The Past Ten Years of Carbohydrate Polymers in *ACS Macro Letters*

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Carbohydrates are the most abundant and one of the most important biomacromolecules in Nature. Although the word carbohydrate sounds simple and has a long history, it covers a very broad research scope with extensions in different research disciplines. In the past ten years, *ACS Macro Letters* has been an outstanding platform for publishing research papers related to carbohydrates from the polymer perspective. To date, we have published more than 120 papers related to the concept of carbohydrate polymers. These papers can be categorized into different topics (Figure 1), from synthesis,

Figure 1. (a) Word cloud of keywords used in the titles and abstracts of carbohydrate polymers published in *ACS Macro Letters* in the past ten years. The size of the word is reflective of the number of publications it appears in. (b) The number of papers categorized by different types of carbohydrate polymers.

physics, and self-assembly of new carbohydrate polymers or polysaccharides to various applications, including targeted delivery, polyplex, immune regulation, etc. In this editorial, the different topics published in *ACS Macro Letters* that involve carbohydrate-related papers will be summarized, giving one way to assess the state-of-the-art research in the field of carbohydrate polymers. The above-mentioned topics do not include polysaccharide-based materials that can show an impressive range of uses, such as those that include cellulose, which is an extremely important aspect of the field and deserves to be discussed separately.

The polymers related to carbohydrates can be roughly divided into three types (Figure 2):[1] (a) the polysaccharides found in Nature, which are normally homopolymers or heteropolymers, including cellulose, dextrin, agarose, etc.; (b) naturally derived synthetic polysaccharides, which are polymers containing a carbohydrate backbone, made by ring-opening polymerization or other methods with monomers made from natural saccharides; and (c) glycopolymers (including glycopeptides), which are synthetic polymers with monosaccharides or oligosaccharides as pendent groups. *ACS Macro Letters* published several important papers on novel synthesis of naturally derived synthetic polysaccharides and glycopolymers. For example, Grinstaff and his colleagues have published a number of *ACS Macro Letters* on their polyamidosaccharides (PASs) over the years. PAS is a type of naturally derived synthetic polysaccharide, made from glucose-/galactose-derived β-lactam monomers, with an amide linkage instead of the natural ether linkage. Based on a PAS backbone mimicking cellulose with alkyl chain modifications, thermotropic LC behavior was observed and reported.[2] Although the structures of glucose and galactose are similar, the property of PASs made of glucose and galactose can be very different. In comparison to the glucose-derived polymers, the galactose-derived polymers of all molecular weights showed high water solubility, which indicated the strong structure−property relationship of naturally derived synthetic polysaccharides.[3] The anionic ring-opening polymerization method to prepare PASs was also successfully extended to a maltose-based β-lactam monomer.[4] The synthesis of other types of naturally derived synthetic polysaccharides can also be found in *ACS Macro Letters*, including unnatural oligoaminosaccharides with N-1,2-glycosidic bonds prepared by cationic ring-opening polymerization of 2-oxazoline-based heterobicyclic carbohydrate monomers[5] and polycarbonates of a D-glucal-derived bicyclic carbonate prepared via organocatalytic ring-opening polymerization.[6] A different class of carbohydrate main chain polymers called glucose-based poly(ester amines) with carbohydrate units and oligoamines as a backbone was also made by diacrylate glucose and benzyl-Boc-protected oligoamine monomers via Michael addition.[7]
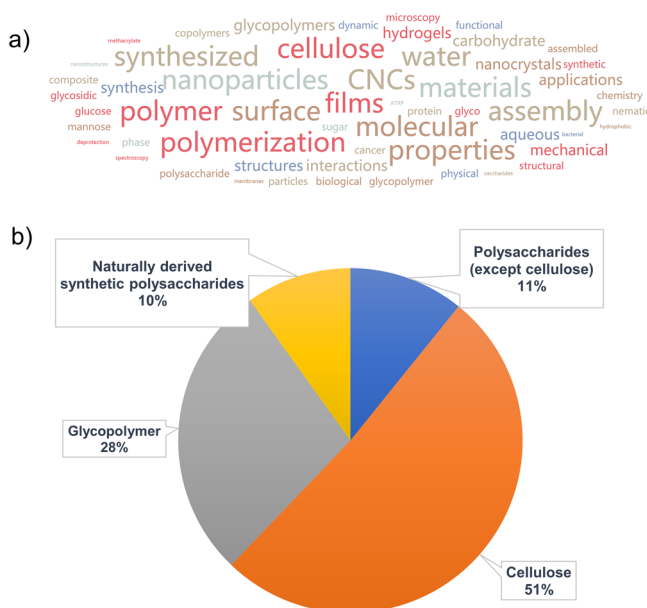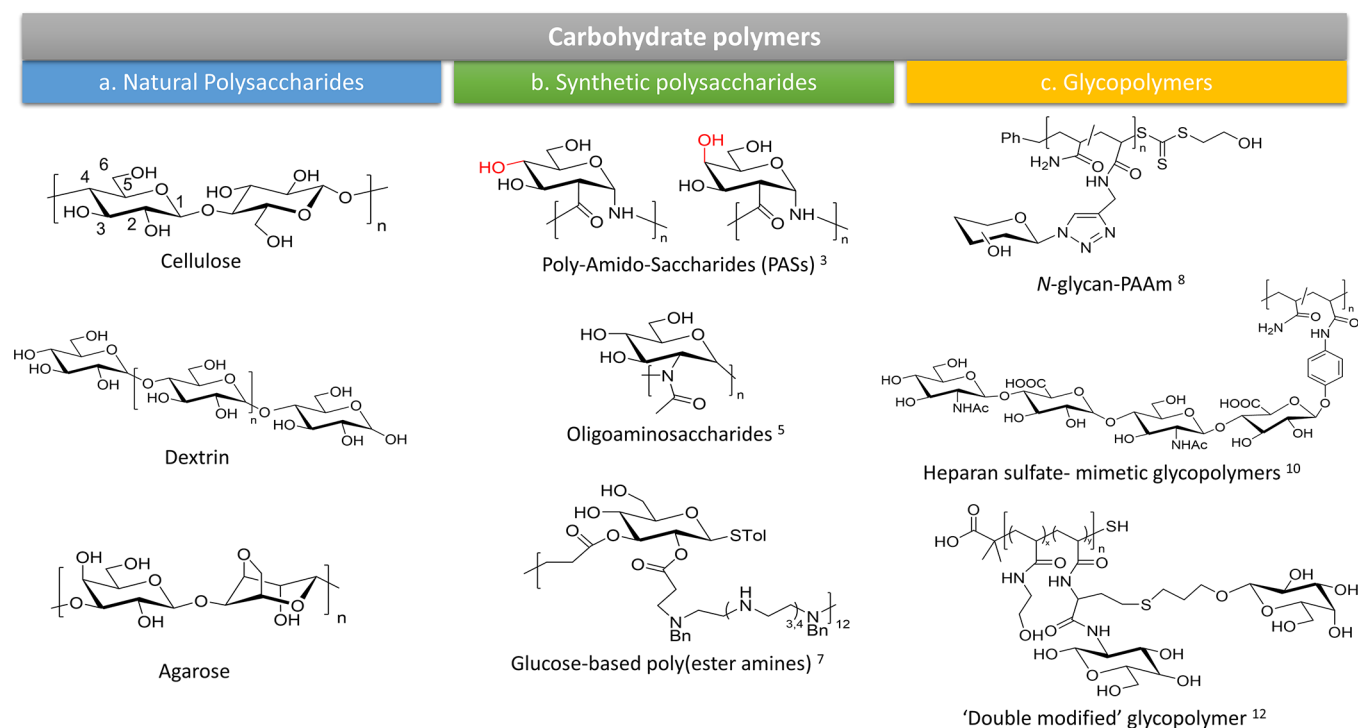
Figure 2. Different types of carbohydrate polymers discussed in this editorial (with the reference mark with each structure).

When it comes to glycopolymers, a range of new reported structures can be found in *ACS Macro Letters*. While naturally derived synthetic polysaccharides are mimicking the backbone of polysaccharides, glycopolymers are more or less designed to mimic the function of carbohydrate-containing biopolymers, especially the protein-binding functions of natural glycans. There are several papers that reported new glycopolymer structures that made significant steps toward mimicking natural glycans (Figure 2, right column). For example, new glycopolymers with *N*-glycan chains as pendent groups have been prepared by converting the *N*-glycan chain into a monomer.[8] One-pot synthesis of *N*-glycan polymers from unprotected carbohydrates was achieved via cyanoxyl free radical polymerization.[9] Chemoenzymatic synthesis of heparan sulfate mimetic glycopolymers[10] and synthesis of fucoidan-mimetic glycopolymers with sulfation patterns via emulsion ring-opening metathesis polymerization[11] have been also reported. In order to mimic the branched GM-1 structure, a glycopolymer with double-modified pendent from thiolactones[12] was prepared to modulate lectin selectivity and affinity.[12] Protein−glycopolymer "end-to-end" conjugation via copper-free click chemistry was reported as a structural mimic of natural glycan.[13] Besides the carbohydrate side chain, other functional components have been employed in glycopolymers. For example, FRET pairs, i.e., donor modified on the oligosaccharide side chain and acceptor on the main chain, were designed and prepared to investigate the activity of α-amylase.[14]

The natural glycosidic bond and hydroxyl groups make carbohydrate polymers an interesting platform from a polymer physics perspective. Cyclic or ring polymers have a topologically interesting structure and physical properties as well, in which the contribution from chain stiffness cannot be overlooked. Cyclic amylose provides an opportunity to investigate the effect of chain stiffness on cyclic polymers as reported by Terao et al., as the cyclic polymer with more than

100 pyranose units can be prepared enzymatically. Transformation of the free hydroxyl groups at the 2, 3, and 6 positions of glucopyranoside to tris(phenylcarbamate) results in a significant increase in chain stiffness as Kuhn length changed from 4 nm for cyclic amylose to 16−22 nm for cyclic amylose tris(phenylcarbamate) (Figure 3).[15] High molecular
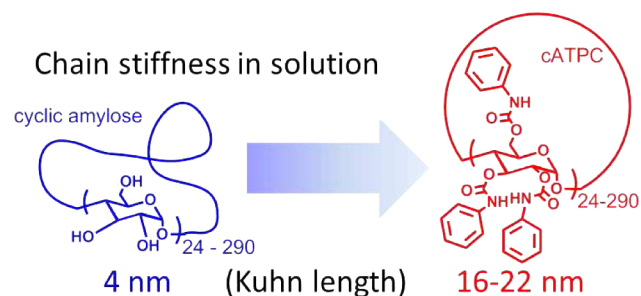

Figure 3. Kuhn length change on cyclic amylose. Reproduced with permission from ref 15. Copyright 2012 American Chemical Society.

weight methylcellulose was also grafted with short poly-(ethylene glycol) chains, as reported by Lodge et al., and while the contour length remained unchanged, the grafting led to an increase in the persistence length by a factor of 4.[16] Furthermore, the conformation change of linear polysaccharide λ-carrageenan controlled by chloroquine and inorganic cations has been reported by Mezzenga et al.[17]

The applications of carbohydrate polymers, especially glycopolymers, have drawn significant attention in the past ten years. These functions can be roughly divided into carbohydrate moieties on the polymer acting as a targeting agent, primarily on account of their ability to bind proteins and/or act as a hydrophilic shell. Polyplexes with a hydrophilic shell of glycopolymers were reported by Reineke et al. with pDNA and poly(2-methacrylamido-2-deoxy glucopyanose)-

modified star-shaped polyamidoamine.[18] Furthermore, a polyplex formed by a glycopolymer was employed for oncogenic epidermal growth factor receptor silencing.[19] The protein (or carbohydrate)-binding function of glycopolymers has been utilized in different applications, including lectin sensing,[20] probing carbohydrate—carbohydrate interactions (Figure 4),[21] elimination of pathogenic bacteria,[22] targeting

Figure 4. Cover art of thermal-triggered probing of carbohydrate—carbohydrate interactions reported by Gibson et al.[21]

HepG2 cells,[23] etc. The receptor binding ability of mannose-6-phosphate has been utilized in glycopolypeptides for lysosome targeting,[24] while a tumor-associated carbohydrate antigen was combined with single-chain polymer particles in order to enhance the weak immunogenicity of the former.[25] In addition to glycopolymers, new functions of polysaccharides have been reported in *ACS Macro Letters*. For example, a galacturonic-acid-presenting polysaccharide showed binding affinities to proangiogenic growth factors.[26]

Self-assembly is one way that connects the synthesis and physical properties of carbohydrate polymers to materials with applications. Considering the complex structure of carbohydrates, which have relative rigid backbones and numerous hydroxyl groups, the understanding of carbohydrate polymer self-assembly becomes an interesting and important topic. For example, the attachment of maltoheptaose to long-chain hydrocarbons (wax) can be used to form micelles and vesicles.[27] Related maltoheptaose-modified poly(ε-caprolactone) block copolymers allow access to self-assembled microphase-separated domains at the 10 nm scale, on account of the high Flory—Huggins interaction parameter (χ) of the block copolymer.[28] New approaches to construct assembled nano-objects based on carbohydrate polymers have been continuously published in *ACS Macro Letters*. The concept of

deprotection-induced glycopolymer self-assembly (DISA), in which the amphiphilicity change of the glyco-block copolymer is induced by deprotection, was first introduced by Chen et al.[29] Soon after, a related approach that resulted in a morphology transition was achieved by chemoenzymatic synthesis of a glycopeptide.[30] Single-chain methods[31,32] and interfacial polyaddition in miniemulsions[33] were also reported as new approaches to access glyco-nanoobjects. Other reversible/dynamic interactions have also been investigated with carbohydrates. For example, the dynamic covalent bonds formed between saccharides and phenylboronic acid have been utilized to construct either layer-by-layer assemblies[34] or hydrogels.[35] Similarly, carbohydrate/lectin binding was employed to access polymeric hydrogels.[36]

Based on the assembled glyco-nanoobjects, the structure—property relationship has been extensively investigated across different scales. For example, at the molecular level, binding of regioisomers of galactopyranoside (Gal)-modified glyco-nanoparticles was compared, showing the different binding ability and cellular transportation pathway of 1-Gal- and 6-Gal-modified nanoparticles.[37] Based on this result, the same group revealed the importance of Gal modification of nanoparticles, in order to achieve the biofilm inhibition activity of *S. aureus*.[38] Meanwhile, virus-like morphologies of glyco-nanoparticles were achieved by Stenzel et al. that exhibit different internalization ability by macrophages.[39] Different fluorescent-labeling properties of glyco-nanoparticles with different morphologies were also reported.[40] The interaction of glyco-nanoparticles of different shapes, from worm-like micelles to platelets with immune cells, has been intensively investigated by O'Reilly and Chen et al.[41,42] These studies revealed the intricate connection between the biological function and the structure of glyco-nanoobjects at different scales, from the structure of carbohydrates to the size, shape, and even phase separation of the nanoobjects.

While the term carbohydrate is a simple name, it covers an extremely large amount of macromolecules. A large number of polysaccharides exist in nature and function as matter, with cellulose being the most abundant. Nanocelluloses, including cellulose nanocrystals (CNCs), are a topic that attracts much interest, in part on account of the robust nature of its crystalline structure (Figure 5).[43] In addition, while surface hydroxyl groups are the dominant functionality in carbohydrate polymers, they can be modified to access, e.g., carboxylate, sulfate half ester, and amine on the CNC surface, providing more versatility for material preparation and properties. For example, pH-responsive cellulose nanocrystal gels and nanocomposites have been prepared based on the protonation/deprotonation of carboxylate- or amine-modified cellulose nanocrystals.[44] Other carbohydrate polymers contain these functionalities naturally. For example, the macroscopic properties of gellan gum hydrogels have been tuned by the rigid, fibrillar quaternary structures of these carboxylic-acid-functionalized polysaccharides, which were induced by divalent ions.[45] Besides, shear-thinning injectable hydrogels with hyaluronic acid were fabricated via tuning electrostatic interactions by Langer et al.[46] Other functionalities can also be exploited: for example, mechanically stable hydrogels based on polysaccharide were achieved by dynamic covalent cross-linking of thiol-aldehyde addition.[47] Meanwhile, 4,6-acetalized Curdlan, i.e., β-1,3 glucan, can be cross-linked via the hydrogen bonds of the hydroxyl groups at the 2 position of this modified Curdlan, forming double or triple helices.[48] To decipher the
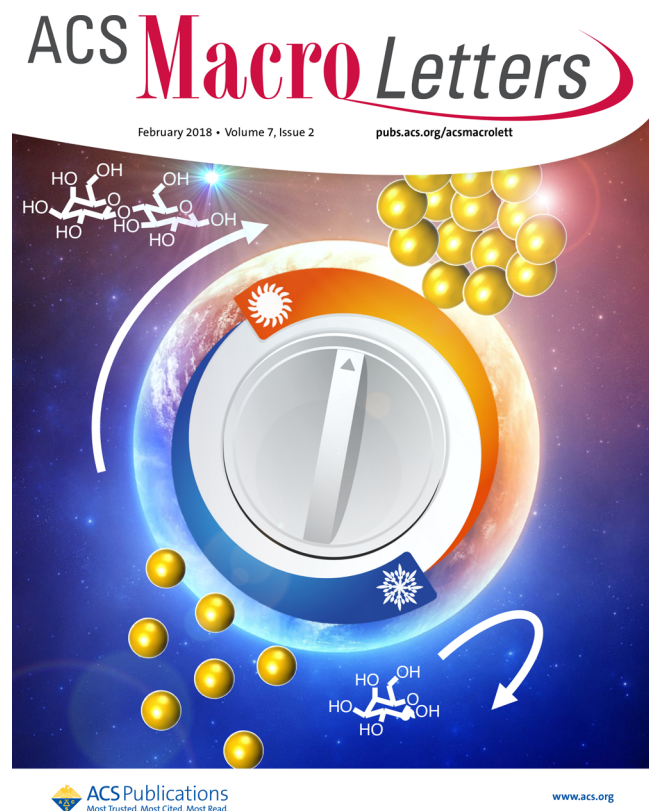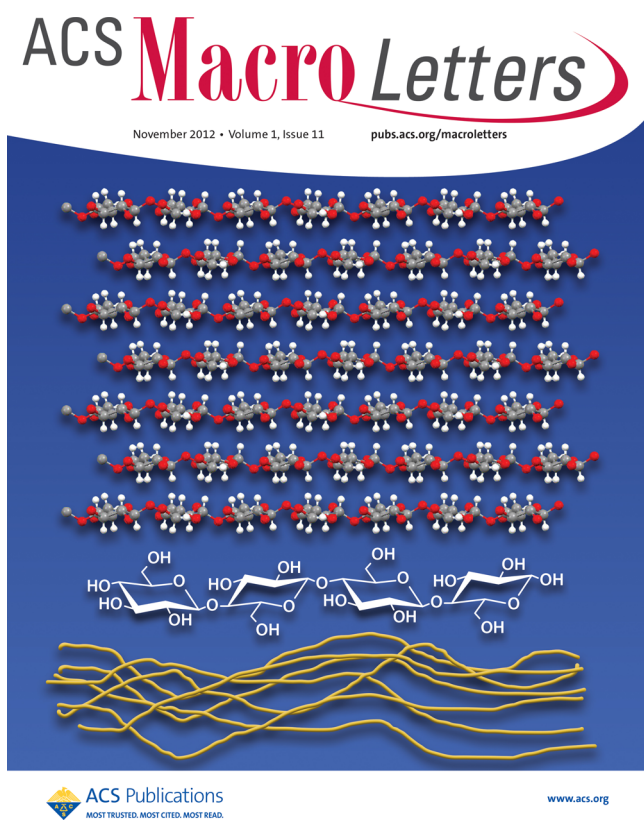
Figure 5. Cover art showing the molecular chains of cellulose in crystalline cellulose.[43]

connection between the regioselectivity of the glucan chain and the property of the final bulk material, a (1−2)-glucopyran derivative was prepared by using cationic polymerization. The self-standing film of the obtained (1−2)-linked glucan chain derivative was found to be highly stretchable and tough, while the film made with the (1−4)-linked glucan chain derivative was brittle. This dramatic difference indicated that the interchain hydrogen bonds in the two glucan chains with different linkages could serve as energy-dissipative bonds (Figure 6).[49] The combination of the polysaccharide with other polymers is also a very active area of research, especially as a way to enhance mechanical properties. 4D printing of robust hydrogels could be achieved by combining agarose nanofibers and polyacrylamide.[50] A remarkable increase in

toughness and stiffness can be achieved by blending of polybutadiene (PB) and cellulose triacetate (CTA), with the triblock copolymer CTA-*b*-PB-*b*-CTA as a compatibilizer.[51]

When the published papers are divided by the category of carbohydrate polymers, as I mentioned in the beginning of this editorial, polysaccharides can be found to be dominate, with more than 60 papers. Among these papers, preparing various materials by using different polysaccharides, especially cellulose or cellulose nanocrystals, contributed significantly (Figure 1). While some aspects of this work were touched upon, there was not enough space to do this area full justice. The focus of this editorial was to give more of a taste of the different types of carbohydrate polymers that have been reported in *ACS Macro Letters* with exploration of their contribution to material functions, which not only stands from the fundamentals of carbohydrate polymers but also gives a broad vision in material science.

I joined the editorial team of *ACS Macro Letters* in 2018. Before that, I was an author and a reviewer. By summarizing the carbohydrate-related papers in the past ten years, we can get some idea of the research trends in this field. *ACS Macro Letters* publishes novel approaches and important breakthroughs in all research aspects of carbohydrate polymers, from synthesis to physics and from assembly to macroscopic materials and biological functions. From the above examples, it is clear that *ACS Macro Letters* is one of the best platforms in which to publish all areas of carbohydrate-related research in polymer science and material science. I hope and also believe that *ACS Macro Letters* will serve this community and will be continuously trusted by our colleagues in this research field in the coming ten years and beyond!

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Notes

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■ REFERENCES

(1) Su, L.; Feng, Y.; Wei, K.; Xu, X.; Liu, R.; Chen, G. Carbohydrate-Based Macromolecular Biomaterials. *Chem. Rev.* **2021**, DOI: 10.1021/acs.chemrev.0c01338.
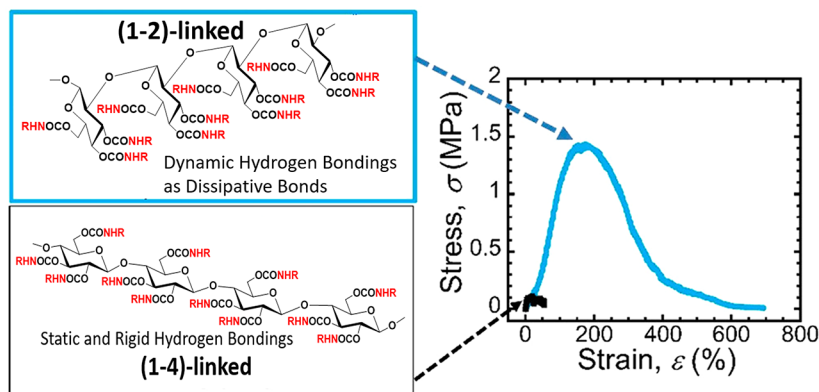
Figure 6. Comparison of the materials made by (1−2)-linked or (1−4)-linked glucans. Reproduced with permission from ref 50. Copyright 2020 American Chemical Society.

(2) Ghobril, C.; Heinrich, B.; Dane, E. L.; Grinstaff, M. W. Synthesis of Hydrophobic Carbohydrate Polymers and Their Formation of Thermotropic Liquid Crystalline Phases. *ACS Macro Lett.* **2014**, *3* (4), 359−363.

(3) Dane, E. L.; Chin, S. L.; Grinstaff, M. W. Synthetic Enantiopure Carbohydrate Polymers that are Highly Soluble in Water and Noncytotoxic. *ACS Macro Lett.* **2013**, *2* (10), 887−890.

(4) Xiao, R.; Zeng, J.; Grinstaff, M. W. Biologically Active Branched Polysaccharide Mimetics: Synthesis via Ring-Opening Polymerization of a Maltose-Based β-Lactam. *ACS Macro Lett.* **2018**, *7* (7), 772−777.

(5) Koda, Y.; Terashima, T.; Ouchi, M. Unnatural Oligoamino-saccharides with N-1,2-Glycosidic Bonds Prepared by Cationic Ring-Opening Polymerization of 2-Oxazoline-Based Heterobicyclic Sugar Monomers. *ACS Macro Lett.* **2019**, *8* (11), 1456−1460.

(6) Lonnecker, A. T.; Lim, Y. H.; Wooley, K. L. Functional Polycarbonate of a d-Glucal-Derived Bicyclic Carbonate via Organo-catalytic Ring-Opening Polymerization. *ACS Macro Lett.* **2017**, *6* (7), 748−753.

(7) Lee, C.-C.; Liu, Y.; Reineke, T. M. Glucose-Based Poly(ester amines): Synthesis, Degradation, and Biological Delivery. *ACS Macro Lett.* **2012**, *1* (12), 1388−1392.

(8) Tanaka, T.; Ishitani, H.; Miura, Y.; Oishi, K.; Takahashi, T.; Suzuki, T.; Shoda, S.-i.; Kimura, Y. Protecting-Group-Free Synthesis of Glycopolymers Bearing Sialyloligosaccharide and Their High Binding with the Influenza Virus. *ACS Macro Lett.* **2014**, *3* (10), 1074−1078.

(9) Tang, J.; Ozhegov, E.; Liu, Y.; Wang, D.; Yao, X.; Sun, X.-L. Straightforward Synthesis of N-Glycan Polymers from Free Glycans via Cyanoxyl Free Radical-Mediated Polymerization. *ACS Macro Lett.* **2017**, *6* (2), 107−111.

(10) Li, J.; Cai, C.; Wang, L.; Yang, C.; Jiang, H.; Li, M.; Xu, D.; Li, G.; Li, C.; Yu, G. Chemoenzymatic Synthesis of Heparan Sulfate Mimetic Glycopolymers and Their Interactions with the Receptor for Advanced Glycation End-Product. *ACS Macro Lett.* **2019**, *8* (12), 1570−1574.

(11) Fan, F.; Cai, C.; Wang, W.; Gao, L.; Li, J.; Li, J.; Gu, F.; Sun, T.; Li, J.; Li, C.; Yu, G. Synthesis of Fucoidan-Mimetic Glycopolymers with Well-Defined Sulfation Patterns via Emulsion Ring-Opening Metathesis Polymerization. *ACS Macro Lett.* **2018**, *7* (3), 330−335.

(12) Wilkins, L. E.; Badi, N.; Du Prez, F.; Gibson, M. I. Double-Modified Glycopolymers from Thiolactones to Modulate Lectin Selectivity and Affinity. *ACS Macro Lett.* **2018**, *7* (12), 1498−1502.

(13) Zhang, H.; Weingart, J.; Gruzdys, V.; Sun, X. Synthesis of an End-to-End Protein−Glycopolymer Conjugate via Bio-Orthogonal Chemistry. *ACS Macro Lett.* **2016**, *5* (1), 73−77.

(14) Matsuoka, K.; Arai, H.; Oka, H.; Koyama, T.; Hatano, K. Synthetic Assembly of Bifluorescence-Labeled Glycopolymers as Substrates for Assaying α-Amylase by Resonance Energy Transfer. *ACS Macro Lett.* **2012**, *1* (2), 266−269.

(15) Terao, K.; Asano, N.; Kitamura, S.; Sato, T. Rigid Cyclic Polymer in Solution: Cycloamylose Tris(phenylcarbamate) in 1,4-Dioxane and 2-Ethoxyethanol. *ACS Macro Lett.* **2012**, *1* (11), 1291−1294.

(16) Morozova, S.; Lodge, T. P. Conformation of Methylcellulose as a Function of Poly(ethylene glycol) Graft Density. *ACS Macro Lett.* **2017**, *6* (11), 1274−1279.

(17) Diener, M.; Adamcik, J.; Mezzenga, R. Formation of Higher Structural Levels in λ-Carrageenan Induced by the Antimalarial Drug Chloroquine. *ACS Macro Lett.* **2020**, *9* (9), 1310−1317.

(18) Buckwalter, D. J.; Sizovs, A.; Ingle, N. P.; Reineke, T. M. MAG versus PEG: Incorporating a Poly(MAG) Layer to Promote Colloidal Stability of Nucleic Acid/"Click Cluster" Complexes. *ACS Macro Lett.* **2012**, *1* (5), 609−613.

(19) Diaz-Dussan, D.; Peng, Y.-Y.; Kumar, P.; Narain, R. Oncogenic Epidermal Growth Factor Receptor Silencing in Cervical Carcinoma Mediated by Dynamic Sugar-Benzoxaborole Polyplexes. *ACS Macro Lett.* **2020**, *9* (10), 1464−1470.

(20) Richards, S.-J.; Gibson, M. I. Optimization of the Polymer Coating for Glycosylated Gold Nanoparticle Biosensors to Ensure Stability and Rapid Optical Readouts. *ACS Macro Lett.* **2014**, *3* (10), 1004−1008.

(21) Won, S.; Hindmarsh, S.; Gibson, M. I. Triggerable Multivalent Glyconanoparticles for Probing Carbohydrate-Carbohydrate Inter-actions. *ACS Macro Lett.* **2018**, *7* (2), 178−183.

(22) Hyun, J. Y.; Lee, C.-H.; Lee, H.; Jang, W.-D.; Shin, I. Bacterial Lectin-Targeting Glycoconjugates for Selective Elimination of Pathogenic Bacteria. *ACS Macro Lett.* **2020**, *9* (10), 1429−1432.

(23) Zhao, C.-M.; Wang, K.-R.; Wang, C.; He, X.; Li, X.-L. Cooling-Induced NIR Emission Enhancement and Targeting Fluorescence Imaging of Biperylene Monoimide and Glycodendrimer Conjugates. *ACS Macro Lett.* **2019**, *8* (4), 381−386.

(24) Das, S.; Parekh, N.; Mondal, B.; Gupta, S. S. Controlled Synthesis of End-Functionalized Mannose-6-phosphate Glycopoly-peptides for Lysosome Targeting. *ACS Macro Lett.* **2016**, *5* (7), 809−813.

(25) Gracia, R.; Marradi, M.; Salerno, G.; Perez-Nicado, R.; Perez-San Vicente, A.; Dupin, D.; Rodriguez, J.; Loinaz, I.; Chiodo, F.; Nativi, C. Biocompatible single-chain polymer nanoparticles loaded with an antigen mimetic as potential anticancer vaccine. *ACS Macro Lett.* **2018**, *7* (2), 196−200.

(26) Li, Q.; Guo, G.; Meng, F.; Wang, H. H.; Niu, Y.; Zhang, Q.; Zhang, J.; Wang, Y.; Dong, L.; Wang, C. A Naturally Derived, Growth Factor-Binding Polysaccharide for Therapeutic Angiogenesis. *ACS Macro Lett.* **2016**, *5* (5), 617−621.

(27) Cushen, J. D.; Shanmuganathan, K.; Janes, D. W.; Willson, C. G.; Ellison, C. J. Synthesis of Amphiphilic Naturally-Derived Oligosaccharide-block-Wax Oligomers and Their Self-Assembly. *ACS Macro Lett.* **2014**, *3* (9), 839−844.

(28) Otsuka, I.; Isono, T.; Rochas, C.; Halila, S.; Fort, S.; Satoh, T.; Kakuchi, T.; Borsali, R. 10 nm Scale Cylinder−Cubic Phase Transition Induced by Caramelization in Sugar-Based Block Copolymers. *ACS Macro Lett.* **2012**, *1* (12), 1379−1382.

(29) Su, L.; Wang, C.; Polzer, F.; Lu, Y.; Chen, G.; Jiang, M. Glyco-Inside Micelles and Vesicles Directed by Protection−Deprotection Chemistry. *ACS Macro Lett.* **2014**, *3* (6), 534−539.

(30) Yang, J.; Du, Q.; Li, L.; Wang, T.; Feng, Y.; Nieh, M.-P.; Sheng, J.; Chen, G. Glycosyltransferase-Induced Morphology Transition of Glycopeptide Self-Assemblies with Proteoglycan Residues. *ACS Macro Lett.* **2020**, *9* (7), 929−936.

(31) Wuest, K. N. R.; Lu, H.; Thomas, D. S.; Goldmann, A. S.; Stenzel, M. H.; Barner-Kowollik, C. Fluorescent Glyco Single-Chain Nanoparticle-Decorated Nanodiamonds. *ACS Macro Lett.* **2017**, *6* (10), 1168−1174.

(32) Kroger, A. P.; Komil, M. I.; Hamelmann, N. M.; Juan, A.; Stenzel, M. H.; Paulusse, J. M. J. Glucose Single-Chain Polymer Nanoparticles for Cellular Targeting. *ACS Macro Lett.* **2019**, *8* (1), 95−101.

(33) Roux, R.; Sallet, L.; Alcouffe, P.; Chambert, S.; Sintes-Zydowicz, N.; Fleury, E.; Bernard, J. Facile and Rapid Access to Glyconanocapsules by CuAAC Interfacial Polyaddition in Mini-emulsion Conditions. *ACS Macro Lett.* **2012**, *1* (8), 1074−1078.

(34) Gou, Y.; Slavin, S.; Geng, J.; Voorhaar, L.; Haddleton, D. M.; Becer, C. R. Controlled Alternate Layer-by-Layer Assembly of Lectins and Glycopolymers Using QCM-D. *ACS Macro Lett.* **2012**, *1* (1), 180−183.

(35) Kotsuchibashi, Y.; Agustin, R. V. C.; Lu, J.-Y.; Hall, D. G.; Narain, R. Temperature, pH, and Glucose Responsive Gels via Simple Mixing of Boroxole- and Glyco-Based Polymers. *ACS Macro Lett.* **2013**, *2* (3), 260−264.

(36) Wei, K.; Li, J.; Chen, G.; Jiang, M. Dual Molecular Recognition Leading to a Protein−Polymer Conjugate and Further Self-Assembly. *ACS Macro Lett.* **2013**, *2* (3), 278−283.

(37) Sun, P.; He, Y.; Lin, M.; Zhao, Y.; Ding, Y.; Chen, G.; Jiang, M. Glyco-regioisomerism Effect on Lectin-Binding and Cell-Uptake Pathway of Glycopolymer-Containing Nanoparticles. *ACS Macro Lett.* **2014**, *3* (1), 96−101.

(38) Tao, G.; Ji, T.; Wang, N.; Yang, G.; Lei, X.; Zheng, W.; Liu, R.; Xu, X.; Yang, L.; Yin, G.-Q.; Liao, X.; Li, X.; Ding, H.-m.; Ding, X.;

Xu, J.; Yang, H.-B.; Chen, G. Self-Assembled Saccharide-Functionalized Amphiphilic Metallacycles as Biofilms Inhibitor via "Sweet Talking. *ACS Macro Lett.* **2020**, *9* (1), 61−69.

(39) Dag, A.; Zhao, J.; Stenzel, M. H. Origami with ABC Triblock Terpolymers Based on Glycopolymers: Creation of Virus-Like Morphologies. *ACS Macro Lett.* **2015**, *4* (5), 579−583.

(40) Chen, H.; Zhang, E.; Yang, G.; Li, L.; Wu, L.; Zhang, Y.; Liu, Y.; Chen, G.; Jiang, M. Aggregation-Induced Emission Luminogen Assisted Self-Assembly and Morphology Transition of Amphiphilic Glycopolypeptide with Bioimaging Application. *ACS Macro Lett.* **2019**, *8* (8), 893−898.

(41) Li, Z.; Sun, L.; Zhang, Y.; Dove, A. P.; O'Reilly, R. K.; Chen, G. Shape Effect of Glyco-Nanoparticles on Macrophage Cellular Uptake and Immune Response. *ACS Macro Lett.* **2016**, *5* (9), 1059−1064.

(42) Li, Z.; Zhang, Y.; Wu, L.; Yu, W.; Wilks, T. R.; Dove, A. P.; Ding, H.-m.; O'Reilly, R. K.; Chen, G.; Jiang, M. Glyco-Platelets with Controlled Morphologies via Crystallization-Driven Self-Assembly and Their Shape-Dependent Interplay with Macrophages. *ACS Macro Lett.* **2019**, 596−602.

(43) Eichhorn, S. J. Stiff as a Board: Perspectives on the Crystalline Modulus of Cellulose. *ACS Macro Lett.* **2012**, *1* (11), 1237−1239.

(44) Way, A. E.; Hsu, L.; Shanmuganathan, K.; Weder, C.; Rowan, S. J. pH-Responsive Cellulose Nanocrystal Gels and Nanocomposites. *ACS Macro Lett.* **2012**, *1* (8), 1001−1006.

(45) Diener, M.; Adamcik, J.; Bergfreund, J.; Catalini, S.; Fischer, P.; Mezzenga, R. Rigid, Fibrillar Quaternary Structures Induced by Divalent Ions in a Carboxylated Linear Polysaccharide. *ACS Macro Lett.* **2020**, *9* (1), 115−121.

(46) Appel, E. A.; Tibbitt, M. W.; Greer, J. M.; Fenton, O. S.; Kreuels, K.; Anderson, D. G.; Langer, R. Exploiting Electrostatic Interactions in Polymer−Nanoparticle Hydrogels. *ACS Macro Lett.* **2015**, *4* (8), 848−852.

(47) Hua, Y.; Gan, Y.; Zhang, Y.; Ouyang, B.; Tu, B.; Zhang, C.; Zhong, X.; Bao, C.; Yang, Y.; Lin, Q.; Zhou, Q.; Zhu, L. Adaptable to Mechanically Stable Hydrogels Based on the Dynamic Covalent Cross-Linking of Thiol-Aldehyde Addition. *ACS Macro Lett.* **2019**, *8* (3), 310−314.

(48) Sakamoto, J.; Kita, R.; Duelamae, I.; Kunitake, M.; Hirano, M.; Yoshihara, D.; Yamamoto, T.; Noguchi, T.; Roy, B.; Shinkai, S. Cohelical Crossover Network by Supramolecular Polymerization of a 4,6-Acetalized β-1,3-Glucan Macromer. *ACS Macro Lett.* **2017**, *6* (1), 21−26.

(49) Ihsan, A. B.; Koyama, Y. Substituent Optimization of $(1 \rightarrow 2)$-Glucopyranan for Tough, Strong, and Highly Stretchable Film with Dynamic Interchain Interactions. *ACS Macro Lett.* **2020**, *9* (5), 720−724.

(50) Guo, J.; Zhang, R.; Zhang, L.; Cao, X. 4D Printing of Robust Hydrogels Consisted of Agarose Nanofibers and Polyacrylamide. *ACS Macro Lett.* **2018**, *7* (4), 442−446.

(51) Arrington, K. J.; Haag, J. V.; French, E. V.; Murayama, M.; Edgar, K. J.; Matson, J. B. Toughening Cellulose: Compatibilizing Polybutadiene and Cellulose Triacetate Blends. *ACS Macro Lett.* **2019**, *8* (4), 447−453.