Materials Science & Engineering R 168 (2026) 101140

Contents lists available at ScienceDirect

Materials Science & Engineering R

journal homepage: www.elsevier.com/locate/mser

Advances in stimuli-responsive polymers for biomedical and environmental applications

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ARTICLE INFO

Keywords:
Stimuli-responsive polymers
Drug delivery
Environmental remediation
Biodegradable materials
Green chemistry

ABSTRACT

Stimuli-responsive polymers (SRPs), also known as "smart polymers," have transformed biomedical and environmental applications by enabling dynamic and adaptable material properties. These polymers respond to external stimuli such as pH, temperature, light, and magnetic fields, allowing precise control over drug delivery, biosensing, pollutant removal, and sustainable material design. This review explores the fundamental principles behind SRP design, their response mechanisms, and cutting-edge fabrication strategies, highlighting their growing impact across multiple disciplines. In biomedicine, SRPs are advancing site-specific drug release, injectable scaffolds for regenerative therapies, and real-time biosensing, contributing to the evolution of personalized medicine. In environmental science, they play a crucial role in water purification, heavy metal adsorption, and biodegradable materials, offering innovative solutions to pressing sustainability challenges. Unlike previous reviews, this work emphasizes the latest breakthroughs in modular synthesis, hybrid nanostructuring, and 4D printing with a particular focus on the advances achieved over the past decade, while addressing key challenges such as scalability, stability, and cost-effectiveness. By integrating molecular engineering with green chemistry and state-of-the-art fabrication techniques, this review provides a forward-looking perspective on the future of SRPs in medicine, industry, and environmental sustainability. As research continues to advance, SRPs are set to redefine next-generation solutions for healthcare, ecological preservation, and smart material applications.

1. Introduction

Recent advancements in materials science and nanotechnology have accelerated the development of functional polymer-based systems to unprecedented levels, particularly in biomedical and environmental applications [1]. Among these, stimuli-responsive polymers (SRPs), also known as "smart polymers," have introduced new dimensions of functionality and complexity by selectively reacting to external triggers (Fig. 1) [2]. These polymers respond to chemical, physical, or biological cues, enabling signal recognition, self-regulation, controlled payload

Abbreviations: AI, artificial intelligence; AMPs, antimicrobial peptides; ATRP, atom transfer radical polymerization; CMC, carboxymethyl cellulose; Con A, concanavalin A; CuAAC, Copper azide–alkyne cycloaddition; DDS, drug delivery systems; EAPs, electroactive polymers; ECMs, extracellular matrices; FGF, fibroblast growth factor; Gox, glucose oxidase; GSH, glutathione; H_2O_2, hydrogen peroxide; HPMCP, hydroxypropyl methylcellulose phthalate; IPMCs, ionomeric polymer-metal composites; LbL, Layer-by-layer; LCST, lower critical solution temperature; ML, machine learning; MMP, matrix metalloproteinase; MOFs, metal-organic frameworks; MPEG-PCLA, methoxy polyethylene glycol-b-polylactide-co-caprolactone; OFET, organic field-effect transistor; PAA, polyacrylic acid; PANI, polyaniline; PBA, phenylboronic acid; PCL, polycaprolactone; PCLA-PEG-PCLA, polylactide-co-caprolactone-b-polyethylene glycol-b-polylactide-co-caprolactone; PDGF, platelet-derived growth factor; PDMAEMA, polyN,N-dimethylaminoethyl methacrylate; PDMS, polydimethylsiloxane; PDT, photodynamic therapy; PEDOT, poly3,4-ethylenedioxythiophene; PEI, polyethylene imine; PLA, polylactic acid; PLGA, polylactic-co-glycolic acid; Pluronic, polyethylene oxide-b-polypropylene oxide-b-polyethylene oxide; PMAA, polymethacrylic acid; PNIPAM, polyN-isopropylacrylamide; POEGMA, polyoligo(ethylene glycol methacrylate); PPy, polypyrrole; PTT, photothermal therapy; PVA, polyvinyl alcohol; PVCL, polyN-vinylcaprolactam; RAFT, reversible addition-fragmentation chain transfer polymerization; RF, radio-frequency; ROMP, ring-opening metathesis polymerization; ROS, reactive oxygen species; SMPs, shape-memory polymers; SRPs, stimuli-responsive polymers; UCST, upper critical solution temperature; VEGF, vascular endothelial growth factor; VOCs, volatile organic compounds.

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https://doi.org/10.1016/j.mser.2025.101140
Received 20 August 2025; Received in revised form 15 October 2025; Accepted 24 October 2025

release, and structural transformations [3]. Due to these unique characteristics, they endow materials with dynamic and adaptive properties that were previously unattainable. Depending on the specific stimulus, such as pH, ionic strength, temperature, electric or magnetic fields, light, biological interactions, metal ions, or redox conditions [4], SRPs can reversibly or irreversibly modify their chain conformation, phase behavior, solubility, interfacial properties, and surface structures [5]. This responsiveness allows them to transcend traditional passive materials, functioning as highly intelligent systems that are increasingly valued in both medical and environmental fields [6].

Polymeric materials have long been used in medical devices and environmental applications, such as water treatment and antifouling coatings, due to their structural robustness and chemical stability [7]. However, the properties of conventional polymers often remain unchanged under dynamic environmental conditions, making them less suitable for applications requiring real-time adaptability [8]. For example, in advanced drug delivery systems, maintaining a constant drug release rate may not be sufficient to maximize therapeutic efficacy [9]. Instead, such systems require precise control over the timing, rate, and direction of drug release in response to external stimuli [10]. Similarly, in environmental remediation and sensing, materials must go beyond passively adsorbing or filtering pollutants, with practical applications requiring rapid detection and response to contamination indicators or the sudden emergence of toxic substances [11].

SRP systems have been developed to address these complex demands [12]. With finely tuned sensitivity and reproducible responses, these polymers undergo structural and functional transformations such as reversible or irreversible conformation changes, phase transitions, variations in crosslinking density, shifts between soluble and insoluble states, and alterations in surface properties under specific stimuli [13]. Achieving precise control at the nano- to microscale further enhances these transformations, enabling a range of advanced functions, including modulation of protein interactions, mimicry of cellular signal transduction, targeted drug delivery, high-sensitivity detection, and cyclical pollutant removal [14].

In the medical field, SRPs have attracted considerable attention as drug delivery systems (DDS) [15]. For instance, polymeric nanoparticles designed to respond to specific tumor microenvironment conditions, such as low pH, specific enzymes, or reactive oxygen species, can release therapeutic agents precisely at the tumor site [16]. This targeted release not only enhances treatment efficacy but also minimizes adverse effects on surrounding healthy tissues. Additionally, integrating thermo-responsive polymers with hyperthermia treatments or photo-responsive polymers with photodynamic therapy enables theranostic approaches [17], consolidating diagnostics and therapy within a single platform [18]. The use of biocompatible and biodegradable responsive polymers further ensures minimal long-term accumulation in the body, enhancing both drug delivery and tissue regeneration strategies. This dynamic responsiveness lays the foundation for personalized and precision medicine [19].

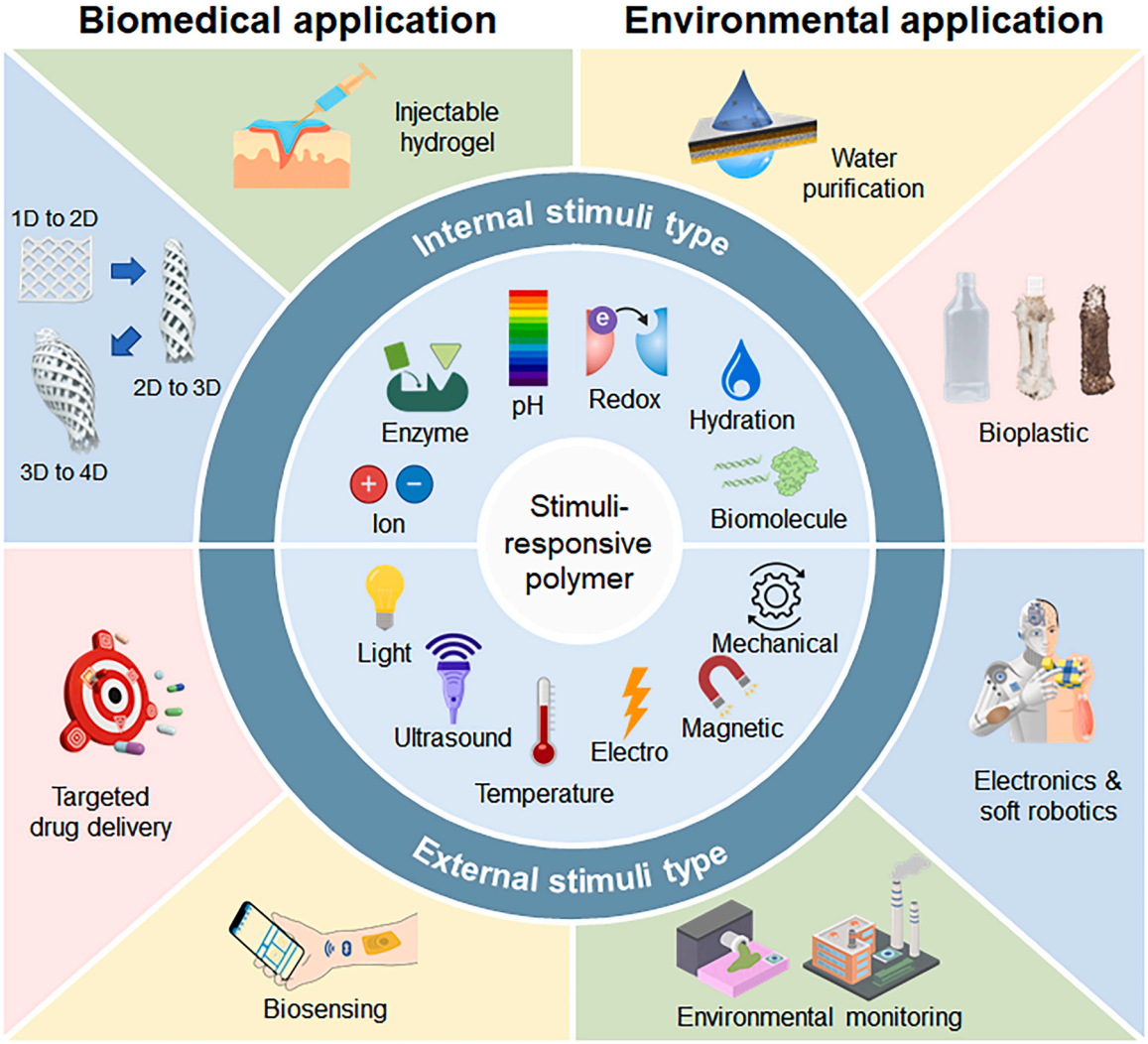


Fig. 1. Applications of stimuli-responsive polymers in biomedical (left) and environmental (right) fields.

In the environmental sector, SRPs are equally transformative, offering innovative solutions for pollutant detection and removal, environmental sensing, self-cleaning surfaces, and eutrophication control [20]. For example, polymer coatings with chelating functionalities can selectively bind and remove heavy metal contaminants from water [21]. Similarly, membranes with tunable permeability or adsorption characteristics, responsive to changes in pH or temperature, can improve resource efficiency in water treatment and recycling processes, reducing energy consumption while enhancing performance [22]. Photo-responsive polymer films can function as intelligent windows that adjust to sunlight exposure or as environmental monitoring devices that detect real-time changes [23], playing a crucial role in sustainable resource management and environmental protection [24].

Despite these significant advancements, several challenges must be addressed before SRPs can be widely commercialized and integrated into clinical and field applications [25]. Enhancing the selectivity and sensitivity of responsive polymers while ensuring long-term stability and reproducibility remains a key priority. Economic viability must also be considered, requiring improvements in manufacturing efficiency [26]. In biomedical applications, reducing toxicity, immunogenicity, and potential side effects is critical [27], while environmental applications require scalability, durability, and recyclability [28]. Overcoming these challenges will require interdisciplinary collaboration across materials science, chemistry, nanotechnology, biology, medicine, and environmental engineering.

This review provides a comprehensive analysis of the design principles, response mechanisms, and applications of SRPs, emphasizing their transformative role in biomedicine and environmental sustainability. Specifically, we explore key case studies, advanced fabrication techniques, and molecular engineering strategies while addressing current limitations and future research directions. By integrating insights from polymer chemistry, biomedical engineering, nanotechnology, and environmental science, this review highlights the potential of SRPs to drive next-generation advancements in precision medicine, sustainable materials, and intelligent industrial applications. As research continues to expand the frontiers of adaptive polymer systems, SRPs are poised to enhance therapeutic efficacy, minimize environmental impact, and enable novel smart technologies, solidifying their role as essential materials for the future.

Over the past decade, SRP design has diversified remarkably, encompassing multi-stimuli hybrid systems, bio-inspired polymers, and environmentally friendly degradable materials. Recent critical reviews have emphasized this growing diversity in polymer chemistries and fabrication strategies (Fig. 2) [29,30]. Building upon these perspectives, our review offers a more integrative synthesis of these developments, distinguishing recent advances while identifying key challenges and future opportunities in both biomedical and environmental domains. Unlike earlier reviews that focus predominantly on either biomedical or environmental applications, this article provides a unified perspective that bridges the two fields. By consolidating the past decade of research, we highlight not only the chemical and structural diversity of SRPs but also their successful translation into real-world technologies. In addition, we emphasize fabrication strategies such as 4D printing, AI-driven material design, and multifunctional hybrid systems, which remain underexplored in prior literature. This dual focus on broad applications and advanced design principles underscores the novelty and significance of our contribution relative to existing reviews.

2. Stimuli-responsive polymers (SRPs): Classification of internal and external triggers

SRPs, often referred to as "smart" or "intelligent" polymers, have attracted significant interest in recent decades due to their ability to undergo predictable and often reversible changes in physical or chemical properties in response to subtle environmental variations [31]. These materials are engineered in such a way that their molecular

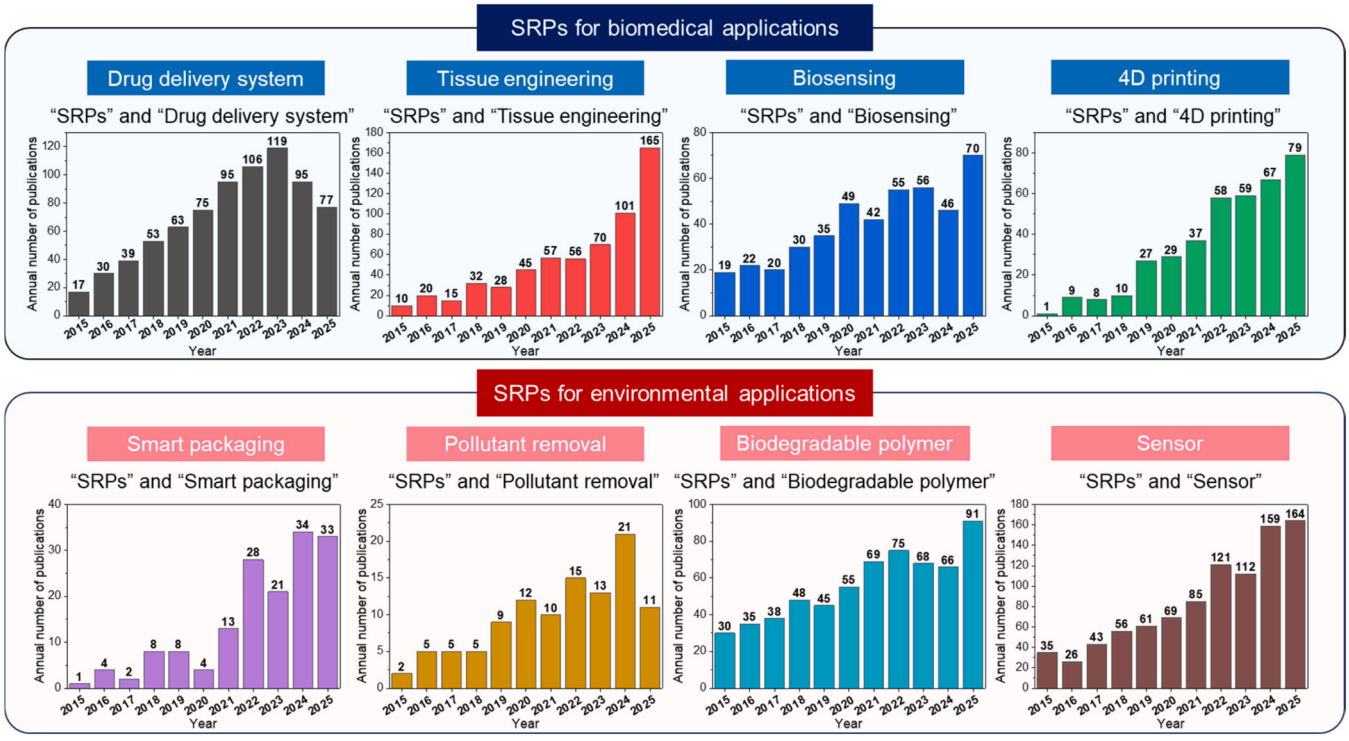


Fig. 2. Graph showing the number of publications on SRPs from 2015 to 2025, categorized by application domains. The upper panel represents biomedical applications, including drug delivery systems, tissue engineering, biosensing, and 4D printing, which have shown a steady increase over the past decade. The lower panel illustrates environmental applications, such as smart packaging, pollutant removal, biodegradable polymers, and sensors, reflecting the growing emphasis on sustainability and eco-friendly technologies. Data were retrieved from the Scopus database using the keyword "SRPs" combined with each application domain, and the graphs were generated based on the annual number of retrieved publications.

structure, conformation, or assembly state can be modulated by various internal and external stimuli, leading to controlled transformations. These transformations may include phase transitions from soluble to insoluble states, changes in hydrophilicity or charge density, variations in crosslinking density or mechanical stiffness, and morphological alterations in self-assembled nanostructures [32]. Such dynamic responses enable on-demand functionality, programmable behavior, and precise control across diverse fields, including drug delivery, regenerative medicine, biosensing, environmental remediation, energy conversion, and smart coating technologies [33].

2.1. Conceptual framework and systematic classification of SRPs

SRPs can be broadly classified based on the type of stimulus that triggers their response. Internal stimuli typically originate from endogenous biological environments and include factors such as pH gradients, redox potentials, enzymatic activity, and fluctuations in biomolecule concentrations [34]. In contrast, external stimuli arise from exogenous materials or the surrounding environment, including temperature changes, light irradiation, magnetic or electric fields, mechanical forces, and variations in ionic strength. By leveraging these triggers, researchers can design polymers with precisely controlled spatial and temporal responses, enabling a new generation of adaptive materials [35]. This section provides an overview of different stimulus types and their characteristics, highlighting how they induce structural and functional changes in SRPs.

2.2. Internal stimuli: Biochemical and physiological triggers for SRPs

Stimuli-responsive polymers (SRPs) are broadly classified based on the origin of the stimulus into internal and external categories (Fig. 3). Internal stimuli originate from within the biological or environmental system and include variations in pH, redox potential, enzymatic activity, biomolecular concentrations, ionic composition, and hydration levels. These endogenous triggers allow for precise spatiotemporal control over polymer behavior, particularly in biomedical applications.

2.2.1. pH-responsive polymers: Acidic microenvironments and controlled release

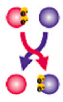
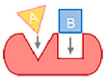
pH-sensitive systems are among the most extensively studied in the context of internal stimuli [36]. Various biological environments, such as the gastrointestinal tract, tumor microenvironments, and intracellular organelles (e.g., endosomes and lysosomes), exhibit distinct pH levels [37]. By incorporating acidic or basic functional groups (e.g., carboxyl or amine moieties) into polymer chains, the solubility, charge state, and swelling behavior of these materials can be precisely tuned to respond to these pH variations [38]. For instance, pH-responsive drug delivery carriers remain stable at physiological pH (~7.4) but undergo structural changes in more acidic tumor tissues or intracellular compartments, triggering targeted drug release. This mechanism enhances therapeutic selectivity while minimizing off-target effects [39].

2.2.2. Redox-responsive polymers: Exploiting cellular redox gradients

The intracellular redox environment, particularly the difference in glutathione (GSH) concentrations between the extracellular space and the cytosol, has inspired the development of redox-responsive polymers [40]. These materials often incorporate disulfide bonds or other redox-sensitive linkages that remain stable under oxidizing conditions but are cleaved in reducing environments [41]. By leveraging this gradient, cargo-loaded nanoparticles remain intact during circulation and selectively release their payload upon internalization into cells, where the reducing conditions trigger polymer network disassembly [42].

2.2.3. Enzyme- and biomolecule-responsive polymers: Precision degradation and targeting

Enzyme- and receptor-responsive polymers leverage the highly specific catalytic or recognition capabilities of biomolecules [43]. These polymers are designed with peptide linkages or other functional moieties that can be selectively cleaved by enzymes overexpressed in diseased tissues, such as cancerous tumors or sites of inflammation, enabling precise degradation and controlled drug release [44]. Similarly, polymers engineered to interact with specific biomolecules, such as glucose-responsive materials for insulin delivery, can undergo conformational or permeability changes in response to variations in target ligand concentrations [45]. This strategy enables highly targeted therapies and adaptive biosensors that dynamically adjust their function in the presence of specific biomarkers, enhancing both therapeutic efficacy and diagnostic precision.

Internal stimuli		Pros	Cons
	**pH-responsive**	• Exploits natural pH gradients • Enables site-specific environments • Simple and reversible mechanism	• Limited pH window in microenvironment • Unpredictable response • Potential burst release under alkaline shift • pH sensitivity affected by formulation stability
	**Redox-responsive**	• Sensitive to oxidative microenvironments • Enables selective response • Reversible redox-triggered degradation	• Variable redox potential • Possible premature activation in ROS-rich environments • Complex synthesis and stability issues
	**Enzyme-responsive**	• High specificity for targets • Enables site-selective activation • Suitable for local, continuous control	• Limited enzyme stability • Complex design and synthesis requirements
	**Ion-responsive**	• Simple mechanism and easy tuning • Good compatibility with matrices	• Possible ion interference with other components • Narrow ion concentration range for activation • Unpredictable response under variable pH or ionic media

External stimuli		Pros	Cons
	**Photo-responsive**	• Precise spatial and temporal control • On-demand, adjustable response	• Limited light penetration depth • Potential phototoxicity or heat generation • Requires specialized light source or device
	**Temperature-responsive**	• Respond to local temperature elevation • Enables site-specific, self-regulated response • Simple trigger without external equipment	• Sensitive temperature difference • Limited control over precise response • Possible premature response under external heat
	**Ultrasound-responsive**	• Non-invasive and controllable external trigger • Deep penetration and localized activation • Enables on-demand, repeated control	• Requires specialized ultrasound equipment • Possible local heating or irritation • Limited spatial selectivity at high intensities
	**Electro-responsive**	• Precise, rapid, and reversible control • Easily tunable stimulus intensity and duration • Enables localized and programmable control	• Requires external power source or electrodes • Risk of localized heating or electrochemical irritation • Complex device integration and cost consideration

Fig. 3. Classification of stimuli for stimuli-responsive polymers. Internal stimuli (e.g., pH, redox, enzymes, ions) originate from within the body, while external stimuli (e.g., light, temperature, ultrasound, electric fields) are applied externally. These triggers induce structural changes in polymers, enabling controlled responses for biomedical and environmental uses.

2.2.4. Advantages, limitations, and applications of internal stimuli-responsive polymers

Internal SRPs exhibit distinct advantages arising from their ability to exploit endogenous biochemical and physiological gradients within biological or environmental systems. These materials respond autonomously to variations in pH, redox potential, enzymatic activity, or ionic composition, enabling *in situ* activation without the need for external intervention. Such self-regulated behavior provides excellent spatial and temporal precision, high biocompatibility, and minimal invasiveness, which are particularly desirable for biomedical uses. Typical examples include pH-responsive hydrogels for tumor or wound microenvironment–specific drug release, redox-cleavable micelles that degrade in glutathione-rich cytosols, and enzyme-triggered linkers enabling localized delivery of bioactive molecules.

Despite these benefits, several limitations restrict broader translation. Internal stimuli often vary among individuals and disease states, leading to inconsistent response intensity or kinetics. Moreover, fine-tuning degradation rates and reversibility remains challenging, and excessive sensitivity may cause premature release or instability under physiological fluctuations. Manufacturing reproducibility and quantitative control of internal signal thresholds also remain technical obstacles.

Representative applications of internal SRPs include targeted and on-demand drug delivery, biosensing and diagnostic platforms, gene or protein transport, and smart scaffolds for tissue regeneration. Future work should emphasize quantitative modeling of endogenous triggers, integration of multi-stimuli couplings, and hybrid systems that combine internal and external responsiveness to achieve reliable and personalized therapeutic performance.

2.3. External stimuli: Physical and environmental triggers for SRPs

In contrast to internal stimuli, external stimuli are applied from outside the system and include physical or environmental cues such as light, temperature, magnetic and electric fields, ultrasound, and ionic strength. These external triggers are particularly attractive for their non-invasive nature and controllability, enabling real-time modulation of polymer behavior in situ.

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2.3.1. Temperature-responsive polymers: Phase transitions and thermo-switching

Temperature-sensitive polymers exhibit a lower critical solution temperature (LCST) or upper critical solution temperature (UCST), at which their solubility undergoes a dramatic change. For example, poly (N-isopropylacrylamide) (PNIPAM) is hydrophilic below its LCST (~32 °C) and hydrophobic above it [46]. Similarly, amphiphilic block copolymers such as poly(lactide-co-caprolactone)-b-poly(ethylene glycol)-b-poly(lactide-co-caprolactone) (PCLA-PEG-PCLA), methoxy poly (ethylene glycol)-b-poly(lactide-co-caprolactone) (mPEG-PCLA), and poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (PEO-PPO-PEO; Pluronic) exhibit temperature-responsive sol-gel transitions driven by micellization and physical crosslinking [47–49]. These transitions typically occur near physiological temperatures, enabling their application as injectable hydrogels and thermogelling drug delivery systems.

These materials have been widely applied in tissue engineering, where body temperature induces in situ gelation, as well as in controlled drug delivery platforms that respond to local hyperthermia [50]. Beyond biomedical applications, temperature-responsive polymers such as PNIPAM, PCLA-based systems, and Pluronic are also utilized in smart membranes and separation technologies, contributing to energy-efficient processes in environmental and industrial settings [51].

2.3.2. Light-responsive polymers: Photocontrol of polymer functionality

Photostimulation provides high spatiotemporal resolution and remote control, making light-responsive polymers particularly attractive [52]. By incorporating photochromic groups (e.g., spiropyrans, azobenzenes, diarylethenes, stilbenes, fulgides, naphthopyrans) [53,54] or photocleavable linkages (e.g., o-nitrobenzyl esters, coumarin dimers, nitroveratryl derivatives, p-hydroxyphenacyl, benzoin esters) [55,56], these polymers can undergo conformational changes, degradation, or switch between isomeric states upon exposure to specific wavelengths. Applications include photo-induced drug release, photo-patternable coatings, holographic data storage, and artificial muscles that flex or relax in response to light [57].

2.3.3. Magnetic and electric field-responsive polymers: Remote-controlled systems

Magnetic nanoparticles embedded within polymer matrices can respond to external magnetic fields, inducing shape changes, alignment, or heat generation (magnetic hyperthermia) on demand [58]. Similarly, electrically responsive polymers (e.g., polypyrrole, polyaniline-based systems) alter their conductivity, volume, or mechanical properties when exposed to applied voltages [59]. These polymers enable electrically controlled drug release, sensors, and actuators.

2.3.4. Ionic strength and mechanical force-responsive polymers: Adaptive mechanics

Changes in ionic strength can modulate electrostatic interactions and osmotic pressure within polyelectrolyte networks, leading to swelling or collapse transitions [60]. Mechanical forces, such as shear stress or compression, can induce changes in polymer configuration, enabling applications in self-healing materials, mechanochromic coatings, and rheology modifiers that adjust viscosity based on applied stress [61]. These properties have significant implications for responsive lubricants, tactile sensors, and adaptive biointerfaces.

2.3.5. Advantages, limitations, and applications of external stimuli-responsive polymers

External stimuli provide unique opportunities in the design of SRPs due to their controllability and non-invasive characteristics; however, each type of stimulus also presents distinct limitations that affect its practical applicability [46]. To facilitate comparison, Table 1 and Table 2 summarizes the representative examples of polymers responsive to various external triggers. This comparative overview illustrates how specific stimuli can be strategically selected according to the desired biomedical or environmental application [49].

For instance, photo-responsive polymers offer exceptional spatial and temporal precision, making them ideal for controlled drug release and biosensing applications. However, their effectiveness in deep tissue is limited by poor light penetration and potential phototoxicity [52]. Temperature-responsive systems particularly those based on PNIPAM and Pluronic copolymers exhibit sharp sol–gel transitions near physiological temperatures, which is advantageous for injectable hydrogels and regenerative scaffolds [46,47]. Nonetheless, their narrow transition range can present challenges in reproducibility. Magneto-responsive polymers allow remote activation and deep tissue penetration, making them particularly useful in targeted drug delivery and hyperthermia therapy. Nevertheless, the incorporation of magnetic nanoparticles raises potential concerns about localized heating and biocompatibility [58]. Electro- and ionic-responsive materials enable precise, programmable actuation, lending themselves to applications in soft robotics, energy devices, and tissue engineering. However, these systems often require electrodes or conductive additives that may reduce cytocompatibility [59]. In contrast, ultrasound-responsive polymers combine non-invasiveness with deep tissue penetration, facilitating

Table 1
Representative examples of polymers responsive to various external triggers.

	Stimulus	Advantages	Limitations	Polymers	References
Internal stimuli	pH	• Utilizes pH differences (stomach, intestine, tumor) for site-specific drug release. • Switches hydrophilic/hydrophobic states, swelling, and solubility with pH. • Drug delivery, scaffolds, sensors, environmental remediation. • Functional groups (amines, carboxyls, imidazoles) enable tunable responsiveness.	• Small physiological differences limit sensitivity/selectivity. • Affected by ionic strength, proteins, temperature. • Repeated pH shifts reduce mechanical/structural integrity. • Complex, costly synthesis, scaling up is challenging.	Poly(acrylic acid) (PAA) Poly(methacrylic acid) (PMAA) Poly(ethylene imine) (PEI) Poly(L-lysine) Poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) Poly(2-vinylpyridine) (P2VP)	[62–66]
	Redox	• Exploits elevated GSH/ROS in tumors or inflamed tissues for precise drug delivery. • Redox-labile bonds (S–S, Se–Se, Te–Te) enable on/off degradation. • Drug delivery, tissue scaffolds, antioxidant coatings, environmental remediation. • Can be combined with pH or enzyme responsiveness.	• GSH/ROS levels differ across tissues and patients. • Possible interference with other redox processes. • Susceptible to oxidation during storage/processing. • Complex, costly synthesis, scale-up difficulties.	Poly(disulfide)s Poly(diselenide)s Poly(ditelluride)s Poly(thioketal)s Poly(ferrocene) Poly(vinyl dithiocarbonate) Polyaniline	[67–71]
	Enzyme	• Enzymes act only on specific substrates, enabling precise targeting. • Utilizes natural enzymes, requiring no external stimuli. • Drug release/degradation rate tuned by enzyme activity. • Drug delivery, scaffolds, diagnostics, biosensors, environmental uses.	• Enzyme levels differ across patients and tissues. • Unwanted degradation from similar enzymes. • Reduced stability during storage/transport. • Complex and costly introduction of enzyme-recognition motifs.	Poly(L-lysine) Poly(glutamic acid) Poly(caprolactone) Poly(lactic acid) Poly(phosphate)s Poly(anhydrides) Poly(ortho esters)	[72–76]
	Biomolecule	• Responds only to specific biomolecules (DNA, ATP, proteins) for precise diagnosis and drug release. • Uses endogenous recognition, no external stimuli required. • Polymer response tuned by biomolecule concentration or expression. • Applicable in diagnosis, targeted drug delivery, biosensors, and environmental monitoring.	• Biomolecule levels vary across patients, tissues, and conditions. • Possible interference with similar biomolecules. • Recognition function may decrease during storage or in vivo. • Incorporating aptamers, peptides, or antibodies is complex and costly.	poly(N-isopropylacrylamide-co-PBA) Dextran–Concanavalin A-based polymers ATP-aptamer functionalized polymers DNA-crosslinked polymers Antibody–polymer conjugates	[77–80]
	Ion	• Specific response to certain metal ions. • Reversible binding controls swelling, solubility, conductivity. • Works with Ca2 + , Zn2 + , Mg2 + for biomedical uses. • Applications in drug delivery, tissue regeneration, sensors, remediation, membranes.	• Affected by ionic strength, pH, competing ions. • Hard to distinguish similar ions (Ca2 + vs. Mg2 +). • Ion–polymer interactions may degrade over time. • Complex synthesis and scaling.	Poly(acrylic acid) (PAA) Poly(methacrylic acid) (PMAA) Poly(styrene sulfonate) Nafion Poly(vinylphosphonic acid) Polyaniline Alginate	[81–85]
	Hydration	• Responds to ubiquitous water changes without external devices. • Swelling/shrinking and property changes are reversible with hydration. • Hydrophilic polymers (e.g., PEG, PVA) are suitable for biomedical use. • Applied in drug delivery, scaffolds, humidity sensors, and smart packaging.	• Water is everywhere, making selective control difficult. • Response affected by temperature, pH, and salts. • Repeated hydration cycles can cause damage and fatigue. • Hard to design uniform networks, scale-up may reduce performance.	Poly(vinyl alcohol) Poly(2-hydroxyethyl methacrylate) (PHEMA) Poly(methacrylic acid) Poly(ethylene glycol) Polyacrylamide (PAAm) Cellulose Gelatin	[86–89]
External stimuli	Photo	• Light enables localized, precise, spatiotemporal regulation. • Photoisomerization and photocrosslinking allow repeated property changes. • Responsive to UV, visible, and NIR, NIR offers deeper tissue penetration. • Applications in drug delivery, photodynamic therapy, sensors, coatings, and actuators.	• UV/visible light poorly penetrates tissues. • UV may cause cell damage, mutations, or heating. • Photoactive groups degrade under prolonged light/heat. • Incorporating photoresponsive units (e.g., azobenzene, spiropyran) is complex and costly.	Poly(azobenzene methacrylate) Spiropyran-functionalized poly (methacrylate)s o-Nitrobenzyl-funtionalized polymers Fulgide-functionalized poly (methacrylate)s Coumarin-funtionalized polymers	[90–93]
	Temperature	• Sensitive to small temperature changes, enabling fine control of drug release and material properties. • Hydrophilic/hydrophobic switching and swelling/shrinking near LCST/UCST. • Temperature is a simple, accessible trigger. • Applied in drug delivery, cell/protein separation, scaffolds, sensors, and smart coatings.	• LCST/UCST easily shifts with pH, salts, or co-solvents. • Temperature lacks molecular or tissue selectivity. • Repeated cycles may cause mechanical damage or fatigue. • Copolymer design is complex for precise LCST/UCST tuning.	Poly(N-isopropylacrylamide) (PNIPAM) Poly(N-vinylcaprolactam) (PVCL) Poly(N,N-diethylacrylamide) (PDEAAm) PEG-based thermosensitive block copolymers (PCLA-PEG-PCLA, Pluronic) Hydroxypropyl cellulose (HPC)	[94–97]
	Magnetic	• Non-invasive, precise regulation via external magnetic fields. • Magnetic fields penetrate tissues, enabling drug delivery and hyperthermia therapy. • Combine magnetic heating with pH or temperature responsiveness.	• Requires magnetic nanoparticles (Fe3O4, γ-Fe2O3), synthesis and dispersion are challenging. • Risk of cytotoxicity and tissue accumulation at high nanoparticle doses.	Polyacrylamide (PAAm)–Fe_3O_4 nanocomposite PAA–Fe_3O_4 nanocomposites Polyurethane (PU)-based composites Polydopamine (PDA)-coated magnetic polymers Silk fibroin-based composites	[98–100]

(*continued on next page*)

Table 1 (*continued*)

	Stimulus	Advantages	Limitations	Polymers	References
		• Applications in drug delivery, cancer therapy, scaffolds, sensors, and environmental remediation.	• Efficiency depends on magnetic field strength and frequency. • Difficult and costly to produce uniformly dispersed MNP–polymer composites.		
	Ionic	• Immediate swelling/shrinking with ion changes. • Properties controlled by ion binding/release. • Selective response to ions (Na^+, K^+, Ca^{2+}, Cl^-) for sensing and regulation. • Applications in drug release, sensors, smart membranes, and energy storage.	• Hard to distinguish between similar ions (e.g., Na^+ vs. K^+). • Influenced by pH, temperature, and electrolyte concentration. • Long-term ion exchange can cause mechanical fatigue. • Complex, costly processes for high ion selectivity.	Poly(acrylic acid) (PAA) Poly(styrene sulfonate) (PSS) Poly(allylamine hydrochloride) (PAH) Nafion Poly(ionic liquid)s (PILs) Chitosan	[20–22, 101,102]
	Electro	• Voltage or current can finely regulate drug release, swelling/shrinking, and conductivity. • Electrical stimulation enables real-time, on-demand control. • Oxidation–reduction and electrochemical doping/de-doping are repeatable. • Used in drug delivery, electro-stimulation, biosensors, electrode materials, soft actuators, and energy storage (supercapacitors, batteries).	• Performance is highly sensitive to electrolyte concentration, pH, and ion type. • High voltage/current may cause tissue damage or heating. • Repeated stimulation can lead to mechanical fatigue and electrochemical degradation. • Achieving uniform conductivity and stable electrode–polymer interfaces is difficult.	Polypyrrole (PPy) Poly(3,4-ethylenedioxythiophene) (PEDOT) Polyaniline (PANI) Poly(phenylene vinylene) (PPV) Polythiophene (PTh) Acrylic elastomer composites	[103–105]
	Ultrasound	• Ultrasound enables localized and precise targeting. • Effectively reaches deep tissues for therapy and drug release. • Utilizes mechanical force, cavitation, and localized heating. • Applied in drug delivery, cancer therapy, tissue regeneration, imaging, and smart hydrogels/microbubbles.	• Responses vary with ultrasound intensity, frequency, and duration. • High-intensity ultrasound may cause tissue damage or heating. • Effectiveness depends on tissue location, blood flow, and environment. • Designing ultrasound-responsive systems is complex and costly.	Poly(ethylene glycol) (PEG) with sonosensitive linkers polyurethane-based polymers with ultrasound-labile bonds Lipid–polymer hybrid microbubbles Polymer–porphyrin conjugates Poly(sebacic anhydride) (PSA)	[106,107]

Table 2
Summary of representative stimuli-responsive polymer systems categorized by trigger type, showing typical stimuli/handles, representative polymers, and major biomedical and environmental applications.

Stimulus	Typical triggers/ handles	Representative polymer	Biomedical applications	Environmental applications	Refs
pH	Acid/base microenvironment	PAA, PMAA, PDMAEMA, P2VP, poly (histidine), chitosan, PEG-b-PAA hydrogels	Tumor/GI site-specific release, endosomal escape, scaffolds, pH-sensing wearables/implants	Acid/alkali wastewater sorbents, pH-gated membranes	[108–111]
Redox	GSH↑ (cytosol), ROS↑ (inflamed/tumor)	Disulfide/diselenide/ditelluride polymers, PEG–SS–PCL micelles	Redox-triggered drug release, antioxidant coatings, tissue engineering	Redox-gated adsorbents, reversible capture/release, catalytic remediation	[112–115]
Enzyme	MMP, cathepsin B, lipase, glycosidase, phosphatase	Peptide-crosslinked gels, PCL/PLA (lipase-degradable), HA/dextran/chitosan, PEG–peptide–PLA	Disease-site cleavage, prodrug release, enzyme-responsive biosensors/theranostics	Enzymatic pollutant capture/degrade, biofouling control	[116–119]
Biomolecule	Glucose, ATP, DNA/RNA, proteins	PBA-copolymers (glucose), aptamer-polymer, DNA-crosslinked gels, antibody–polymer	Glucose monitoring & insulin delivery, aptamer diagnostics, precision release	Biosensors for food/water biomolecules, affinity separations	[120–122]
Ion	Ca^{2+}, Mg^{2+}, Na^+/K^+, Fe^{3+}	Alginate (Ca^{2+}), carrageenan, PAA/PSS, crown-ether polymers, polyaniline/polypyrrole	Mineralized scaffolds, ion-gated delivery, bioelectronics	Ion-exchange membranes, heavy-metal capture	[123–125]
Hydration	Water activity, RH	PEG, PVA, PHEMA, cellulose derivates, PNIPAM blends	Moisture-gated release, wound dressings, humidity sensors	Smart packaging films, humidity-gated membranes	[126–129]
Temperature	LCST/UCST	PNIPAM, PVCL, PDEAAm, PNAGA, ELPs, PNIPAM-IPN gels	Thermo-gated DDS (≈37 ℃), injectable hydrogels, cell sheets, thermoactuators	Thermo-valves, compostable/biodegradable films	[130–132]
Light	UV/Vis/NIR	Azobenzene, spiropyran, coumarin, diarylethene, o-nitrobenzyl, NIR nanocomposites	PDT/photothermal release, photoactuators, patternable gels	Photo-switchable coatings/membranes, sunlight-degradable films	[133–135]
Magnetic	AC/DC field, hyperthermia	PVA/alginate/PNIPAM–Fe_3O_4 gels, PDMS–MNP elastomers, PLGA–MNP	Magnetothermal therapy, targeted delivery, actuators	Magnetic separations, pollutant capture	[136–139]
Electric	Voltage/current	PPy, PANI, PEDOT:PSS, electroactive gels, dielectric elastomers	On-demand release, neural/electrostimulation, soft actuators	Electro-valves, antifouling/electrode interfaces	[140–143]
Ultrasound	Cavitation, acoustic heating	PEG/PU with sonolabile linkers, PEG–PLA/PCL micelles, PLGA-PEG microbubbles, HA/alginate gels	US-triggered delivery, sonodynamic therapy, imaging contrast	US-assisted remediation, responsive filters	[144–147]
CO_2 / gas	CO_2 partial pressure	CO_2-responsive amidines/guanidines, PDEAEMA blends	CO_2-gated micelles, respiratory sensors	Flue-gas separations, CO_2-switchable membranes	[148–150]
Mechanical/Shear	Shear/strain, pressure	Mechanophore-polymers (spiropyran mechanochemistry), tough hydrogels	Mechano-release, strain sensors, tissue-mimetic scaffolds	Flow-gated separations, damage-sensing coatings	[151–153]

their use in on-demand drug release and imaging-guided therapy, although the risks of local heating and the need for specialized instrumentation remain challenges [50].

Future work should prioritize the translation of external stimuli-responsive polymers into versatile platforms for real-world applications, including precision medicine, sustainable environmental remediation, and intelligent material systems. In parallel, future research should emphasize the development of integrative frameworks that quantitatively model multi-stimuli interactions, enabling the rational design of hybrid SRP systems capable of dynamic adaptation across biomedical, environmental, and industrial contexts [46,61]. Moreover, efforts should be directed toward optimizing the design trade-offs between internal and external stimuli to achieve an ideal balance among responsiveness, safety, and functionality.

2.4. Architectural design and mechanistic control

The success of SRPs depends on rational molecular design and precise architectural engineering [154]. For example, block copolymers can self-assemble into micelles, vesicles, or nanotubes, with their stability and morphology shifting under specific stimuli. Random copolymers and homopolymers with responsive side groups can undergo coil-to-globule transitions [155]. Crosslinked network hydrogels can expand or contract selectively, controlling the transport of molecules or ions [156]. Advanced synthesis techniques, such as controlled radical polymerization, click chemistry, and bioconjugation strategies, allow for the precise placement of stimuli-responsive elements and functional groups [157]. This level of control ensures that the polymer's response can be tailored not only in terms of the magnitude of the change but also its kinetics, reversibility, and threshold sensitivity.

2.5. Comparative evaluation of stimuli-responsive methods

SRPs exhibit distinct mechanisms and performance characteristics depending on the type of stimulus they respond to. This comparative framework highlights not only the diversity of SRP triggers but also their translational potential in advanced additive manufacturing [29,30].

As shown in Fig. 3, each type of stimulus presents unique strengths and limitations. pH- and redox-responsive polymers are particularly advantageous for intracellular delivery and tumor targeting because they exploit natural biochemical gradients [36]. Temperature- and light-responsive systems enable precise control over gelation and release, making them well suited for injectable hydrogel depots and light-triggered on-demand drug delivery platforms, respectively [57]. Enzyme-responsive systems leverage biological specificity but require careful consideration of inter-patient variability [43]. In contrast, magnetic-, electric-, and ultrasound-responsive materials allow remote, non-invasive actuation, offering great potential for targeted therapy, biosensing, and adaptive wound-healing systems, where dynamic responsiveness is critical [58,61].

Overall, this comparative framework emphasizes that no single stimulus is universally optimal; rather, the choice should be guided by the intended biomedical application and fabrication approach. Furthermore, the integration of multiple triggers into multi-stimuli-responsive polymers holds considerable promise for overcoming the inherent limitations of individual stimuli, thereby advancing the development of next-generation 3D/4D printed biomedical constructs [17,18,29]. A detailed comparison of major stimulus-responsive mechanisms, including their key characteristics, advantages, disadvantages, and representative biomedical or 3D/4D printing applications, is summarized in Table 3.

3. Design principles of SRPs

The ability of polymers to respond predictably to external or internal stimuli is fundamentally rooted in their molecular design and synthesis. Achieving the desired responsiveness requires a careful selection of monomers, functional groups, crosslinkers, and synthetic strategies that position stimuli-reactive units at specific locations within the polymer chain or network [187]. By controlling these structural elements and their arrangement, researchers can tailor the type, sensitivity, kinetics, and reversibility of the polymer's response [188]. In this section, we will discuss the fundamental design principles for SRPs, focusing on the roles of chemical structures and functionalities, the incorporation of specialized stimuli-responsive moieties, strategies for fine-tuning responsiveness through various synthetic approaches, and methods for creating polymers capable of addressing multiple triggers simultaneously.

3.1. Chemical structures and functional moieties driving responsiveness

The first step in designing an SRP is identifying the specific trigger (or triggers) and the corresponding molecular motifs that can translate these triggers into macroscopic property changes. The key chemical structures that influence responsiveness are discussed below.

3.1.1. Stimuli-responsive functional groups

Certain functional groups undergo reversible or irreversible chemical transformations in response to specific environmental stimuli, such as pH, redox potential, light, and temperature **(**Fig. 4**)**. These moieties serve as the molecular "switches" in SRPs, enabling dynamic transitions in properties such as solubility, hydrophilicity, crosslinking density, or degradation rate [189]. The representative types and their mechanisms are summarized below:

- **pH-responsive groups:** Carboxyl (–COOH), amino ($–NH_2$), and sulfonic acid ($–SO_3H$) groups are commonly employed due to their pH-dependent ionization behavior. Polymers containing these groups can reversibly switch between soluble and insoluble states or undergo volumetric changes (swelling and contraction) in response to environmental pH variations, enabling controlled release and structural modulation [37].
- **Redox-sensitive linkages:** Disulfide (–S–S–), diselenide (–Se–Se–), and ditelluride (–Te–Te–) bonds, as well as thiol groups and quinone derivatives, are redox-responsive linkages that remain stable under oxidative conditions but cleave or undergo transformation under reducing environments, enabling controlled degradation or payload release in stimuli-responsive polymer systems [190,191].
- **Photochromic moieties:** Photoresponsive moieties such as azobenzene, spiropyran, coumarin, and o-nitrobenzyl derivatives undergo structural rearrangements including isomerization or bond cleavage upon absorption of light energy, which excites electrons and induces specific photochemical reactions. These transformations lead to reversible or irreversible changes in optical, mechanical, or solubility properties of the polymer matrix [53,192].
- **Thermo-responsive groups:** Polymers like PNIPAM and its derivatives show LCST or UCST behavior, where solubility changes with temperature. Amphiphilic block copolymers such as PCLA-PEG-PCLA, mPEG-PCLA, and Pluronic also exhibit temperature-triggered micellization and sol-gel transitions near body temperature, making them useful for injectable hydrogels, drug delivery, and tissue engineering [47,193,194].

3.1.2. Stimuli-responsive initiators and crosslinkers

Initiators and crosslinkers incorporating responsive bonds or groups can also impart responsiveness to a polymer. For example, using an initiator with photocleavable bonds can produce polymer chains that fragment upon UV irradiation [195]. Similarly, redox- or enzyme-cleavable crosslinkers can alter a hydrogel network's structure under specific conditions [196]. By carefully selecting these initiators and crosslinkers, researchers gain additional control over polymer structure and the resulting responses.

Table 3
Comprehensive comparison of various stimulus-responsive mechanisms applied in 3D/4D printing of SRPs, summarizing their key characteristics, advantages, limitations, representative materials, and biomedical applications.

Stimulus	Key Mechanism / Functional Handle	Advantages in 3D/4D Printed SRPs	Limitations / Challenges	Representative Materials / Systems	Biomedical Applications (3D/4D Printing Context)	Refs
Temperature	Phase transition near LCST/UCST; hydrogen bonding or hydrophobic collapse	• Enables thermally triggered shape change and self-folding • Compatible with body temperature (~37 °C) • Enables self-expanding stents and actuators	• Slow thermal diffusion in bulk structures • Poor control in heterogeneous tissues • Possible fatigue over repeated cycles	PNIPAM, PVCL, PDEAAm, PEG–PCL copolymers, SMP-based composites	• Self-deploying stents, thermally adaptive scaffolds • Shape-memory implants and tissue expanders • Thermo-triggered drug release systems	[158–160]
pH	Protonation/deprotonation of carboxyl/amine groups	• Site-specific release in acidic (tumor) or basic (intestinal) environments • Enables local therapeutic precision • Stable in neutral physiological conditions	• Limited ΔpH window in vivo • Possible buffering effects of body fluids • Long-term mechanical instability in swelling media	PAA, PMAA, PDMAEMA, poly (histidine), chitosan-based hydrogels	• 4D-printed drug capsules releasing in tumor pH • pH-sensitive scaffolds for local therapy • GI-targeted delivery systems	[161–163]
Enzyme	Cleavage of peptide, ester, or glycosidic bonds by specific enzymes (e.g., MMPs, lipases)	• High biological specificity • Enables stimuli-specific degradation in disease microenvironments • Natural coupling to biochemical pathways	• Enzyme concentration varies across tissues • Possible non-specific hydrolysis • Limited stability during processing	Peptide-crosslinked PEG hydrogels, PCL/PLA blends, HA–dextran networks	• Enzyme-triggered tissue scaffolds • • Biodegradable implants • Sequential or multi-drug releasing 4D constructs	[164–166]
Light	Photoisomerization or photolysis (azobenzene, spiropyran, o-nitrobenzyl)	• Remote, on-demand spatial control • Enables photopatterning and localized activation • Compatible with microfabrication	• Limited tissue penetration (UV/Vis) • Potential phototoxicity • Need for precise optical exposure	Azobenzene- or coumarin-modified hydrogels, NIR-responsive nanocomposites	• Light-triggered drug release • Photoactuated microvalves or microneedle arrays • 4D-printed soft robotics for minimally invasive therapy	[167–169]
Redox	Reversible cleavage of disulfide/diselenide/thioketal bonds under GSH/ROS variations	• Enables intracellular drug delivery • Applicable to oxidative stress sites • Provides degradation "on/off" control	• Sensitive to premature oxidation • Requires controlled storage and processing • Possible batch variability	PEG–SS–PCL micelles, poly(diselenide) hydrogels, thioketal elastomers	• Redox-cleavable drug scaffolds • Antioxidant coatings • Self-degradable biomedical constructs	[170–172]
Hydration	Water absorption-induced swelling/shrinking; hydrogen-bond rearrangement	• Biocompatible and easily processed • Enables swelling-controlled release and actuation • Suitable for hydrophilic SRP inks in 4D printing	• Difficult to maintain dimensional stability • Fatigue after repetitive hydration cycles • Sensitivity to ionic strength	PEG, PVA, PHEMA, cellulose-based hydrogels	• Wound dressings with moisture regulation • Hydration-triggered actuators for biosensing • Self-folding 4D hydrogel constructs	[173–175]
Magnetic	Movement or heating under external magnetic field	• Non-invasive control • Enables remote actuation and hyperthermia • Useful in deep-tissue systems	• Requires nanoparticle dispersion stability • Risk of cytotoxicity at high MNP loading • Equipment cost	Fe_3O_4/γ-Fe_2O_3–PVA hydrogels, magnetic SMP composites	• Magnetically guided drug delivery • 4D-printed actuators and microbots • Remote-controlled stents	[176–178]
Electric	Electrochemical oxidation/reduction; ion migration	• Precise real-time control • Fast response rate • Compatible with biosensors and electrodes	• Needs stable electrode–polymer interface • Risk of tissue heating or corrosion • High energy requirement	PPy, PEDOT:PSS, PANI composites	• Electrostimulated release systems • Neural interfaces and electroactive scaffolds • Bioelectronic actuators	[140, 179–181]
Multi-stimuli combined	Integration of dual/triple responsiveness (pH + temperature, redox + enzyme, etc.)	• Highly adaptive and programmable • Enables logic-gated or sequential responses • Suitable for complex tissue microenvironments	• Complex synthesis and tuning • Cross-interference between triggers • • Difficult to model dynamic coupling	pH + ROS-responsive PEG–PCLA gels, thermo + photo SMP composites	• Sequential drug delivery • Logic-gated therapeutic scaffolds • Self-adaptive 4D printed implants	[182–186]

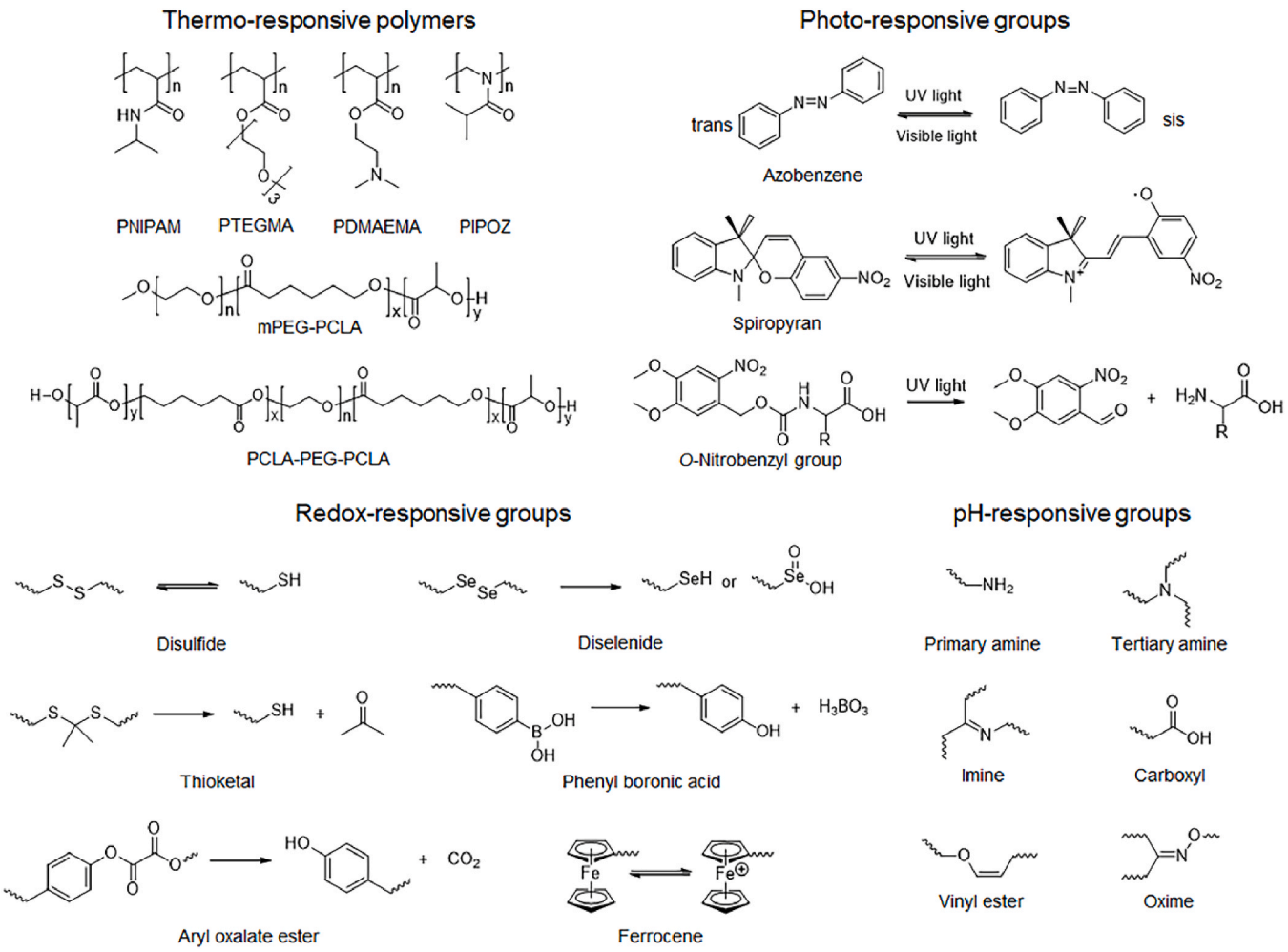

Fig. 4. Stimuli-responsive functional groups and mechanisms. Chemical groups such as acetal, disulfide, and boronate respond to pH, redox, enzymes, or light through reversible or irreversible reactions. Light-sensitive groups like nitrobenzyl and coumarin degrade under UV or visible light. Thermoresponsive, ion-sensitive, and click-reactive groups further enable dynamic control in smart polymer systems.

3.2. Mechanisms pathways of stimuli-induced polymer transformations

Stimulus recognition at the molecular level must translate into measurable changes in polymer behavior. The underlying mechanisms often involve:

- **Conformational transitions:** Changes in the charge state, hydrogen bonding, or polarity of certain groups can induce coil-to-globule transitions in linear polymer chains. This switch in conformation alters solubility, viscosity, or hydrodynamic size, enabling applications in separations, controlled release, or nanoparticle assembly [197].
- **Phase separation and aggregation:** Polymers with thermoresponsive components may undergo phase separation upon heating above their LCST [46]. Similarly, pH shifts can lead to micelle formation or disassembly in amphiphilic block copolymers [198], with hydrophobic segments collapsing or exposing hydrophobic domains under specific conditions [199].
- **Network expansion or contraction:** In hydrogels, reversible swelling and deswelling occur when ionic or hydrogen bonding interactions change in response to stimuli [200]. This enables the polymer to regulate the diffusion of solutes, making it useful in drug delivery systems, sensors, and tissue scaffolds where regulated mass transport is essential [201].
- **Chemical bond cleavage or formation:** Certain stimuli can break or form covalent bonds within the polymer, leading to irreversible changes such as polymer degradation or reversible linking/unlinking events that convert macroscopic properties such as modulus or permeability on demand [8,202].

3.3. Synthetic strategies to customize polymer reactivity and responsiveness

Optimizing polymer responsiveness requires selecting appropriate synthetic routes to incorporate functional groups with spatial and compositional precision. Three primary synthetic strategies are commonly employed.

3.3.1. Grafting

Grafting is a widely employed strategy to functionalize polymer backbones with stimuli-responsive moieties, thereby imparting environmental sensitivity to otherwise inert macromolecules [203]. This can be achieved through three principal approaches: “grafting onto,” “grafting from,” and “grafting through,” each offering different levels of control, efficiency, and architectural complexity **(**Fig. 5**a)** [204].

- The “grafting onto” method involves the post-polymerization attachment of preformed functional chains onto a reactive polymer backbone. This approach offers high modularity and compatibility,

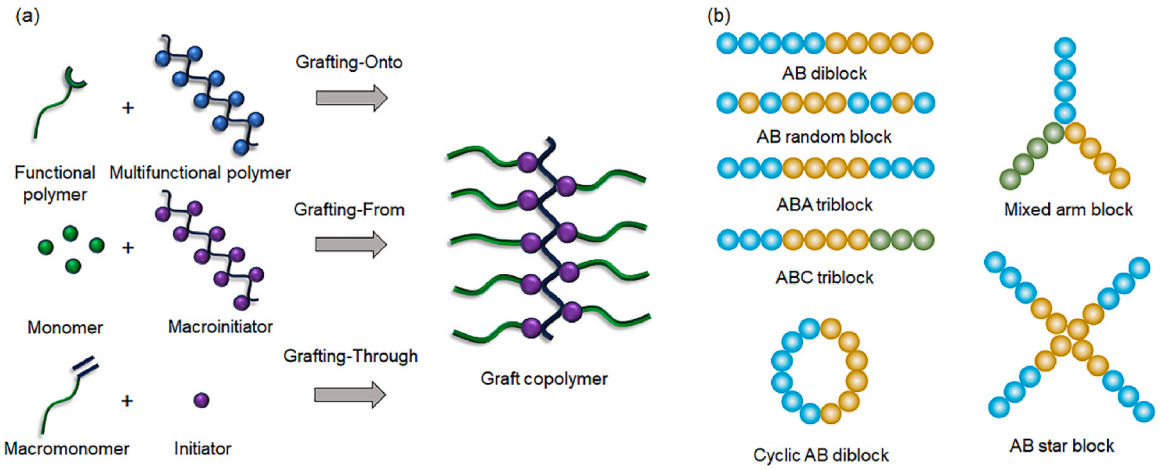

Fig. 5. Grafting strategies and copolymer architectures in stimuli-responsive polymer systems. (a) Grafting methods including "grafting to," "grafting from," and "grafting through" approaches enable functional chain incorporation onto polymer backbones. (b) Representative copolymer structures: random, alternating, block, gradient, star-shaped, cyclic, and crosslinked architectures used to tune physical and responsive properties.

allowing for the selective incorporation of photoresponsive or thermoresponsive segments without altering the base polymer structure.

- The "grafting from" strategy initiates polymerization directly from reactive sites along the backbone, enabling dense and uniform grafting of responsive side chains, such as pH-sensitive or redox-sensitive blocks. This method is advantageous for achieving high grafting density and tailored stimuli-responsiveness.
- In the "grafting through" approach, macromonomers bearing reactive groups are polymerized to simultaneously form the backbone and incorporate side chains, allowing precise control over architecture and composition in a single step.

Grafting strategies are often combined with diverse copolymer architectures, such as random, alternating, block, gradient, star-shaped, cyclic, or crosslinked networks, which can be engineered to finely tune the mechanical, transport, and stimuli-responsive properties of the resulting materials **(**Fig. 5**b)** [205]. For instance, block or gradient copolymers can segregate into distinct domains upon stimulus exposure, while star or cyclic topologies may exhibit enhanced elasticity or compactness for biomedical applications.

3.3.2. *Copolymers and block architectures*

Copolymers are a powerful tool for designing materials that combine multiple functionalities. By creating block copolymers, where each block responds differently to a given stimulus, hierarchical and multi-stage responses can be achieved [206]. For instance, a diblock copolymer may consist of a hydrophilic, pH-sensitive block and a thermo-sensitive block, forming micelles whose size and structure can be modulated by both pH and temperature [207]. Control over composition, sequence, and block lengths through living polymerization techniques (e.g., atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and ring-opening metathesis polymerization (ROMP) enables precise tuning of the polymer's responsiveness [208].

3.3.3. *Crosslinking and network formation*

Crosslinking polymers into a 3D network (hydrogels or elastomers) creates a robust scaffold in which responsiveness can be controlled by the density and type of crosslinks [209]. Incorporating stimuli-responsive crosslinkers (e.g., disulfide bonds for redox response, photolabile bonds for UV-triggered release) enables the creation of networks that swell, degrade, or stiffen under predefined conditions [210]. By adjusting crosslink density and distribution, researchers can fine-tune the magnitude and kinetics of swelling or degradation responses, allowing the design of hydrogels for controlled release, tissue engineering scaffolds, or membrane valves that open or close in response to a given trigger [211].

3.4. *Strategies for designing multi-stimuli-responsive polymers*

In complex biological and environmental systems, multiple factors may change simultaneously. To address these challenges, polymers must be engineered to respond to more than one stimulus, providing enhanced control and specificity [212]. Therefore, this session will introduce various approaches to achieve multi-stimuli responsiveness.

3.4.1. *Incorporation of multiple responsive units*

A widely used approach to achieve multi-stimuli responsiveness involves the integration of distinct functional moieties or domains into a single polymer matrix, each sensitive to a different external or internal trigger [213]. For example, diblock and triblock copolymers can be designed to contain a pH-responsive segment (e.g., -COOH or -NH_2), a thermo-responsive domain (e.g., PNIPAM or PCLA-based blocks), and a photoresponsive unit (e.g., azobenzene or coumarin), thereby enabling orthogonal and finely tunable control over polymer behavior in complex environments [214–216].

Such multifunctional designs allow polymeric systems to exhibit sequential, synergistic, or orthogonal responses when exposed to combinations of stimuli, enhancing their functional complexity for applications such as targeted drug delivery, biosensing, and smart coatings. A notable example includes drug carriers that remain inert during systemic circulation, accumulate at pathological sites due to a pH gradient, and release their cargo upon external light or thermal activation, offering spatiotemporal control and improved therapeutic efficacy [217].

The overall strategies and representative molecular mechanisms for designing such polymers are illustrated in Fig. 6, where various stimuli-responsive moieties including enzyme-cleavable peptides, pH-sensitive linkers, redox-labile bonds, photo-cleavable groups, and thermo-responsive segments are embedded within the polymer framework. This multi-responsive integration provides a robust platform for engineering smart polymer systems tailored to the demands of advanced biomedical and environmental technologies.

3.4.2. *Cascade or hierarchical responses*

A more sophisticated approach involves constructing polymers with hierarchical triggers. In this design, an initial stimulus (e.g., mild heating) induces a structural rearrangement that exposes new reactive sites for a secondary stimulus (e.g., pH shift) [31]. This controlled, sequential

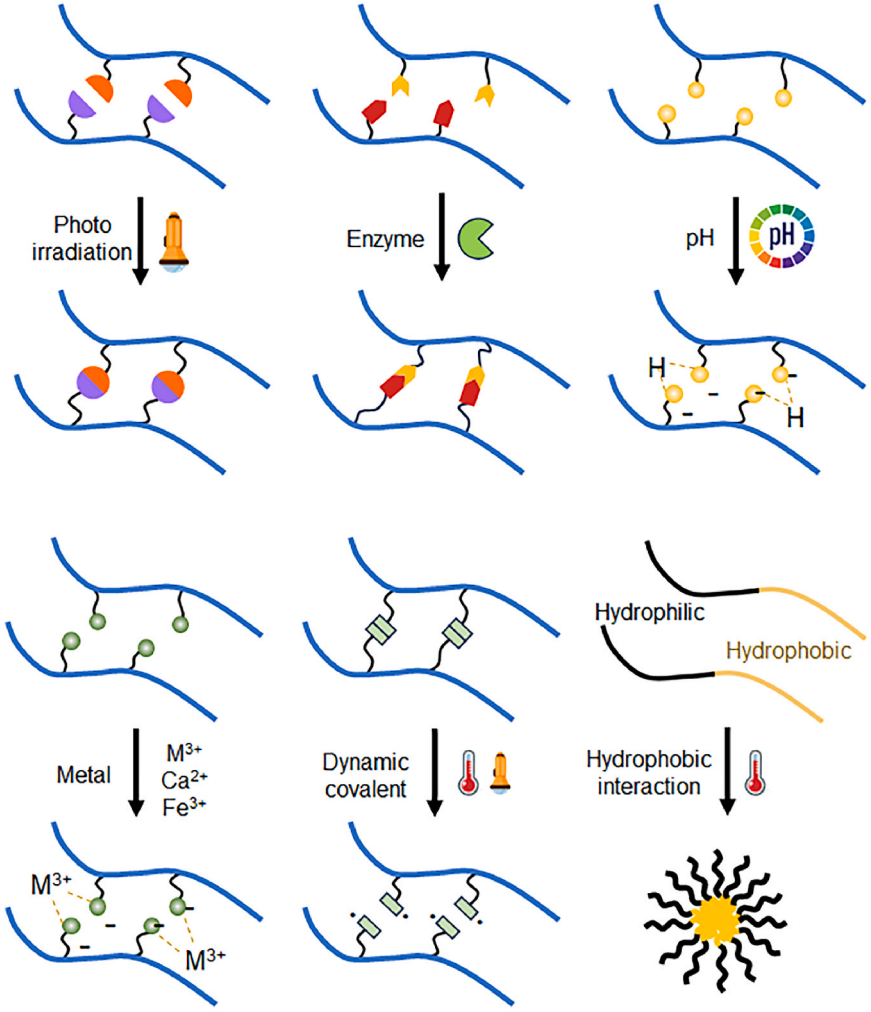

Fig. 6. Strategies for incorporating multiple stimuli-responsive units into polymer systems. Examples include the integration of photo-, enzyme-, pH-, redox-, and thermo-responsive moieties into a single polymer backbone, enabling multi-triggered responses. Such designs allow for sequential, synergistic, or orthogonal activation in response to different stimuli, enhancing functional complexity for advanced biomedical or environmental applications.

responsiveness mimics biological signal transduction pathways and is particularly valuable for applications requiring multi-step functionality. Examples include stepwise drug release or dynamic sensors that adapt their mode of operation based on changing environmental conditions [218].

3.4.3. *Use of hybrid materials and nanocomposites*

Polymers can be endowed with multiple responsive modalities by integrating inorganic nanoparticles, quantum dots, or metallic nanorods that respond to magnetic or optical stimuli [219]. For instance, a hydrogel loaded with magnetic nanoparticles and temperature-sensitive moieties can respond to both magnetic fields (through heating or shape change) and temperature variations, enabling remote control of drug release or mechanical properties [220]. Similarly, incorporating enzymes or biomolecules that selectively degrade polymer segments in response to target analytes adds another layer of responsiveness [221].

4. Synthesis and fabrication techniques

The development of SRPs heavily depends on innovative synthesis and fabrication techniques that allow precise control over their molecular architecture, responsiveness, and functionality [13]. By integrating advanced synthetic strategies with state-of-the-art fabrication methods, researchers can design materials tailored for specific medical and environmental applications [222]. This section discusses the synthesis methods and fabrication techniques that enable the realization of these intelligent polymer systems.

4.1. *Modular synthesis strategies*

SRPs are designed using carefully selected synthetic strategies that incorporate functional groups and structural features essential for responsiveness. These strategies prioritize versatility, precision, and scalability.

4.1.1. *Click chemistry approaches*

Click chemistry has emerged as a versatile platform for functionalizing SRPs, offering highly efficient, selective, and modular reactions that proceed under mild conditions [223]. Representative strategies include azide–alkyne cycloaddition (CuAAC), thiol-ene coupling, Diels-Alder reactions, and oxime or hydrazone formation, which facilitate the orthogonal attachment of diverse functional groups to polymer backbones or side chains [224].

By leveraging these reactions, SRPs can be precisely modified with stimuli-sensitive moieties, such as redox-labile disulfide bonds introduced via thiol-based reactions, enabling targeted degradation in reducing environments (e.g., intracellular compartments) for controlled drug release [225]. Fig. 7 illustrates these widely used click reactions and their role in enabling customizable and biocompatible SRP architectures for advanced biomedical applications.

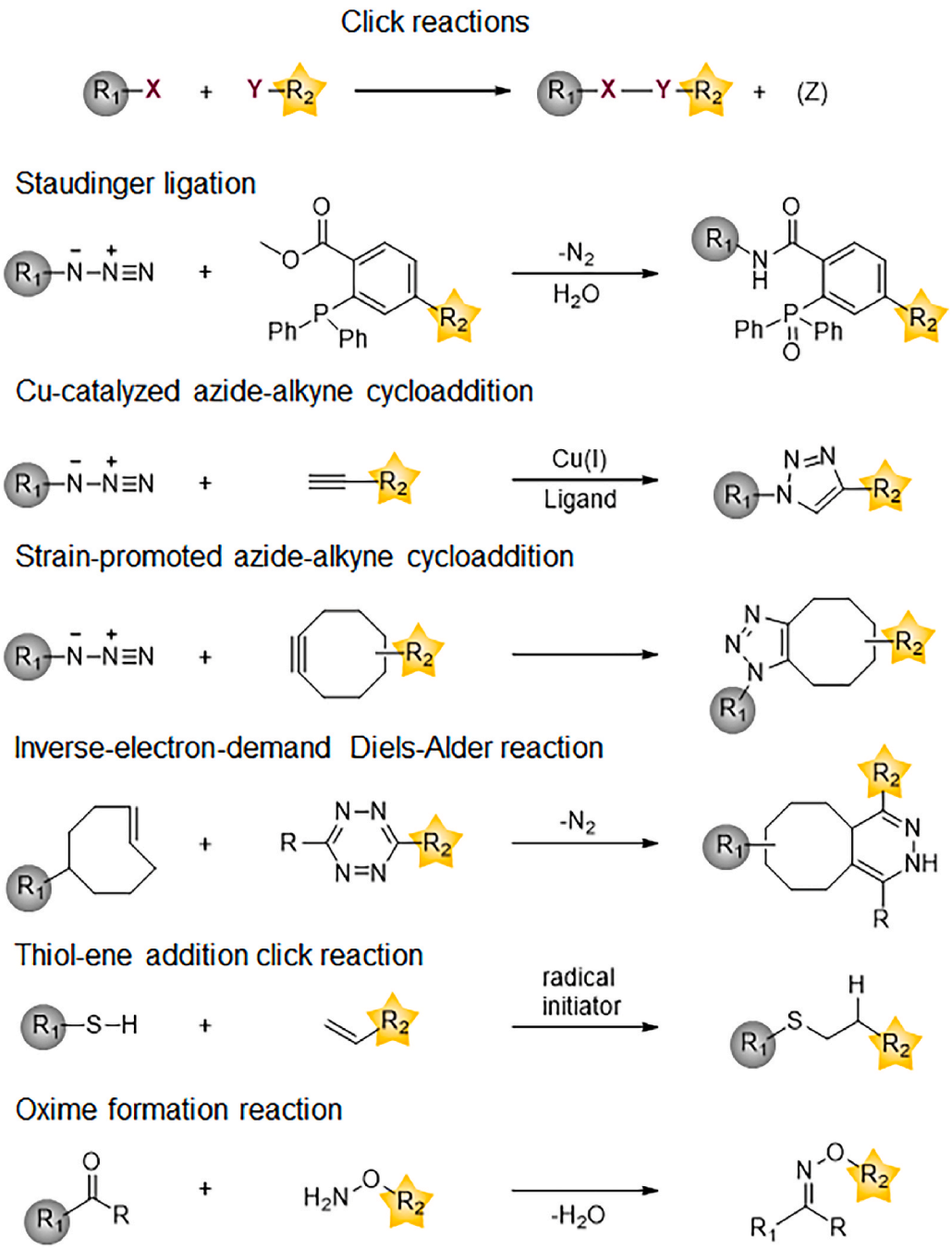

Fig. 7. Representative click chemistry reactions for polymer functionalization. Various efficient and selective click reactions including azide-alkyne cycloaddition (CuAAC), thiol-ene, Diels–Alder, oxime formation, and related cycloadditions enable modular and orthogonal conjugation of functional groups (R_1 and R_2) to polymer backbones or side chains. These reactions proceed under mild conditions and are widely used in stimuli-responsive polymer design and bioconjugation.

4.1.2. Living polymerization techniques

Living/controlled polymerization techniques such as RAFT, ATRP, and ROMP have enabled precise control over polymer chain length, architecture, composition, and end-group functionality, making them invaluable in the synthesis of stimuli-responsive polymers [226]. These methods allow the construction of diverse polymer topologies, including block, graft, brush, and star-shaped polymers, with tailored segmental properties for multi-functional applications [208].

For instance, ATRP has been widely used to fabricate amphiphilic block copolymers integrating both temperature-sensitive and pH-responsive domains, yielding materials capable of dual-stimuli response for applications in targeted drug delivery, environmental sensing, and smart nanocarriers [227]. As illustrated in Fig. 8, these polymerization strategies offer a versatile foundation for engineering complex macromolecular structures such as random, block, graft, and dendritic polymers with programmable stimuli sensitivity.

4.1.3. Bio-inspired synthesis

Bio-inspired approaches to polymer synthesis mimic natural systems by incorporating motifs such as peptide sequences, saccharides, or biomimetic functional groups. These materials are designed to respond to specific biological cues, such as enzymatic activity or biomolecule concentrations [228]. For instance, polymers with enzyme-cleavable peptide bonds can selectively degrade in disease-specific microenvironments, allowing targeted therapeutic delivery. This approach leverages the specificity and efficiency of natural systems to create highly

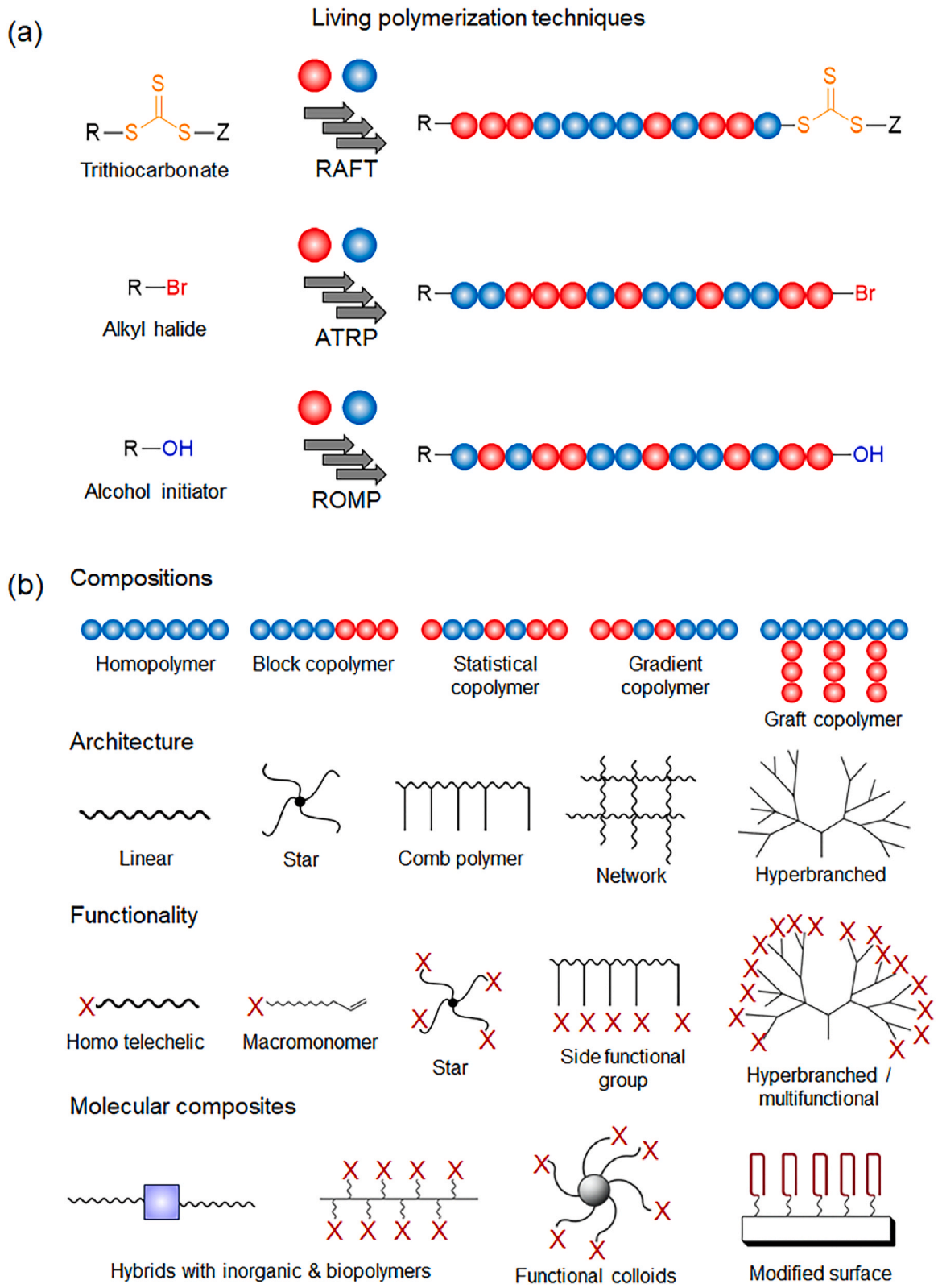

Fig. 8. Living polymerization techniques for stimuli-responsive polymer synthesis. (a) Major living polymerization methods RAFT, ATRP, and ROP enable precise control over polymer length, sequence, and end-group functionality. (b) Resulting polymer architectures: linear, block, random, graft, star, brush, dendritic, and surface-grafted forms, allowing tailored material properties for advanced applications.

adaptive materials [229].

4.1.4. *Multi-stimuli integration*

Advanced polymer designs often integrate multiple responsive units to achieve complex functionality. By combining distinct functional groups, such as pH-sensitive carboxyl groups, thermo-responsive PNIPAM segments, and photochromic azobenzene moieties, researchers can create polymers that respond to multiple triggers simultaneously or

sequentially [230]. This multi-stimulus responsiveness is especially useful for applications requiring sophisticated control, such as smart drug delivery systems that release payloads in a stepwise manner in response to pH, temperature, and light [231].

4.2. Advanced fabrication techniques

Fabrication techniques are crucial for transforming synthesized polymers into functional materials with the desired properties. These methods ensure the preservation and optimization of polymer responsiveness for practical applications.

4.2.1. Solvent casting

Solvent casting is a conventional method for fabricating thin films of stimuli-responsive polymers by dissolving the polymer in a volatile solvent, casting it into a mold or flat surface, and allowing the solvent to evaporate, forming a homogeneous film layer [232]. As shown in Fig. 9**a**, this technique enables control over film morphology through solvent selection and drying conditions, directly impacting surface properties and mechanical characteristics. Solvent-cast films are particularly suited for applications such as pH-responsive membranes and temperature-sensitive coatings for environmental or biomedical use [233,234].

4.2.2. Electrospinning

Electrospinning utilizes a high-voltage electric field to generate continuous polymer nanofibers from solution, producing mats with high porosity and surface area, as depicted in Fig. 9**b**. This technique is highly effective in engineering stimuli-responsive nanofibers for targeted drug delivery, tissue scaffolding, and biosensing applications. For example, electrospun mats made from temperature-sensitive polymers can regulate drug release profiles in response to local thermal cues [235,236].

4.2.3. Layer-by-layer assembly

Layer-by-layer (LbL) assembly involves the sequential deposition of oppositely charged polyelectrolytes to construct multilayered films with precise nanoscale control over thickness and composition, as illustrated in Fig. 9**c**. By incorporating different SRPs in alternating layers, LbL systems can be engineered for multi-functional or hierarchical responses to various stimuli [237]. These films are particularly valuable for applications requiring dual or sequential triggering, such as pH- and light-responsive drug delivery coatings [238].

4.2.4. 3D Printing and additive manufacturing

Advanced additive manufacturing technologies, including stereolithography and direct ink writing, allow precise spatial patterning of SRP-based structures, as shown in Fig. 9**d**. These techniques enable the integration of complex architectures and multiple responsive materials into a single construct, making them especially advantageous in tissue engineering and regenerative medicine [239]. For example, 3D-printed hydrogels embedded with pH- and temperature-sensitive domains can be engineered for controlled cell growth, spatiotemporal drug delivery, and organoid development [240,241].

A key consideration in designing SRPs for biomedical additive manufacturing is ensuring alignment between the type of stimulus and the chosen printing technology [30,50]. Light-responsive polymers, for example, are especially suitable for digital light processing (DLP) and two-photon polymerization (2PP), where photo-crosslinking enables

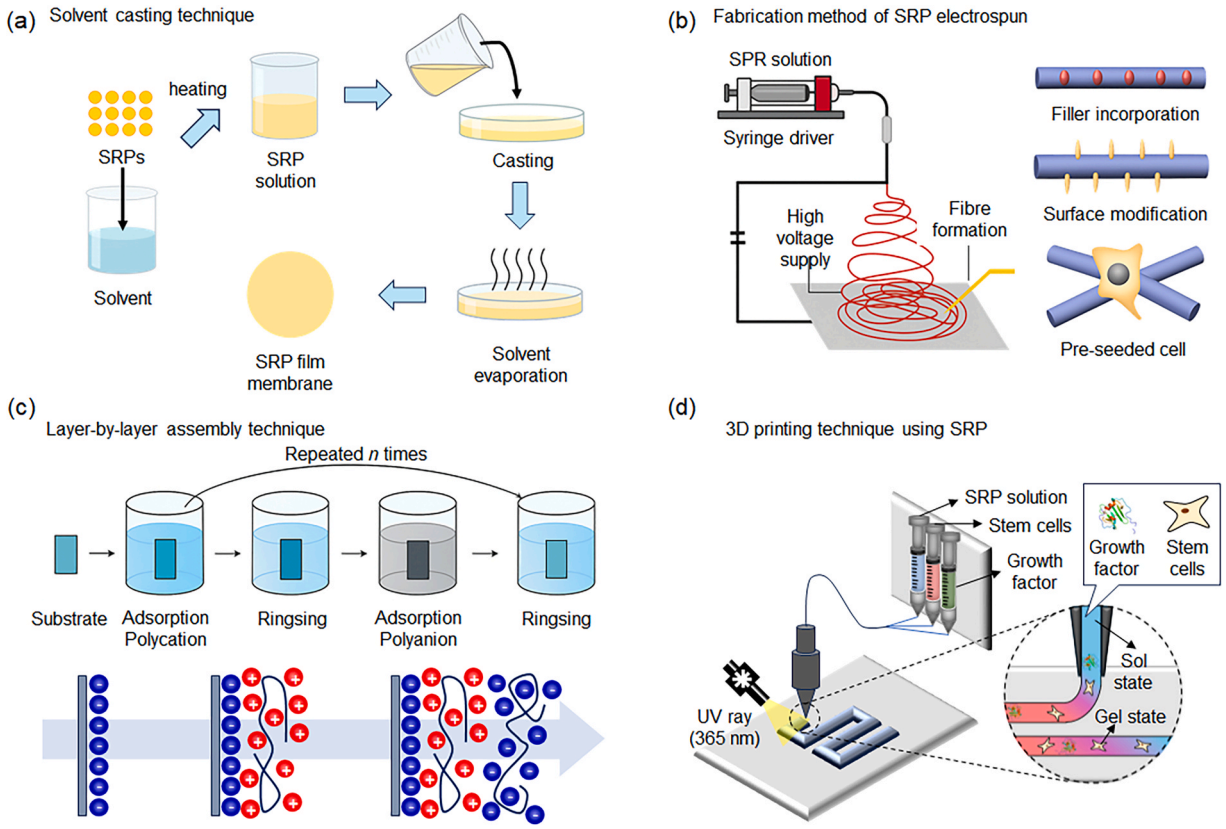

Fig. 9. Advanced fabrication techniques for stimuli-responsive polymer systems. (a) Solvent casting: Polymer solutions are poured into molds and dried to form thin films. (b) Electrospinning: High-voltage electrostatic force draws polymer fibers from solution to create nanofiber mats used in drug delivery and tissue scaffolds. (c) Layer-by-layer assembly: Polyelectrolyte multilayers are built up through alternating immersion in oppositely charged solutions, allowing nanoscale control over film composition and thickness. (d) 3D printing and photopatterning: Light-assisted 3D printing enables precise spatial structuring of stimuli-responsive hydrogels loaded with cells or bioactive factors for tissue engineering and biomedical applications.

high-resolution constructs with precise spatial and temporal control [52,56]. In contrast, thermo-responsive hydrogels, such as PNIPAM- and Pluronic-based systems, are well suited for extrusion-based bioprinting, as their sol–gel transitions near physiological temperatures enhance printability and support in situ gelation [47,49]. Magnetic- and electric-responsive composites open new possibilities for 4D printing, allowing printed constructs to be remotely actuated or dynamically reconfigured under external fields, an approach that offers exciting potential for smart biomedical devices [61]. Likewise, enzyme- and pH-responsive systems can be incorporated into bioinks to enable on-demand degradation or controlled release after implantation, coupling biological specificity with fabrication versatility [42]. By strategically aligning stimulus characteristics with suitable 3D/4D printing modalities, SRPs can be more effectively translated into practical biomedical constructs that combine adaptive responsiveness, structural fidelity, and clinical functionality [29,30].

4.3. Hybridization and composite fabrication

The hybridization of SRPs with other materials is an innovative strategy to enhance their functionality and broaden their range of applications. By combining polymers with complementary components, these hybrids can exhibit properties that surpass those of the individual materials. This section explores the design and applications of polymer-nanoparticle hybrids, responsive hydrogels, and post-fabrication surface modifications, emphasizing their unique capabilities and versatility.

4.3.1. Polymer-nanoparticle hybrids

SRPs can be functionalized into hybrid materials by incorporating nanoparticles such as gold nanorods, magnetic nanoparticles, and quantum dots thereby imparting synergistic properties including external responsiveness and enhanced diagnostic or therapeutic capability [242,243]. For example, gold nanorods confer photothermal functionality via localized surface plasmon resonance, enabling efficient light-to-heat conversion for applications like photothermal therapy [244]. Magnetic nanoparticles embedded within polymer matrices enable remote actuation or magnetic hyperthermia, while quantum dots offer tunable fluorescence useful for real-time bioimaging and environmental sensing [245].

These multifunctional polymer-nanoparticle hybrids find broad utility in theranostics, smart coatings, and environmental remediation, owing to their ability to respond to external triggers such as temperature, light, or magnetic fields. As shown in Fig. 10, these systems have been widely applied in drug and gene delivery, biosensing, photothermal/photodynamic therapy (PTT/PDT), and bioimaging, offering enhanced stability, targeted functionality, and on-demand activation [246]. Nevertheless, uniform nanoparticle dispersion and long-term stability within the polymer matrix remain key challenges that necessitate continued optimization in synthesis protocols and compatibility tuning.

4.3.2. Responsive hydrogels

Responsive hydrogels are highly adaptable materials that swell or shrink in response to specific stimuli, making them ideal for applications requiring dynamic behavior. These hydrogels can be further enhanced by incorporating functional fillers such as enzyme-loaded microcapsules, metal-organic frameworks (MOFs), or bioactive particles [247]. For example, enzyme-loaded microcapsules allow the hydrogel to respond to enzymatic triggers, enabling targeted drug delivery or biosensing applications [248]. MOFs, characterized by their tunable pore structures and high surface areas, serve as versatile additives that can significantly reinforce hydrogel matrices, enhance their biocompatibility, and introduce new functionalities [249]. As illustrated in Fig. 11a, the incorporation of MOFs into SRP hydrogels results in composite materials with improved mechanical stability and advanced chemical reactivity.

Moreover, bioactive fillers like hydroxyapatite or silica nanoparticles further improve the structural integrity and biological performance of hydrogels, broadening their utility in biomedical engineering [250]. The resulting MOF-SRP hybrid hydrogels enable a wide array of high-value applications, as summarized in Fig. 11b, including wound healing, controlled drug delivery, biosensing, antimicrobial barrier materials, cartilage regeneration, enzymatic biocatalysis, and precision 3D printing platforms. These multifunctional systems are especially promising

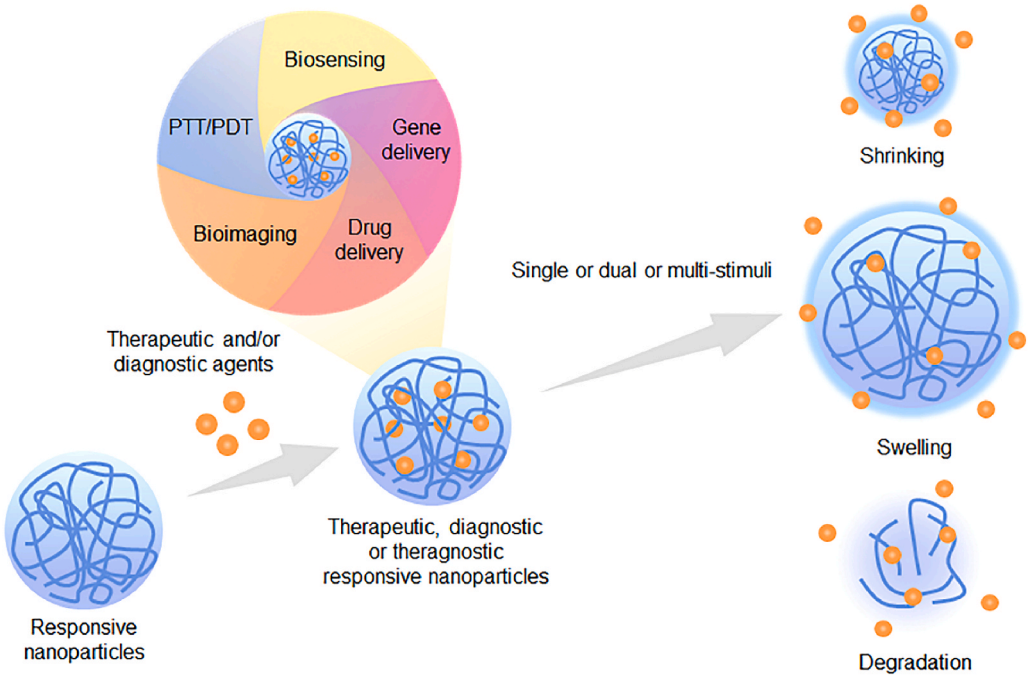

Fig. 10. Applications of polymer-nanoparticle hybrids. These systems enable drug and gene delivery, bioimaging, biosensing, and PTT/PDT, offering enhanced stability, responsiveness, and multifunctionality.

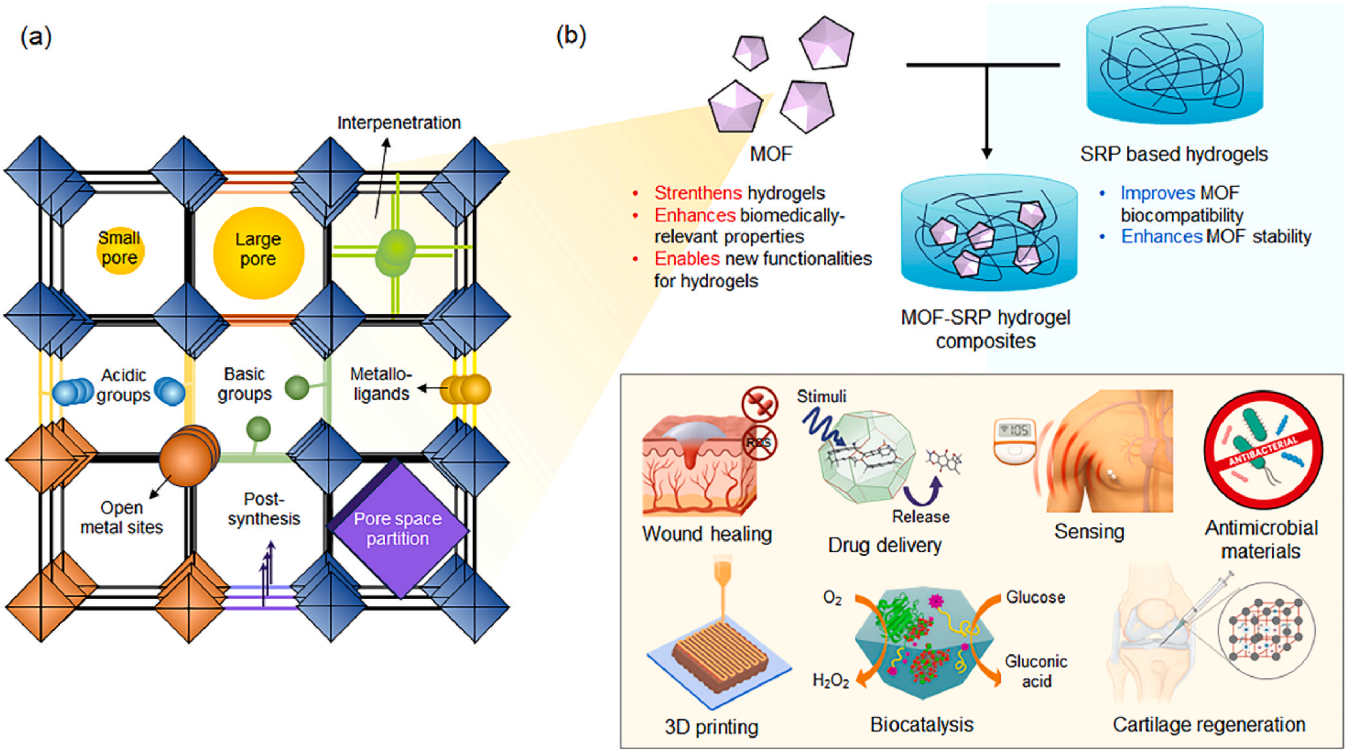

Fig. 11. MOF-integrated stimuli-responsive hydrogels and their biomedical applications. (a) MOFs with tunable pore structures and functional metallo-ligands used to enhance SRP-based hydrogels. MOF-SRP composites improve hydrogel strength, biocompatibility, and functionality. (b) Applications of MOF-hydrogel composites in wound healing, drug delivery, biosensing, antimicrobial materials, cartilage regeneration, biocatalysis, and 3D printing.

for next-generation smart biomedical devices and regenerative scaffolds [251]. Nevertheless, achieving a precise balance between the hydrogel's stimuli-responsiveness and mechanical robustness remains a critical design challenge, necessitating optimized synthesis strategies and matrix-filler compatibility.

4.3.3. *Post-fabrication surface modification*

Post-fabrication surface modification is an essential technique for enhancing the functionality of pre-fabricated SRPs. This approach allows for selective tuning of surface properties without altering the bulk characteristics of the material, thereby enabling adaptation to diverse

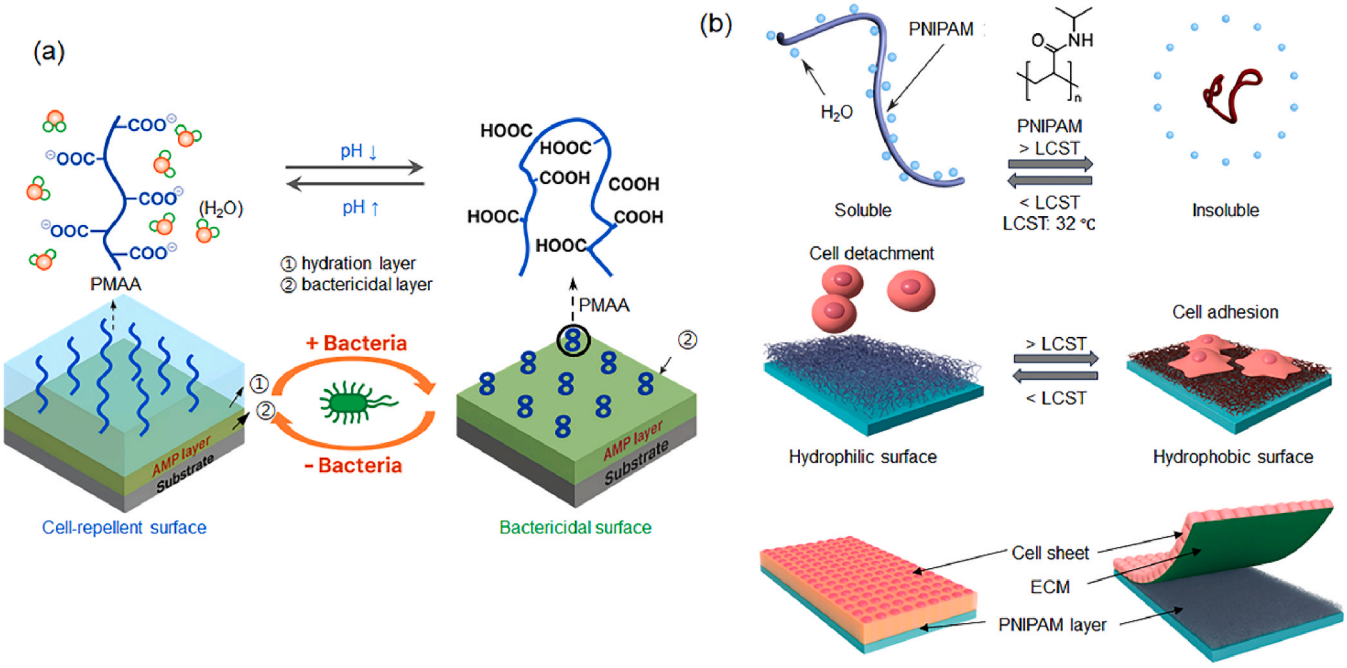

Fig. 12. Post-fabrication surface modifications of stimuli-responsive polymer systems. (a) pH-responsive surfaces utilizing AMPs for reversible transitions between cell-repellent and bactericidal states depending on pH [258]. (b) Temperature-responsive PNIPAM-modified surfaces that switch between hydrophilic (cell-adhesive) and hydrophobic (cell-repellent) states, enabling dynamic cell patterning and detachment [259]. Copyright 2018, Elsevier Ltd.

application environments [252]. Techniques such as plasma treatment, grafting, and LbL assembly are frequently employed [253,254]. For instance, plasma treatment introduces polar functional groups onto the polymer surface, improving hydrophilicity or facilitating secondary chemical modifications [255]. Grafting enables the introduction of responsive moieties such as pH-sensitive or photoresponsive groups directly onto the surface, expanding functional adaptability. Similarly, LbL assembly provides nanoscale control over surface composition and gradient functionalities, which is advantageous in sensors and drug release systems [256,257].

As illustrated in Fig. 12a, pH-responsive coatings using antimicrobial peptides (AMPs) can reversibly switch between a bactericidal state and a cell-repellent state, depending on environmental pH, offering a promising strategy for infection-responsive medical coatings [258]. In Fig. 12b, temperature-responsive surfaces grafted with PNIPAM demonstrate reversible switching between hydrophilic (cell-adhesive) and hydrophobic (cell-repellent) states, enabling dynamic control of cell attachment and detachment for biomedical devices or tissue engineering platforms [259]. These surface modifications have shown considerable promise in the development of anti-fouling membranes, environmental sensors, and stimuli-triggered therapeutic surfaces.

Nevertheless, maintaining surface functionality over prolonged use remains a significant challenge, particularly under fluctuating environmental conditions. Continued innovation in post-fabrication chemistry and surface engineering is vital to improving the durability, responsiveness, and application scope of these smart polymeric materials [260].

4.4. Optimization of processing conditions

The performance and long-term stability of SRPs are heavily influenced by their processing conditions. Optimizing these conditions is crucial for ensuring uniform material properties, enhancing responsiveness to stimuli, and minimizing defects or inconsistencies in the final product. This section highlights the key factors involved in optimizing processing conditions, including the control of drying and annealing processes, environmental tuning during fabrication, and scalable manufacturing techniques.

4.4.1. Control of drying and annealing

Drying and annealing are essential steps in the fabrication of SRPs, as they significantly influence the material's structural integrity, responsiveness, and physical properties. Improper control of these processes can lead to residual stresses, uneven structures, or reduced performance [261].

During the drying process, careful management of solvent removal from the polymer matrix is crucial. Slow and controlled solvent evaporation is often necessary to prevent surface defects such as cracks, voids, or uneven thickness in polymer films. Optimized drying temperatures help ensure complete solvent removal without compromising sensitive functional groups or stimuli-responsive elements [262]. For instance, temperature-sensitive polymers require precise temperature control to avoid degradation or undesirable changes in their critical solution temperature [263].

Annealing is equally important, as it enhances the crystallinity and phase separation of polymers. By exposing the material to elevated temperatures for a controlled period, annealing can improve thermal and mechanical properties, such as tensile strength and elasticity [264]. Additionally, annealing can alleviate residual stresses introduced during fabrication, leading to more consistent and reproducible material behavior under applied stimuli [265].

4.4.2. Environmental tuning

The fabrication environment plays a critical role in the stability and functionality of SRPs [266]. Controlled atmospheres, such as inert gas environments or humidity-regulated chambers, are commonly used to minimize unwanted side reactions and preserve sensitive functional groups during synthesis or processing [267].

For example, polymers with redox-sensitive or pH-responsive moieties may degrade or lose functionality when exposed to oxygen, moisture, or other reactive species during processing. Using inert gases such as nitrogen or argon helps prevent oxidative degradation, ensuring the integrity of these functional groups [268]. Similarly, controlling humidity is vital for hydrophilic or hygroscopic polymers, as excess moisture can alter their swelling behavior, responsiveness, or mechanical properties [269].

Beyond preserving the material's chemical structure, environmental tuning can enhance the reproducibility of fabrication processes. For instance, maintaining consistent environmental conditions during film casting or extrusion ensures uniform thickness, surface morphology, and responsiveness in the final product [270].

4.4.3. Scalable manufacturing

To facilitate the transition of SRPs from laboratory-scale research to industrial-scale applications, the development of scalable manufacturing processes is essential. These processes must preserve the desired material properties while enabling cost-effective and reproducible production at a larger scale [271].

Continuous flow synthesis is a promising approach for scaling up the polymerization process. This technique allows for precise control over key reaction parameters, such as temperature, flow rate, and mixing, which ensures consistent molecular weights and structures of the resulting polymers [272]. Furthermore, continuous flow systems minimize batch-to-batch variations, thereby enhancing the reproducibility and uniformity of the final product.

For the large-scale production of films or membranes, roll-to-roll processing has proven to be an effective method. This technique involves the continuous deposition and processing of polymer solutions onto a substrate, enabling the fabrication of large-area films with uniform thickness and consistent properties [273]. Roll-to-roll processing is particularly advantageous for applications requiring scalability and cost efficiency, such as smart coatings, responsive membranes, and thin-film sensors [274].

Additionally, emerging additive manufacturing techniques, such as 3D printing, present new opportunities for the scalable production of complex polymer structures [275]. Methods such as direct ink writing and stereolithography allow for the creation of intricate geometries with precise spatial control over the material's responsiveness, making them suitable for advanced medical devices and environmental applications.

5. Biomedical applications of SRPs: Toward precision medicine

SRPs have become a transformative class of materials in biomedical applications due to their ability to dynamically adapt to physiological or external stimuli. These intelligent polymers can undergo controlled structural or chemical changes, enabling their use in drug delivery, tissue engineering, biosensing, and wound healing. This section discusses solutions for controlled, targeted, and on-demand therapeutic release using SRPs.

5.1. Controlled delivery with SRPs: Controlled, targeted, and on-demand release

pH-responsive polymers exploit the varying pH levels in different biological environments, such as the acidic tumor microenvironment (pH ~6.5) or the intracellular lysosomes and endosomes (pH ~5.0) [276]. These polymers incorporate functional groups such as carboxylic acids or amino groups that undergo ionization, swelling, or dissolution in response to acidic conditions.

For instance, pH-sensitive polymeric nanoparticles can be designed with a core-shell structure. These nanoparticles remain stable at neutral physiological pH (7.4) during circulation, ensuring drug stability [277].

Upon reaching acidic environments, such as those found in tumor tissues or intracellular compartments, the polymer shell disassembles, releasing the encapsulated drug precisely at the target site. This mechanism not only enhances drug concentrations at the affected location but also minimizes unintended effects on healthy tissues [278]. Common materials used in these systems include poly(β-amino ester)s and poly (lactic-co-glycolic acid) (PLGA)-based copolymers, which have shown significant success in delivering chemotherapeutic agents such as doxorubicin [279].

5.1.1. pH-responsive drug carriers

Various biological environments, such as the acidic tumor microenvironment (pH ~6.5) or intracellular lysosomes (pH ~5.0), exhibit distinct pH profiles. Polymers incorporating pH-sensitive groups, such as carboxyl or amino moieties, undergo solubility or swelling changes under these conditions [31,276]. For instance, pH-responsive polymeric nanoparticles remain stable at physiological pH (7.4) but release their payload in acidic environments, ensuring precise targeting of cancer cells or infected tissues [278].

5.1.2. Redox-responsive carriers

Redox-responsive polymers leverage the differences in redox potential between intracellular and extracellular environments. The cytosol contains high concentrations of reducing agents, such as GSH, which are 100–1000 times more concentrated than those in the extracellular matrix [190,280]. Redox-sensitive polymers incorporate disulfide bonds into their structure, which remain stable in oxidative conditions but break down in reductive environments [210].

For example, micelles formed from amphiphilic block copolymers with disulfide-linked hydrophobic cores can encapsulate hydrophobic drugs. When these micelles are internalized by cells, the high GSH levels in the cytosol cleave the disulfide bonds, disassembling the micelles and releasing the drug payload [281]. This mechanism ensures that drug release occurs specifically within cells, making it highly effective for cancer therapies or intracellular gene delivery Similar strategies have been used to develop polymeric vectors for delivering siRNA or DNA, improving delivery efficiency and minimizing cytotoxicity [282].

5.1.3. Temperature- and light-responsive systems

Thermoresponsive polymers such as PNIPAM, PCLA-PEG-PCLA, mPEG-PCLA, and Pluronic exhibit distinct phase transitions governed by a LCST, typically near 32 ℃ [47,283]. Below this LCST, the polymers exist in a hydrated and soluble coil conformation, while exceeding the threshold induces a coil-to-globule transition, leading to hydrophobic aggregation and macroscopic phase separation [197]. This reversible transformation provides a powerful means for modulating sol-gel behavior and drug release kinetics based on local temperature changes.

As shown in Fig. 13a, triblock amphiphilic copolymers self-assemble into micelles at physiological temperature, forming physically crosslinked hydrogels through temperature-induced gelation. Likewise, Fig. 13b illustrates that diblock copolymers can also undergo thermally responsive micellization and reversible aggregation behavior, contributing to tunable gelation characteristics. These polymers are particularly suitable for injectable hydrogel formulations that remain in a sol state at room temperature but undergo rapid in situ gelation upon administration at ~37 ℃, as depicted in Fig. 13c [284].

The resulting hydrogels serve as localized drug depots, offering sustained release profiles, improved therapeutic efficacy, and reduced systemic exposure. This property is highly advantageous for site-specific treatment in oncology or inflammatory diseases, where controlled drug retention and spatiotemporal precision are critical [285].

In addition, light-responsive systems incorporating photochromic or photocleavable groups such as azobenzene or coumarin enable non-invasive activation by UV or NIR light [286]. This mechanism is leveraged in micelle disassembly and on-demand drug release, enhancing therapeutic precision. Furthermore, these systems play a pivotal role in photodynamic therapy (PDT), combining light-triggered drug release with ROS-mediated tumor ablation [287].

5.2. SRPs in tissue engineering and regenerative medicine

SRPs have opened new horizons in tissue engineering and

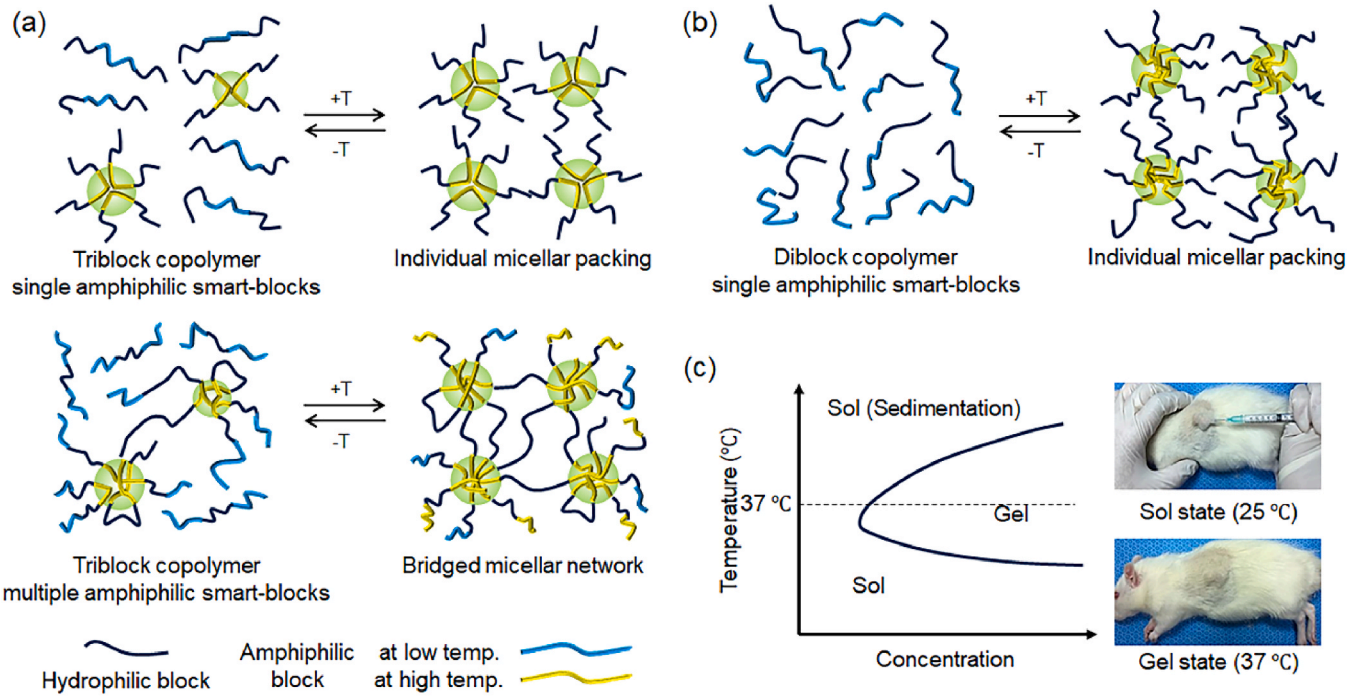

Fig. 13. Schematic illustration of temperature-responsive polymer systems. (a) Temperature-induced micellization and gelation behavior of triblock amphiphilic polymers forming physically crosslinked hydrogels at physiological temperature. (b) Temperature-responsive behavior of diblock copolymers undergoing micelle aggregation and reversible gelation. (c) Injectable hydrogel formation and in vivo retention via temperature-triggered sol-to-gel transition.

regenerative medicine by mimicking the dynamic and complex environments of cellular microenvironments. These advanced materials can interact with cells and tissues in response to physiological or external stimuli, providing enhanced control over cellular processes such as adhesion, proliferation, and differentiation [36,288]. By facilitating the fabrication of adaptive scaffolds, hydrogels, and matrices, SRPs offer versatile solutions for tissue repair, regeneration, and modeling. This section will explore the methods and characteristics of SRPs in tissue engineering and regenerative medicine.

5.2.1. *Injectable hydrogels*

Hydrogels composed of temperature-sensitive polymers, such as PCLA-PEG-PCLA and methoxy mPEG-PCLA, utilize their LCST behavior to enable injectable applications [47]. These polymers remain soluble below their LCST (e.g., at room temperature) and rapidly transition to a gel state when heated above their LCST, such as at body temperature (~37 ℃), forming a localized 3D matrix at the target site [289]. This transition facilitates the minimally invasive delivery of therapeutic agents or cells, while promoting enhanced retention and site-specific action.

As depicted in Fig. 14, injectable hydrogels can be constructed using biocompatible building blocks and crosslinked through either chemical or physical interactions, such as covalent bonds or hydrophobic associations [290]. These crosslinking strategies enable hydrogels to be finely tuned for in situ gelation at physiological conditions [291]. The platform also allows for stimuli-responsive behavior, where external triggers such as pH, temperature, or redox potential regulate the hydrogel structure and drug release profile.

For example, PCLA-PEG-PCLA or mPEG-PCLA-based hydrogels are frequently used to encapsulate bioactive cargos including growth factors or stem cells, aiding in regenerative therapies by providing a structural matrix that supports cellular infiltration, proliferation, and differentiation upon injection into damaged tissues such as cartilage or bone [292]. In addition, pH-sensitive injectable hydrogels functionalized with carboxyl or amine groups can swell or degrade in acidic microenvironments, such as wounds or ischemic tissues, enabling on-demand release of angiogenic factors to stimulate vascular regeneration [293].

Overall, these injectable systems represent a versatile platform for controlled drug delivery, wound healing, and tissue engineering, with Fig. 14's bottom panel providing a concise summary of design components ranging from building blocks to stimuli types and application targets highlighting the modularity and adaptability of these advanced hydrogel systems.

5.2.2. *Responsive scaffolds*

Scaffolds play a critical role in tissue engineering by providing a structural framework that supports cell attachment, migration, and organization. The integration of SRPs into scaffolds introduces an adaptive dimension, allowing them to actively regulate cellular behavior in response to specific triggers [34].

Electroresponsive scaffolds incorporate conductive polymers, such as polypyrrole (PPy), polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and polythiophene derivatives, enabling them to respond to applied electric fields [294]. These scaffolds are particularly advantageous for neural or cardiac tissue engineering, where electrical stimulation is essential for cell function and tissue repair. For instance, applying an electric field to electroresponsive scaffolds can promote neuronal outgrowth or enhance the alignment and contractility of cardiac myocytes, thereby facilitating the regeneration of functional tissues [295].

Photoresponsive polymer-based scaffolds enable spatiotemporal control of cellular environments via light stimuli. Incorporating photochromic groups such as azobenzene, spiropyran, diarylethene, stilbene, fulgides, or naphthopyran, as well as photocleavable moieties like nitrobenzyl derivatives, allows reversible structural changes or bond cleavage under specific wavelengths [53,196]. For example, UV or visible light can trigger the controlled release of growth factors embedded in the scaffold, enabling sequential delivery to guide cell proliferation and differentiation during tissue repair [296]. Photoresponsive scaffolds are also used in wound healing, where light can stimulate the scaffold to release antimicrobial agents or cytokines, accelerating the healing process [297]. Incorporating stimuli-responsive biodegradable polymers into scaffolds ensures their degradation in response to physiological triggers, leaving behind regenerated tissue without the need for surgical removal [298]. Additionally, shape-memory polymers represent another class of responsive materials

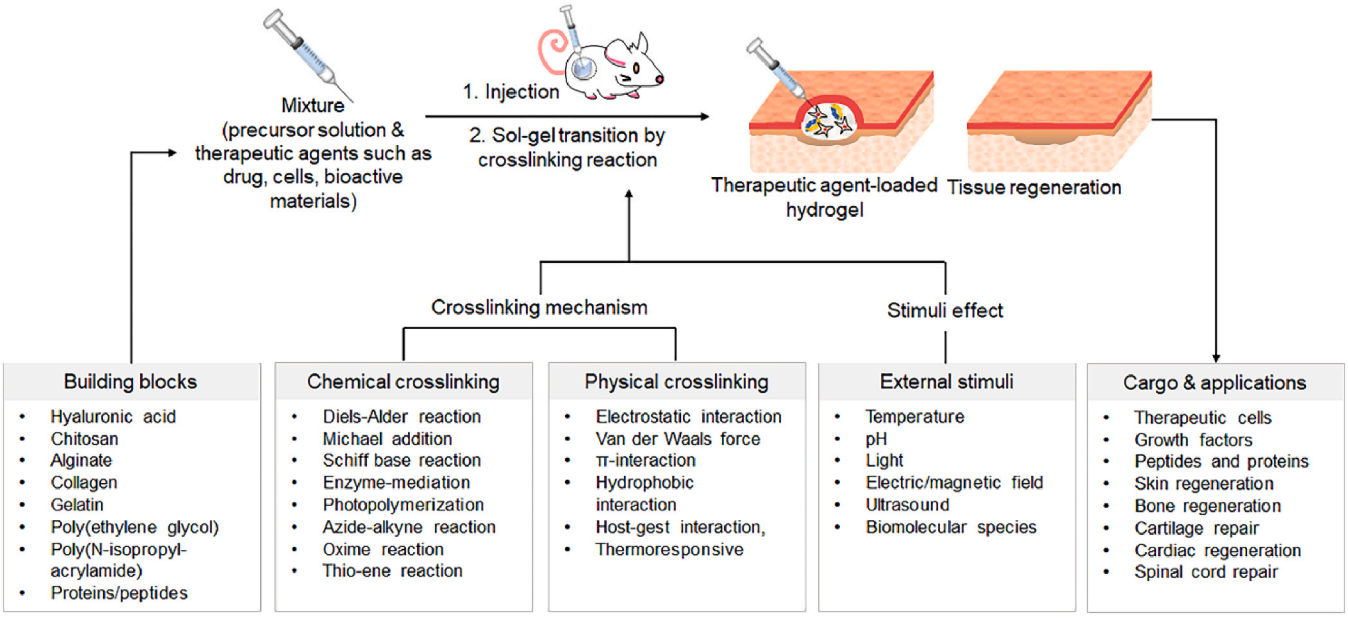

Fig. 14. Schematic illustration of injectable hydrogels for biomedical applications. Injectable hydrogels can be formed via chemical or physical crosslinking mechanisms using biocompatible building blocks. These hydrogels can respond to external stimuli (e.g., pH, temperature, redox) and enable in situ gelation at the target site for controlled drug release, tissue regeneration, or wound healing. The table summarizes key components and application strategies of stimuli-responsive injectable hydrogels.

that can conform to complex defect geometries under specific stimuli, such as heat or pH changes, thereby providing a custom-fit scaffold for irregular tissue defects [299].

5.2.3. Dynamic tissue models

SRPs are increasingly employed in the development of dynamic tissue models and organ-on-a-chip systems, which mimic the mechanical, chemical, and biological properties of native tissues. These models respond to external stimuli, offering a versatile platform for studying tissue behavior, disease progression, and drug responses [300].

Organ-on-a-chip systems integrate stimuli-responsive hydrogels to mimic the microenvironments of organs such as the liver, lungs, and kidneys [301]. These hydrogels can replicate the elasticity, porosity, and biochemical cues of extracellular matrices (ECMs), allowing researchers to observe cell-cell and cell-matrix interactions in real time [302]. For example, hydrogels that stiffen in response to light or enzymatic activity can simulate the fibrotic progression of liver tissues, providing insights into disease mechanisms and potential therapeutic interventions [303].

Stimuli-responsive hydrogels are also used to create dynamic tissue models that can simulate real-time changes in properties such as stiffness or permeability in response to external factors [304]. These models are particularly valuable for drug testing, as they enable researchers to evaluate how drugs interact with tissues under different conditions, such as during inflammation or tumor progression [305]. For instance, pH-sensitive hydrogels such as those composed of poly(methacrylic acid) (PMAA), poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA), poly(ethylene imine) (PEI), alginate, or poly(glutamic acid) can mimic the acidic microenvironment of tumors, providing a more physiologically relevant platform for evaluating pH-targeted therapies [306,307]. These hydrogels undergo swelling or deswelling depending on local pH conditions, enabling controlled release, cell behavior modulation, or signal responsiveness tailored to pathological environments.

The incorporation of multiple SRPs into hydrogels has led to the development of 4D tissue models, which change over time in response to external stimuli [308]. For example, hydrogels responsive to temperature, pH, and enzymatic activity can mimic the dynamic remodeling of tissues during healing or development [309]. These 4D models offer a more realistic representation of tissue behavior, enabling advanced research in regenerative medicine and tissue engineering.

5.3. SRPs as biosensors for physiological and metabolic changes

SRPs have become a cornerstone in the development of biosensors capable of detecting and adapting to physiological changes in real time. By leveraging their ability to undergo controlled structural or functional transformations in response to specific biological cues, these materials facilitate the monitoring of key parameters such as pH, glucose levels, and biomarker concentrations [310]. Such biosensors are particularly valuable in personalized medicine, where real-time and precise feedback is essential for optimizing treatment strategies [311]. In this section, we explore recent advancements in glucose monitoring, enzyme-responsive diagnostics, and the integration of SRPs into wearable and implantable biosensors.

5.3.1. Glucose-responsive systems

Glucose-responsive polymers play a crucial role in diabetes management by enabling continuous glucose sensing and regulated insulin delivery. These materials are commonly engineered with phenylboronic acid (PBA)-functionalized polymers, such as poly(acrylamide-co-phenylboronic acid), poly(N-isopropylacrylamide)-b-phenylboronic acid, and PBA-modified chitosan or alginate, which reversibly bind glucose via dynamic boronate ester formation [312,313]. In addition, concanavalin A (Con A)-based hydrogels and glucose oxidase (GOx)--incorporated systems have been utilized to generate glucose-sensitive swelling, degradation, or signal generation [314]. These reversible interactions allow the polymers to function as glucose sensors, translating glucose concentration changes into quantifiable signals or controlled therapeutic responses.

As schematically depicted in Fig. 15, glucose-responsive drug delivery systems exploit two main mechanisms: (1) phenylboronic acid-based linkers that undergo competitive displacement by glucose, resulting in the release of conjugated therapeutic agents, and (2) enzyme-mediated systems, where glucose is oxidized by glucose oxidase to produce gluconic acid and hydrogen peroxide (H_2O_2). The resulting acidic and oxidative microenvironments induce pH-triggered and ROS-sensitive degradation of the hydrogel network, facilitating drug release at hyperglycemic conditions [315].

The integration of glucose-sensitive polymers into hydrogel matrices has led to the development of advanced continuous glucose monitoring devices. These hydrogels undergo structural changes, such as swelling, shifts in optical properties, or alterations in mechanical or electrical characteristics, in response to fluctuating glucose levels [316]. For example, boronic acid-based hydrogels can exhibit refractive index changes upon glucose binding, enabling real-time optical detection of glucose concentrations. Such non-invasive systems provide continuous feedback, helping patients maintain stable blood sugar levels more effectively [317].

Beyond monitoring, glucose-responsive polymers are also being utilized for automated insulin delivery. Hydrogels embedded with glucose-sensitive elements can encapsulate insulin and release it in response to rising glucose levels in the surrounding environment [318]. The system illustrated in Fig. 15 exemplifies how dynamic glucose recognition and enzymatic oxidation converge to enable on-demand drug release, minimizing manual intervention and enhancing treatment compliance.

5.3.2. Enzyme-responsive biosensors

Enzyme-responsive polymers are designed to detect and respond to the activity of specific enzymes, many of which serve as critical biomarkers for diseases such as cancer, inflammatory disorders, and metabolic conditions [43,44]. These polymers undergo structural or chemical changes upon enzymatic interaction or cleavage, producing measurable signals or triggering functional transformations that correlate with enzyme activity [319]. Typically, enzyme-sensitive polymers incorporate cleavable peptide sequences or chemical bonds that are selectively degraded by specific enzymes [320].

Various enzyme-responsive systems have been developed based on disease-relevant enzymatic triggers. For instance, polymers containing matrix metalloproteinase (MMP)-sensitive linkers degrade in tumor microenvironments due to elevated MMP expression, enabling site-specific drug release [321]. Cathepsin B-sensitive polymers respond to lysosomal protease activity in cancer cells, while esterase-sensitive systems such as poly(ortho esters) and poly(β-amino esters) undergo backbone cleavage in inflamed or intracellular conditions [322]. Additionally, phosphatase-sensitive polymers alter their structure through dephosphorylation reactions mediated by alkaline phosphatases, which are upregulated in certain pathological states. This enzymatic responsiveness enables tailored applications such as controlled drug delivery, bioimaging, and diagnostic sensing [323].

One of the key advantages of enzyme-responsive biosensors is their high specificity, allowing for the detection of subtle biochemical changes associated with disease progression. For instance, biosensors that respond to proteases secreted by cancer cells can facilitate early tumor detection or monitor therapeutic response over time [324]. Similarly, polymers sensitive to inflammatory enzymes, such as elastase or myeloperoxidase, enable real-time monitoring of inflammation in conditions such as rheumatoid arthritis or chronic wounds [325].

Enzyme-responsive polymers are also widely applied in theranostic systems, which integrate both diagnostic and therapeutic functions. These systems not only detect disease-specific enzymes but also trigger localized drug release in response to enzymatic activity, ensuring

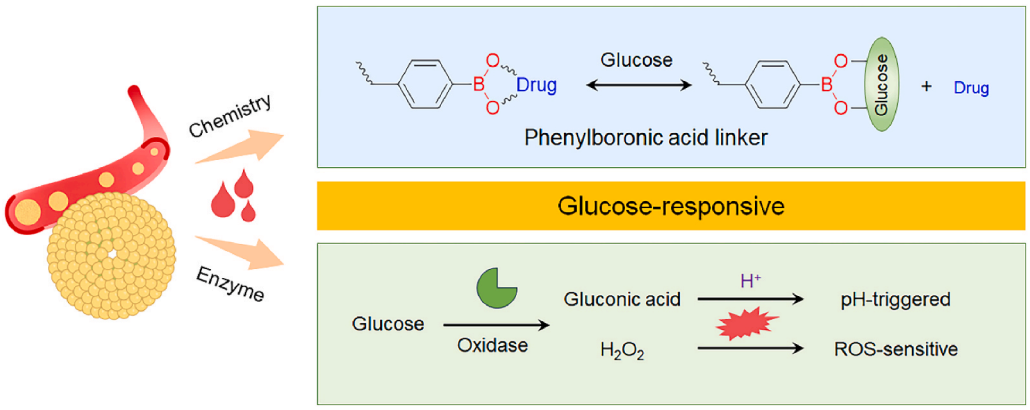

Fig. 15. Schematic illustration of glucose-responsive drug delivery systems. Phenylboronic acid linkers reversibly bind glucose, enabling glucose-triggered drug release via competitive displacement. Glucose oxidation by glucose oxidase produces gluconic acid and H_2O_2, triggering drug release through pH changes and ROS-sensitive degradation pathways.

targeted treatment while minimizing systemic side effects [326].

5.3.3. *Wearable and implantable devices*

The integration of SRPs into wearable and implantable biosensors has transformed health monitoring by enabling continuous, real-time tracking of physiological changes. These devices using pH-sensitive polymers such as poly(acrylic acid) (PAA), chitosan, PMAA, PDMAEMA, and PEI are designed to be non-invasive or minimally invasive, ensuring patient comfort while providing critical health data [327,328].

Wearable biosensors utilize SRPs to analyze biomarkers in sweat, saliva, or interstitial fluid. For example, pH-sensitive polymers embedded in wearable patches can detect fluctuations in sweat pH, which may signal dehydration, electrolyte imbalance, or stress levels [329]. Similarly, ion-sensitive polymers are employed in wearable devices to monitor electrolyte concentrations, offering valuable insights for athletes, individuals with chronic illnesses, or those exposed to extreme conditions [330].

Implantable biosensors equipped with SRPs enable long-term monitoring of essential physiological parameters such as glucose levels, oxygen saturation, and pH within the body [331]. For instance, glucose-responsive hydrogels in implantable sensors adjust their optical or electrical properties in response to glucose concentration. These innovations enable continuous monitoring without frequent recalibrations or replacements, significantly improving the quality of life for patients with chronic conditions [332].

Advancements in polymer science have led to the development of multifunctional wearable and implantable biosensors. These devices integrate multiple SRPs to simultaneously track various biomarkers [333]. For example, hybrid sensors can monitor glucose, lactate, and pH levels in real time, providing a comprehensive assessment of a patient's metabolic status [329]. Additionally, combining biosensing capabilities with drug delivery functions allows for the creation of closed-loop systems that autonomously administer medication based on detected biomarker levels, enhancing personalized treatment strategies [334].

5.4. *Stimuli-responsive materials for advanced wound healing therapies*

Wound healing is a complex physiological process that progresses through distinct stages, including inflammation, proliferation, and remodeling. SRPs have marked a turning point in wound care by offering materials that dynamically adjust to the wound environment [335]. These polymers respond to local changes in temperature, pH, moisture, or biochemical activity, enabling targeted therapeutic delivery, enhanced protection, and accelerated tissue repair [336]. This section explores the role of SRPs in wound healing, focusing on antibacterial coatings, moisture-responsive dressings, and bioactive hydrogels.

5.4.1. *Antibacterial and antifouling coatings*

Infections are a significant complication in wound healing, often leading to prolonged recovery and an increased risk of systemic complications. SRPs provide a targeted strategy for infection control by releasing antibacterial agents in response to specific triggers, such as pH shifts associated with bacterial activity [337].

Infected wounds often exhibit an acidic microenvironment (pH ~5.0–6.5), which has prompted the development of pH-sensitive polymers for targeted antibacterial coatings. Polymers such as PAA and PMAA contain ionizable carboxylic acid groups that swell or degrade under acidic conditions, enabling site-specific drug release [338]. Chitosan, a natural polymer with inherent antimicrobial properties, becomes soluble in mildly acidic environments, enhancing its utility in wound dressings [339]. Other pH-responsive materials, including PDMAEMA, hydroxypropyl methylcellulose phthalate (HPMCP), and Eudragit® S100, have also been used to create polymeric films or hydrogels that release antibacterial agents such as silver nanoparticles or antibiotics specifically at infection sites, thereby improving therapeutic efficacy while minimizing systemic side effects [340,341].

As illustrated in Fig. 16**a**, the hydrogel network undergoes a conformational change in response to local acidity at the wound site, enabling pH-triggered drug release through dynamic modulation of polymer-drug interactions [342]. In addition, as shown in Fig. 16**b**, wound dressings can be integrated with colorimetric pH indicators to allow real-time monitoring of wound healing status. These smart dressings provide visible feedback via color change, facilitating early detection of infection and timely therapeutic response [343].

In addition to antibacterial properties, antifouling SRP coatings prevent bacterial adhesion and biofilm formation on wound dressings and medical devices. Materials such as zwitterionic hydrogels and PEG derivatives create hydrophilic, non-adhesive surfaces that resist bacterial attachment [344]. Additionally, stimuli-responsive antifouling coatings can adapt to environmental changes, releasing antimicrobial agents upon bacterial detection, further improving their efficacy in wound management.

5.4.2. *Moisture-responsive dressings*

Maintaining an optimal moisture balance at the wound site is essential for effective healing [345]. Excessive exudate can lead to maceration, while insufficient moisture may cause desiccation and hinder cell migration. Moisture-responsive dressings made from SRPs dynamically regulate hydration levels, ensuring an ideal wound environment [346].

Hydrogels formulated with moisture-sensitive polymers absorb

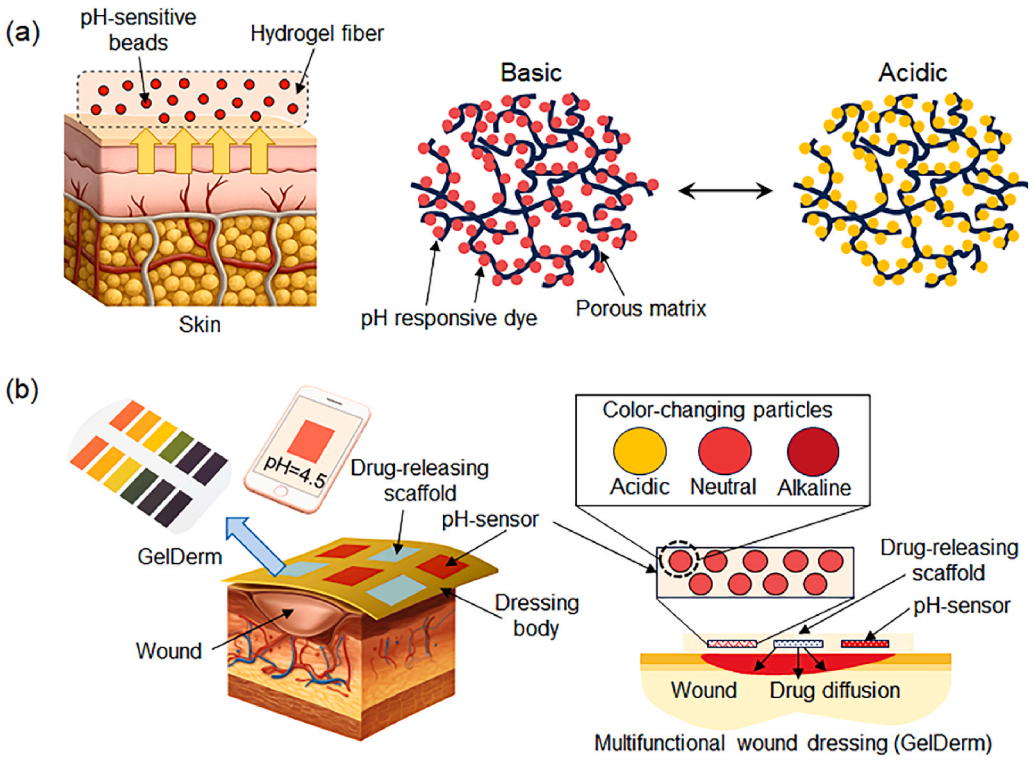

Fig. 16. (a) pH-responsive wound dressings for controlled drug delivery. The hydrogel network responds to acidic environments at wound sites, enabling targeted drug release through changes in polymer-drug interactions [342]. (b) Colorimetric pH-indicating systems integrated into wound dressings enable real-time monitoring of wound healing status, providing visual feedback through color changes and assisting in pH-triggered therapeutic response [343]. Copyright 2015, Kluwer Academic Publishers.

excess exudate while retaining sufficient moisture to support cell proliferation and tissue repair. These materials often incorporate crosslinked networks that swell upon contact with wound fluids, forming a soft and hydrated interface with the wound bed [347]. For instance, dressings based on polyacrylic acid or alginate derivatives expand significantly in response to exudate, preventing maceration of surrounding tissues while maintaining a moist healing environment [348]. In addition to these, carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), HPMC, chitosan, and polyethylene glycol PEG-based hydrogels have also been widely employed as moisture-responsive materials due to their high water absorbency, biocompatibility, and ability to form protective, hydrated barriers [349,350]. These materials not only manage wound exudate effectively but also contribute to antimicrobial activity, hemostasis, and accelerated tissue regeneration, making them highly suitable for advanced wound care applications.

For wounds with minimal exudate, moisture-responsive polymers can release water or hydrating agents to prevent desiccation. These materials commonly blend hydrophilic polymers, such as PVA or PEG, with moisture-retaining additives like glycerol or hyaluronic acid [351]. This mechanism ensures sustained hydration of the wound bed, facilitating fibroblast migration and epithelialization [352].

Advanced moisture-responsive dressings integrate additional functionalities, such as antimicrobial or growth factor-releasing properties. For example, dressings that simultaneously absorb exudate and release antibacterial agents in response to microbial activity offer a comprehensive approach to wound management, reducing the need for frequent dressing changes and improving treatment outcomes [353].

5.4.3. *Bioactive stimuli-responsive gels*

Bioactive hydrogels incorporating SRPs are engineered to release therapeutic agents such as growth factors, enzymes, or bioactive molecules in response to specific wound-site conditions. These hydrogels enhance the healing process by promoting angiogenesis, reducing inflammation, and facilitating tissue regeneration [354].

Chronic wounds, such as diabetic ulcers or pressure sores, often exhibit elevated protease levels that degrade the extracellular matrix and impede healing [355]. To counteract this, protease-sensitive hydrogels release therapeutic agents upon enzymatic activation. For example, hydrogels loaded with vascular endothelial growth factor (VEGF) or platelet-derived growth factor (PDGF) deliver these angiogenic molecules in response to protease activity, stimulating blood vessel formation and improving oxygen supply to the wound [356].

Chronic inflammation often leads to excessive ROS, causing oxidative damage and delayed healing. To mitigate this, ROS-responsive hydrogels have been developed that degrade or activate upon ROS exposure, enabling site-specific release of therapeutic agents [357].

Thiol-containing polymers are commonly used, as their oxidation to disulfides facilitates polymer breakdown and antioxidant delivery. Diselenide and ditelluride bonds offer higher redox sensitivity and tunable degradation; ditellurides, with their lower bond energy, are especially suited for highly oxidative environments [190,191].

Other ROS-cleavable motifs include boronic esters, peroxalate esters, aryl oxalates, thioketals, and selenides. These systems aid wound healing by scavenging ROS and delivering antioxidants or anti-inflammatory agents in a controlled manner [358].

Hydrogels designed with pH- or enzyme-sensitive release mechanisms enable the controlled delivery of growth factors that support cellular processes such as proliferation and differentiation [359]. For instance, pH-sensitive hydrogels release fibroblast growth factor (FGF) in response to acidic conditions, stimulating collagen synthesis and granulation tissue formation [360]. Similarly, enzyme-responsive gels facilitate on-demand delivery of anti-inflammatory cytokines or antimicrobial peptides, further enhancing wound healing [361].

6. Environmental applications of SRPs: Toward sustainable solutions

Due to their ability to adapt dynamically to changing conditions, SRPs have garnered increasing attention as promising materials to address environmental challenges. These intelligent materials contribute to sustainability by facilitating pollutant removal, environmental monitoring, and waste reduction [362]. This section explores their applications in biodegradable materials, pollutant adsorption, environmental sensing, and smart packaging.

6.1. Biodegradable SRPs for eco-friendly material design

Biodegradable SRPs represent a significant advancement in sustainable material science, providing environmentally friendly alternatives to conventional polymers. These materials are designed to degrade under specific environmental conditions, such as changes in temperature, pH, or light exposure, ensuring minimal long-term ecological impact [363]. By combining biodegradability with responsiveness, these polymers address the growing demand for sustainable materials in applications ranging from agricultural films to single-use packaging [364]. This section examines the mechanisms, applications, and potential of biodegradable SRPs.

6.1.1. Temperature-responsive biodegradable polymers

Temperature-responsive biodegradable polymers exhibit degradation rates that vary with ambient temperature. Commonly used materials include polylactic acid (PLA) and polycaprolactone (PCL), which offer natural biodegradability and tunable thermal properties [365]. These polymers function by incorporating thermally labile bonds or by modifying their crystallinity to enhance heat sensitivity [366,367]. At elevated temperatures, such as those found in industrial composting facilities, their degradation accelerates significantly. For instance, PLA-based films designed for temperature sensitivity efficiently degrade in environments ranging from 50 °C to 70 °C, making them ideal for industrial composting [368].

In addition to PLA and PCL, poly(lactic-co-glycolic acid) (PLGA) is widely used due to its temperature-sensitive hydrolytic degradation, which can be tuned by adjusting the lactide:glycolide ratio [369,370]. Polyanhydrides, with hydrolytically labile anhydride bonds, also exhibit accelerated breakdown at elevated temperatures and are utilized in drug delivery and surface-eroding implants. Poly(ortho esters) are another class of biodegradable polymers with temperature-dependent surface erosion, making them suitable for applications requiring controlled release under varying thermal conditions [371].

Applications of these polymers include compostable food packaging, biodegradable agricultural mulch films, and resorbable medical implants. In agriculture, mulch films degrade in the field after the growing season, eliminating the need for manual removal and reducing soil contamination [372]. In biomedical applications, temperature-sensitive polymers enable controlled degradation within the human body, supporting drug delivery or implant resorption over time [373].

Despite these advantages, challenges remain in optimizing these polymers for stability during use while ensuring rapid degradation post-use. Ongoing research aims to refine their thermal responsiveness and mechanical properties to better suit specific applications [374].

6.1.2. pH-responsive biodegradable polymers

pH-responsive biodegradable polymers are engineered to undergo selective degradation under acidic or alkaline conditions, enabled by the incorporation of labile functional groups such as carboxyl, amine, ester, or pH-sensitive bonds (see Section 3.1.1) [36,37]. These materials are particularly valuable in environments with fluctuating pH such as industrial effluents, alkaline water bodies, and biologically relevant acidic microenvironments where they allow for site-specific and controlled breakdown [375].

Common examples include poly(acrylic acid), chitosan, and poly(β-amino esters), which are extensively used in drug delivery, smart coatings, and environmental remediation [328,376]. Polymers containing ester, acetal, or ortho ester linkages degrade more rapidly in acidic conditions via hydrolysis, making them suitable for applications such as wastewater treatment, where they can remove pollutants and subsequently decompose without generating secondary waste [377]. This tunable degradation behavior enables precise control over release profiles or material clearance, depending on the pH of the surrounding environment.

In biomedical applications, pH-sensitive polymers play a crucial role in targeted drug delivery. These materials are designed to release therapeutic agents in acidic environments, such as tumor tissues, where the lower pH triggers the breakdown of the polymer matrix. This controlled release improves drug efficacy while minimizing side effects on healthy tissues [378]. Despite their versatility, challenges remain in ensuring consistent degradation across different pH environments and maintaining structural stability during storage and use. Advances in copolymer design and the incorporation of stabilizers are being explored to address these limitations and enhance their practical applications [379].

6.1.3. Photo-responsive biodegradable polymers

Photo-responsive biodegradable polymers are engineered to degrade upon exposure to light, particularly UV or sunlight. This property arises from the incorporation of light-cleavable bonds such as o-nitrobenzyl esters or azobenzene-based linkages which undergo bond cleavage upon absorbing specific wavelengths, enabling spatiotemporal control over degradation in biomedical or environmental settings (see Section 3.1.1) [380,381]. These materials are particularly useful in outdoor applications where controlled degradation is desirable. For instance, agricultural films made from photo-responsive polymers gradually break down under sunlight after the growing season, eliminating the need for manual removal and reducing environmental pollution [382]. Similarly, single-use plastics embedded with light-sensitive components can degrade upon exposure to natural light, helping mitigate plastic waste accumulation [383].

In the medical field, photo-responsive polymers are used for temporary implants and scaffolds that degrade when exposed to specific wavelengths of light, enabling non-invasive removal. These materials are also being considered for smart packaging applications, where UV-sensitive polymers can facilitate controlled degradation under outdoor storage conditions [384].

Challenges associated with photo-responsive polymers include ensuring uniform degradation under varying light intensities and making these materials scalable for industrial use. Current research focuses on optimizing light sensitivity and enhancing material stability in different environmental conditions to expand their real-world applications [385].

6.2. SRPs as functional adsorbents for pollutant removal

SRPs offer innovative strategies for pollutant removal by adjusting their adsorption properties in response to environmental changes. These materials are designed to selectively target specific contaminants while maintaining high efficiency and reusability, making them valuable for water treatment and environmental remediation [386]. Their ability to respond to external stimuli such as pH, redox potential, and temperature allows for controlled adsorption and desorption processes, enhancing their effectiveness in industrial wastewater treatment [387]. The following sections discuss different types of SRPs used as adsorbents and their roles in pollutant removal.

6.2.1. pH-responsive adsorbents

Polymers with pH-sensitive functional groups, such as carboxyl, amine, and sulfonic acid groups, exhibit tunable ion exchange and adsorption properties, enabling selective pollutant capture in

environments with fluctuating pH levels (see Section 3.1.1) In acidic industrial effluents, for example, these functional groups undergo protonation or deprotonation, regulating the polymer's interactions with charged pollutants [32,388]. These materials are particularly effective for the selective removal of heavy metals such as lead (Pb^{2+}), cadmium (Cd^{2+}), and chromium (Cr^{3+}) from aqueous solutions [389].

As shown in Fig. 17, pH-responsive bio-based adsorbents can be engineered by functionalizing biomass-derived substrates with pH-sensitive and crosslinkable moieties to form porous hydrogel-like structures. These materials demonstrate reversible adsorption and desorption behaviors depending on the surrounding pH, allowing for the selective capture and release of target molecules under acidic or basic conditions [390].

Hydrogels containing pH-sensitive groups can swell significantly under acidic conditions, increasing their surface area and exposing more active binding sites for pollutant adsorption, thereby improving efficiency. This swelling behavior allows the material to adapt dynamically to variations in wastewater composition, making it highly effective for industrial applications where pH fluctuations are common [391]. Additionally, these pH-responsive polymers are incorporated into membrane systems to function as selective barriers, regulating the passage of ions or molecules and enhancing precision in water treatment processes [392]. The integration of such tunable and environmentally friendly adsorbents presents a promising strategy for sustainable remediation and resource recovery.

6.2.2. *Redox-responsive materials for pollutant removal*

Redox-sensitive polymers provide an adaptable approach to pollutant removal by incorporating functional groups such as disulfide bonds, thiol groups, or quinone derivatives (see Section 3.1.1), which undergo reversible chemical changes under oxidative or reductive conditions [190,393]. These polymers are particularly suited for environments with redox gradients, such as mining wastewater, where heavy metal contamination is prevalent. For example, redox-sensitive hydrogels can capture heavy metals through chelation or ion exchange in oxidizing conditions and release them in reducing environments, allowing for efficient adsorbent regeneration [394].

This reversible adsorption-desorption capability enhances the reusability of redox-responsive materials, improving both the sustainability and cost-effectiveness of water treatment systems. Additionally, these polymers are effective in removing organic pollutants, particularly persistent contaminants such as dyes and hydrocarbons, which can be broken down or released through redox-induced structural modifications [395]. Integrating redox-responsive materials into filtration membranes or composite adsorbents combines dynamic pollutant capture with structural stability, making them highly versatile for complex remediation challenges.

6.2.3. *Temperature-responsive adsorbents*

Temperature-sensitive polymers, such as PNIPAM, PCL-PEG-PCL, polyanhydrides, and poly(ortho esters), exhibit dynamic solubility and swelling behavior in response to temperature fluctuations, enabling controlled adsorption and release of pollutants in thermally regulated systems (see Section 3.1.1) [396–398]. These polymers often incorporate thermally labile bonds or crystalline domains that modulate chain mobility and hydrophilicity. For instance, PNIPAM hydrogels, which have a LCST near physiological levels, swell below this threshold due to their hydrophilic nature and contract above it as they become hydrophobic [399].

This reversible transition is particularly advantageous for water purification systems requiring precise control over adsorption and desorption processes. At lower temperatures, PNIPAM-based materials swell to capture dyes, oils, and organic pollutants from wastewater, while at higher temperatures, they release these adsorbed substances, facilitating adsorbent regeneration. This thermal responsiveness minimizes reliance on harsh chemical regenerants and enhances the energy efficiency of water treatment processes [400,401]. Additionally, temperature-responsive adsorbents are increasingly incorporated into hybrid systems, such as polymer-nanoparticle composites, to enhance mechanical stability, adsorption capacity, and thermal conductivity, ensuring reliable performance in industrial and environmental applications [402].

6.3. *Smart SRP sensors for environmental monitoring*

SRPs are increasingly employed in environmental sensing

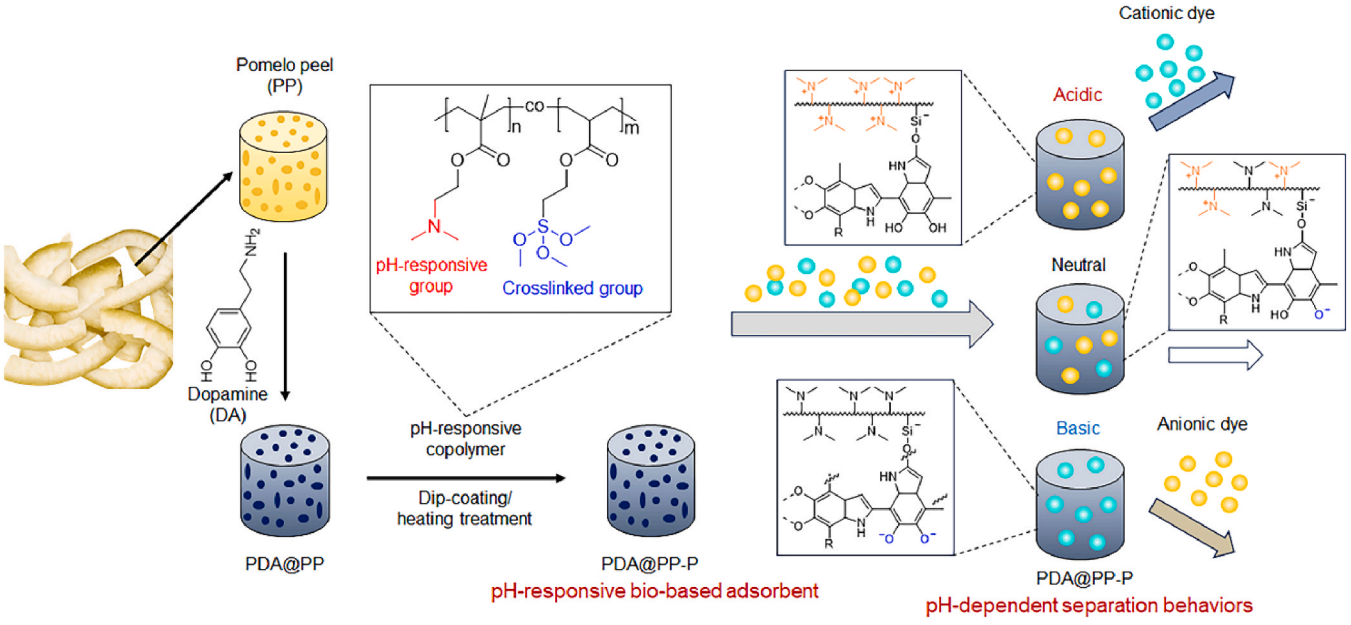

Fig. 17. Schematic illustration of pH-responsive bio-based adsorbents for selective separation. Biomass-derived substrates are functionalized with pH-sensitive and crosslinkable groups to form porous hydrogel-like adsorbents. These materials exhibit reversible adsorption and desorption behaviors depending on the environmental pH, enabling selective capture and release of target molecules under acidic or basic conditions. This strategy offers a sustainable and tunable approach for environmental remediation and separation processes.

applications due to their ability to detect pollutants, toxins, and environmental fluctuations with high sensitivity and specificity. These materials undergo distinct physical or chemical transformations upon exposure to environmental stimuli, enabling real-time monitoring and accurate feedback crucial for addressing ecological challenges [403]. Their applications extend across water quality assessment, air pollution detection, soil monitoring, and industrial process control, making them valuable tools for sustainable environmental management [404]. The following sections discuss the emerging trends and potential applications of SRP-based sensors in environmental monitoring.

6.3.1. *pH-responsive sensors*

pH-responsive polymer sensors play a crucial role in monitoring acidity and alkalinity across diverse environmental settings, including water bodies, agricultural soils, and industrial effluents. These sensors incorporate pH-sensitive functional groups or dyes that undergo measurable transformations in response to pH fluctuations [405]. For example, hydrogel-based sensors embedded with colorimetric dyes such as bromothymol blue or phenolphthalein exhibit visible color changes when exposed to acidic or basic environments. This rapid, visual response enables the immediate detection of contamination in water supplies or soil acidification that could affect crop health [406].

Fluorescent pH-responsive polymers provide even greater sensitivity by emitting light at specific wavelengths in response to pH variations. These materials, often used in optical sensors, allow for precise quantification of minor pH shifts in highly sensitive applications, such as monitoring aquaculture water quality or detecting fluctuations in industrial effluent discharge [407]. Recent advances in microfluidic technology have further enabled the development of portable, pH-responsive sensors capable of real-time, on-site monitoring with minimal maintenance, facilitating timely interventions in environmental management [408].

In parallel, redox-responsive polymer systems have emerged as powerful tools for environmental pollutant sensing and removal. As illustrated in Fig. 18, redox-active materials undergo reversible oxidation and reduction cycles that facilitate ion exchange processes, allowing for the selective adsorption and separation of various anionic pollutants such as chloride, fluoride, nitrate, and sulfate. These materials capture contaminants upon oxidation and can be regenerated via reduction, restoring their adsorption capacity for repeated use. Such redox-coupled mechanisms enhance the versatility and reusability of functional polymers in environmental remediation [409].

6.3.2. *Heavy metal detection*

Detecting heavy metals such as mercury (Hg^{2+}), lead (Pb^{2+}), arsenic (As^{3+}), and cadmium (Cd^{2+}) is critical for environmental monitoring due to their toxicity and persistence in ecosystems [410]. SRPs functionalized with chelating groups such as thiols, amines, carboxylic acids, phosphonic acids, crown ethers, imidazole rings, and dihydroxybenzenes (e.g., catechols) exhibit high selectivity and affinity for binding metal ions [411]. These polymers are often incorporated into biosensors that generate optical or electrochemical signals upon metal ion recognition, enabling highly sensitive and selective detection in complex environments [404].

For example, polymer coatings integrated with thiol-based ligands effectively chelate mercury ions from contaminated water, triggering a color change or fluorescence quenching as a visual detection mechanism [412]. Similarly, amine-functionalized polymer matrices serve as electrochemical sensors for lead ions, with binding events inducing measurable changes in electrical conductivity or electrochemical potential. These sensors are particularly valuable for field applications, such as testing drinking water quality or monitoring industrial discharge for regulatory compliance [413]. The incorporation of nanomaterials such as gold nanoparticles or graphene into the polymer matrix enhances signal amplification and sensitivity, enabling the detection of trace heavy metal concentrations down to parts-per-billion levels [414].

6.3.3. *Gas sensors*

Gas-responsive polymers are widely used for detecting and monitoring volatile organic compounds (VOCs), greenhouse gases (e.g., CO_2 and CH_4), and toxic industrial emissions (e.g., ammonia and sulfur dioxide). Upon gas exposure, these polymers undergo changes in

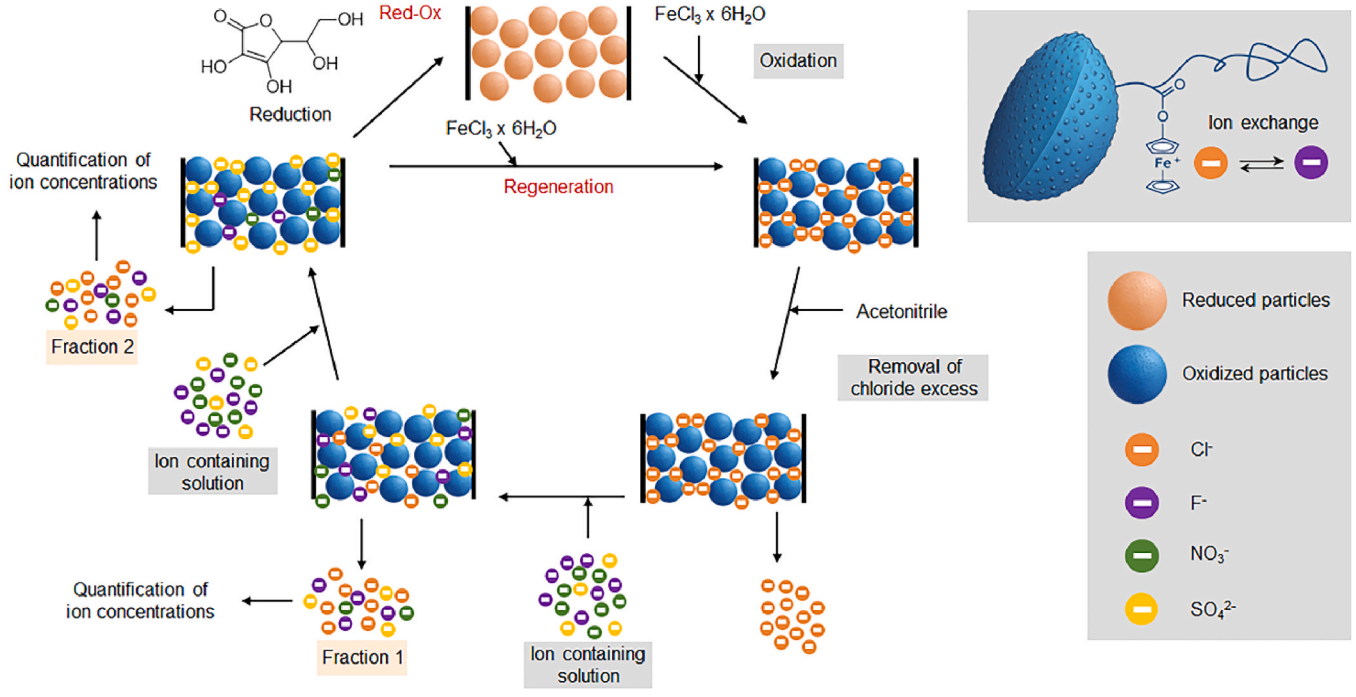

Fig. 18. Redox-responsive materials for pollutant removal. Redox-active particles undergo reversible oxidation and reduction cycles, enabling ion exchange for selective adsorption of anionic pollutants such as Cl^-, F^-, NO_3^-, and SO_4^{2-}. Upon oxidation, particles capture contaminants via ion exchange; regeneration through reduction restores adsorption capacity for repeated use [409]. Copyright 2024, Elsevier BV.

properties such as conductivity, swelling, or optical behavior, which can be converted into quantifiable signals [415,416].

For instance, polymers embedded with conductive materials such as quantum dots or graphene exhibit variations in electrical resistance when exposed to specific gases [417]. Quantum dots provide high surface reactivity and tunable optical/electronic properties, while graphene offers exceptional electrical conductivity and sensitivity to surface adsorption. These attributes enhance the sensor's ability to detect trace gas concentrations with high precision [418]. These sensors are commonly deployed in industrial environments to monitor emissions and ensure regulatory compliance, as well as in urban areas for air quality assessment. Swelling-based gas sensors, constructed from materials such as polydimethylsiloxane (PDMS), absorb VOCs, leading to dimensional changes that can be detected using piezoelectric or capacitive transducers [419].

Gas sensors are also essential for detecting greenhouse gases such as CO_2 in the agricultural and energy sectors. SRPs integrated with CO_2-capture groups, such as amines, can selectively bind and release CO_2 under controlled conditions, enabling real-time monitoring of gas levels. These sensors are vital for optimizing processes like carbon sequestration and air quality management in enclosed environments, such as greenhouses and industrial plants [420,421].

As illustrated in Fig. 19, organic field-effect transistor (OFET)-based sensors using redox-responsive semiconducting polymers represent a promising platform for gas detection. Upon exposure to oxidative or reductive gases, the carrier concentration in the semiconductor layer changes, modulating conductivity depending on the semiconductor type p-type (hole carriers) or n-type (electron carriers). These gas-induced charge modulation effects are exploited for the sensitive detection of environmental pollutants, offering a versatile and reusable sensing platform. In addition to environmental monitoring, such OFET-based sensors have potential applications in healthcare diagnostics and food quality monitoring, due to their high sensitivity, portability, and tunability [422].

6.3.4. *Multi-stimuli sensors*

In complex environmental systems, multi-stimuli-responsive sensors are essential for simultaneously detecting multiple parameters, such as pH, temperature, and pollutant concentration. These advanced sensors integrate various stimuli-responsive functionalities within a single material, allowing for comprehensive monitoring and adaptive responses to changing environmental conditions [423].

For example, multi-stimuli sensors incorporating both pH-responsive and heavy metal-chelating functionalities can detect simultaneous changes in water acidity and metal ion concentrations, providing a holistic assessment of water quality in aquaculture systems or wastewater treatment plants [424]. Similarly, temperature- and gas-responsive sensors are used in industrial settings to monitor process conditions while detecting hazardous emissions [425].

Recent advancements in sensor technology have led to the development of portable, real-time monitoring devices that combine optical, electrochemical, and piezoelectric transduction mechanisms. These devices leverage SRP composites to achieve high sensitivity and specificity for multiple environmental indicators, making them valuable for

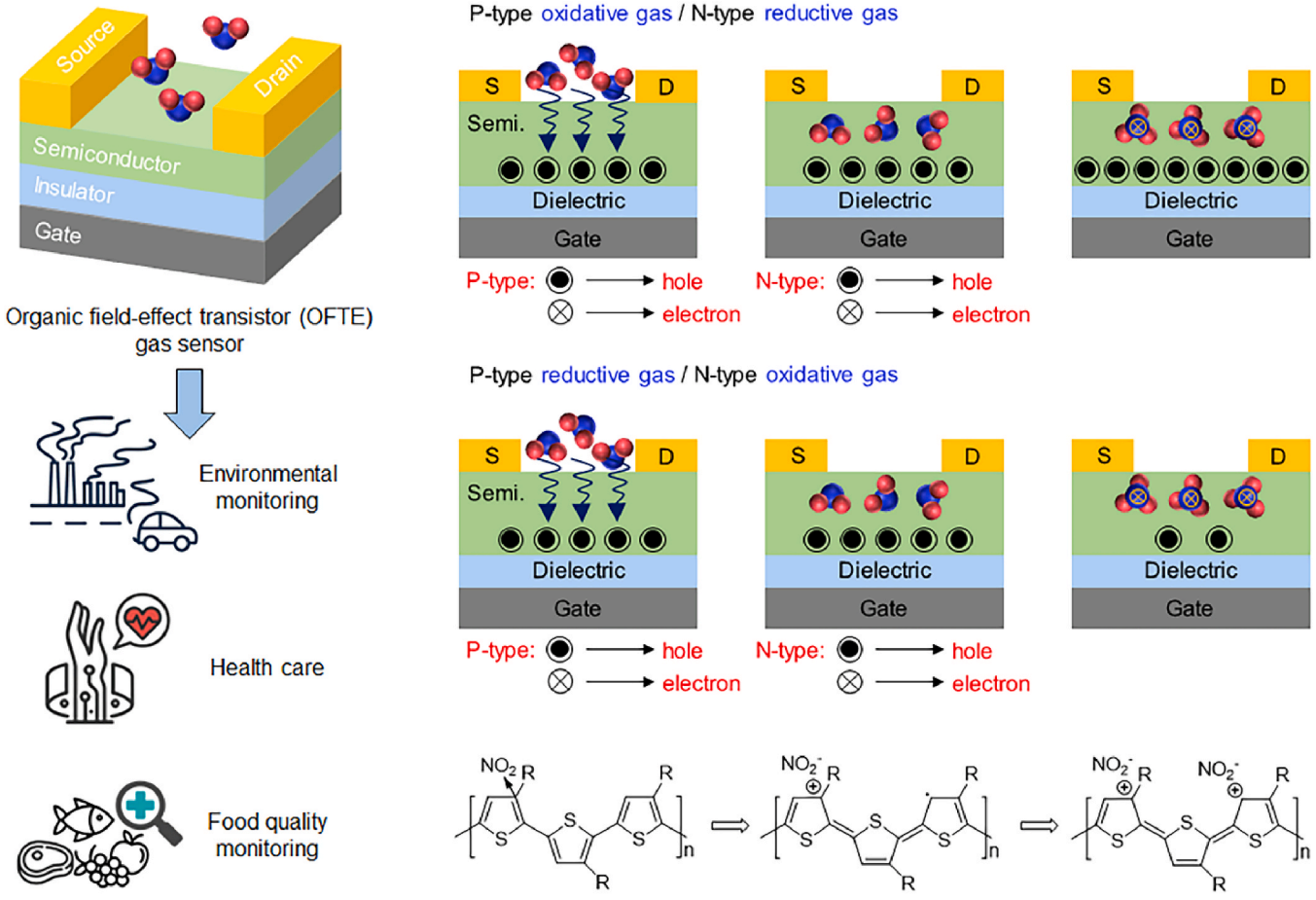

Fig. 19. Schematic overview of gas sensing mechanisms using OFET platforms based on redox-responsive semiconducting polymers. Upon exposure to oxidative or reductive gases, changes in carrier concentration (holes or electrons) alter the OFET conductivity depending on the semiconductor type (p-type or n-type). These responsive systems enable applications in environmental monitoring, healthcare, and food quality control. The bottom panel shows a redox-active conjugated polymer undergoing reversible oxidation states for sensing applications.

applications ranging from environmental remediation to resource management [426]. For instance, a single sensor could simultaneously detect pH fluctuations, monitor ammonia concentrations in wastewater, and assess the presence of trace heavy metals, providing comprehensive data for informed decision-making [427].

6.4. *Stimuli-responsive packaging for freshness and spoilage indication*

Smart packaging materials incorporating SRPs represent a significant advancement in food safety and waste reduction, offering real-time, visible indicators of product freshness, spoilage, and optimal storage conditions. These intelligent materials react to environmental triggers such as pH changes, temperature fluctuations, and moisture levels, allowing consumers and suppliers to effectively monitor the quality of perishable goods [428]. By integrating these polymers into packaging systems, the food industry can enhance product safety, extend shelf life, and minimize waste through timely spoilage detection and condition monitoring [429]. The following section will explore current innovations and future directions in the application of SRP-based smart packaging materials.

6.4.1. *pH-sensitive packaging*

Perishable food items such as meat, fish, dairy, and certain vegetables release acidic or basic compounds as they degrade, leading to measurable pH changes in their immediate environment. Stimuli-responsive packaging materials incorporating pH-sensitive polymers can detect these changes and provide a visual indication of spoilage [430]. For example, films embedded with pH-sensitive dyes, such as bromothymol blue or methyl red, undergo distinct color shifts as the pH of the packaging environment changes. A packaging film might transition from green to red to indicate meat spoilage or from yellow to blue for seafood, offering consumers a clear and immediate freshness indicator [431].

Beyond visual cues, advanced pH-sensitive packaging systems integrate electrochemical sensors that generate digital signals, enabling remote monitoring via smart devices. These sensors not only provide real-time freshness data but also assist retailers and distributors in managing inventory more efficiently by identifying items nearing spoilage [432]. Such applications help reduce food waste and enhance supply chain efficiency by enabling proactive decision-making [433].

As depicted in Fig. 20, the integration of active and intelligent packaging strategies using biodegradable pH-sensitive films functionalized with natural pigments and plasticizers offers a multifunctional approach that combines food protection, real-time freshness monitoring, and environmental sustainability [434].

6.4.2. *Temperature-responsive packaging*

Temperature-sensitive polymers in packaging materials play a crucial role in ensuring that perishable goods remain within specified temperature ranges during storage and transport. These materials respond to temperature deviations by undergoing physical or optical changes, which act as clear indicators of thermal abuse [435]. For example, polymers such as PNIPAM, poly(N-vinylcaprolactam) (PVCL), Pluronic, and poly(oligo(ethylene glycol) methacrylate) (POEGMA) exhibit LCST behavior, becoming opaque or undergoing phase transitions when exposed to temperatures above their threshold [436]. Packaging films incorporating PVCL or Pluronic copolymers signal improper storage conditions by undergoing a visible sol–gel transition or phase change, such as becoming opaque, thereby alerting handlers to potential quality degradation during transport or storage [437].

In addition to visible changes, temperature-sensitive packaging can incorporate irreversible indicators that document thermal history. These indicators utilize thermochromic or shape-memory polymers that permanently record temperature exposure, providing a detailed storage history [438]. Such systems are particularly beneficial for cold chain logistics, where maintaining strict temperature control is essential for preserving the quality of vaccines, dairy products, and frozen foods [439]. By ensuring that products reaching consumers meet safety and quality standards, temperature-responsive packaging helps mitigate foodborne illness risks while improving supply chain reliability [440].

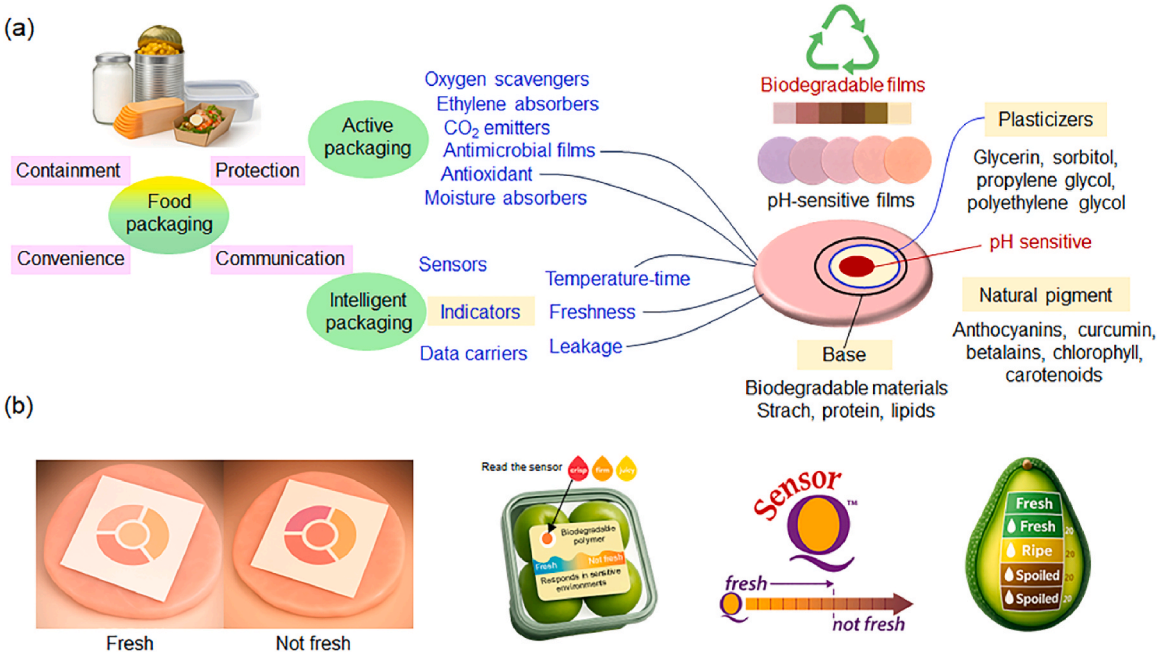

Fig. 20. (a) Conceptual overview of food packaging functions, highlighting the integration of active and intelligent packaging technologies. Active packaging incorporates oxygen scavengers, ethylene absorbers, antimicrobial films, and moisture regulators to preserve food quality. Intelligent packaging employs sensors and indicators (e.g., temperature-time, freshness, leakage) to communicate food status. Biodegradable films composed of starch, protein, or lipid matrices can be enhanced with pH-sensitive natural pigments (e.g., anthocyanins, curcumin) and plasticizers for functional applications [434]. (b) Visual examples of pH-responsive packaging indicators that monitor food freshness by color change, enabling real-time quality assessment and enhancing consumer safety. Copyright 2024, Elsevier BV.

6.4.3. Moisture-responsive materials

Moisture-sensitive polymers in packaging materials address the critical challenge of humidity control, which significantly affects the freshness of many perishable products. Excess moisture within packaging can promote microbial growth, leading to spoilage, while insufficient moisture can cause dehydration and quality loss [441]. Stimuli-responsive packaging materials equipped with moisture-sensitive components can actively regulate humidity levels and provide real-time feedback on storage conditions [442].

For instance, films made from hydrophilic polymers such as PEG, CMC, and HPMC absorb excess moisture, preventing the accumulation of condensation that could foster mold growth on fresh produce. Conversely, these materials can release stored water vapor when humidity drops, helping maintain an optimal microclimate for delicate items like leafy greens or berries [443].

Some moisture-responsive materials include visual indicators, such as hygroscopic dyes, which change color as humidity levels fluctuate. These indicators help consumers and supply chain managers identify products exposed to suboptimal storage conditions [444]. Additionally, integrating moisture-responsive polymers with antimicrobial agents provides dual functionality, regulating humidity while simultaneously preventing microbial contamination [445].

6.4.4. Multi-stimuli packaging

Advanced smart packaging systems combine multiple stimuli-responsive properties to provide comprehensive monitoring of food quality and safety. These materials respond to a combination of pH, temperature, and gas changes associated with spoilage, offering a holistic approach to freshness detection [446]. For example, multi-stimuli packaging materials might include CO_2-sensitive polymers that detect the release of carbon dioxide, a common byproduct of microbial activity, alongside temperature- and pH-sensitive dyes [447].

Such packaging can display a color change when exposed to elevated CO_2 levels, signaling spoilage, while also recording thermal abuse via temperature-sensitive components. This layered approach to quality monitoring ensures that consumers and suppliers are informed of various factors that could compromise product safety [448]. Moreover, integrating digital technologies, such as QR codes or RFID tags linked to sensors embedded in the packaging, allows for real-time data collection and remote monitoring of storage conditions throughout the supply chain These multi-functional packaging solutions are particularly beneficial for high-value or sensitive products, such as seafood, pharmaceuticals, or ready-to-eat meals [449]. By providing actionable information about product quality and safety, multi-stimuli packaging systems empower consumers to make informed decisions, reduce food waste, and improve sustainability in the food supply chain [450].

7. Industrial and consumer applications of SRPs: From smart textiles to robotics

The integration of SRPs into textiles has led to the development of smart fabrics capable of dynamically adapting to external stimuli, including environmental conditions and physiological changes. These advanced materials offer functionalities such as automatic temperature regulation, efficient moisture management, and real-time chemical sensing. Such properties make SRPs essential in wearable technology and functional clothing, particularly for sportswear, outdoor apparel, and health-monitoring garments [451]. This section explores the current use and applicability of SRPs in consumer and high-tech applications.

7.1. Smart textiles and wearable technology

Smart textiles and coatings represent a significant advancement in functional materials for consumer goods. By incorporating SRPs, these products can dynamically respond to environmental changes, enhancing functionality, durability, and user comfort. The versatility of these polymers allows for their application in adaptive clothing, protective surfaces, and advanced textiles, addressing modern consumer demands for energy efficiency, sustainability, and high performance [452].

7.1.1. Temperature-responsive coatings and textiles

Temperature-responsive polymers are a cornerstone of smart textile and coating technology due to their ability to undergo reversible phase transitions in response to temperature fluctuations. For instance, PNIPAM, PCLA-PEG-PCLA, and Pluronic exhibit a LCST of approximately 32 °C [453,454]. Below this threshold, these polymers are hydrophilic, retaining moisture, while above the LCST, they become hydrophobic and repel water. This property enables dynamic thermal regulation, making them highly suitable for applications in climate-adaptive clothing and self-regulating textiles [455].

In textiles, temperature-responsive polymers enable the development of adaptive clothing that modulates thermal insulation based on environmental conditions. Garments embedded with these polymers can enhance breathability and cooling in warm climates while providing thermal insulation by trapping air in colder conditions. This dynamic adjustment reduces the need for layering, improving user comfort across varying temperatures [456]. Such textiles are particularly valuable in outdoor apparel, sportswear, and military uniforms, where maintaining thermal balance is essential for both performance and comfort [457].

In addition to textiles, temperature-responsive coatings have broad applications in architecture and energy management. Thermochromic coatings, for instance, utilize polymers that change color with temperature fluctuations [458]. Applied to windows, these coatings transition from transparent to opaque as temperatures rise, reducing heat gain in buildings and lowering cooling energy demands. Similarly, in automotive applications, smart sunroofs use these coatings to adjust light transmission, helping regulate cabin temperature efficiently [459].

Another innovative application of temperature-responsive coatings is in anti-icing systems. Coatings containing PNIPAM derivatives prevent ice adhesion by becoming hydrophobic at low temperatures, allowing ice to slide off surfaces easily. These coatings are particularly beneficial in aviation, transportation, and outdoor infrastructure, reducing reliance on energy-intensive de-icing processes and improving safety in extreme weather conditions [460].

7.1.2. Moisture-responsive textiles

Moisture-responsive polymers have significantly advanced functional textiles by enabling fabrics to adapt dynamically to changes in humidity. These materials often incorporate hygroscopic polymers such as PVA, PEG, chitosan, CMC, HPMC, PAA, and other natural polysaccharides. These polymers interact with moisture through swelling, conformational shifts, or hydrogen bonding, which induces reversible structural or mechanical changes in the textile matrix [461].

Textiles embedded with moisture-responsive polymers are designed to wick moisture away from the skin during physical activity, enhancing comfort and preventing overheating. These fabrics are widely used in activewear and sportswear, where efficient moisture management is critical for maintaining user performance [462]. Additionally, they can regulate humidity by releasing stored moisture when conditions become dry, making them suitable for applications such as medical garments or wearable sensors that require controlled hydration [463].

In smart bandages, moisture-responsive polymers serve a dual function: they maintain a moist environment conducive to wound healing while absorbing excess exudate to prevent maceration. These polymers are often integrated with antibacterial agents to provide infection prevention, making them highly valuable in advanced wound care [464].

Moisture-sensitive textiles are also employed in adaptive building elements, such as curtains and wall coverings, which regulate indoor humidity by absorbing excess moisture and releasing it when the air becomes dry. This capability improves indoor air quality and reduces reliance on mechanical humidification systems, contributing to greater

energy efficiency [465].

7.1.3. Self-healing coatings and fibers

Self-healing materials have emerged as a sustainable solution to enhance the durability and lifespan of coatings and textiles. In addition to disulfide bonds, hydrogen bonds, and Diels-Alder adducts, other reversible interactions such as imine linkages (Schiff bases), boronic esters, metal-ligand coordination, π-π stacking, and host-guest interactions (e.g., cyclodextrin complexes) are frequently employed [466]. These dynamic bonds enable the material to autonomously repair cracks or surface damage in response to stimuli like heat, moisture, or light, thereby maintaining performance and reducing the need for external maintenance [467]. As illustrated in Fig. 21, these self-healing mechanisms rely on either dynamic covalent bonds or noncovalent interactions to reconnect disrupted polymer networks, facilitating the recovery of mechanical and functional properties after damage [468].

In coatings, self-healing polymers are used to repair minor abrasions, scratches, or surface cracks. For instance, coatings embedded with disulfide-containing polymers can restore their structural integrity when exposed to heat, UV light, or mechanical pressure. These coatings are widely applied to high-wear surfaces, including automotive paints, consumer electronics, and construction materials, helping to maintain both aesthetic and functional performance over time [469]. Advanced self-healing coatings also offer anti-corrosion properties, making them ideal for protecting metallic surfaces in marine, industrial, and infrastructure applications [470].

In textiles, self-healing fibers can recover from physical damage such as tears, cuts, or abrasions. These fibers are designed to restore their mechanical properties when exposed to external stimuli such as heat or moisture [471]. For example, fibers incorporating reversible hydrogen-bonding networks can self-repair upon contact with water, which activates bonding sites and facilitates polymer chain reconnection. These self-healing properties are particularly beneficial in high-performance textiles, including military uniforms, protective gear, and industrial fabrics, where durability and reliability are essential [472].

The integration of self-healing polymers into textiles also supports sustainability by reducing waste and extending the lifespan of garments and upholstery. As demand for circular economies grows, self-healing textiles are becoming a key innovation in sustainable materials, ensuring that products remain functional for longer and minimizing the environmental impact of textile production and disposal [473].

7.2. High-performance polymers for automotive and aerospace applications

In the automotive and aerospace industries, the need for materials that enhance performance, ensure safety, and promote sustainability has driven the adoption of high-performance SRPs. These advanced materials dynamically respond to operational conditions such as pressure, temperature, and mechanical stress, offering solutions that improve efficiency, reliability, and adaptability. Their integration into critical systems has not only transformed design and manufacturing processes but also paved the way for smarter, more sustainable vehicles and aircraft [474].

7.2.1. Pressure- and stress-responsive materials

Pressure- and stress-responsive polymers are designed to detect and respond to external mechanical forces, such as compression, tension, or shear, by undergoing changes in their structural, optical, or electrical properties [475]. Common examples include piezoelectric polymers like poly(vinylidene fluoride) (PVDF), which generate electrical signals upon deformation; mechanophore-containing polymers incorporating spiropyran or cyclobutane units that undergo bond cleavage or color changes under stress; and conductive polymer composites with fillers such as carbon nanotubes or graphene, which exhibit resistance changes in response to pressure [476]. Additionally, elastomeric materials like PDMS and supramolecular polymers with reversible non-covalent interactions contribute to real-time sensing and adaptive functions in applications such as soft robotics, wearable sensors, and structural health monitoring [477].

In aerospace applications, these polymers are utilized in coatings and sensors to monitor the structural integrity of aircraft components. For example, piezoelectric polymers such as PVDF, when embedded in composite structures, can generate electrical signals in response to mechanical deformation, enabling real-time monitoring of stress and strain. This feature supports predictive maintenance by detecting early signs of fatigue or structural damage [478]. Similarly, mechanophore-containing polymers such as those incorporating spiropyran or cyclobutane units can exhibit visible color changes under stress, serving as stress-responsive coatings for intuitive, non-destructive inspection of surfaces, including aircraft exteriors during routine maintenance [479]. Conductive polymer composites with carbon nanotubes or graphene fillers also detect pressure through resistance changes, further enhancing sensing capabilities in safety-critical systems.

In the automotive industry, pressure-responsive materials are

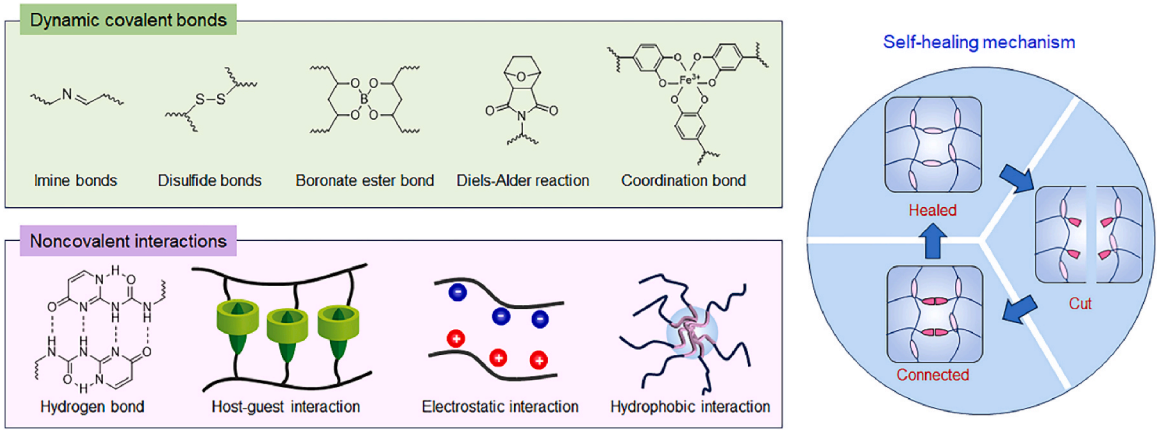

Fig. 21. Self-healing mechanisms in polymeric systems. Self-healing materials utilize either dynamic covalent bonds (e.g., imine, disulfide, boronate ester, Diels-Alder, and coordination bonds) or noncovalent interactions (e.g., hydrogen bonding, host-guest complexation, electrostatic and hydrophobic interactions) to restore network integrity after damage. These reversible interactions enable polymer chains to reconnect after mechanical disruption, promoting autonomous healing and extending material longevity.

utilized in suspension systems, brake components, and tire monitoring systems. For instance, polymers with mechanochemical properties can adapt to varying load conditions, optimizing suspension performance for different driving environments. These materials also enhance tire safety by detecting pressure changes and alerting drivers to potential issues such as underinflation or overloading [480]. Additionally, adaptive polymer composites in crash-resistant panels absorb and dissipate impact energy, minimizing vehicle damage and improving passenger safety during collisions [481].

7.2.2. Temperature-responsive components

Temperature-responsive polymers are essential in the development of adaptive systems for vehicles and aircraft, especially where precise thermal regulation and responsive structural behavior are required. Among them, shape-memory polymers (SMPs) stand out for their ability to recover pre-programmed shapes upon exposure to specific temperature thresholds. These materials exhibit reversible changes in shape, stiffness, or elasticity based on thermal stimuli, allowing components to deploy, contract, or self-adjust under varying conditions [482]. Common SMPs include polyurethane-based systems, PCL, and epoxy composites, which are engineered to respond at tailored activation temperatures [483]. As illustrated in Fig. 22, shape-memory behavior typically involves a thermomechanical cycle consisting of permanent shape fixation, programming via deformation above the melting temperature, and shape recovery upon reheating, as demonstrated using PCL-co-PGMA copolymer systems. Their integration enhances performance, reduces mechanical complexity, and contributes to lightweight, energy-efficient design in aerospace, automotive, and robotics applications [484].

In aerospace engineering, SMPs are used in actuators and self-deploying structures, such as morphing wing panels or deployable satellites. These materials can change shape upon heating, allowing for the controlled deployment of components without the need for complex mechanical systems. For example, SMP-based actuators in aircraft wing flaps can adjust their geometry to optimize airflow and reduce drag under varying thermal conditions, improving fuel efficiency and aerodynamic performance [485].

In the automotive sector, SMPs are integrated into thermal management systems for engine components and air conditioning ducts. These polymers adjust airflow or heat dissipation in response to temperature changes, ensuring efficient operation and reducing energy consumption. For instance, SMPs in vehicle air ducts expand or contract based on cabin temperature, maintaining passenger comfort while minimizing energy usage. Similarly, temperature-sensitive materials are employed in battery management systems for electric vehicles, helping regulate heat generation and prevent overheating [486].

Advanced temperature-responsive polymers are also used in safety systems, such as thermally activated airbags and fire-resistant coatings. These materials ensure rapid responses to extreme temperatures, enhancing passenger protection and reducing risks in critical situations [487].

7.2.3. Lightweight and adaptive materials

The pursuit of fuel efficiency and reduced carbon emissions has driven the development of lightweight and adaptive materials for automotive and aerospace applications. SRPs offer a unique combination of lightweight properties and adaptability, making them ideal for high-stress components and structural elements [488].

In aerospace technology, multi-stimuli-responsive composites that combine thermal, mechanical, and chemical adaptability such as shape-memory alloys integrated with polymer matrices, ionomer-based smart materials, and stimuli-responsive epoxy systems are increasingly used in turbine blades, fuselage panels, and heat shields [489].

For instance, polymer composites reinforced with carbon or glass fibers, as well as with aramid fibers, basalt fibers, or nanomaterials like carbon nanotubes and graphene, exhibit excellent strength-to-weight ratios and can respond to thermal or mechanical stimuli by altering their stiffness or geometry. These materials can withstand extreme operating conditions, such as high temperatures and mechanical loads, while adapting to environmental changes. This adaptability reduces wear and tear, extending the lifespan of critical components [490].

In the automotive industry, lightweight SRPs are used in crash-resistant panels, adaptive chassis systems, and aerodynamic components. These materials contribute to significant weight reductions, improving vehicle fuel efficiency and reducing greenhouse gas emissions. For example, adaptive polymer panels in electric vehicles optimize energy absorption during collisions, enhancing passenger safety while maintaining a lightweight design [491].

The integration of SRPs into exterior components, such as hoods and bumpers, also offers additional benefits, including self-healing properties that repair minor damages caused by impacts or abrasions. This self-repair capability minimizes maintenance costs and improves the aesthetic durability of vehicles [492].

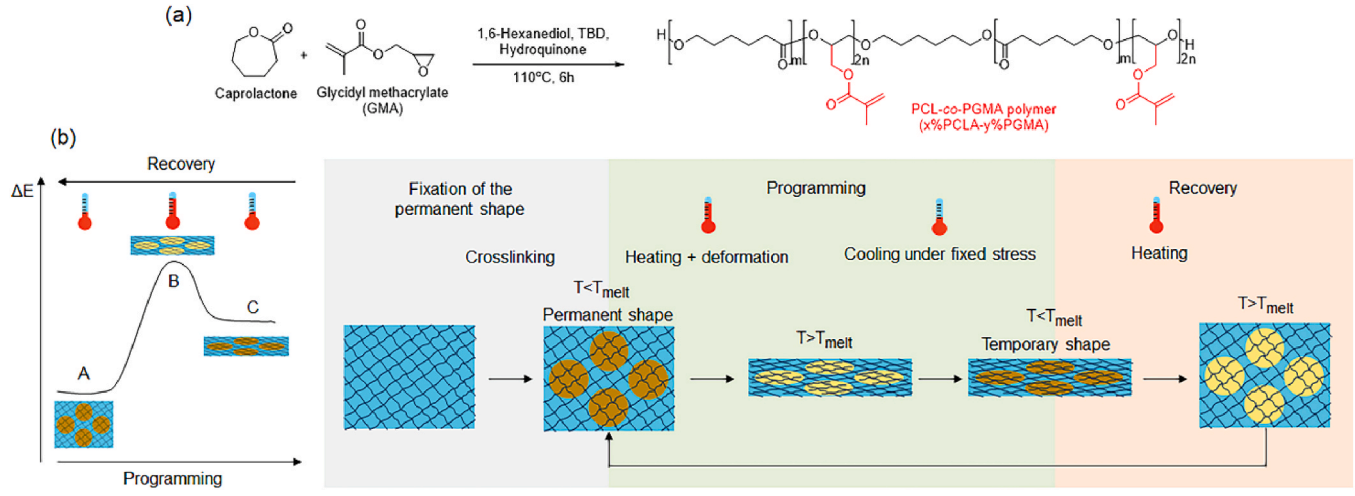

Fig. 22. Thermally induced shape memory polymer system. (a) Synthetic scheme of a PCL-*co*-PGMA copolymer from caprolactone and glycidyl methacrylate. (b) Shape memory cycle including permanent shape fixation via crosslinking, programming through heating and deformation above T_{melt}, cooling under stress to fix the temporary shape, and recovery to the original shape upon reheating.

7.3. SRPs for wearable electronics and soft robotics

The integration of SRPs into wearable electronics and soft robotics has significantly advanced the design and functionality of flexible, adaptive, and multi-functional systems. These polymers offer unique capabilities, such as dynamic responsiveness to environmental stimuli, self-healing properties, and energy-harvesting potential, making them essential for progress in personalized healthcare, human-machine interaction, and next-generation robotic technologies. Their use in wearable devices and soft robotics improves comfort, adaptability, and sustainability, while enabling a wide range of functionalities, from real-time physiological monitoring to autonomous robotic movement [493].

7.3.1. Flexible and stretchable electronics

SRPs play a pivotal role in enabling flexible and stretchable electronic devices by preserving functionality under mechanical deformation. Materials such as conductive hydrogels (e.g., PEDOT:PSS, PANI, and polyacrylamide-silver nanowire composites) offer intrinsic stretchability alongside electrical conductivity [494]. Elastomers like PDMS, polyurethane, and SEBS provide mechanical flexibility suitable for wearable sensors, while SMPs, including PCL- and polyurethane-based systems, facilitate reversible shape changes in response to environmental triggers [495]. As illustrated in Fig. 23, the development of flexible and deformable electronic systems relies on two complementary strategies: (1) materials stretchability, which leverages elastic polymers and nanostructures to ensure mechanical compliance, and (2) structural stretchability, which utilizes geometrically engineered configurations such as serpentine, wavy, and mesh patterns to accommodate strain without compromising function [496].

These integrated approaches support a wide range of wearable applications. Conductive hydrogels and elastomers, which combine conductivity and flexibility, are employed in biosensors that monitor parameters such as heart rate, temperature, and muscular activity [497]. Incorporation of stimuli-responsive elements like temperature-sensitive PVCL or pH-responsive chitosan enables real-time adaptation to environmental changes. For example, self-regulating heating elements based on thermoresponsive hydrogels provide thermal comfort in wearable garments, while piezoresistive polymers enhance tactile sensing in prosthetics and virtual interfaces [498].

Stretchable circuits fabricated from SRPs preserve electrical continuity under extensive deformation, making them ideal for long-term wearable electronics. Moreover, polymers featuring reversible cross-linking (e.g., hydrogen bonding, ionic interactions) offer resilience against cracking and delamination. SRPs are also being actively explored for use in deformable energy storage devices, serving as flexible electrolytes or separators that maintain high ionic conductivity and conformability [499].

7.3.2. Adaptive materials for soft robotics

Soft robotics relies on materials that emulate the adaptability and fluidity of biological systems, enabling robots to perform tasks requiring flexibility, dexterity, and safe interaction with humans and dynamic environments. As depicted in Fig. 24, adaptive materials serve as a critical bridge between soft and rigid systems, facilitating core functionalities such as motion, sensing, and communication across wearable devices, soft robotic platforms, and healthcare technologies [500].

SRPs including electroactive polymers (EAPs), thermally responsive polymers, and light-sensitive gels have emerged as essential materials for actuators, grippers, and artificial muscles in soft robotics [501]. EAPs, which undergo shape or stiffness changes in response to electric fields, are particularly effective in enabling reversible, fast, and controllable deformation. Ionic EAPs, such as polyelectrolyte gels, ionomeric polymer-metal composites (IPMCs), Nafion® membranes, and PVA-based ionogels, function at low voltages and are highly suitable for bioinspired motion in soft actuators. For example, IPMCs generate large bending deformations at millivolt inputs, making them ideal for artificial muscles and robotic limbs [502].

Thermally responsive polymers, including shape-memory alloys and SMPs, provide temperature-triggered actuation by transitioning between rigid and flexible phases. These materials are used in applications such as deployable soft robotic structures, adaptive exoskeletons, and morphing devices [503]. Similarly, light-responsive gels that change shape or modulus upon exposure to specific wavelengths enable precise, wireless control of soft actuators. Such systems have been applied in phototunable grippers and reconfigurable robotic appendages [504].

To further enhance the versatility of soft robots, hybrid SRPs are

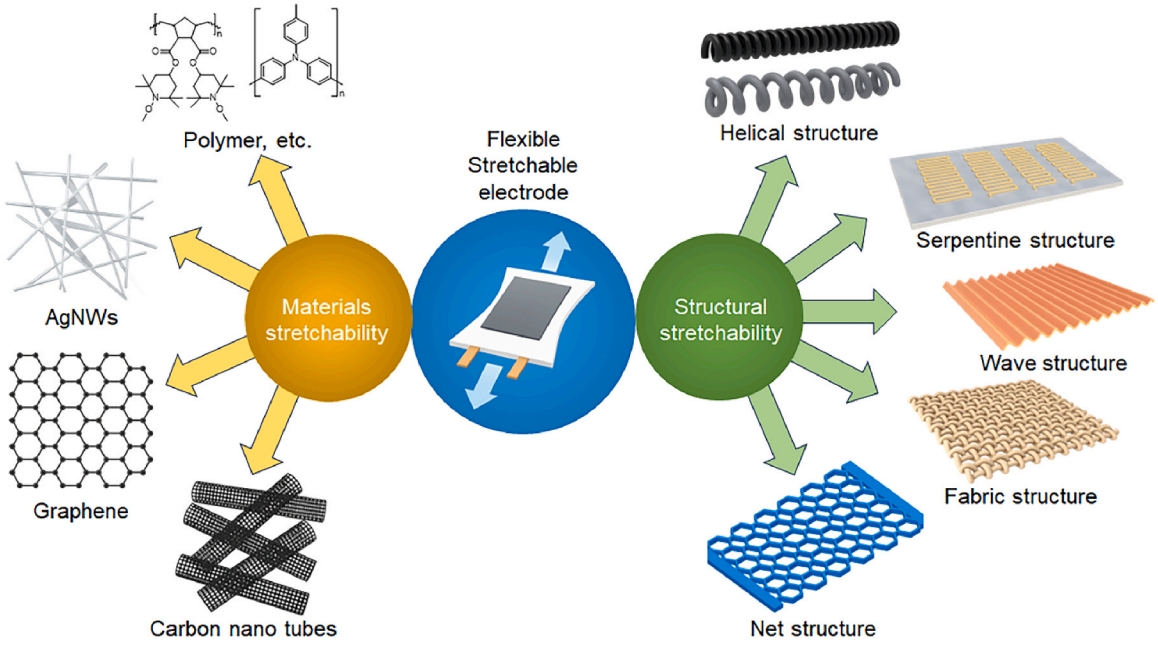

Fig. 23. Approaches to flexible and stretchable electronics. Stretchability is achieved through material strategies using elastic polymers and nanomaterials, and structural designs like serpentine, wavy, and mesh patterns, enabling flexible and deformable electronic devices [496]. Copyright 2010, American Association for the Advancement of Science.

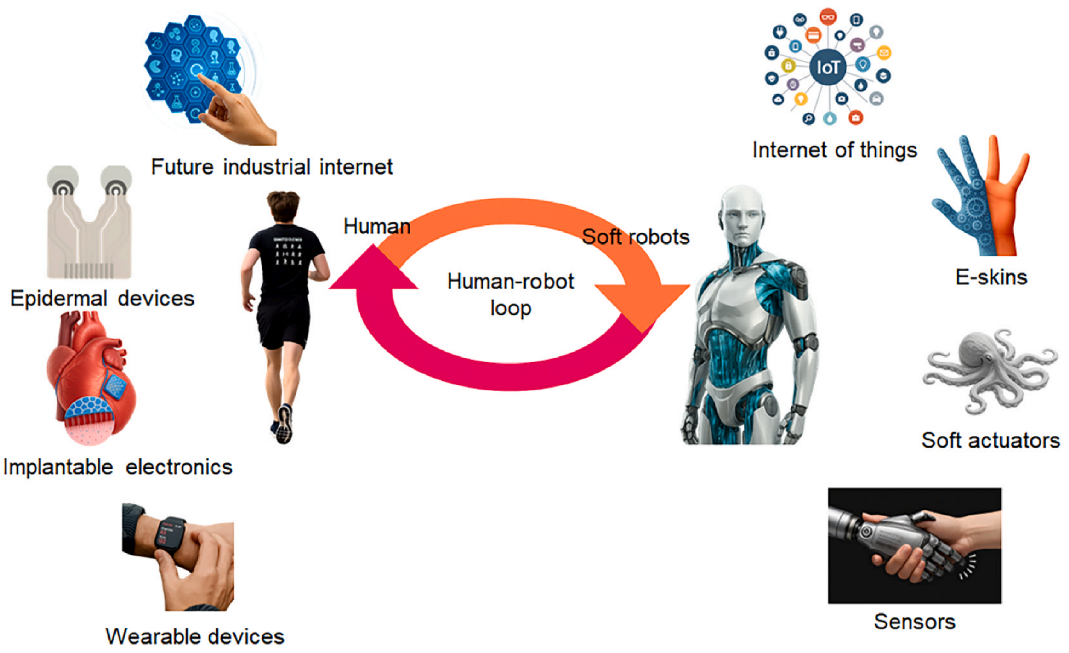

Fig. 24. Adaptive materials enabling soft robotics. Adaptive materials bridge soft and hard systems, enabling functions such as motion, sensing, and communication in wearable devices, soft robots, and healthcare systems. Their flexibility, responsiveness, and integration with electronics are key to future human-machine interfaces.

being developed to respond to multiple stimuli electrical, thermal, or optical. These multifunctional materials allow robots to dynamically adjust shape, stiffness, and motion strategy to suit changing environmental conditions. Ultimately, adaptive materials integrated with sensing and electronic systems enable the realization of next-generation human-machine interfaces that are flexible, interactive, and intelligent [505].

7.3.3. *Self-healing and energy-harvesting polymers*

The incorporation of self-healing and energy-harvesting SRPs into wearable electronics and soft robotics significantly enhances device durability, sustainability, and autonomy. These materials enable devices to maintain functionality despite physical damage and generate power from ambient energy sources, reducing reliance on external power supplies [506].

Self-healing polymers, which autonomously repair minor damage through reversible chemical bonds or phase transitions, are essential for extending the lifespan of wearable and robotic devices. These materials often use dynamic covalent bonds, such as disulfide linkages or Diels-Alder reactions, to restore structural integrity after damage. For example, wearable sensors made from self-healing hydrogels can recover their conductivity and mechanical properties after being cut or

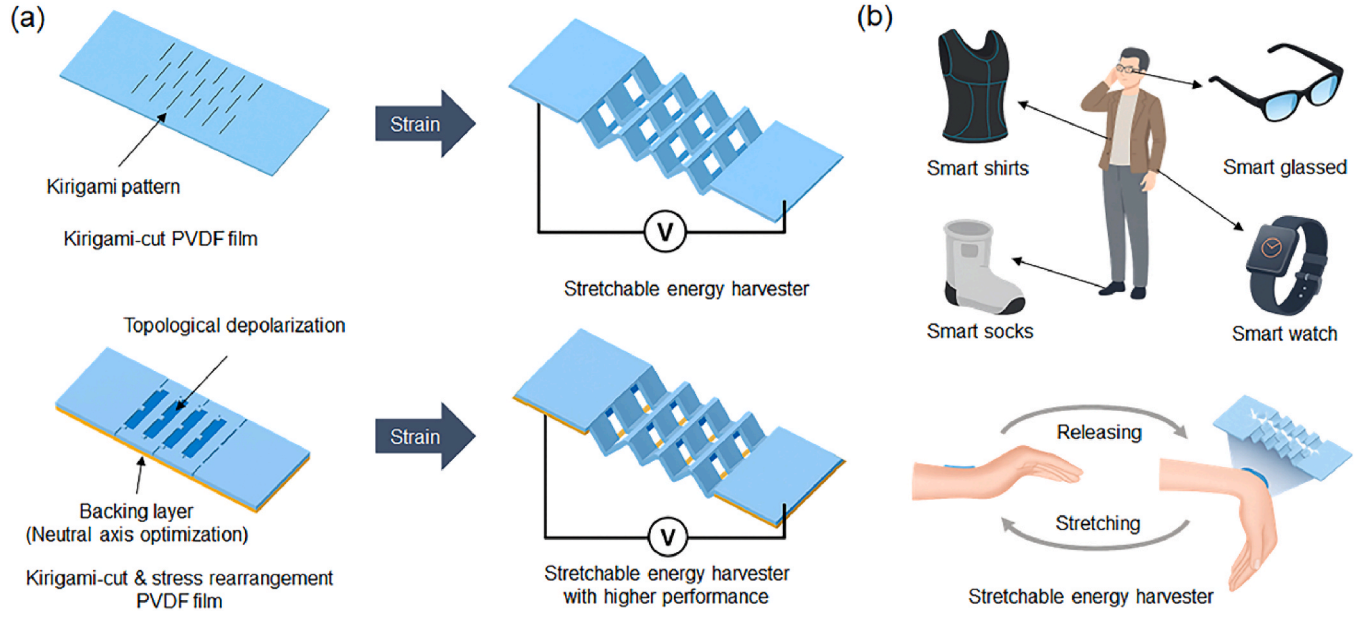

Fig. 25. Kirigami-inspired strain sensors for wearable electronics. (a) Schematic of kirigami-patterned structures that unfold upon mechanical strain, converting deformation into electrical signals for strain sensing. (b) Integration of kirigami-based sensors into wearable systems for monitoring joint motion, posture, and health-related movements in real-time applications [510]. Copyright 2019, Royal Society of Chemistry.

punctured, ensuring continuous monitoring without the need for replacement [507]. In soft robotics, self-healing elastomers enable actuators and grippers to withstand repeated mechanical stresses and accidental tears, reducing maintenance costs and improving reliability [508].

In parallel, energy-harvesting polymers are used to convert biomechanical energy into electricity. Piezoelectric and triboelectric materials such as PVDF, PVDF-TrFE, and PLLA are integrated into devices to generate power from motions like walking or bending. These technologies allow for the creation of self-powered medical monitoring systems, fitness trackers, and soft robotic skins, particularly valuable in remote or power-constrained environments [509]. Notably, kirigami-inspired strain sensors (Fig. 25) exemplify the integration of mechanical deformation and energy transduction. These systems use strategically patterned cuts to unfold under strain, converting mechanical input into detectable electrical signals for real-time strain sensing. Their incorporation into wearable electronics supports applications such as joint motion tracking, posture monitoring, and movement-based diagnostics [510].

The combination of self-healing and energy-harvesting properties in a single material creates multi-functional systems that are both resilient and self-sustaining. For example, a soft robotic arm made from a hybrid polymer can repair damage autonomously while simultaneously generating energy from its movements to power embedded sensors. These integrated systems represent the future of wearable electronics and soft robotics, offering unprecedented levels of functionality, adaptability, and sustainability [511].

8. Advancements in SRP technology: Innovations, hybrid systems, and 4D printing

Recent progress in SRP technology has vastly broadened its range of applications and functionalities, driving innovation across multiple fields such as energy storage, optical systems, and data storage. This section explores the transformative impact of SRPs in these areas, focusing on novel material designs, the expansion of their use cases, and case studies that highlight their real-world potential [512].

8.1. Integration with artificial intelligence and machine learning

8.1.1. Advancements in polymer design through computational insights

The integration of artificial intelligence (AI) and machine learning (ML) with SRP technology is reshaping the way these materials are developed and applied. With the use of advanced computational tools, researchers can now go beyond traditional trial-and-error methods, achieving remarkable precision and efficiency in polymer design. ML models, trained on extensive polymer databases, can uncover complex structure-property relationships [513]. For example, by analyzing the molecular structure and functional groups of polymers, ML can predict how they will react to various stimuli such as temperature, pH, light, or mechanical stress. This predictive capability allows for the precise design of SRPs for targeted applications, saving both time and resources during development [514].

Additionally, AI-driven simulations and modeling techniques can optimize polymer synthesis by identifying the best reaction conditions and predicting outcomes in different environments. These methods also help evaluate the scalability and reproducibility of polymer production, ensuring that laboratory results can be successfully scaled up for industrial applications [515]. A comprehensive data-driven pipeline integrating data collection, feature engineering, and ML-based prediction and optimization is illustrated in Fig. 26, highlighting how AI accelerates property prediction, material discovery, and autonomous experimentation. Therefore, AI-driven technologies not only streamline the discovery of new materials but also address practical considerations for their deployment in real-world applications [516].

8.1.2. Enhancing performance predictions in complex environments

AI and ML are proving invaluable in predicting how SRPs will behave in dynamic, complex environments. Traditional experimental methods often fall short in accurately modeling the complex conditions found in

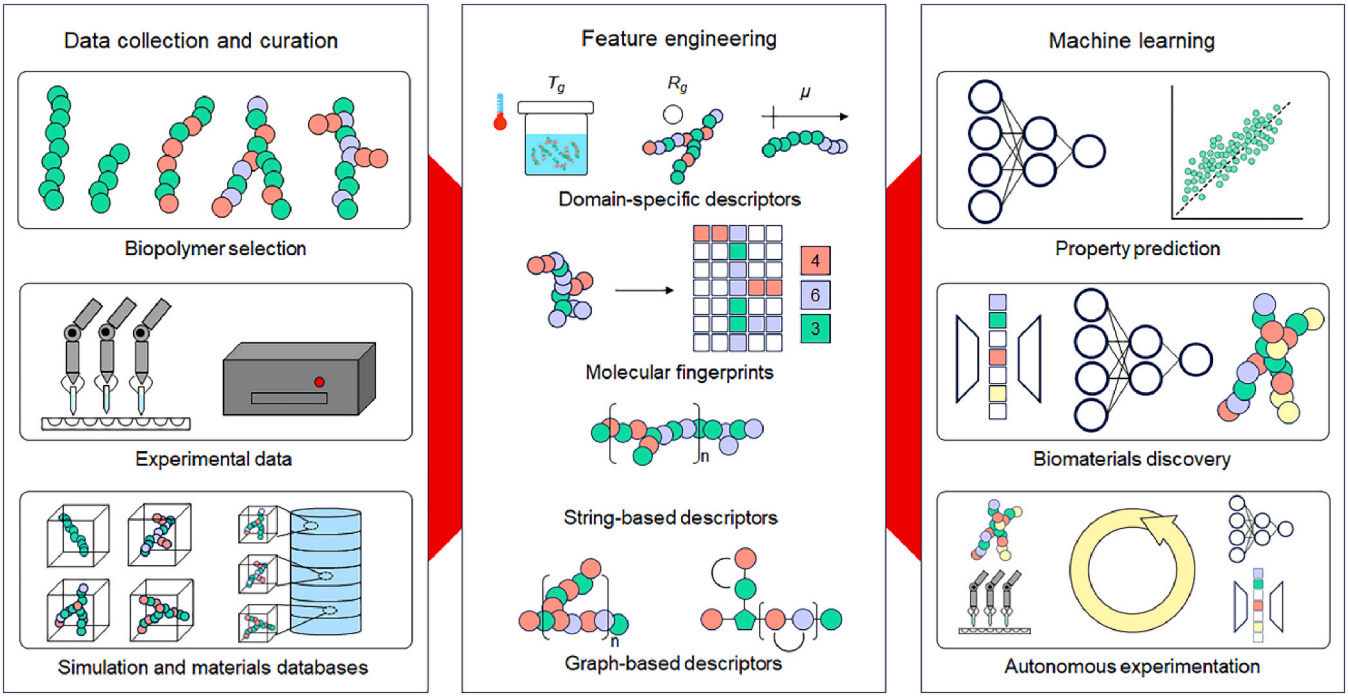

Fig. 26. Advancements in polymer design through computational insights. Overview of a data-driven pipeline for biomaterial discovery integrating (left) data collection and curation from experiments, simulations, and databases; (middle) feature engineering using domain-specific descriptors, molecular fingerprints, and graph/string-based representations; and (right) machine learning approaches for predicting properties, discovering new biomaterials, and enabling autonomous experimentation.

biological systems or polluted ecosystems. AI models can process vast datasets, including variables such as temperature fluctuations, pH levels, and the presence of reactive biomolecules, to simulate polymer performance under realistic conditions [517].

For example, in biomedical applications, AI simulations can predict how a polymer carrying drugs will interact in the acidic microenvironment of a tumor or under oxidative stress in inflamed tissues. This helps fine-tune polymer properties such as degradation rates, drug release profiles, and biocompatibility, ensuring both therapeutic effectiveness and safety [518]. Similarly, in environmental applications, AI can simulate how stimuli-responsive polymers will react with pollutants in water treatment systems, considering factors like ionic strength, contaminant concentrations, and the presence of competing chemicals. These predictive capabilities are crucial for enhancing the selectivity and efficiency of polymer-based solutions for environmental remediation [519].

8.1.3. Real-time control in adaptive systems

AI and ML play an instrumental role not only in the design and analysis of SRPs but also in their real-time applications. By embedding AI-driven control systems, adaptive materials and devices can dynamically adjust their properties in response to environmental feedback. This capability is particularly advantageous for self-healing materials, smart actuators, and responsive drug delivery systems [520].

For example, AI-integrated wearable medical devices can continuously monitor physiological signals such as glucose levels or body temperature and adjust drug release from SRPs accordingly. This closed-loop system enhances treatment precision and personalization, ultimately improving patient outcomes [521]. In industrial applications, smart coatings and membranes embedded with AI-responsive polymers can automatically adapt to changes in temperature, humidity, or chemical exposure, ensuring consistent performance without requiring manual adjustments [522].

8.1.4. Accelerating innovation through data-driven approaches

The integration of AI and ML into polymer science has also accelerated material discovery by enabling high-throughput screening and virtual experimentation. These advanced techniques allow researchers to efficiently explore vast chemical spaces, identifying promising polymer candidates much faster than conventional trial-and-error methods. By automating data analysis and pattern recognition, AI systems can reveal previously unnoticed correlations and trends, guiding the development of next-generation SRPs [523].

Additionally, AI-powered platforms facilitate interdisciplinary collaboration by integrating datasets from fields such as materials science, biomedicine, and environmental engineering [524]. For instance, a polymer initially designed for biomedical applications may also exhibit properties suitable for environmental remediation, which are connections that AI can quickly identify. This cross-disciplinary insight fosters innovation and broadens the potential applications of SRP technologies [525].

8.2. Hybrid and multifunctional polymer systems

8.2.1. Enhancing functionality through hybrid systems

The integration of SRPs with complementary materials such as nanomaterials, biopolymers, and MOFs has garnered increasing attention as a powerful strategy for overcoming the limitations of single-component materials. These hybrid polymer systems leverage the synergistic properties of their components to achieve advanced functionalities tailored for complex biomedical and environmental applications [526]. By combining the environmental responsiveness of SRPs with the unique physical or chemical properties of nanomaterials, the resulting multifunctional materials can perform simultaneous or sequential tasks with greater efficiency [527].

One of the key advantages of hybrid polymer systems is their modularity, which enables the seamless incorporation of diverse functional components into a single material. This adaptability is particularly beneficial for applications requiring multimodal capabilities, such as theranostics, adaptive coatings, and environmental remediation [528].

8.2.2. Dual stimuli-responsive materials for precision control

One of the most significant advancements in hybrid polymer systems is the development of materials that respond to two or more external stimuli in a coordinated manner. By incorporating functional components such as magnetic nanoparticles, quantum dots, or plasmonic nanostructures into SRPs, these materials can exhibit dual or multi-stimuli responsiveness [529]. For instance, embedding magnetic nanoparticles within thermo-responsive polymers enables a material to react to both temperature and magnetic fields. This feature is particularly valuable in biomedical applications such as targeted drug delivery, where an external magnetic field directs nanoparticles to a specific location, after which temperature changes trigger the controlled release of therapeutic agents [530].

In environmental applications, dual-stimuli systems facilitate the development of smart adsorbents and membranes capable of adapting to fluctuating conditions. For example, a hybrid polymer incorporating pH-sensitive groups and magnetic nanoparticles can selectively capture heavy metals from industrial wastewater under acidic conditions, while the application of a magnetic field enables the efficient recovery and regeneration of the adsorbent for repeated use [531].

8.2.3. Hybrid hydrogels for tissue engineering and regenerative medicine

Hybrid hydrogels have revolutionized tissue engineering by offering dynamic, biomimetic platforms that closely replicate the complexity of native tissues [532]. By integrating enzyme-sensitive polymers with bioactive nanoparticles, these hydrogels provide enhanced performance in applications such as wound healing, tissue scaffolding, and organ regeneration. These systems not only enable localized, stimuli-triggered drug release but also promote cell adhesion, proliferation, and differentiation, which are essential for tissue regeneration [533].

For example, enzyme-responsive hydrogels embedded with growth factor-loaded nanoparticles can selectively release bioactive molecules in response to specific enzymatic activity at wound sites or within inflamed tissues. This targeted delivery accelerates healing while minimizing systemic side effects [534]. Additionally, incorporating biocompatible nanostructures, such as hydroxyapatite or silica nanoparticles, strengthens the hydrogel's mechanical properties and enhances osteoinductive capabilities, making them ideal candidates for bone regeneration [535].

8.2.4. Theranostic platforms for simultaneous diagnosis and treatment

Hybrid polymer systems incorporating quantum dots, fluorescent dyes, and other imaging agents have enabled the development of theranostic platforms that seamlessly integrate diagnostic and therapeutic functions. These systems facilitate real-time monitoring of treatment efficacy, offering substantial advantages in personalized medicine [536]. For instance, polymers conjugated with fluorescent nanoparticles can track drug release dynamics in cancer therapy, ensuring precise delivery to tumor sites and minimizing off-target effects [537].

Additionally, hybrid systems that integrate MOFs with pH-responsive polymers can encapsulate and release drugs selectively in the acidic microenvironments of tumors while simultaneously enhancing contrast in imaging techniques such as MRI or fluorescence microscopy [538]. By providing clinicians with real-time feedback on drug distribution and tumor response, these theranostic materials enable dynamic adjustments to treatment strategies, ultimately improving patient outcomes [539].

8.2.5. Advanced environmental applications of hybrid systems

In environmental science, hybrid polymer systems are proving instrumental in addressing pollution and resource management challenges. By combining the adsorption capabilities of polymers with the catalytic and sensing properties of nanomaterials, these systems offer enhanced performance in pollutant detection and remediation [540].

For example, hybrid membranes incorporating MOFs and pH-responsive polymers can dynamically regulate their permeability to optimize contaminant separation in water treatment. Similarly, polymers functionalized with catalytic nanoparticles, such as titanium dioxide or gold nanorods, enable the photodegradation of organic pollutants under light exposure, providing an active approach to water purification [541].

Hybrid systems are also being employed in the development of responsive coatings for environmental monitoring devices. These coatings, which integrate temperature-sensitive polymers with fluorescent sensors, can detect and report real-time fluctuations in environmental parameters such as temperature, pH, and pollutant levels [542]. The combination of adaptive responsiveness and sensing functionality makes these materials invaluable for sustainable environmental monitoring and resource management.

8.3. Sustainability and green chemistry approaches

8.3.1. Transitioning toward eco-friendly SRPs

The increasing global focus on sustainability has driven significant advancements in the development of SRPs using green chemistry principles. Researchers are prioritizing the creation of polymers that maintain high functionality while minimizing environmental impact. This transition is particularly crucial as SRPs gain widespread use in medical, industrial, and environmental applications, where long-term ecological effects must be considered [543]. By incorporating bio-based feedstocks, environmentally benign synthesis methods, and innovative processing techniques, next-generation SRPs are designed to address pressing sustainability challenges [544]. The foundational framework for this transition is outlined by the twelve principles of green chemistry, which serve as a guideline for designing safer, more efficient, and degradable SRPs with reduced waste and energy consumption (Fig. 27). These principles collectively support the realization of environmentally friendly applications in future smart material systems [545].

8.3.2. Bio-based monomers for biodegradable polymers

A key strategy for sustainable polymer development is the use of bio-based monomers derived from renewable resources. Unlike conventional petroleum-based monomers, these alternatives offer inherent biodegradability and a reduced carbon footprint. Natural sources such as lignin, chitosan, cellulose, and plant oils have been extensively explored for synthesizing responsive polymers [546].

For example, chitosan, a polysaccharide derived from crustacean exoskeletons, has been used to develop pH-responsive polymers for drug delivery and water treatment applications. Beyond native chitosan, quaternized chitosan, carboxymethyl chitosan, and chitosan-grafted synthetic polymers (e.g., PEG or PAA) have been engineered to enhance solubility, antimicrobial activity, and environmental responsiveness, broadening their applicability in biomedical coatings, wound dressings, and biosensors [547].

Similarly, lignin, a byproduct of the paper and biofuel industries, has been incorporated into polymer formulations due to its abundance, UV-blocking properties, and chemical modifiability [548]. Lignin has been utilized in various forms such as kraft lignin, organosolv lignin, lignosulfonates, and enzymatic hydrolysis lignin, which differ in molecular weight, solubility, and reactivity. These derivatives are frequently used to prepare lignin-based polyurethanes, thermoplastics, or nanocomposites, offering improved antioxidant, flame-retardant, or mechanical properties in packaging, agriculture, and electronics [549]. As illustrated in Fig. 28, lignin is composed of three major units H (p-hydroxyphenyl), G (guaiacyl), and S (syringyl) and can be extracted through various methods such as alkali, organosolv, enzymatic, and sulfite processes. These structural features confer lignin with intrinsic responsiveness to stimuli such as pH, temperature, enzymes, gases, and light, making it a promising multifunctional monomer for the design of biodegradable and stimuli-responsive polymers across biomedical, pharmaceutical, and environmental applications [550].

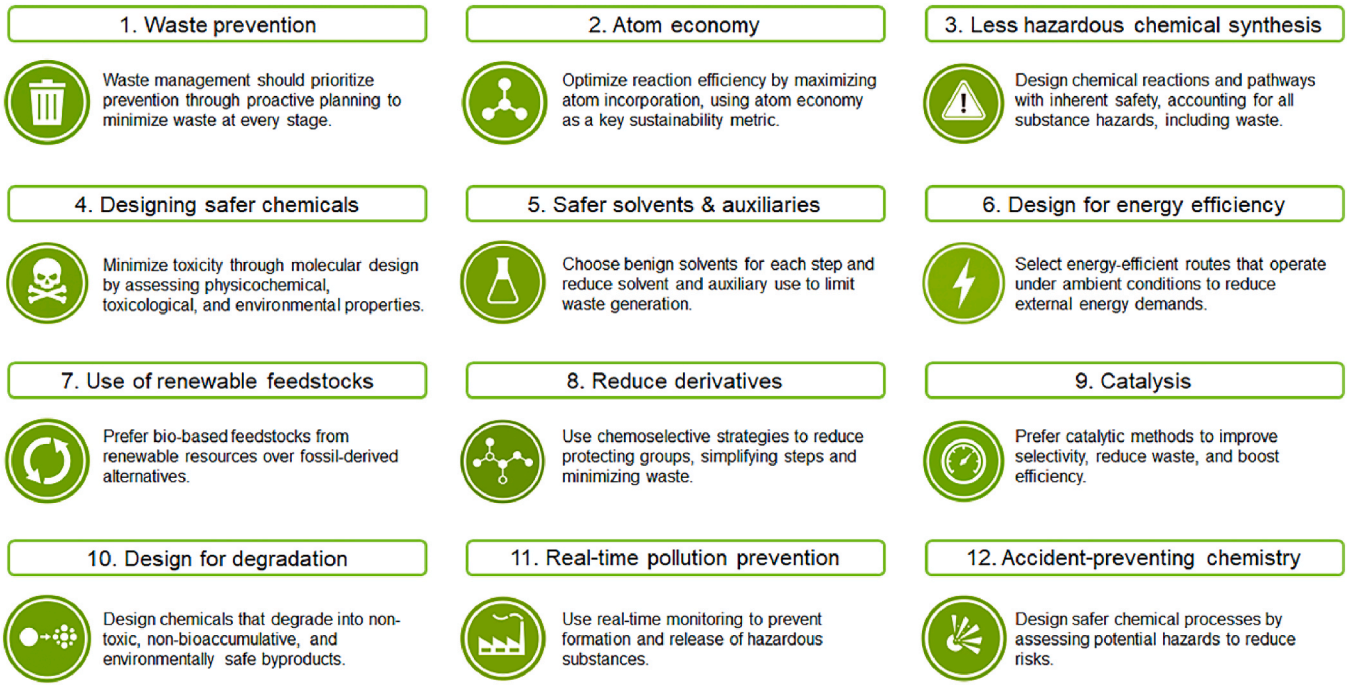

Fig. 27. Green chemistry principles guiding eco-friendly SRP development. Twelve principles support the design of sustainable stimuli-responsive polymers by promoting safer materials, reduced waste, energy efficiency, and enhanced degradability for environmentally friendly applications.

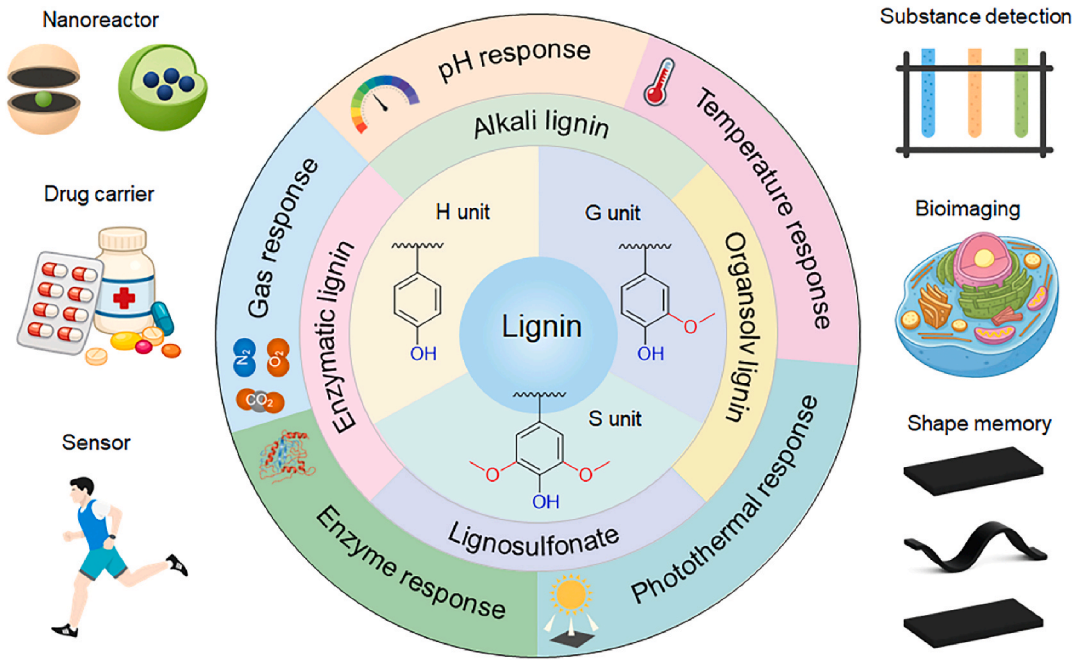

Fig. 28. Bio-based lignin as a multifunctional monomer for biodegradable stimuli-responsive polymers. Lignin, composed of H, G, and S units, is extracted via various methods (alkali, organosolv, enzymatic, and sulfite) and enables diverse responsiveness to pH, temperature, enzymes, gases, and light. These properties support its use in biomedical, pharmaceutical, and environmentally responsive applications [550]. Copyright 2023, MDPI Open Access Publishing.

8.3.3. Green polymerization techniques

Sustainability in polymer science extends beyond raw materials to include environmentally friendly synthesis methods. Traditional polymerization techniques often involve toxic solvents, high energy consumption, and hazardous reagents, all of which contribute to environmental degradation [551]. Advances in green chemistry have led to the development of eco-friendly alternatives that minimize these issues.

One such approach is solvent-free polymerization, where reactions occur without VOCs, reducing harmful emissions and simplifying purification processes. This method is particularly beneficial for producing bulk materials such as hydrogels and elastomers used in medical and environmental applications [552].

Another innovation is aqueous polymerization, which replaces organic solvents with water-based reaction media. This technique significantly lowers the ecological footprint while improving polymer morphology control. Aqueous emulsion polymerization, for instance, has been widely employed to synthesize temperature- and pH-sensitive polymers for drug delivery and coating applications [553].

Additionally, photo-initiated polymerization, which utilizes light to drive the reaction, has gained attention for its energy efficiency and ability to proceed under mild conditions. This technique is particularly advantageous for fabricating responsive coatings and thin films, where precision and environmental sustainability are critical [554].

8.3.4. Sustainable fabrication techniques

The sustainability of SRPs is further enhanced through advanced fabrication techniques that prioritize energy efficiency and waste reduction. Methods such as additive manufacturing (3D printing), electrospinning, and layer-by-layer assembly enable precise material production while minimizing resource consumption and environmental impact [555].

For example, 3D printing allows for the fabrication of complex polymer structures with minimal material waste. This technique is particularly advantageous in personalized medicine, where patient-specific devices (e.g., drug delivery systems or tissue scaffolds) can be produced on demand. By integrating green synthesis approaches with 3D printing, researchers can develop biodegradable, stimuli-responsive materials that align with sustainability objectives [556].

Electrospinning, another environmentally friendly technique, produces nanofibers with high surface area-to-volume ratios, making them ideal for environmental applications such as pollutant adsorption and filtration. The use of water-based spinning solutions or bio-based polymers ensures that the process remains eco-conscious while delivering high-performance materials [557].

8.3.5. Applications in environmental sustainability

SRPs developed through green chemistry approaches play a crucial role in addressing environmental challenges, particularly in water treatment, pollutant sensing, and sustainable packaging. These applications demonstrate the synergy between high performance and eco-friendliness [558].

In water treatment, biodegradable pH- and temperature-sensitive hydrogels are employed to capture heavy metals, organic pollutants, and microplastics. These materials degrade harmlessly after use, preventing secondary contamination. Similarly, environmentally responsive membranes, which adjust their permeability in response to ionic strength or pH fluctuations, contribute to resource-efficient water recycling [559].

In sustainable packaging, SRPs derived from renewable sources are designed to degrade under specific environmental conditions, such as exposure to sunlight or moisture. For instance, biodegradable packaging films incorporating pH-sensitive dyes provide real-time spoilage detection for perishable goods, helping to reduce food waste while ensuring environmental safety [560].

8.4. Enhanced biocompatibility and reduced cytotoxicity

8.4.1. Addressing challenges in biomedical applications

Ensuring biocompatibility and minimizing cytotoxicity are essential for the successful implementation of SRPs in biomedical applications. While these materials hold great promise in drug delivery, tissue engineering, and implantable devices, their interactions with biological systems often present challenges, including inflammatory responses,

immunogenicity, and cellular toxicity. These issues may arise from factors such as the composition of synthetic polymers, residual monomers or catalysts, and degradation byproducts. To address these concerns, recent advancements have focused on integrating synthetic and natural polymers, refining surface modification techniques, and adopting bioinspired approaches to enhance safety and compatibility [561].

8.4.2. Incorporating natural polymers into hybrid systems

A highly effective approach to improving biocompatibility is the incorporation of natural polymers, such as hyaluronic acid, silk fibroin, alginate, and chitosan, into synthetic polymer systems. These natural components offer inherent biocompatibility, biodegradability, and the ability to mimic the ECM, making them ideal for biomedical applications [562]. Commonly used synthetic polymers in such hybrid systems include PLGA, PEG, PCL, and PVA, which provide mechanical strength, tunable degradation rates, and processability. When combined, natural-synthetic hybrids synergistically integrate the biofunctionality of natural polymers with the structural and physicochemical advantages of synthetic matrices, leading to enhanced performance in tissue engineering scaffolds, injectable hydrogels, and drug delivery systems [563].

For instance, hybrid hydrogels integrating silk fibroin with temperature-responsive polymers such as PVCL or PEG-based block copolymers (PCLA-PEG-PCLA and Pluronic) exhibit enhanced biocompatibility and mechanical strength, making them well-suited for tissue scaffolding and wound healing [564]. Similarly, pH-responsive polymers integrated with hyaluronic acid have shown significant potential in drug delivery, particularly for treating inflammatory diseases. Since hyaluronic acid interacts with CD44 receptors on inflamed cells, it facilitates targeted therapeutic delivery while minimizing systemic side effects [565].

In addition to immune responses, these hybrid systems also improve SRP functionality by providing bioactive cues that promote cell adhesion, proliferation, and differentiation. By strategically combining synthetic and natural components, researchers can fine-tune material properties, such as degradation rates, mechanical strength, and stimulus responsiveness, to meet specific biomedical needs [566].

8.4.3. Surface modification for biocompatibility

Surface modification is a key strategy for enhancing the biocompatibility of SRPs. By altering the polymer's outermost layer, researchers can reduce cytotoxicity, improve cell compatibility, and minimize immune responses while preserving the material's core functionality. One widely used approach is grafting biocompatible coatings onto polymer surfaces [567]. For example, grafting PEG chains onto stimuli-responsive hydrogels creates a hydrophilic barrier that prevents protein adsorption and reduces immune activation. This PEGylation technique is commonly employed in drug delivery systems to prolong circulation times and improve compatibility with biological fluids [568].

Another effective strategy involves integrating anti-inflammatory agents or bioactive molecules into the polymer matrix. For example, polymers functionalized with anti-inflammatory drugs such as dexamethasone or nitric oxide-releasing compounds actively reduce inflammation at implantation sites. These functionalized materials are particularly beneficial for long-term implantable devices, such as drug-eluting stents and tissue-engineered scaffolds, where chronic inflammation could otherwise compromise performance and patient outcomes [569].

Additionally, surface modification with cell-adhesive peptides, such as RGD (arginine-glycine-aspartate) sequences, enhances cellular interactions and promotes tissue integration. This approach has been widely applied in hydrogels and scaffolds for tissue engineering, facilitating more effective regeneration of bone, cartilage, and soft tissues by improving cell adhesion and proliferation [570].

8.4.4. Advances in non-toxic degradation byproducts

Addressing the toxicity of polymer degradation byproducts is another crucial aspect of enhancing biocompatibility. Many synthetic polymers degrade into acidic or reactive molecules, which can cause local pH imbalances or oxidative stress, leading to tissue damage. To mitigate these effects, researchers have developed polymers that degrade into neutral or bioactive byproducts [571].

For example, PEG-PLGA copolymers are designed to degrade into lactic acid and glycolic acid, both of which are naturally metabolized by the body. As illustrated in Fig. 29, PLGA is synthesized via the ring-opening polymerization of lactide and glycolide monomers, typically catalyzed by $Sn(Oct)_2$. Upon hydrolytic degradation, PLGA yields lactic acid and glycolic acid, which are subsequently converted through metabolic pathways into non-toxic end products such as CO_2, H_2O, pyruvate, glycine, and urea. These pathways enable the safe clearance of degradation products without eliciting harmful physiological responses [572].

To further neutralize any potential acidity, buffering agents can be incorporated into the polymer matrix, ensuring a degradation process that does not compromise surrounding tissues [573]. Similarly, natural polymer-based systems, such as those incorporating alginate or collagen, degrade into molecules that can be resorbed or utilized by the body for tissue repair. These materials are particularly advantageous for applications like wound healing, where non-toxic degradation supports the natural healing cascade without causing adverse inflammatory responses [574].

8.4.5. Applications in advanced biomedical fields

Advancements in biocompatibility and reduced cytotoxicity have significantly expanded the potential applications of SRPs in biomedical fields. In wound healing, biocompatible hydrogels that respond to pH or enzymatic activity are used for the controlled delivery of growth factors and antimicrobial agents [575]. For example, hyaluronic acid-based hydrogels can simultaneously promote cell migration and hydration while releasing therapeutic agents in response to wound exudate [576]. In tissue engineering, biocompatible scaffolds that mimic the ECM are being developed to regenerate complex tissues, such as cartilage, skin, and neural networks. These scaffolds provide structural support while responding to local biochemical cues to release bioactive molecules or adjust their mechanical properties as needed [577]. For implantable devices, including stents, prosthetics, and biosensors, surface-modified polymers help minimize foreign body reactions and ensure long-term functionality. Stimuli-responsive coatings that release anti-inflammatory or anticoagulant agents have proven particularly effective in improving the performance of cardiovascular implants by reducing complications such as thrombosis and chronic inflammation [578].

8.5. 4D printing of SRPs

8.5.1. Advancing material fabrication with 4D printing

The introduction of 4D printing technology has redefined SRP fabrication by incorporating time-dependent changes into traditionally static 3D-printed materials. Unlike conventional 3D printing, where fixed structures are produced, 4D printing enables the creation of materials that can change shape, properties, or functionality over time in response to specific environmental stimuli, such as temperature, light, humidity, or pH [579]. By programming responsive behaviors directly into printed structures, 4D printing allows the development of dynamic, adaptive materials tailored for complex and evolving applications [580]. As illustrated in Figs. 30, 4D printing integrates four key pillars smart materials, structural design, external stimuli, and 3D printing technology to enable multifunctional capabilities such as self-folding, self-assembling, and self-repairing behaviors. For example, the blooming flower model conceptually demonstrates how printed structures can be engineered to morph over time when triggered by stimuli, closely

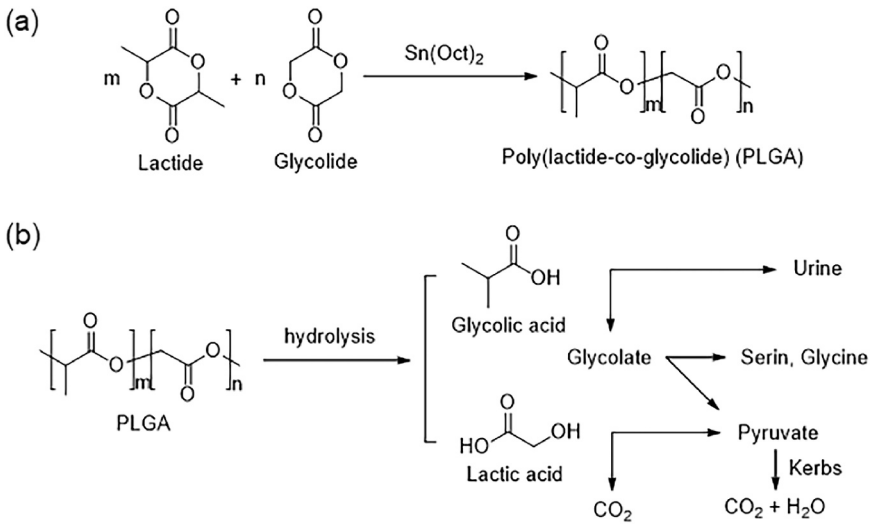

Fig. 29. Advances in non-toxic degradation byproducts of PLGA. (a) Synthesis of PLGA via ring-opening polymerization of lactide and glycolide monomers using Sn $(Oct)_2$ as a catalyst. (b) Hydrolytic degradation of PLGA into lactic acid and glycolic acid, which are metabolized into non-toxic byproducts (CO_2, H_2O, pyruvate, glycine, and urea) via natural physiological pathways.

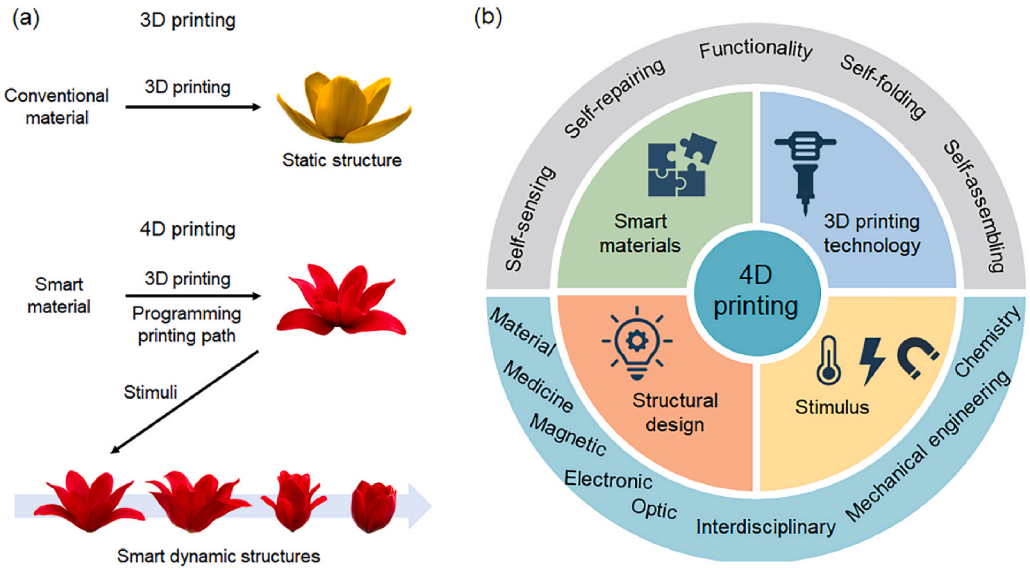

Fig. 30. Advancing material fabrication with 4D printing. (a) Conceptual illustration of 4D printing where printed structures change shape over time in response to external stimuli, mimicking flower blooming behavior. (b) Core components and interdisciplinary aspects of 4D printing, integrating smart materials, structural design, stimuli-responsiveness, and 3D printing technologies for self-folding, self-assembling, and functional materials [581]. Copyright 2023, American Association for the Advancement of Science.

mimicking natural biological transformations [581]. This interdisciplinary approach combining materials science, mechanical engineering, chemistry, and electronics expands the potential of SRPs beyond static applications.

This innovation leverages advanced SRPs, including SMPs, hydrogels, and liquid crystal elastomers, to achieve time-dependent transformations. These materials undergo reversible or irreversible changes in their molecular or structural arrangement when exposed to external triggers, enabling functionalities such as self-healing, shape-shifting, and controlled release. The precision and scalability of 4D printing make it a powerful tool across diverse fields, including medicine, environmental science, and industrial manufacturing [582]. Different classes of external stimuli enable unique fabrication and actuation modes within 4D-printed systems. For instance, photothermal and photopolymerizable hydrogels are well suited for light-based printing, while thermo-responsive systems enable extrusion-based gelation control. Meanwhile, magnetic and electric fields facilitate the fabrication of remotely actuated scaffolds capable of dynamic movement or therapeutic release.

8.5.2. Tailoring personalized medical devices

4D printing offers significant potential in personalized medicine by enabling the fabrication of patient-specific devices that adapt to individual physiological conditions. For example, 4D-printed stents made from thermo-responsive polymers can expand or contract in response to body temperature, ensuring a precise fit and optimal functionality. Similarly, self-expanding implants or prosthetics that respond to heat or hydration provide greater comfort and usability compared to static alternatives [583].

One promising application is in drug delivery systems, where 4D-printed capsules or scaffolds release therapeutic agents in a controlled manner based on specific stimuli, such as pH or enzymatic activity

[584]. For instance, a pH-sensitive hydrogel scaffold can release drugs only in acidic tumor environments, minimizing off-target effects and maximizing treatment efficacy. These systems can also be designed to release multiple drugs sequentially, offering advanced solutions for complex therapies, such as cancer treatment or chronic disease management [585].

Additionally, 4D-printed tissue scaffolds that mimic the dynamic properties of native tissues are being developed for regenerative medicine. These scaffolds can adjust their mechanical properties, porosity, or degradation rates in response to local biochemical cues, promoting cell growth and tissue regeneration. For example, scaffolds that stiffen in response to mechanical stress can better support the growth of load-bearing tissues such as bone or cartilage [586].

8.5.3. Advancing environmental applications

In environmental science, 4D printing enables the development of adaptive materials for pollution control and resource management. For example, 4D-printed filtration membranes can dynamically adjust their pore sizes or permeability in response to changes in temperature, pH, or ionic strength, optimizing performance across various water treatment scenarios. This adaptability allows for the efficient removal of contaminants such as heavy metals, organic pollutants, and microplastics, even under fluctuating environmental conditions [587].

Similarly, 4D-printed adsorbents made from SRPs can capture and release pollutants cyclically. For example, a temperature-responsive adsorbent can bind heavy metals at low temperatures and release them at higher temperatures, allowing for easy regeneration and reuse. These systems are particularly valuable for industrial wastewater treatment, where operational conditions often vary significantly [588].

Another innovative application involves self-healing coatings for environmental sensors. These coatings, made from light- or heat-responsive polymers, can autonomously repair minor damages, ensuring long-term reliability in harsh environments such as oceans, deserts, or industrial sites [589]. Additionally, 4D-printed structures integrated with sensing capabilities can monitor environmental parameters, such as humidity, temperature, or pollutant levels, and adapt their behavior in real-time to optimize performance [590].

8.5.4. Multi-stimuli-responsive architectures

A key advantage of 4D printing is its ability to produce complex architectures with multi-stimuli responsiveness. By integrating different responsive elements into a single material, researchers can design systems that react to multiple environmental cues simultaneously or sequentially [591]. For instance, a 4D-printed material could combine temperature-responsive and pH-responsive polymers to create a filtration system that adjusts its properties based on both thermal and chemical conditions [592].

These multi-functional materials are particularly valuable in applications where environmental conditions are unpredictable or dynamic, such as disaster recovery, space exploration, or military operations [593]. For example, 4D-printed shelters that respond to temperature and humidity could provide adaptive protection in extreme environments, while self-healing components in vehicles or equipment could reduce maintenance needs and improve durability [594].

8.5.5. Scalability and precision in industrial manufacturing

The precision and scalability of 4D printing make it an ideal technology for industrial manufacturing. Advanced techniques such as direct ink writing, stereolithography, and selective laser sintering enable the creation of highly detailed and complex structures with minimal material waste. These methods also allow for the integration of multiple materials within a single print, expanding the functional possibilities of 4D-printed systems [595].

For instance, in the aerospace and automotive industries, 4D-printed components made from shape-memory alloys or polymers can adapt their aerodynamic properties in real time, optimizing fuel efficiency and performance [596]. Similarly, in consumer electronics, 4D-printed cases or components that respond to heat or pressure can enhance durability and improve the user experience [597].

8.6. Remote-controlled responsive systems

8.6.1. Advancing material functionality with remote control

The development of remote-controlled SRP systems has introduced unprecedented capabilities in the design and application of intelligent materials. These systems use wireless signals such as ultrasound, radiofrequency (RF), NIR light, or magnetic fields to activate and control polymer responses in a non-invasive and highly targeted manner [598]. This innovation expands the versatility of SRPs, enabling precise manipulation of their properties in diverse environments, including the human body and remote ecological settings. By eliminating the need for direct physical interaction, remote-controlled systems enhance the efficiency, safety, and adaptability of applications across biomedical, environmental, and industrial fields [599].

8.6.2. Ultrasound-responsive polymers for targeted drug delivery

Ultrasound-responsive polymer systems represent a breakthrough in non-invasive therapeutic delivery. Ultrasound waves, which can penetrate deep into tissues, provide a means of activating polymer responses precisely at the desired site [600]. Hydrogels incorporating ultrasound-sensitive moieties, such as gas-filled microbubbles or cross-linked networks that degrade under acoustic energy, have been developed for controlled drug release [601].

For instance, a hydrogel loaded with chemotherapeutic agents can remain stable during systemic circulation but disintegrate and release its payload when exposed to ultrasound waves at a tumor site. This approach minimizes off-target effects and enhances therapeutic efficacy. The ability to control release profiles by varying ultrasound intensity and duration allows for personalized treatment regimens, ultimately improving patient outcomes [602]. As illustrated in Fig. 31, these systems are designed to remain stable during systemic circulation and undergo disintegration only upon localized ultrasound exposure. This strategy enables site-specific drug release, particularly at tumor tissues, enhancing drug accumulation while minimizing off-target effects and systemic toxicity. The illustration highlights how ultrasound irradiation triggers the rupture of polymer carriers, leading to the release of chemotherapeutic agents directly at the tumor site, offering precise spatiotemporal control of drug delivery [603].

The ability to control release profiles by varying ultrasound intensity and duration allows for personalized treatment regimens, ultimately improving patient outcomes [604]. Additionally, ultrasound-responsive polymers have been explored for applications in regenerative medicine. Hydrogels that release growth factors or stem cells in response to ultrasound stimulation can accelerate tissue repair in conditions such as chronic wounds or bone fractures [605]. This targeted delivery reduces the need for repeated interventions and promotes more efficient healing.

8.6.3. Light-activated systems for precision control

Polymers that respond to light, particularly NIR wavelengths, offer an innovative approach for remote-controlled activation. NIR light is especially advantageous in biomedical contexts due to its deep tissue penetration and minimal phototoxicity [606]. Polymers functionalized with photoresponsive groups, such as azobenzenes, spiropyrans, o-nitrobenzyl derivatives, coumarin dimers, diarylethenes, and nitroaryl-based moieties, undergo conformational changes, cleavage, or solubility shifts upon light exposure [607].

A prominent biomedical application of this technology is photothermal therapy, where NIR-responsive polymers loaded with photothermal agents (e.g., gold nanoparticles, carbon nanomaterials) generate localized heat upon irradiation [608]. As depicted in Fig. 32, these agents, when administered into tumor-bearing mice and exposed to NIR light, produce heat that raises local temperature above 42 ℃,

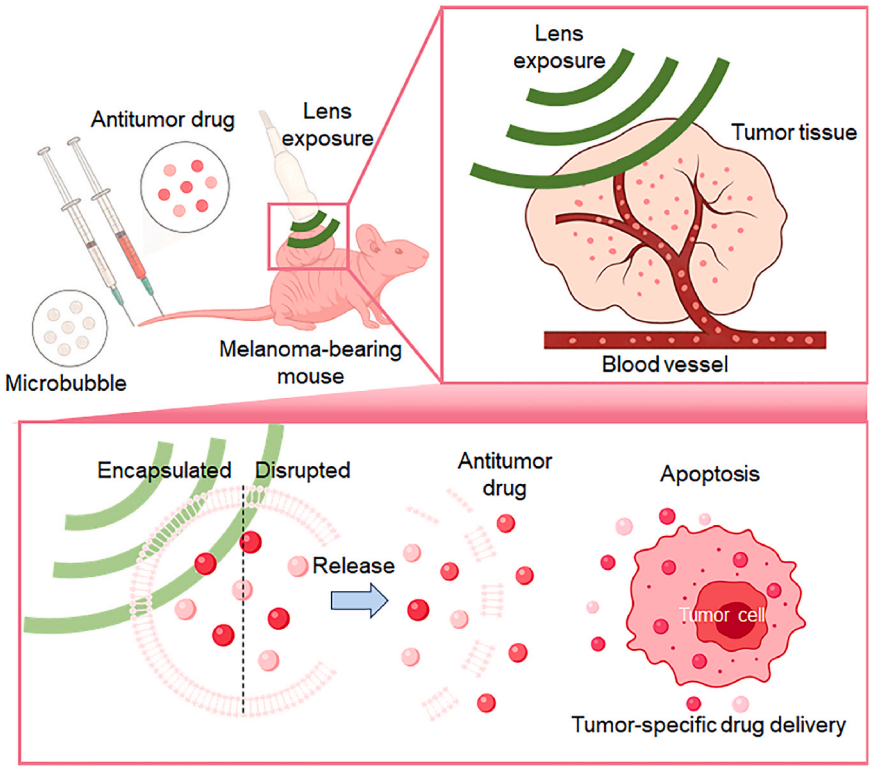

Fig. 31. Ultrasound-responsive polymers for targeted drug delivery. Schematic illustration of ultrasound-triggered drug delivery using responsive polymer-based carriers. Upon local ultrasound irradiation, the drug-loaded polymers release therapeutic agents at the tumor site in vivo, enabling spatiotemporal control over drug release and enhanced accumulation in tumor tissue, thereby improving treatment precision and reducing systemic toxicity.

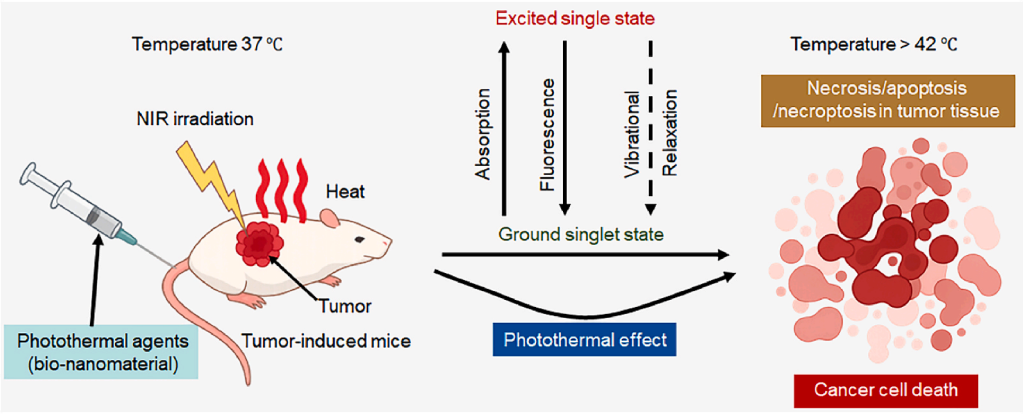

Fig. 32. Light-activated systems for precision control. NIR-triggered photothermal agents generate localized heat in tumors, inducing cancer cell death via necrosis or apoptosis.

leading to necrosis, apoptosis, or necroptosis in tumor tissue and ultimately resulting in cancer cell death. This approach allows for precise spatial and temporal control over therapeutic activation, enhancing treatment specificity while minimizing systemic side effects [609].

In addition to cancer therapy, NIR-responsive hydrogels have shown potential in wound healing applications by releasing antimicrobial or bioactive agents upon light exposure, thereby promoting faster tissue regeneration. Beyond healthcare, light-responsive polymers are being employed in smart coatings and sensors in industrial and environmental sectors [610]. Coatings that alter their fluorescence or color in response to light can serve as real-time indicators for detecting pollutants or hazardous substances, offering robust monitoring capabilities in complex environments.

8.6.4. *Magnetically controlled polymers for non-invasive applications*

Magnetic fields offer a versatile, non-invasive method for controlling polymer systems. Polymers embedded with magnetic nanoparticles or ferrofluids respond to external magnetic fields, enabling remote manipulation of their physical properties. These materials have a wide range of applications in both biomedical and environmental settings [611].

In drug delivery, magnetically responsive nanoparticles encapsulated within polymer matrices can be directed to specific areas of the body using external magnetic fields. Once localized, applying an alternating magnetic field generates heat (through magnetic hyperthermia) or disrupts the polymer matrix, triggering the controlled release of therapeutic agents. This combination of targeting and controlled release makes magnetic systems highly effective for localized cancer treatments

and other therapies [612].

In environmental science, magnetically responsive polymers are being used to develop adaptive sensors and pollutant adsorbents. For example, a magnetic polymer membrane can dynamically alter its permeability or adsorption capacity in response to fluctuating pollutant levels, optimizing filtration processes. These systems are especially valuable in difficult-to-reach locations, such as contaminated industrial sites or deep-sea environments, where traditional monitoring and intervention are not feasible [613].

8.6.5. Radio frequency (RF)-responsive systems for advanced control

RF-responsive polymers represent another innovative category of remote-controlled materials. RF energy can penetrate tissues and other barriers without causing significant heating or damage, making it ideal for both biomedical and industrial applications [614]. Polymers embedded with conductive fillers, such as metallic nanoparticles (e.g., gold or silver), carbon nanotubes, or graphene, are capable of absorbing RF energy and converting it into heat or mechanical motion [615]. Additionally, magnetically responsive composites incorporating iron oxide (Fe_3O_4) nanoparticles or ferrites have been engineered to absorb RF signals efficiently, enabling applications such as RF-triggered drug release, hyperthermia therapy, or wireless actuation in soft robotics. Some stimuli-responsive hydrogels formulated with ionic liquids or polyaniline also exhibit tunable RF sensitivity due to enhanced dielectric or conductive properties under alternating electromagnetic fields [616].

In biomedical applications, RF-responsive hydrogels have been employed for on-demand drug release. For example, a polymer loaded with antibiotics can be activated in response to RF signals, releasing its contents directly at the infection site. This targeted release reduces the need for systemic administration and minimizes side effects. RF-responsive systems are also being explored for smart implants, which can adjust their mechanical properties or release therapeutic agents based on external signals, enabling a personalized approach to treatment [617].

In industrial settings, RF-responsive polymers are used in self-healing coatings, where the heat generated by RF energy repairs microcracks or restores functionality. These materials are particularly valuable in high-performance environments, such as aerospace and automotive industries, where durability and reliability are essential [618].

8.6.6. Environmental monitoring and data collection

Remote-controlled responsive systems are revolutionizing environmental monitoring by enabling real-time data collection in difficult-to-reach or hazardous locations. For example, light-activated polymers integrated into underwater sensors can detect changes in water quality parameters such as pH, temperature, or pollutant levels, and relay this information to surface monitoring stations [619]. Similarly, magnetically responsive polymers can be used in robotic systems for sampling and analyzing environmental contaminants in remote areas, such as polar regions or deep-sea ecosystems [620].

These systems not only enhance monitoring efficiency but also reduce the need for human intervention, minimizing risks and costs associated with environmental management. Their ability to provide continuous, remote feedback makes them invaluable tools for addressing global challenges, including pollution control, climate monitoring, and resource conservation [621].

8.7. Modular and plug-and-play designs

8.7.1. Transforming SRPs with modular design

Modular design in SRPs is a groundbreaking strategy that enables the creation of customizable systems with interchangeable components. This “plug-and-play” approach allows researchers to design materials that can be easily reconfigured or adapted to meet specific needs [622]. By incorporating stimuli-responsive modules into polymer matrices, a single material can be engineered to respond to multiple environmental cues, such as pH, temperature, or light, while maintaining the flexibility to modify its behavior through the addition of new components [623].

This modularity is particularly beneficial in applications where versatility and customization are critical, such as personalized medicine, adaptive industrial systems, and dynamic environmental solutions. The approach not only simplifies material development but also accelerates the transition of these advanced polymers from laboratory research to practical implementation [624].

8.7.2. Modular hydrogels for sequential drug delivery

One of the most promising applications of modular polymer design is the development of hydrogels for personalized and sequential drug delivery. These hydrogels are made from polymer networks that contain interchangeable responsive units, each programmed to react to a specific stimulus [625]. For example, a modular hydrogel can integrate pH-sensitive segments for releasing a chemotherapeutic drug in acidic tumor microenvironments, alongside temperature-sensitive modules for delivering anti-inflammatory agents to feverish tissues [626].

The ability to load and release multiple drugs sequentially in response to distinct triggers is particularly valuable for treating complex diseases such as cancer or chronic infections. In these cases, a stepwise therapeutic approach, where one drug prepares the target site for another, can significantly enhance treatment efficacy [627]. For instance, a modular hydrogel could first release a drug to disrupt the tumor’s extracellular matrix, making it easier for a second therapeutic agent to penetrate. Such precise control over drug release minimizes side effects and improves patient outcomes [628].

In addition to drug delivery, modular hydrogels are being explored for regenerative medicine applications. By incorporating bioactive modules, such as growth factors or cell adhesion peptides, these hydrogels can provide tailored support for tissue repair. The modular design allows for the integration of specific cues that promote cell proliferation, differentiation, or angiogenesis, depending on the target tissue [629].

8.7.3. Adaptive coatings with customizable functionality

The modular approach has also revolutionized the design of coatings for medical devices, industrial surfaces, and infrastructure. By combining interchangeable stimuli-responsive components, researchers can create multi-functional coatings that address various challenges, such as biofouling, corrosion, or microbial contamination [630].

For example, a modular coating for marine equipment might integrate anti-fouling modules that release biocides in response to the presence of biofilms, self-healing modules that repair scratches or abrasions when exposed to UV light, and anti-corrosion modules that release inhibitors in response to changes in pH or salinity. These customizable coatings reduce maintenance costs, extend the lifespan of equipment, and improve operational efficiency in harsh environments [631].

In the medical field, modular coatings for implants and devices offer tailored protection and functionality. For instance, a cardiovascular stent could be coated with a modular system that releases anticoagulants in response to mechanical stress, while simultaneously preventing bacterial adhesion through antimicrobial modules [632]. Similarly, orthopedic implants with modular coatings can release anti-inflammatory drugs to minimize post-surgical complications, enhancing patient recovery and reducing the risk of implant failure [633].

8.7.4. Dynamic materials for environmental and industrial applications

Modular polymer systems are increasingly being used in environmental and industrial applications, where adaptability and efficiency are crucial. For example, modular membranes for water purification can incorporate multiple responsive units to target different types of pollutants. A single membrane may combine pH-sensitive components for capturing heavy metals, temperature-sensitive modules for removing organic contaminants, and light-sensitive units for degrading persistent

pollutants under UV exposure [634].

Similarly, modular adsorbents for air pollution control can be tailored to remove specific gases or particulate matter based on the operational environment. For example, a modular filter could include CO_2-adsorbing units for greenhouse gas mitigation alongside modules that capture VOCs from industrial emissions [635].

In industrial processes, modular polymer systems are also used to develop adaptive lubricants and adhesives. By integrating temperature- and pressure-sensitive modules, these materials can dynamically adjust their viscosity or bonding strength in response to changing conditions, optimizing performance and reducing energy consumption [636].

8.7.5. Advantages of plug-and-play polymer systems

The modular, plug-and-play approach offers several key advantages over traditional polymer design. Notably, it provides exceptional flexibility, allowing researchers to easily swap or combine components to create tailored materials for specific applications. This adaptability reduces the time and cost of developing entirely new polymers for each use case [637].

Furthermore, modular systems enhance scalability and reproducibility. By standardizing individual modules, manufacturers can streamline production processes while maintaining consistency across different products. This standardization is especially beneficial in industries such as pharmaceuticals, where regulatory compliance and batch-to-batch uniformity are critical [638].

Modular design also enables rapid adaptation to emerging challenges. For example, during a pandemic, a modular hydrogel system could be quickly modified to deliver new antiviral drugs or vaccines simply by incorporating the relevant responsive modules. Similarly, in environmental applications, modular systems can be reconfigured to address newly identified pollutants or evolving regulatory requirements [639].

8.8. Enhanced responsiveness through nanostructuring

8.8.1. Role of nanostructuring in SRPs

Nanostructuring has become a key strategy for enhancing the responsiveness, precision, and overall performance of SRPs. By manipulating polymer morphology at the nanoscale, researchers can develop materials with superior properties, including faster response times, increased sensitivity to external stimuli, and greater control over property changes [640]. These improvements are particularly valuable in fields where precision and efficiency are critical, such as medicine, environmental science, and advanced manufacturing [448].

Nanostructuring leverages the unique characteristics of nanoscale materials, such as their high surface area-to-volume ratios and tunable surface properties. These features allow polymers to respond more rapidly and effectively to stimuli such as pH, temperature, light, or chemical gradients, expanding their potential applications and improving functionality [641].

8.8.2. Advanced techniques for nanostructuring polymers

Nanostructuring SRPs involves a variety of fabrication techniques, each designed to achieve specific morphological and functional outcomes. The key methods are discussed below.

Electrospinning is a versatile technique used to create nanofibrous structures with high surface area and porosity. In this process, a polymer solution is subjected to a high electric field, forming fine fibers that are deposited onto a collector. The resulting nanofibers exhibit rapid swelling or deswelling in response to environmental stimuli, making them ideal for drug delivery, wound healing, and filtration applications [642]. For example, temperature-sensitive nanofibers made from PCLA-PEG-PCLA, Pluronic F127, or PVCL can release encapsulated drugs when heated above their critical temperature, providing localized and controlled therapeutic effects [643,644].

Block copolymer self-assembly is another powerful nanostructuring method in which distinct polymer blocks spontaneously organize into well-defined nanostructures such as micelles, vesicles, or lamellar phases. These structures can be tailored to exhibit highly specific responses to stimuli [645]. For instance, pH-sensitive block copolymer micelles can encapsulate hydrophobic drugs within their cores and release them in acidic environments, such as tumor microenvironments, ensuring targeted delivery [646].

Embedding nanoparticles within polymer matrices enhances responsiveness by introducing additional functionalities. Magnetic nanoparticles, for example, can be incorporated into thermo-responsive polymers to create materials that respond to both temperature and magnetic fields. These hybrid systems have been employed in applications ranging from magnetic hyperthermia treatments to pollutant adsorption systems that combine selectivity with ease of recovery using external magnets [647].

Nanopatterning techniques, such as electron beam lithography and nanoimprinting, allow for the precise design of polymer surfaces at the nanoscale. These patterned surfaces can exhibit tailored wetting, adhesion, or optical properties in response to stimuli [648]. For example, nanopatterned hydrogels with periodic structures can regulate cell behavior in tissue engineering applications, providing dynamic control over cell adhesion and proliferation [649].

8.8.3. Biomedical applications of nanostructured polymers

Nanostructuring has greatly expanded the use of SRPs in medicine, particularly in drug delivery, biosensing, and regenerative medicine. Nanostructured polymers are highly effective in developing drug delivery systems that respond rapidly to physiological triggers [650]. For instance, nanogels (hydrogels structured at the nanoscale) exhibit quick swelling or deswelling behaviors due to their high surface area and porous structures. This property allows for precise control over drug release in response to pH, temperature, or enzymatic activity. In cancer therapy, nanostructured carriers can selectively release chemotherapeutics in acidic tumor environments while minimizing off-target effects [651].

In biosensing, nanostructured SRPs have enabled the detection of biomolecules with exceptional sensitivity and specificity. For example, nanopatterned polymer surfaces functionalized with responsive groups can detect changes in glucose levels, pH, or specific biomarkers, providing real-time feedback for medical diagnostics. These materials are particularly valuable in wearable or implantable biosensors, where rapid and accurate detection is critical for personalized healthcare [652].

In regenerative medicine, nanostructured scaffolds made from SRPs provide dynamic control over cellular environments. Electrospun nanofibrous scaffolds that respond to temperature or light can modulate their stiffness, porosity, or bioactivity in real time, promoting tissue repair and regeneration. These scaffolds mimic the extracellular matrix at the nanoscale, providing cells with cues that enhance their proliferation and differentiation [653].

8.8.4. Environmental applications of nanostructured polymers

Nanostructuring has also improved the performance of SRPs in environmental science, particularly in water treatment, pollutant removal, and environmental monitoring. Nanostructured polymer membranes offer superior filtration performance due to their high surface area and tunable pore structures [654]. By incorporating stimuli-responsive components, these membranes can dynamically adjust their permeability or adsorption capacity in response to environmental changes, such as variations in pH or ionic strength [655]. For instance, pH-responsive membranes functionalized with carboxylic acid groups can selectively capture heavy metals from industrial wastewater, while temperature-responsive membranes can prevent fouling by adjusting their hydrophobicity [656].

Nanostructured adsorbents made from SRPs enhance pollutant removal efficiency and selectivity. For example, nanogels functionalized

with magnetic nanoparticles can capture organic pollutants or heavy metals from water and be easily retrieved using external magnets. These systems are not only effective but also reusable, reducing operational costs and environmental impact [657]. Nanostructured SRPs are increasingly used in sensors for monitoring environmental parameters such as temperature, humidity, and pollutant levels. Nanopatterned surfaces or nanoparticles embedded in polymer matrices enhance the sensitivity and response time of these sensors, making them suitable for real-time monitoring in remote or hazardous locations [658].

9. Challenges and future perspectives in SRP development and translation

SRPs are rapidly evolving materials with significant potential across diverse applications, from biomedical devices to environmental sustainability. However, despite substantial progress in the field, several challenges remain in their development, scalability, and practical implementation. This section outlines key obstacles in SRP research and highlights promising future directions that could drive the next generation of SRP technologies [659].

9.1. Challenges in SRP development

9.1.1. Scalability and reproducibility

One of the major challenges in SRP development is the scalability of synthesis processes. While many SRPs exhibit excellent properties at the laboratory scale, transitioning to large-scale industrial production presents significant challenges. Ensuring reproducibility in polymer properties, achieving uniform synthesis, and maintaining cost-effective manufacturing are critical for making SRPs commercially viable [660]. Additionally, consistent performance across production batches is essential, particularly in industrial and biomedical applications, where variability can lead to functional failures in large-scale systems [661].

9.1.2. Stability and longevity

The long-term stability and durability of SRPs are crucial for their successful deployment in real-world applications, especially in environments exposed to harsh conditions such as high temperatures, fluctuating pH levels, and mechanical stresses [662]. In biomedical applications, particularly those involving implants or drug delivery systems, maintaining SRP stability within the human body is a key concern. These materials must remain functional for the intended lifespan of the device, and any degradation products should be non-toxic and biocompatible [663]. Similarly, for environmental applications such as pollutant removal and sensing, SRPs must retain their functionality over extended periods without significant degradation to ensure reliability and effectiveness.

9.1.3. Functionalization and multi-stimuli responsiveness

While significant progress has been made in designing SRPs that respond to a single external stimulus, developing materials capable of responding to multiple stimuli simultaneously remains a challenge. Integrating multiple responsive units within a single polymer matrix requires sophisticated design strategies and a deep understanding of the interactions between different responsive components [664]. Achieving precise control over these complex materials is essential for applications requiring adaptive behavior, such as drug delivery systems where the controlled, sequential release of therapeutic agents is necessary [665].

9.1.4. Toxicity and biocompatibility

In biomedical applications, the potential toxicity of SRPs remains a major concern. While many SRPs are designed to be biodegradable and biocompatible, some degradation byproducts can cause inflammation, oxidative stress, or other adverse effects [666]. Additionally, the use of certain synthetic polymers or nanomaterials in biomedical devices may trigger immune responses, potentially compromising device performance and posing health risks. Research into non-toxic degradation pathways and the development of biocompatible additives are essential to mitigating these risks and ensuring the safe application of SRPs in medical settings [667].

9.1.5. Environmental impact and sustainability

As SRPs gain widespread use in industries such as packaging, water treatment, and electronics, their environmental impact must be carefully evaluated. While biodegradable SRPs offer a potential solution to plastic waste, their full environmental footprint, including production processes and potential byproducts, requires thorough assessment [668]. Additionally, most current SRPs are derived from petrochemical sources, raising concerns about their long-term sustainability. To address these challenges, the development of bio-based SRPs and the adoption of green chemistry principles in their synthesis are critical to ensuring these materials contribute to broader environmental sustainability goals [669].

9.2. Future directions

9.2.1. Smart and personalized medicine

The future of SRPs in the biomedical field lies in the integration of advanced functionalities into smart, personalized medical devices. SRPs have the potential to revolutionize drug delivery systems by offering tailored, on-demand drug release in response to specific physiological conditions [670]. This could be particularly beneficial in treating chronic diseases or cancer, where precise timing and localization of drug delivery can significantly improve therapeutic outcomes while reducing side effects. Personalized medicine, enabled by SRPs, will require the development of materials that can dynamically adapt to the patient's condition, offering real-time control over drug release, biosensing, and tissue regeneration [671].

Additionally, SRPs that respond to specific biomolecular signals, such as those found in disease microenvironments (e.g., cancerous tissues or infected areas), could enable highly targeted, localized treatments. This approach may reduce the need for systemic drug administration, thereby lowering toxicity risks and improving patient recovery [672].

9.2.2. Integration with artificial intelligence and machine learning

The integration of AI and ML into SRP design and application holds immense potential. AI can accelerate the discovery of new SRPs by predicting material properties based on extensive datasets and simulations, while ML algorithms can optimize polymer synthesis, improving efficiency, scalability, and reproducibility [513,514]. Moreover, AI-driven models can predict SRP behavior in complex, dynamic environments, such as the human body or industrial settings, allowing for the development of highly specialized materials with precise, on-demand responses to stimuli [673].

Furthermore, AI systems could be incorporated into adaptive materials, enabling real-time, autonomous adjustments based on environmental feedback. This advancement would significantly enhance the functionality of SRPs across various applications, from personalized healthcare to environmental monitoring [674].

9.2.3. Multi-stimuli and hybrid systems

Future research should focus on developing SRPs that respond to multiple stimuli simultaneously, enabling complex, adaptive behaviors. Multi-stimuli-responsive systems are particularly important for applications requiring sequential or synergistic responses, such as drug delivery systems where different drugs must be released at specific times or under distinct environmental conditions [424,529]. Additionally, hybrid systems that combine SRPs with other functional materials, such as nanomaterials, bio-based polymers, or MOFs, could lead to multifunctional materials capable of addressing multiple challenges simultaneously. These hybrid materials could be applied to areas such as

pollutant removal, advanced wound healing, and next-generation biosensing technologies [675].

9.2.4. Sustainable and green chemistry approaches

As sustainability becomes a global priority, the development of SRPs using renewable resources and green chemistry principles will be crucial for their future. Biodegradable SRPs derived from plant-based or waste-based feedstocks, such as lignin or chitosan, are expected to gain prominence. These materials not only reduce the environmental impact of production but also help mitigate plastic waste accumulation in ecosystems [551,552].

Green polymerization techniques, including solvent-free and aqueous-based methods, can further minimize the ecological footprint of SRP synthesis. Additionally, innovations in recycling and reusability could enhance the sustainability of SRPs, particularly in large-scale industrial applications such as smart packaging and water treatment systems [676].

9.2.5. Advanced manufacturing techniques

Advancements in manufacturing technologies, particularly 4D printing, will enable the creation of dynamic, responsive systems that can change their shape, function, or properties over time. The ability to fabricate stimuli-responsive materials with high precision and scalability will open new possibilities for personalized medical devices, adaptive coatings, and environmental monitoring systems [676].

4D printing, which incorporates time-dependent transformations into traditional 3D printing, will allow for the design of structures that autonomously respond to environmental stimuli. This innovation could lead to self-healing materials, programmable drug delivery systems, and intelligent environmental sensors that adapt to fluctuating conditions without manual intervention [308,309].

9.2.6. Environmental remediation and sustainability

SRPs will continue to play an essential role in addressing global environmental challenges, particularly in water treatment, pollutant removal, and waste management. The development of SRPs that respond to environmental stimuli such as pH, temperature, or chemical gradients will enable more efficient and targeted remediation of pollutants, including heavy metals, organic compounds, and microplastics. These materials will be essential for both point-of-use filtration systems and large-scale environmental cleanup operations [677].

Additionally, sustainable packaging solutions based on SRPs can help reduce waste and improve resource efficiency. Smart packaging materials that respond to changes in temperature, humidity, or gas composition could extend the shelf life of perishable goods and enable real-time food safety monitoring. This, in turn, could reduce food waste and enhance supply chain sustainability [678].

10. Conclusion and perspectives: Translational opportunities and outlook

SRPs represent a transformative class of materials capable of undergoing reversible physical or chemical transitions in response to environmental stimuli such as temperature, pH, light, and mechanical stress. Their remarkable versatility has opened new frontiers across diverse fields, including drug delivery, regenerative medicine, environmental sustainability, smart packaging, and adaptive textiles. By dynamically adjusting to changing internal and external conditions, SRPs present unparalleled opportunities to advance healthcare, address ecological challenges, and enable next-generation intelligent materials.

As summarized in Table 4, over the past decade, various SRP has evolved beyond the concept of a simple responsive system to become an intelligent, programmable material capable of sensing, adapting, and healing in biological and environmental contexts. This unique combination of responsiveness, biocompatibility, and sustainability positions SRP as a cornerstone of next-generation functional materials.

10.1. Key advances and achievements

Recent progress in SRP technology has led to breakthroughs across multiple fields. In biomedicine, SRPs have significantly enhanced controlled drug delivery systems, tissue engineering, and wound healing, enabling precise treatments with reduced side effects. Their responsiveness to physiological changes, such as variations in pH or temperature in diseased tissues, allows for targeted therapies that improve treatment efficacy. Additionally, SRPs are advancing implantable devices and regenerative medicine scaffolds, paving the way for personalized medical care. Today, pH-, enzyme-, and redox-responsive systems enable on-demand drug release specifically at tumor sites, inflamed tissues, or intracellular compartments, minimizing off-target toxicity. Smart hydrogel scaffolds and shape-memory polymers that dynamically adjust stiffness or degradation rates in response to cellular signals are now being explored for bone, cartilage, and soft-tissue regeneration. Self-healing, adhesive, and bio-inspired SRPs are also being developed for microneedle patches, wound dressings, and implantable biosensors that recover functionality after deformation or stress. When combined with 4D printing, these adaptive polymers can be fabricated into patient-specific scaffolds and medical implants capable of evolving in vivo.

In environmental applications, SRPs are contributing to pollutant removal, wastewater treatment, and environmental sensing. Their ability to respond to fluctuating environmental conditions enhances the efficiency of systems designed to eliminate industrial pollutants, heavy metals, and organic contaminants, promoting cleaner water and air. Moreover, SRPs support sustainability efforts by facilitating the development of biodegradable materials that help mitigate plastic pollution and improve waste management practices. Beyond pollution control, redox- and ion-responsive SRPs are being applied to reversible adsorption and release processes for heavy-metal capture and catalytic remediation. CO_2- and humidity-responsive polymers are being investigated for smart membranes that modulate permeability under variable gas or moisture levels, enabling energy-efficient separation and carbon capture. Meanwhile, biodegradable SRPs synthesized from renewable feedstocks such as cellulose, lignin, or chitosan are reinforcing the transition toward a circular polymer economy. Light-, photo-, and electro-responsive coatings are also emerging as smart platforms for antifouling, photocatalytic, and self-cleaning surface technologies.

SRPs are also transforming the packaging industry, particularly in food and pharmaceutical applications. Smart packaging systems incorporating SRPs can provide real-time indicators of spoilage, quality, and safety, extending product shelf life and reducing waste. These innovations not only benefit consumers but also enhance supply chain efficiency and lower environmental impact. In addition, thermo- and gas-responsive packaging films capable of visual color change or self-sealing are being developed for food freshness monitoring. Electro- and moisture-responsive SRPs are enabling adaptive textiles, wearables, and soft robotic actuators that adjust to environmental and physiological changes bridging the gap between comfort, performance, and sustainability. These diverse applications collectively demonstrate that SRPs are evolving from laboratory materials into key enablers of intelligent, eco-compatible, and human-interactive technologies.

Furthermore, SRPs have driven advancements in adaptive textiles and wearable technologies. These materials can regulate temperature, manage moisture, and respond to physiological changes, enhancing comfort and performance in applications ranging from sportswear to medical garments and military uniforms. Recent research trends also show integration with conductive or piezoelectric fillers, creating self-powered fabrics and wearable biosensors that harvest mechanical or thermal energy from the human body. Such multifunctional designs open new opportunities for continuous health monitoring, motion detection, and real-time feedback systems.

Table 4
Summary of design principles and recent advances of stimuli-responsive polymer systems, highlighting their key functional motifs, representative synthesis routes, common architectures, response metrics, tunable parameters, major pitfalls, and emerging innovations across biomedical and environmental applications.

Stimulus	Key functional motifs	Typical synthesis routes	Common architectures	Key properties / response metrics	Tunability knobs	Pitfalls	Recent advances / innovations	Refs
pH	COOH, tertiary amines, imidazole, histidine	RAFT/ATRP of (meth)acrylates, peptide coupling, polysaccharide modification	Linear, block (PEG-b-PAA/ PDMAEMA), IPN hydrogels	pKa-matched swelling, ζ-potential switching, solubility/CMC shift	Monomer ratio, block length, crosslink density, ionic strength	Narrow ΔpH in vivo, protein fouling	AI/ML-driven pKa design, microneedle & wearable pH sensors, multi-drug nanogels	[108,109, 161,679]
Redox	Disulfide, diselenide, ditelluride, thioketal	Step-growth linking, click/thiol-ene, RAFT chain transfer	Micelles (PEG–SS–PCL), crosslinked gels, nanoparticles	GSH/ROS-triggered cleavage, on/off release, k_redox	Bond type (S/ Se/Te), hydrophobic core, particle size	Premature oxidation, batch variability	Selective ROS-cleavable linkers (boronate/ thioketal), redox-logic gates, antioxidant coatings	[112,113, 170–172]
Enzyme	Peptide linkers, esters, glycosidic, phosphoesters	Solid-phase peptide grafting, ROP (PLA/PCL), polysaccharide derivatization	Peptide-crosslinked gels, lipase-labile polyesters, HA/ DEX/CS gels	Enzyme-specific cleavage, Michaelis–Menten-coupled degradation	Sequence, sterics, crosslink topology, MW	Off-target cleavage, fluid heterogeneity	Disease-specific peptide libraries, theranostic probes, protein corona-resistant design	[116,164, 165,680]
Biomolecule	PBA (glucose), aptamer/ antibody, DNA crosslinks	Post-polymer conjugation, iniferter-RAFT, DNA hybridization	Aptamer-gels, DNA-crosslinked hydrogels, ligand-decorated micelles	Analyte affinity (Kd), reversible binding, amplification	Ligand density, spacer length, ionic strength	Non-specific binding, ligand instability	Closed-loop insulin systems, multiplex analyte detection, nanoamplifiers (UCNP/QD)	[120,121, 681]
Ion	Carboxylate, sulfonate, phosphate, crown/ calixarene	Copolymerization with ionic monomers, host–guest grafting, polyelectrolyte complexation	Ion-exchange membranes, PEC hydrogels, crown-ether brushes	Selective swelling, permselectivity, conductivity	Charge density, counter-ion type, crosslink density	Competing ions, Donnan effects	MOF@polymer hybrid ion filters, electro–ionic dual gating, bone mineralization scaffolds	[82,83, 124,579, 682]
Hydration	PEG/PVA/ PHEMA, cellulose deriv.	cellulose deriv. Free-radical/RAFT, IPN (PVA-PAA), freeze–thaw	Hydrogels, films, IPNs	Water uptake, reversible modulus, permeability	Hydrophilic fraction, mesh size, crystallinity	Fatigue, dehydration	Smart wound dressings (moisture-color), food packaging freshness films, hydration-induced self-healing	[88,127, 174]
Temperature	LCST/UCST (PNIPAM, PVCL, PNAGA)	RAFT/ATRP, block assembly, ELP recombinants	Micelles, nanogels, cell-sheet hydrogels	LCST/T_cloud, Δsize, reversible turbidity	Hydrophilic/ hydrophobic balance, salts, comonomers	LCST drift in fluids, hysteresis	Injectable in situ gels, 4D printing, hyperthermia-integrated DDS	[131,132, 159,683]
Light	Azobenzene, spiropyran, coumarin, diarylethene, o-nitrobenzyl	Post-functionalization, CRP, step-growth	Photochromic brushes, photocleavable gels, patternable films	Isomerization yield, fatigue resistance, photolysis rate	Wavelength, chromophore loading, matrix Tg	UV phototoxicity, shallow penetration	NIR/2-photon activation, photo-thermal/ photodynamic synergy, light-guided tissue scaffolds	[91,134, 135,168]
Magnetic	Fe_3O_4/γ-Fe_2O_3 nanoparticles	In-situ co-precipitation, ligand-stabilized blending, sol–gel	MNP-hydrogels, elastomers, micelles	SAR, magnetothermal ΔT, field-driven actuation	MNP size/ loading, H/f, viscosity	Agglomeration, biosafety	Dual magnetothermal/ thermo response, MRI-visible DDS, magnetic soft actuators	[138,139, 177,684]
Electric	PPy, PANI, PEDOT:PSS, ionic liquids	Oxidative/electro-polymerization, dopant exchange	Conductive gels, coatings, dielectric elastomers	σ, actuation strain, on-demand release	Doping level, crosslink, electrolyte	Electrochemical aging, interface instability	Bioelectronics/ nerve scaffolds, RF-responsive CNT/ graphene hybrids, self-monitoring electrodes	[142,180, 432,685]
Ultrasound	Sonolabile linkers, micro/ nanobubbles	ONB/thioketal linkers, double emulsion	US-cleavable micelles, PLGA–PEG bubbles, HA/ alginate gels	Cavitation release, SDT-ROS, imaging	Linker chemistry, bubble size/ shell	Dose/ISI control, safety	Targeted ultrasound-triggered DDS, US-aided regenerative therapy, AI-calibrated dosing	[107,144, 145,686]
CO_2 / gas	Amidine/ guanidine, tertiary amines	Post-quaternization, CO_2-switchable blocks	CO_2-switchable micelles/ membranes	On/off assembly, permselectivity	Amine pKa, solvent, pressure	Moisture sensitivity	CO_2-switchable membranes with MOFs, carbon	[149,150, 687]

(*continued on next page*)

Table 4 (*continued*)

Stimulus	Key functional motifs	Typical synthesis routes	Common architectures	Key properties / response metrics	Tunability knobs	Pitfalls	Recent advances / innovations	Refs
							capture–recycling integration	
Mechanical/ Shear	Spiropyran, DTE mechanophores	Covalent embedding in backbones/ crosslinks	Mechano-reporting gels, mechano-release carriers	Force-activated color/release, toughness	Mechanophore content, network design	Irreversible, calibration	Self-healing coatings, digital-twin fatigue prediction	[152,153, 688]
Bioadhesive	Catechol, aldehyde/amine	Mussel-inspired grafting, Schiff-base crosslinking	Tissue glues, wet coatings	Adhesion under water, hemostasis	Catechol density, oxidation state	Oxidative darkening	Transparent catechol adhesives, anticoagulant co-functionalization	[155,156, 689]

10.2. Challenges and limitations

Despite significant advancements, several key challenges must be addressed to fully unlock the potential of SRPs in biomedical and environmental applications. One of the primary hurdles is scalability, as transitioning from laboratory-scale synthesis to cost-effective, reproducible large-scale manufacturing remains a complex task. The adoption of green synthesis techniques, continuous-flow polymerization, and advanced 3D/4D printing technologies offer promising solutions for improving scalability while reducing production costs. Future success will depend on integrating sustainable feedstocks and solvent-free or enzyme-catalyzed polymerization routes that maintain functionality while minimizing waste generation. Industrial scalability will also require automation, real-time process monitoring, and machine-learning-driven optimization for consistent product quality.

Another critical challenge is ensuring the long-term stability and durability of SRPs under real-world conditions. Environmental factors such as humidity, UV exposure, and temperature fluctuations can affect their responsiveness. To address this, researchers are exploring cross-linking strategies, nanocomposite reinforcements, and bioinspired self-healing mechanisms to enhance material robustness. Advances in supramolecular chemistry and dynamic covalent networks now enable polymers to autonomously repair damage and retain performance even after repeated stress. Such approaches are essential for extending the lifetime of SRP-based devices in medical implants, packaging, and energy applications.

Achieving multifunctionality and precise control over stimuli-triggered transformations remains a complex issue due to material integration challenges, cross-reactivity, and difficulties in fine-tuning responses. Advanced computational modeling, machine-learning-driven material design, and hybrid nanostructuring are emerging as powerful tools to facilitate the development of SRPs capable of responding to multiple stimuli in a coordinated manner. In particular, AI-assisted design frameworks are beginning to predict polymer–stimuli correlations, enabling rapid discovery of multi-responsive SRPs that combine pH, temperature, redox, and mechanical sensitivity within a single platform. This data-guided approach will accelerate optimization for specific biomedical or environmental functions.

Finally, biocompatibility and environmental safety are crucial concerns. Developing biodegradable alternatives, identifying non-toxic degradation pathways, and ensuring compliance with regulatory standards will be essential to the safe and sustainable deployment of SRPs in medical and ecological applications. Addressing these challenges through interdisciplinary collaboration will be key to advancing the next generation of high-performance, sustainable SRPs. Researchers are increasingly turning toward bio-based monomers and dynamic cross-linkers that degrade into non-toxic fragments, enabling safe resorption in vivo and eco-friendly decomposition in environmental contexts. These efforts align SRP development with the global transition toward sustainable material life cycles.

Looking forward, the integration of AI-guided materials design, hybrid polymer architectures, and green fabrication technologies will propel SRPs into a new era of intelligent functionality. By coupling responsiveness with programmability and sustainability, SRPs will serve as a foundation for precision medicine, adaptive energy systems, and smart environmental technologies. As interdisciplinary collaborations deepen, SRPs will no longer merely respond to stimuli but will actively sense, decide, and adapt, marking the dawn of truly autonomous materials capable of transforming how polymers interact with living and environmental systems.

10.3. Future directions and opportunities

Ongoing advancements in materials science, digital technologies, and sustainability-driven innovations are expected to play a crucial role in shaping the future of SRPs. As the demand for adaptive, intelligent, and environmentally responsible materials increases, SRPs are expected to evolve beyond simple stimuli-responsive systems toward self-adaptive, self-healing, and self-degradable materials capable of functioning in complex biomedical and environmental environments. As research progresses, interdisciplinary collaborations between polymer chemistry, nanotechnology, AI, and biomedical engineering will accelerate the development of next-generation SRPs with enhanced functionality, adaptability, and environmental compatibility.

One of the most transformative directions for SRP design and application is the integration of AI and ML. AI-driven models can predict material properties, optimize polymer structures, and simulate response behaviors under real-world conditions. Machine learning and deep-learning frameworks can analyze high-throughput polymer data to identify structure–property–response correlations, thus significantly reducing the empirical trial-and-error approach. Predictive algorithms are expected to forecast transition temperatures, degradation rates, swelling ratios, and multi-stimuli coupling behaviors, accelerating discovery of new SRP compositions. In biomedicine, AI-powered SRP formulations will enable personalized drug delivery systems that adapt in real-time to patient-specific conditions, such as pH changes, enzyme concentrations, or temperature fluctuations. AI-assisted optimization will also guide molecular design for precision implants, biosensors, and adaptive scaffolds that respond dynamically to physiological feedback, thereby enabling next-generation precision medicine.

Future SRPs will likely incorporate hybrid and multifunctional materials, combining nanomaterials, biopolymers, and MOFs to achieve enhanced performance. These hybrid SRPs will exhibit multi-modal responsiveness (e.g., pH–temperature–redox coupling) and operate effectively in heterogeneous biological and environmental conditions. The integration of soft polymer matrices with rigid inorganic or nanostructured components will improve both mechanical stability and responsiveness, expanding SRP utility in tissue regeneration, bioelectronics, and environmental sensing. For example, a hybrid polymer that integrates pH, temperature, and light responsiveness could enable on-demand drug delivery, tissue regeneration, and pollutant removal within a single system. The synergy between these materials will unlock new opportunities in biosensing, regenerative medicine, and environmental monitoring, making SRPs highly adaptable to a wide range of

applications.

With the increasing global focus on sustainability, future SRPs will be designed with biodegradability, recyclability, and eco-friendliness in mind. Researchers are exploring renewable feedstocks, such as cellulose, lignin, and chitosan, to synthesize biodegradable SRPs that reduce plastic waste. Moreover, green synthesis techniques, including solvent-free polymerization and enzymatic catalysis, are expected to further reduce the environmental footprint of SRP production. In particular, enzyme-catalyzed, photo-initiated, and solvent-free polymerization routes will advance the transition toward greener, energy-efficient manufacturing. SRPs incorporating self-degradable or stimuli-triggered disassembly mechanisms will replace conventional plastics and contribute to circular polymer economies. In packaging and smart coatings, SRPs with self-degrading properties can replace conventional plastics, significantly reducing pollution. Smart food packaging with temperature-sensitive indicators can enhance food safety by signaling spoilage, while biodegradable medical implants can dissolve safely after their therapeutic function is complete. Such innovations represent a move toward sustainable materials that combine environmental protection with advanced functional performance.

In parallel, clinical translation challenges—including regulatory approval, long-term safety, reproducibility, and scalability—remain significant barriers to real-world adoption. Large-scale manufacturing requires standardized synthesis protocols, quality control, and cost-effective production routes. Industrial sustainability will depend on life-cycle assessment and the use of renewable or recyclable precursors to ensure economic and environmental feasibility. Regulatory perspectives, particularly for biomedical SRPs, must account for long-term biocompatibility, degradation product safety, and adherence to green-chemistry principles. Ethical frameworks surrounding AI-driven material discovery and automated decision-making in polymer design will also become increasingly important as data-guided approaches expand.

One of the most promising technological advancements is 4D printing, where SRPs are printed into structures that change over time in response to external stimuli. Unlike traditional 3D printing, 4D-printed materials can undergo shape transformation, self-healing, or controlled drug release, making them ideal for biomedical implants, robotics, and smart structures. Through programmable chemistry, 4D-printed SRPs can morph, repair, and release therapeutics autonomously under physical or chemical triggers. In regenerative medicine, 4D scaffolds will dynamically adjust to cellular growth and microenvironmental cues, enhancing integration and healing. In soft robotics and wearable electronics, 4D-printed SRPs can serve as actuators and self-healing components capable of adaptive motion and real-time responsiveness. For example, self-healing hydrogels printed via 4D technology can be used in wearable biosensors that recover functionality after mechanical damage. In regenerative medicine, stimuli-responsive scaffolds can dynamically adapt to tissue growth, improving integration with the human body. As 4D printing becomes more cost-effective and scalable, it will drive the next generation of SRP-based medical and industrial applications.

SRPs are also expected to play a key role in addressing environmental challenges, particularly in water purification, air filtration, and pollution monitoring. Smart polymer membranes that can selectively capture heavy metals and organic pollutants will enhance the efficiency of wastewater treatment. Furthermore, SRP-based real-time sensors will enable early detection of toxic contaminants in industrial and agricultural environments, preventing potential hazards before they escalate. Beyond purification, responsive polymeric adsorbents and catalytic systems are expected to allow reversible pollutant capture and regeneration, supporting circular water treatment strategies.

Additionally, photoresponsive and electroactive polymers are likely to be incorporated into smart grids and renewable energy systems, improving both energy efficiency and sustainability. These materials could be used for energy harvesting, where mechanical movement or light exposure generates electricity, thus reducing reliance on fossil fuels. Such systems could bridge the gap between stimuli-responsive polymers and energy materials, enabling self-powered sensors, flexible electronics, and sustainable energy storage devices.

Despite these advancements, key challenges remain. Complex synthesis, reproducibility issues, and limited scalability hinder industrial translation. Long-term stability, biocompatibility, and standardized response quantification are essential for reliable deployment. Future progress will depend on integrating computational modeling, sustainable chemistry, AI-guided design, and regulatory frameworks to accelerate the safe, scalable, and responsible translation of SRPs into clinical and environmental practice.

The future of SRPs will be shaped by advancements in technology, sustainability, and multifunctionality. Innovations such as AI-driven material design, hybrid polymer systems, and 4D printing are set to transform medicine, industry, and environmental science. Through these convergent developments, SRPs will evolve from reactive materials into intelligent, autonomous systems capable of perceiving, adapting, and responding to their surroundings. These advancements will allow SRPs to become more efficient, adaptive, and responsive. As interdisciplinary collaborations continue to grow, SRPs will unlock new possibilities in personalized healthcare, smart materials, and ecological sustainability, leading to the development of high-performance, intelligent, and environmentally friendly polymer solutions. Ultimately, these innovations will redefine the role of polymers in addressing global challenges, establishing SRPs as a cornerstone of next-generation sustainable material technology.

CRediT authorship contribution statement

Kinam Park: Writing – original draft, Visualization. **Moon Suk Kim:** Writing – review & editing, Supervision. **Tae Woong Kang:** Writing – original draft, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was supported by the National Research Foundation of Korea (NRF) grants, STEAM Program (RS-2024–00458419), and Ministry of SMEs and Startups (20224371).

Data availability

Data will be made available on request.

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