Preface: Special Issue on Associating Polymers

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Associative polymers represent a very promising class of systems, since they offer exciting opportunities for stimuli-responsive structures, and exhibit reversible properties, from rubber to liquidlike properties. They also present interesting self-healing properties. Nevertheless, many open questions must be addressed in order to understand their complex behavior and to exploit their large potential.

The objective of this Special Issue is to present recent works, which bring new insight on the complex dynamics of associating polymers.

In addition to the manuscripts, the issue also presents the discussions that we had about these works during the final conference of the European Initial Training Network SUPOLEN [*Supramolecular assembly of polymeric structures: a novel route to enhance soft materials properties*, FP7, 607937].

Either based on experimental investigation or on simulation, these 18 works study the dynamics of associating polymers. The interesting point is that each system studied seems to have its own specificities, despite the fact that all these samples have a similar composition. As the reader will quickly realize, by playing with the entangled state of the building polymers, as well as with the position, density, and lifetime of the stickers, a very rich panel of viscoelastic responses can be obtained.

As shown through these different papers, an interesting way to classify these different behaviors is to discuss them, based on the comparison between experimental time (or rate of deformation), lifetime of the reversible association, and relaxation time of the building polymers.

(1) The ratio between these different times can strongly vary, in function of the nature of the reversible junctions. Typically, these physical bonds are hydrogen bonding, hydrophobic, van der Waals or electrostatic interactions, or metal-ligand interactions. As illustrated in Fig. 1, their corresponding binding energies are very different,[1] which gives us access to a whole range of association lifetimes. Their association times also depend on other parameters such as the functionality, number and localization of supramolecular bonds, the temperature or pH, the polymer concentration, and the nature of the solvent.

The large versatility of the association lifetime is well illustrated in the work of Wang *et al.* [2], who study the properties of a triblock Pluronic copolymer with a weak polyacid able to associate via H-bonded complexes. The authors show that with such systems, the sticker lifetime is strongly affected by the pH of the aqueous solutions as well as by the addition to the solution of a cosolvent able to accept H bonding. In particular, the authors show that at low pH level, the polyelectrolyte system exhibits strong physical associations, leading to the agglomeration of H-bond complexes and consequently, high elasticity and shear viscosity, with good self-healing properties, which is of potential interest for application.

Another highly tunable system is presented by Brassinne *et al.* [3], who study the linear viscoelastic properties of ultrahigh molecular weight polymers sparsely decorated with chelating ligand in aqueous solution. Adding metal ions to this sample leads to the creation of a reversible network, thanks to the formation of metal-ligand complexes. By playing with the nature and proportion of metal ions, the molar mass of the backbone, and the temperature, the authors demonstrate that it is possible to control its dynamics, with a terminal relaxation time which can vary by several orders of
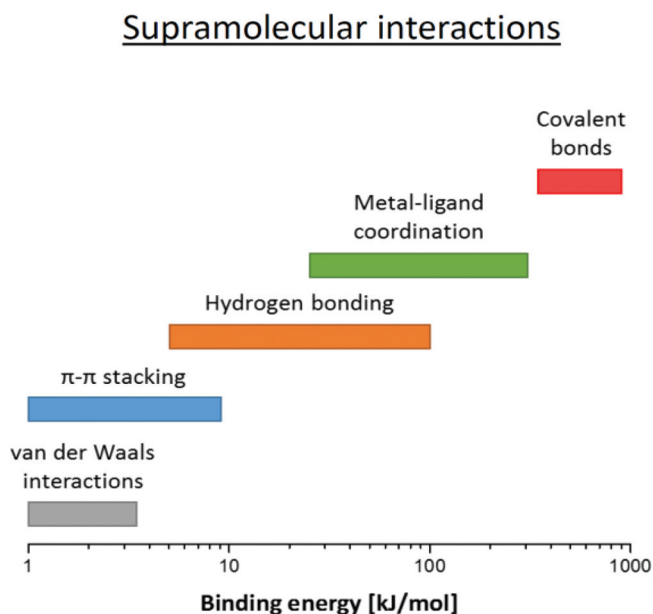

FIG. 1. Binding energies corresponding to reversible junctions of different nature [1].

magnitude. In particular, they show that adding metal ions in excess compared to their stoichiometric amount speeds up the reversible dynamics of the bonds.

As an example in the melt state, Chile *et al.* [4] study the dynamics of poly(lactide)s end-capped with different arylated chain ends. Depending on the nature of the chain ends, the influence of the stickers is found to be more or less important. In particular, it is found that the end-groups have a stronger influence on the properties of the low molar mass sample. The authors attribute this observation to the larger density of end groups in these last samples.

(2) Chain mobility is also very important, in particular, if the building polymers associate into supramolecular assemblies (rather than a percolated network). In such a case, there is a competition between two different relaxation mechanisms, as it has been described by Cates [5]: either the assemblies relax as complex covalentlike architectures or they relax through the dissociation of their reversible bonds followed by the relaxation of their building polymers, the relative importance of these two processes depending on the ratio between sticker lifetime and relaxation time of the assemblies.

This idea is further investigated by Watanabe *et al.* [6], who study and model the viscoelastic and dielectric properties of unentangled head-carboxylated high-cis polyisoprene chains. These monofunctional linear chains, called the "unimers," are able to temporary undergo head-to-head association in order to create "dimers." Through this work, the authors show that the lifetime of the sticker is short enough to compete with the relaxation time of the dimers. Consequently, these samples are not relaxing as their corresponding blend of (covalent) unimers and dimers, and both relaxation mechanisms must be accounted for.

This competing process is also discussed in the work of Louhichi *et al.* [7] on supramolecular living polymers composed of bisurea monomer (EHUT). These supramolecular gelators are able to relax both by reptation and chain scission. But, in addition to these two relaxation mechanisms, the authors show that the presence of a very tiny amount of water is sufficient to significantly speed up the relaxation of the supramolecular gelator (EHUT). It is shown that acting as a chain stopper, the presence of water leads to a reduction of the molar mass of the assemblies, which are then able to relax faster. This example demonstrates how it is important to carefully characterize such sensitive polymers.

Based on a similar strategy, Staropoli *et al.* [8] synthesized and characterized transiently branched comb polymers, able to relax either as comb molecules or as blends of long and short linear chains, depending on the association lifetime. Interestingly, the authors find that the viscoelastic moduli of these supramolecular combs are similar to the response of their covalent counterpart, despite the fact that the sticker lifetime is shorter than the terminal relaxation time of the samples. The authors attributed this peculiar behavior to the similar values of the association lifetime and arm retraction time, both processes affecting the backbone motion in a similar way.

(3) In the case of a percolated transient network, the stickers must dissociate in order to allow the chains moving. The relaxation of this transient network can be divided into two regimes: While at short times ($t \ll \tau_{\text{sticker}}$), the segmental dynamics fully governs the local motion of the polymer strands between two stickers, at longer time, both segmental and supramolecular dynamics enter into play in order to allow the entire chains to relax.

The major consequence of these two regimes is the appearance of a thermorheological complex behavior at intermediate frequency, at which the stickers start dissociating and reassociating.

This failure of tTS principle is analyzed in details by Zhang *et al.* [9], who demonstrate that in the case of unentangled associative chains, the shift factors used in the terminal regime for building a mastercurve are influenced by both the transient bond dynamics and the segmental dynamics. In consequence, these shift factors cannot be directly used to determine the sticker activation energy. To do so, the authors show that one should rather consider the temperature influence on the ratio between the sticker lifetime and the segmental time.

In case of entangled associative chains, the failure of tTS principle can be even more pronounced, without any possibility to build a mastercurve in the low frequency regime of deformation. The importance of this failure seems to depend on the lifetime of the stickers along the chains, compared to the disentanglement time of the unassociated chains.

Gold *et al.* [10] study the dynamics of a first system of entangled sticky chains, which contain urazole groups along the chain backbone. These sticky groups form short lifetime associations via H bonding. In consequence, at the time a chain is diffusing, all its stickers already associated/dissociated several times, leading to chain motion governed by the disentanglement dynamics, with a (global) additional friction coming from the stickers dynamics. Therefore, it is found that these samples display a quasisimple thermorheological behavior.

On the other hand, based on their slip-link model, Shivokhin *et al.* [11] demonstrate that in case of entangled chains with long lifetime stickers along their backbone, entanglement and stickers dynamics are nonadditive, showing a strong synergetic effect. For these samples, mastercurve cannot be built at low frequency.

Similar conclusions are found by Zhuge *et al.* [12] who analyzed and modeled the viscoelastic data of telechelic entangled PnBA star polymers able to associate via metal-ligand interactions. By playing with the temperature and the nature of the metal ion, they systematically vary the lifetime of the stickers, and thus the ratio between disentanglement time of the building blocks and sticker dynamics. They show that this ratio has a direct consequence on the relative contribution from both processes to the terminal relaxation of the sample. Consequently, the sticker activation energy cannot be directly drawn from these terminal relaxation times, even if the T-dependence of the segmental dynamics is taken into account, as proposed in Quan *et al.* in case of unentangled

polymers. The contribution from the entanglement dynamics must also be removed.

(4) While in the linear regime of deformation, the viscoelastic properties of associating polymers are influenced by the ratio between association and disentanglement times, fracture mechanisms are found to strongly depend on the Weissenberg number $\text{Wi}_{\text{terminal}}$, defined as equal to $\tau_{\text{terminal}}\,\dot{\varepsilon}$.

This is shown in the work of Arora et al. [13], who observed that under extension, wormlike micelles linked by telechelic polymers display a brittle behavior (rather than necking) at deformation rate larger than $\text{Wi}_{\text{terminal}}$, while filament thinning is observed at lower rates. The authors attributed this drastic change of behavior to the fact that at high strain rate, viscous dissipation is negligible, so the filaments always fracture in the elastic limit. Furthermore, they highlight the influence of sticker density on the hardening behavior of their samples: while weakly associated chains exhibit significant strain hardening before fracture, the micelles linked by a large amount of telechelic polymers already break in the linear viscoelastic regime.

Similar conclusion are drawn by Shabbir et al. [14] with nonentangled polyester ionomers based on polyethers and sulphonated phthalates with counterions, under large extension: the ability of the chains to strain harden before the sample breakage decreases when the strain rate increases toward the inverse sticker lifetime, and samples are becoming brittle when stretched too fast. Furthermore, by comparing the influence of two different counterions (Na and Li), they demonstrate that the strain hardening behavior of these unentangled sticky chains is fully dominated by the lifetime of the stickers.

The influence of the sticker density on the ability of the samples to show strain hardening is also studied by Park and Ianniruberto [15] based on Brownian dynamics simulation for telechelic associating polymers under large shear. The authors attribute the origin and limit of strain hardening to the finite extensible nonlinear elasticity of the chains. This result well agrees with the former observation by Arora et al. and Shabbir et al.: at low proportion of stickers, the molecular strands between two associated stickers are longer, and consequently the "reservoir of deformation" before reaching finite extensibility is also larger.

Similar arguments are also used by Wagner and McKinley [16] who study the extensional behavior of human saliva: they show that this last one can be modeled by considering saliva as physically associating network of finite extensible elastic segments. In this work, the authors also study the time effect on the filament thinning behavior of these samples. They observe a significant decrease of elasticity, which is attributed to the time dependent decrease of the molar mass of the mucin molecules.

However, the ability of the associated chains to resist to large deformation and eventually show strain hardening behavior also depends on the ability of these physical bonds to survive to high temperature as well as to the stretch conditions.

This is discussed by Aime et al. [17], who study the extensional behavior of model thermoplastic elastomers: By increasing temperature, the strength and lifetime of the hard segment associations are reduced and consequently, the strain at break of the samples strongly decreases. In such a case, it is found that larger strain at break is reached if the samples are deformed very fast. The authors model these properties by studying the loss of connectivity in the transient network. This concept allows them to show that not only the sticker lifetime is important in the rupture properties of these associating chains, but also their length, since it defines the number of stickers per chain and therefore, their ability to connect to neighboring chains.

Similar arguments are used by Biswas et al. [18], who investigate the influence of tacticity, concentration, and molar mass of poly(N-isopropylacrylamide) chains diluted in benzyl alcohol on their rheological properties. These chains are able to reversely associate through partial phase separation. The authors study their elastic behavior in terms of network connectivity, looking at the ability of the chains to bridge different clusters.

The influence of temperature on the physical bonds breaking time is also studied by Pratchayanan et al. [19], in case of transient networks created through Diel–Alder adducts. As Aime et al., the authors find that stress relaxation is much faster at a high temperature, the lifetime of the physical bonds becoming very short. In such a case, the chain motion seems to be more affected by the chain relaxation (segmental dynamics) than by the sticker dynamics.

Thus, these different works tell us that the dynamics of the reversible bonds must be fast enough in order to avoid brittle fracture, while at the same time, network connectivity must be ensured in order to avoid the breakage of the sample.

A smart way to fulfill these two conditions is discussed by Zhao et al. [20], who investigate the elongation properties of dual crosslinked hydrogels, containing both permanent and transient crosslinks. As shown by the authors, the extensibility of a weakly chemically crosslinked gel is considerably enhanced by adding few reversible bonds. However, if the network connectivity is increased further by adding more physical crosslinks, a reduction of the maximum extensibility is then observed. This can be related to our previous statements, according to which the maximum strain at break is limited by the finite extensibility of the molecular strand located between two surviving associated stickers.

To conclude, it is clear that associating polymers exhibit a very rich and diverse behavior, which cannot be understood only based on the lifetime of the stickers. It rather depends on a delicate interplay between transient dynamics, chain mobility, network connectivity, and flow-induced properties.

ACKNOWLEDGMENTS

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