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Perspective

Polymers with Dynamic Bonds: Adaptive Functional Materials for a Sustainable Future

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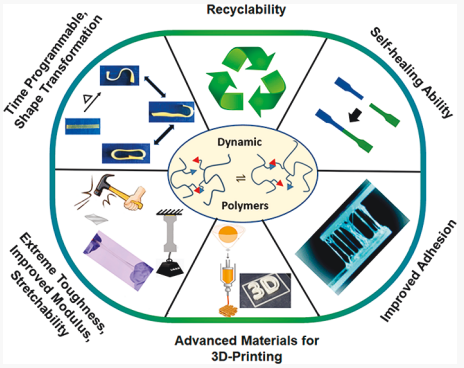
ABSTRACT: Polymeric materials play critical role in many current technologies. Among them, adaptive polymeric materials with dynamic (reversible) bonds exhibit unique properties and provide exciting opportunities for various future technologies. Dynamic bonds enable structural rearrangements in polymer networks in specific conditions. Replacement of a few covalent bonds by dynamic bonds can enhance polymeric properties, e.g., strongly improve the toughness and the adhesive properties of polymers. Moreover, they provide recyclability and enable new properties, such as self-healing and shape memory. We briefly overview new developments in the field of polymers with dynamic bonds and current understanding of their dynamic properties. We further highlight several examples of unique properties of polymers with dynamic bonds and provide our perspectives for them to be used in many current and future applications.



I. INTRODUCTION

Last year (2020) celebrated 100 years anniversary of Staudinger's breakthrough hypothesis about the existence of macromolecules—long molecules with backbone atoms connected by covalent bonds.[1] This idea was the birth of Polymer Science and Staudinger was awarded Nobel Prize in Chemistry in 1953. Although people used natural polymers (e.g., silk) for centuries before this publication, it stimulated strong progress in the development of synthetic polymers and their broad industrial use. Already, in the 1980s, the volume of polymer production surpassed that of steel. Currently, polymers have penetrated almost every corner of our lives. and their applications range from trash bags and bottles to membranes for water desalination and to bodies of aircraft and wind turbine blades. Such broad use of polymers stems from their unique viscoelastic and mechanical properties, their intrinsic light weight (they are mostly constructed from the lightest atoms, such as H, C, O, and N), and their having an extremely wide range of tunable properties and easy processability.

Recent advances in polymer chemistry provided a possibility to use dynamic (reversible) bonds, substituting some of the covalent (irreversible) bonds or cross-linking in the polymeric material.[2−10] These dynamic bonds are stable in the required range of parameters, but they can be reversibly dissociated and rearranged by changing the environment (e.g., high temperature, particular solvent, and pH or being under UV-light illumination[11]). These reversible bonds enable facile recyclability of the polymeric materials in specific conditions. Importantly, they enable several new properties, including self-healing and time-programmable properties.[10] Adding dynamic bonds to traditional polymers introduces several new time and length scales that enable additional control of their viscoelastic properties. They also can provide high toughness and extensibility of the materials,[8,12−14] strong adhesion properties,[15−17] etc. Even for thermoset materials, which usually contain permanent chemical cross-links, the introduction of dynamic bonds makes them reconfigurable in specific conditions, often known as covalent adaptable networks.[18,19] Thus, the insertion of dynamic bonds in traditional polymer-based materials provides a transformative new approach in the design and synthesis of novel functional materials with unique, time-programmable properties not available for usual polymers, and enables recyclability.[10]

In this Perspective, we discuss polymers with different dynamic bonds, their unique properties and briefly overview the models designed to describe these properties. We present a unified qualitative description of the mechanisms controlling the unique properties of polymers with dynamic bonds. We also outline some limitations and gaps in our understanding of these complex materials. Finally, we emphasize that adding dynamic bonds to the toolbox of polymer synthesis enables the design of materials with novel and unique functionalities that

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are critical for our sustainability and many future advanced technologies.

II. DYNAMIC (REVERSIBLE) BONDS IN POLYMERS

Viscoelastic properties of usual polymers are controlled by segmental and chain dynamics. The former represents local structural changes involving several monomers and leads to a transition region when the shear modulus drops from the GPa to the MPa range. Freezing of segmental relaxation defines the glass transition temperature, T_g, of the material. On the other hand, chain relaxation modes define viscosity and terminal relaxation of polymeric systems, and in cross-linked networks, the rubbery plateau level is controlled by the chain relaxation between cross-links. Inserting dynamic bonds introduces several new relaxation processes and enables additional control of viscoelastic properties and structural rearrangements of the materials.

Dynamic (reversible) bonds are defined as any class of bond that can go through dissociation and reassociation and can include several classes of bonds, such as $\pi-\pi$ interactions, hydrogen and ionic bonds, metal−ligand coordination, and even many covalent bonds (Figure 1a).[20] On a large scale, the

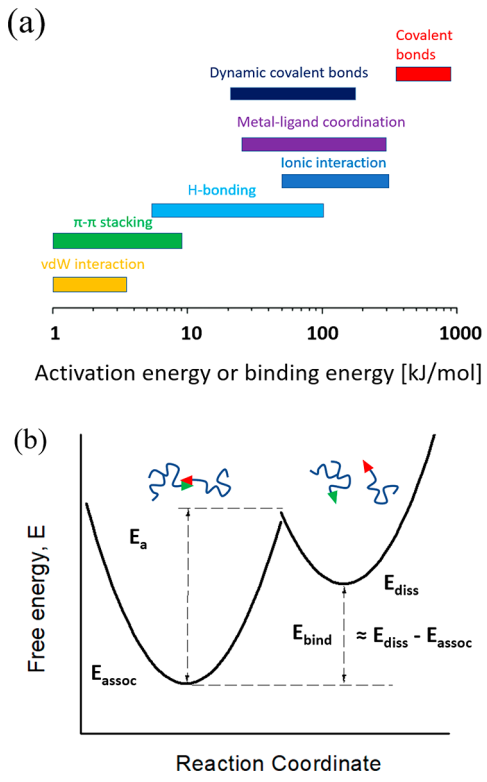

Figure 1. (a) Activation energy of dissociation and binding energy for various types of bonds and interactions. (b) Schematics of free energies of the associated and dissociated states of reversible bonds.

dynamic bonds can be classified into two broad categories: noncovalent bonds and dynamic covalent bonds. The noncovalent bonds include any bonding mechanisms including ionic bonds, hydrogen bonds, van der Waals interactions and $\pi-\pi$ interactions, or metal−ligand coordination bonds (although sometimes classified as a subset of covalent bonding) that differ from typical covalent bonding where electron pair(s) are shared between atoms. The noncovalent bonds are usually weaker, and their equilibrium state can be easily altered by diverse stimuli, including thermal conditions, solvents, and pH. The dynamic covalent bonds can be dynamic and reversible like noncovalent bonds under appropriate conditions (e.g., certain temperatures, catalysts, light, and redox conditions), unlike traditional irreversible covalent bonds. Since breaking/reforming covalent bonds costs more energy than noncovalent bonds, their dynamic bonding behavior is usually slower than that of noncovalent bonds.[21] The examples of dynamic covalent bond chemistry include dynamic C−C bonds (e.g., Aldol, Diels−Alder, Friedel−Crafts reactions), dynamic C−N bonds (e.g., urea/imine exchange, aminal and amide formation), dynamic C−O bonds (e.g., ester, acetal formation, Nicholas ether exchange, alkoxyamine exchange), dynamic C−S bonds (e.g., thioacetal, thiazolidine exchange, and the Thia-Michael reaction) dynamic B−O bonds (e.g., boronic ester exchange), and dynamic S−S bonds (e.g., disulfide exchange).[22]

The dynamic bonds differ significantly in their activation energy of dissociation (E_a), which is usually significantly lower than traditional irreversible covalent bonds (Figure 1a). As a result, this activation energy (Figure 1b), controls many macroscopic properties of polymers with dynamic bonds. Another important parameter is the difference in free energy between associated (E_{assoc}) and dissociated (E_{diss}) states, which is often called a binding energy (E_{bind}) (Figure 1b). In most cases, E_{assoc} is much lower than E_{diss} favoring bonding, while the opposite limit ($E_{assoc} > E_{diss}$) results in no binding. An interesting case is when $E_{bind} = E_{diss} - E_{assoc} \sim RT$ (R is the gas constant and T is the temperature), resulting in many dissociated groups, and the number of bonds (or cross-links) being temperature dependent regardless of the activation energy barrier.

However, for most of the dynamic bonds, $E_{assoc} \ll E_{diss}$, and the activation energy for dissociation plays a critical role in the properties of polymers with dynamic bonds. E_a defines the lifetime of the dynamic bond (τ_{dis}) and in this way controls the viscoelastic properties of the polymer.[23] If τ_{dis} is extremely long (e.g., months or years) under ambient conditions, the material will behave as a polymer with very long chains or as a cross-linked network. However, a strong decrease in τ_{dis} (e.g., by increasing T, or using specific solvents) can strongly reduce the viscosity of the material or reduce the lifetime of the cross-links, making materials easily processable, reformable, and recyclable. Thus, tuning the activation energy enables control of materials mechanical and viscoelastic properties over a wide range. For example, by tuning the strength of hydrogen bonding of end groups in relatively short telechelic poly(propylene glycol) (PPG), Xing et al. demonstrated a significant change of viscoelastic properties, and they even observed the appearance of a rubbery plateau in systems with the molecular weight far below the entanglement limit (Figure 2a).[24] The terminal relaxation time of the polymer was shifted by more than 100 times relative to the same polymer with nonassociating chain ends (Figure 2a), indicating the formation of longer chains through the chain ends association. Even stronger effects can be observed using metal coordination effects (Figure 2b). For example, using a linear copolymer with (2-acetoacetoxy)ethyl methacrylate as a bidentate ligand for metal coordination, the Silberstein group highlighted the effects of coordination geometry on viscoelastic properties of reversible metallopolymer networks. Changing the divalent metal species from Zn(II) to Cu(II) to Ni(II), the coordination geometry changes from tetrahedral to square

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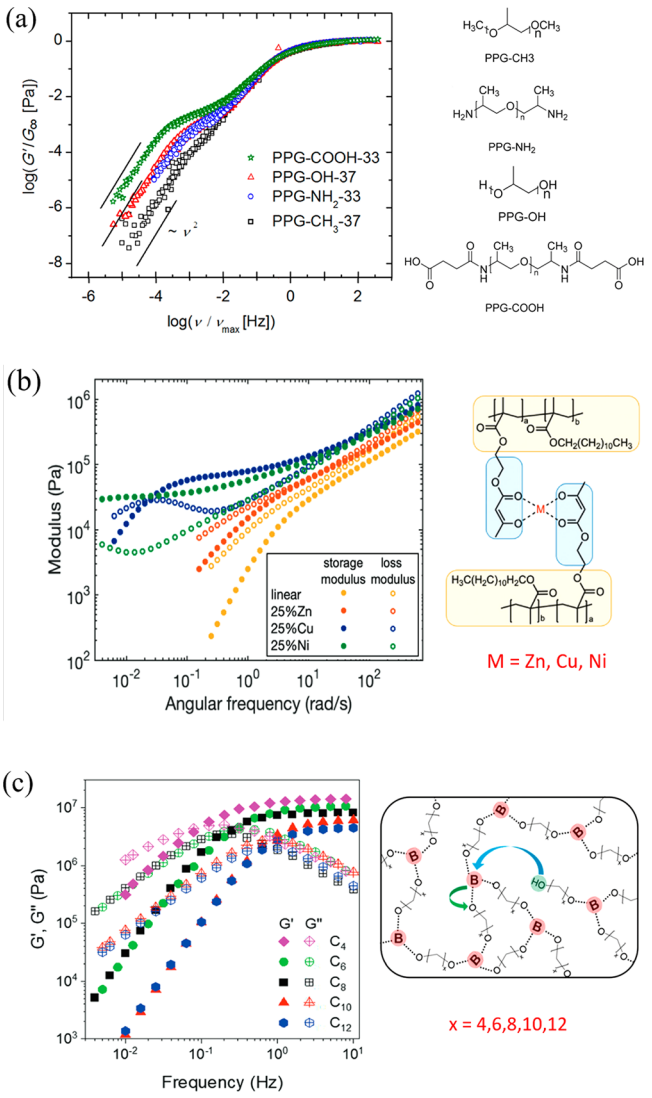

Figure 2. Examples of viscoelastic spectra for polymers with dynamic bonds: (a) Normalized storage modulus master curves $G'(\nu/\nu_{max})/G_\infty$ of telechelic polypropylene glycol (PPG) with the same degree of polymerization (DP = 33) and different end groups. Due to chain end association of the H-bonding groups (−OH, $-NH_2$, and −COOH), the terminal relaxation shifts to lower frequencies compared to nonassociating PPG−CH_3. Reprinted with permission from ref 24. Copyright 2018 American Chemical Society. (b) Change in storage and loss modulus spectra of copolymer poly[(lauryl methacrylate)-*co*-(2-acetoacetoxy)ethyl methacrylate] coordinated with different metal cations due to the difference in the coordination geometry. Reprinted with permission from ref 25. Copyright 2020 Royal Society of Chemistry. (c) Evolution of storage and loss modulus of ethylene vitrimer with increase in linker length (decreasing cross-linking density) from C_4 to C_{12}. Whereas, rubbery plateau modulus increases with increasing cross-linking density, the terminal relaxation shifts to lower frequencies. Reprinted with permission from ref 26. Copyright 2020 Royal Society of Chemistry.

planar to octahedral arrangement, resulting in alteration of the activation energy of the metal-complexes. This affects their rheological spectra, changing the characteristic relaxation time by 3 orders of magnitude (from ∼1 s to >30 min) (Figure 2b).[25] The viscoelastic properties of the network can also be tuned by varying the position and density of associative groups. By introducing boronic ester cross-links in the precise position of a telechelic ethylene vitrimer, Soman and Evans demonstrated that by decreasing the linker spacing from 12 carbon chains to four carbon chains (i.e., by increasing the cross-linking density), the rubbery plateau modulus could be increased from ∼4 to 14 MPa and the terminal relaxation can be pushed to lower frequencies (Figure 2c).[26]

Although the activation energy of the bond dissociation plays a critical role in the viscoelastic properties of polymers with dynamic bonds, many reported studies estimate E_a directly from the slope of the measured temperature dependence of the stress−relaxation time (or viscosity) (Figure 3a). This is incorrect for two reasons. First, the measured dissociation time $\tau_{dis}(T)$ depends on E_a and segmental mobility of the system. It is obvious that if segments are frozen (e.g., the system is below the polymer T_g), no bond dissociation is possible. Thus, $\tau_{dis}(T)$ depends also on segmental relaxation time of the polymer backbone $\tau_\alpha(T)$:[27]

$$\tau_{dis}(T) = \tau_\alpha(T)\exp\left(\frac{E_a}{RT}\right) = \tau_0 \exp\left(\frac{B}{T - T_0}\right)\exp\left(\frac{E_a}{RT}\right) \quad (1)$$

In eq 1, the temperature dependence of segmental relaxation time is expressed through the usual Vogel−Fulcher−Tammann (VFT) expression with material-dependent parameters B, T_0, and τ_0. Thus, the slope of the temperature dependence of $\tau_{dis}(T)$ reflects dissociation rate modulated by segmental relaxation rate, and the correct estimation of the activation energy requires an explicit account of the polymer segmental relaxation:

$$E_a = RT \times \ln\frac{\tau_{dis}(T)}{\tau_\alpha(T)} \quad (2)$$

Second, in some cases, τ_{dis} appears to be much shorter than structural rearrangements time (e.g., terminal relaxation time), τ_{Rheo}, measured in rheology.[28,29] If the dissociated functional group reconnects back with the same partner, no stress−relaxation happens. Only when the sticker changes the partner can structural rearrangement and stress−relaxation occur.[30,31] This point will be discussed in more detail in the next section. All these results clearly suggest that measurements of the temperature dependence of structural rearrangement time using rheology do not provide true estimates of the activation energy of dissociation, and τ_{Rheo} is modulated by several other phenomena.

This character of the temperature dependence of the dissociation time (eq 1) explains two different regimes for the temperature dependence of viscosity or terminal relaxation time known for vitrimers (Figure 3b). In the case of high activation energy, $E_a \gg RT_g$, the system remains cross-linked at temperatures close to T_g and starts to flow only at $T \gg T_g$ (Figure 3b). In this temperature range, the polymer segmental relaxation has already relatively weak temperature dependence, and temperature variation of $\tau_{dis}(T)$ is dominated by the activation energy for bond dissociation (eq 1). As a result, $\tau_{dis}(T)$ exhibits almost Arrhenius T dependence (blue solid line in Figure 3b). However, if E_a/RT_g is not very high, the system will start to flow or have measurable terminal relaxation already at temperatures close to T_g. In that case, the temperature dependence of $\tau_{dis}(T)$ close to T_g might be dominated by strong VFT dependence of segmental dynamics and will cross over to Arrhenius-like behavior dominated by the activation energy of bond dissociation only at a much higher T (red solid line in Figure 3b). As an example, Nishimura et al. designed a

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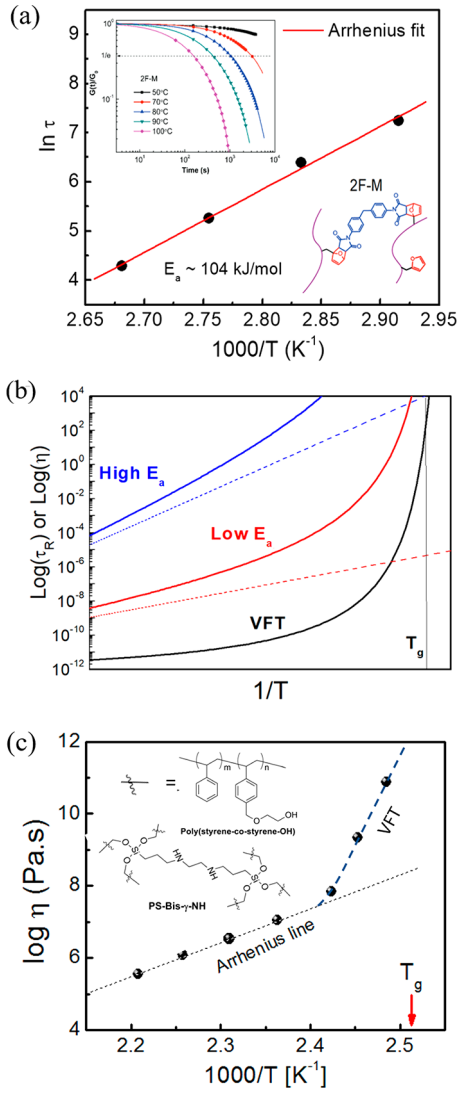

Figure 3. (a) Example of Arrhenius temperature dependence of the stress−relaxation time in a Diels−Alder type (furan−maleimide molar ratio 2:1) covalent adaptive network. Adapted with permission from ref 33. Copyright 2017 Royal Society of Chemistry. The estimated apparent activation energy does not present the activation energy for bond dissociation (see the text). (b) Schematic presentation of temperature dependence of terminal relaxation time or viscosity in vitrimers with relatively high E_a/RT_g (blue line) and relatively low E_a/RT_g (red line). The dashed and dotted lines present the Arrhenius slopes associated with these dissociation energies. The black line presents the VFT dependence of the polymer segmental relaxation. (c) Experimental observation of the VFT to Arrhenius crossover of viscosity in a silyl−ether exchange based vitrimer. Adapted with permission from ref 32. Copyright 2017 American Chemical Society.

silyl−ether exchange-based vitrimer (PS-Bis-γ-NH), in which they introduced a bis(alkoxysilane) cross-linker with neighboring amino groups. This vitrimer design enables them to experimentally observe the VFT to Arrhenius-like transition in viscosity with increasing temperature (Figure 3c).[32]

In the case of weaker dynamic bonds, change in entropy during bond association/dissociation may contribute appreciably to the free energy. Freed and co-workers developed lattice cluster theory for telechelic associating polymers, where they emphasized that the stiffness of the sticky bonds (reduced conformational entropy) plays a significant role in the thermodynamics and self-assembly of the short telechelic chains.[34] Using entropy-dominated noncovalent interaction between polymer dodecyl-modified hydroxypropyl methylcellulose (HPMC-C_{12}) and polystyrene nanoparticle, Yu et al. produced a physical hydrogel exhibiting temperature independent viscoelasticity.[35] Similarly, simulation and mean field theory of a linker-mediated vitrimer system also indicated the importance of translational entropy of free linker in explaining the experimentally observed reentrant sol−gel transition in these systems and provide important guidelines to design novel materials with desired mechanical properties.[36] On the other hand, Kim et al. prepared a supramolecular polymer with high mechanical robustness almost comparable to cross-link elastomeric system, whereas the dimer formation between the vicinal diol stickers randomly spaced within polybutadiene backbone is both enthalpically and entropically favorable.[37]

Even stronger variations in the viscoelastic properties appear when the associating groups are immiscible with polymer backbone and phase separate, forming clusters of dynamic bonds.[38] This phase separation has been reported in ionomers,[39] associating polymers with hydrogen bonds,[40] and vitrimers[41] and even in metal-coordinated supramolecular polymers.[42] For example, hydrophobic poly(dimethylsiloxane) (PDMS) oligomers with polar ureidopyrimidinone (UPy) end groups form microphase separated hard domains of dynamic bonds and ordered structures with domain spacing controlled by the oligomer lengths.[43] These clusters of dynamic bonds can be crystalline or amorphous and are usually detected by small-angle X-ray scattering (SAXS) measurements as a peak at low scattering wave vector.[44,45] Their presence can be also detected in DSC measurements as an additional glass transition step or melting/crystallization process.[46] The cluster's glass transition or melting (T_m) temperatures are usually higher than polymer T_g, and characteristic structural relaxation in these clusters controls the dissociation time of the segregated dynamic bonds. By systematically tuning the steric crowding at the C6-position of the pyrimidone group within UPy, Kan et al. controlled the extent of microphase separation of the UPy groups attached to hydrogenated polyisobutylene telechelic polymer. The authors observed that with the increase in degree of microphase separation, the storage modulus could be enhanced exponentially.[47]

The presence of these clusters has a tremendous impact on the viscoelastic behavior of the polymers. For example, Tress et al. studied the viscoelastic behavior of telechelic PDMS with $NHCO(CH_2)_2COOH$ associating groups and showed that by varying the chain length of the PDMS backbone, the level of the rubbery plateau modulus and its longevity can be modified by orders of magnitude (Figure 4a).[44] Moreover, studies of these associating polymers reveal that their terminal relaxation time and viscosity are controlled by structural relaxation time and T_g of the clusters (Figure 4b), and not by the backbone properties. Only when functional groups within the clusters become mobile will polymers flow and structure can be rearranged.[29] Studies of similar structures with microphase-separated hydrogen bonds also revealed that characteristic self-healing time is defined by the terminal relaxation time of the system (Figure 4c).[45] Thus, clusters of dynamic bonds provide additional opportunities to tune materials properties by changing structural relaxation time in these clusters.

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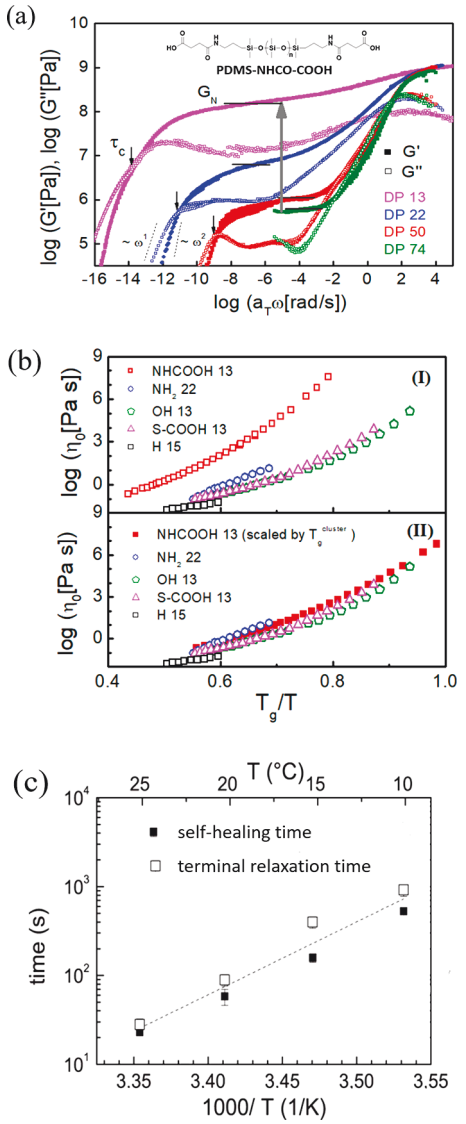

Figure 4. (a) Example of rheological data for storage and loss moduli in telechelic PDMS with phase separating end groups, where changing the degree of polymerization (DP) of the PDMS backbone leads to significantly higher and longer rubbery plateau. Adapted with permission from ref 44. Copyright 2021 American Chemical Society. (b) Scaling of the temperature dependence of viscosity by T_g of the backbone does not remove the difference in polymer behavior, while the use of dynamic bonds cluster T_g removes the difference. Reprinted with permission from ref 29. Copyright 2019 Springer. (c) Comparison of the self-healing time (filled squares) and terminal relaxation time (open squares) in telechelic polyisobutylene with H-bonding end groups. Adapted with permission from ref 45. Copyright 2016 Nature Publishing Group.

III. MODELS DESCRIBING THE BEHAVIOR OF POLYMERS WITH DYNAMIC BONDS

As was mentioned above, introducing dynamic bonds in polymeric systems introduces additional time scales associated with bond dissociation time and bond rearrangement time. This makes the description of the materials with dynamic bonds more complicated than that of regular polymers. Qualitatively one can consider several regimes of bond dissociations and rearrangements in the case of dynamic bonds (Figure 5a–d). The case of bonds with low activation energy, $E_a < RT \times \ln N_x$ (N_x is the average number of polymer segments between dynamic bonds), is not interesting because these bonds dissociate on the time scale shorter than the relaxation time of the chain with N_x segments and play no significant role in viscoelastic properties. However, the intermediate activation energy, $RT \times \ln N_x < E_a < 2RT \times \ln N_x$, presents an interesting regime when the time scale of dissociation becomes longer than the chain relaxation time but shorter than the diffusion time required to find another associating functional group (sticker).[30] This leads to a coexistence of a significant amount of associated and dissociated dynamic bonds and is usually classified as "dissociative exchange" (Figure 5a). Many hydrogen bonds will fall in this category. A similar dissociative exchange appears in the case when the difference in energy between dissociated and associated states is small, $E_{diss} - E_{assoc} \sim$ several RT, and both states are populated (Figure 5a) regardless of the activation energy barrier for dissociation, E_a. Diels–Alder reaction and urethane/urea dissociations are classic examples of this type of bond exchange process.[48]

"Associative exchange" presents another type of bond rearrangement, when both the activation energy and the energy difference between dissociated and associated states are high. In this case, the exchange is completely controlled by the dissociation time, which is much longer than the characteristic diffusion time of functional groups. In this respect, the exchange can be considered as happening on contact with one of the associating groups that are in excess and always have some free nonbonded species (Figure 5b) or on contact between different pairs of dynamic bonds (Figure 5c). This kind of bond exchange is often called the hopping mechanism.[30] The contact of the dynamic bond with other associating groups might reduce the energy barrier for dissociation and in this way accelerate structural rearrangements. Catalysts can be introduced in vitrimers to reduce the activation energy, and this approach is used for many dynamic covalent bonds.[49−51] In the associative exchange regime, the number of associated bonds (or dynamic cross-linking density) remains constant. Examples of these bonds include transamination, imine exchange, transesterification, boronic ester exchange, etc.[18]

Theoretical models like sticky Rouse and sticky reptation models have been proposed to describe changes in polymer dynamics and viscoelastic properties caused by reversible interactions for unentangled and entangled polymers, respectively.[52,53] These models consider a chain with several stickers (dynamic bonds) and the average number of segments between stickers N_x. According to these models, the presence of reversible interactions slows down the relaxation for parts of the chain (subchains) longer than the average number of segments between reversible bonds (subchains with $N > N_x$), because this relaxation requires sticker dissociation. The parts of the chain between the stickers (i.e., shorter subchains with $N < N_x$) follow the classical Rouse dynamics, while the longer length scale motions (motions of the parts of the chain with stickers) are constrained by the lifetime of the dynamic cross-links, τ_{dis}. This leads to the renormalization of the Rouse times and the appearance of the rubbery plateau in a nonentangled polymer.[52] These changes in the Rouse dynamics are qualitatively shown in Figure 6.[25] Extending similar ideas to associating polymers with the molecular weight above entanglement, the sticky reptation model has been developed and applied to describe their linear viscoelastic response.[53] In

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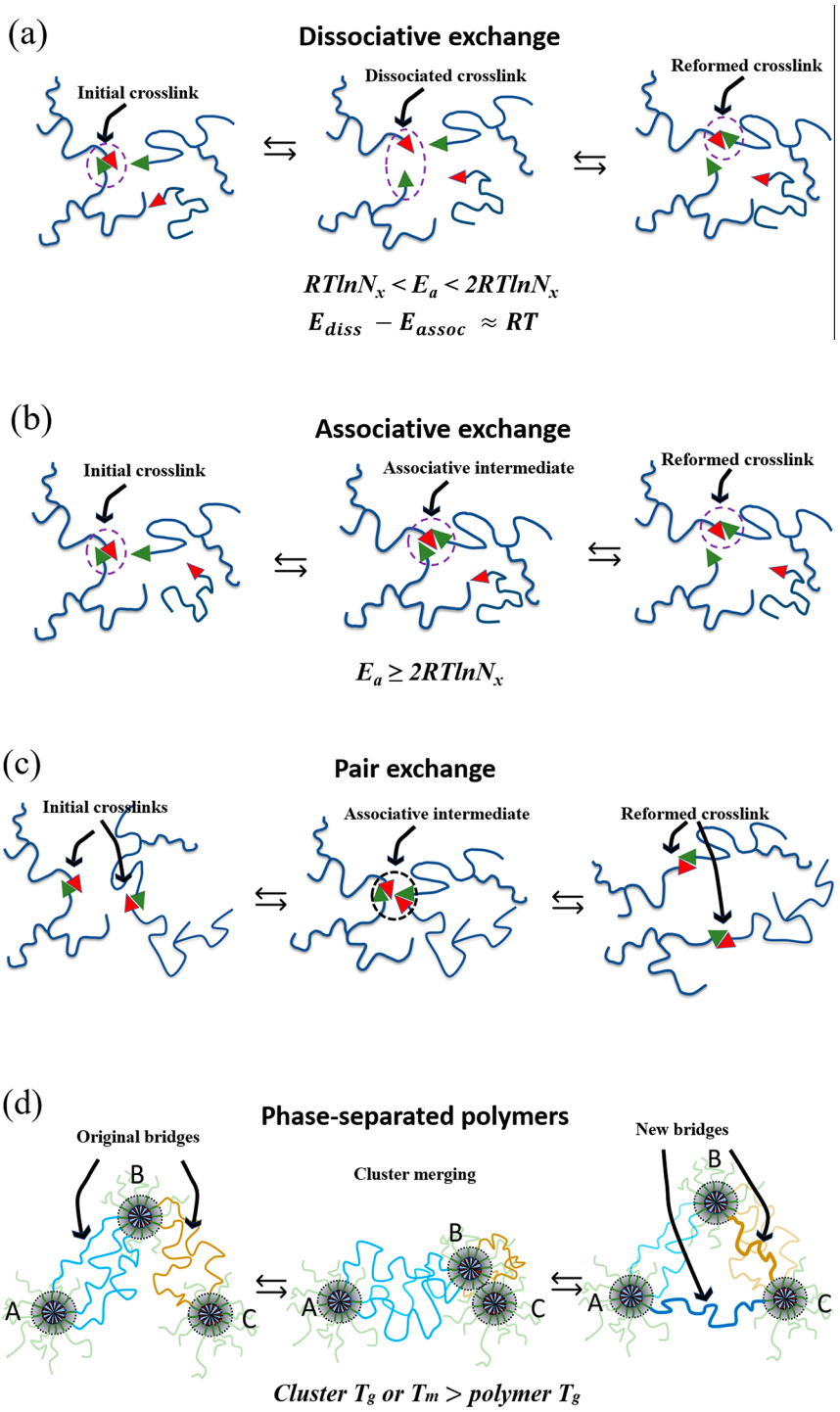

Figure 5. Different regimes of dissociations and structural rearrangements in polymers with dynamic bonds. (a) When the binding energy, $E_{bind} = E_{diss} - E_{assoc}$, is relatively low, the structural rearrangements happen by first breaking the dynamic bond and then finding a different partner (dissociative exchange mechanism). In the cases of high binding energy, the sticker exchange process happens either through (b) association of a nearby free sticker (associative exchange) or (c) on contact with a different sticker pair. (d) In the case of polymers, where stickers phase-segregate and form clusters, bond exchange takes place through cluster fusion and separation above T_g (or T_m) of these clusters.

particular, it predicts the existence of two rubbery plateaus in some conditions.[27,54]

Later it was realized that the dissociation of stickers does not lead to a stress−relaxation, because the sticker can reconnect back with the same partner. No change of structure and no stress−relaxation happen in this case. Only when the sticker can change the partner, do structural rearrangement and stress−relaxation occur. To describe this process, the concept of a renormalized bond lifetime, $\tau_R(T)$, was introduced.[30] The idea behind this concept is that a sticker can dissociate and reassociate several times with the same partner (which does not relax stress) before changing its partner. Only the latter leads to the stress−relaxation. Thus, the stress−relaxation time can be expressed as[30]

$$\tau_R \approx J(\tau_{open})\tau_{dis} + \tau_{open} \quad (3)$$

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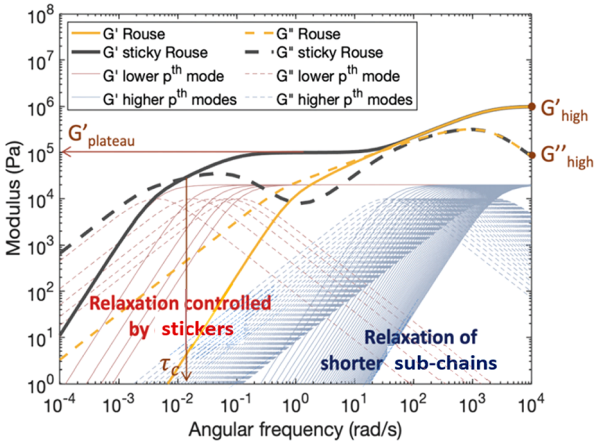

Figure 6. Changes in dynamics from regular Rouse behavior (yellow lines) to sticky Rouse dynamics (black lines) due to dynamic bonds in unentangled polymers. Adapted with permission from ref 25. Copyright 2020 Royal Society of Chemistry.

where $J(\tau_{open})$ indicates the number of returns made by the dissociated sticker to its original partner, which also depends on the average lifetime of an open sticker τ_{open}. With the increasing distances between stickers, the diffusion time to find another sticker increases, thus increasing the number of returns (higher J value) to its initial partner. Recent experiments[28,55] confirmed this model, and data analysis revealed that indeed stickers can reconnect hundreds and thousands of times before they switch the partner, resulting in the stress−relaxation time being hundreds or thousands times longer than the bond dissociation time. The latter in many cases can be measured by dielectric spectroscopy.[29] Applying the sticky Rouse model along with the concept of bond lifetime renormalization, the linear viscoelastic responses of ionomers,[56] metallopolymers,[25] H-bonded supramolecular polymers[57] has been successfully captured. Recently, this model has been also applied to vitrimers.[58]

Neutron scattering usually provides detailed microscopic information on relaxation processes. Using neutron spin echo technique to study Rouse-like dynamics of telechelic poly(ethylene glycol) with hydrogen bonding chain ends, Monkenbusch et al. demonstrated that the intermediate scattering function provides information on distribution of "effective" chain length and also on the lifetime of hydrogen bonds.[59] Their analysis suggests that the instantaneous distribution of chain length governs the macroscopic response of the system. Moreover, the analysis provided reasonable estimates of the hydrogen bond dissociating energy, and it also emphasized the importance of the entropic contribution in the studied system.[59]

Another scenario of dynamic bond rearrangement appears when dynamic bonds form segregated clusters (Figure 5d). Structural rearrangement of the macroscopic network, in this case, is controlled by the local structural relaxation of dynamic bonds in these clusters. In the temperature range below T_g of the cluster (or T_m in the case of crystalline clusters), the dynamic bonds are frozen and cannot dissociate. So, the structure is essentially permanent. However, at temperatures above the cluster's T_g (or T_m) dynamic bonds in the clusters become mobile, enabling structural rearrangements by exchanging bonding groups between different clusters (Figure 5d).

To the best of our knowledge, there is no good model describing the dynamics of systems with phase-separated clusters of dynamic bonds. A sticker within a phase-separated cluster will interact with multiple stickers. Obviously, the effective energy barrier for dissociation will be much higher than in the individual stickers and can be considered as a strong interaction case. Recent studies confirmed that structural relaxation time in clusters of dynamic bonds controls the terminal relaxation and flow of these systems, although terminal relaxation time was found to be slower by an order of magnitude than the structural relaxation time of the clusters in some cases.[46] As the amount of energy needed for a sticker to break free from the cluster is tremendously high, an energetically more favorable pathway of exchanging stickers through association and dissociation of clusters was proposed in simulations (Figure 5d).[60] However, direct experimental evidence in this regard is scarce. Thus, it remains a challenge to understand microscopic details of dynamics in systems with phase-separated dynamic bonds.

IV. IMPROVING USUAL AND ENABLING NEW PROPERTIES WITH DYNAMIC BONDS

Inserting dynamic bonds in polymeric systems resulted in many improvements of polymeric materials, and it enables many new functionalities not existing in regular polymers. This makes the polymers with dynamic bonds attractive for many traditional and future applications, and they might replace traditional polymers in many technologies. Reversible bonds allow easy recycling and reforming of polymer parts and products in a specific environment (e.g., at high T, or in specific solvents), while keeping the system or parts stable at the required working conditions.[61,62] As an example, Christensen et al. synthesized polymers based on dynamic covalent diketoenamine bond cross-links, which can be reorganized using amine groups from a different molecule. Interestingly, this network can be depolymerized in the presence of a strong aqueous acid (0.5−5 M H_2SO_4) with excellent yield (>90%) of monomers, which may pave a way for close-looped recycling of plastics.[63]

Dynamic bonds also enable intrinsic self-healing properties of the material, with the time of self-healing defined by the characteristic time of bond rearrangements. However, the same fast bond rearrangement leads to rather soft mechanical properties of the networks, and higher mechanical strength usually inhibits the self-healing kinetics. Thus, there is a trade-off between network rigidity and self-healing kinetics, and it is challenging to design mechanically robust polymers with fast self-healing time.[7,64−66] In addition, self-healing kinetics also depends on the waiting time between the sample cut and when the separated parts are brought together.[30] This effect is controlled by the number of open stickers that decreases with waiting time and by structural rearrangements that move the materials in separated parts to a new equilibrium. The self-healing process started after relatively long waiting time will be slower, requiring rearrangements of stickers and chains, and will be similar to a regular adhesion process.[30] In any case, the self-healing process in systems with dynamic bonds is a complex phenomenon that requires detailed studies and understanding.

Another interesting aspect of adding dynamic bonds in a polymer network is an increase in fracture toughness.[67,68] Rearrangements of dynamic bonds lead to significant energy dissipation.[69,70] Moreover, they help in redistributing the stress

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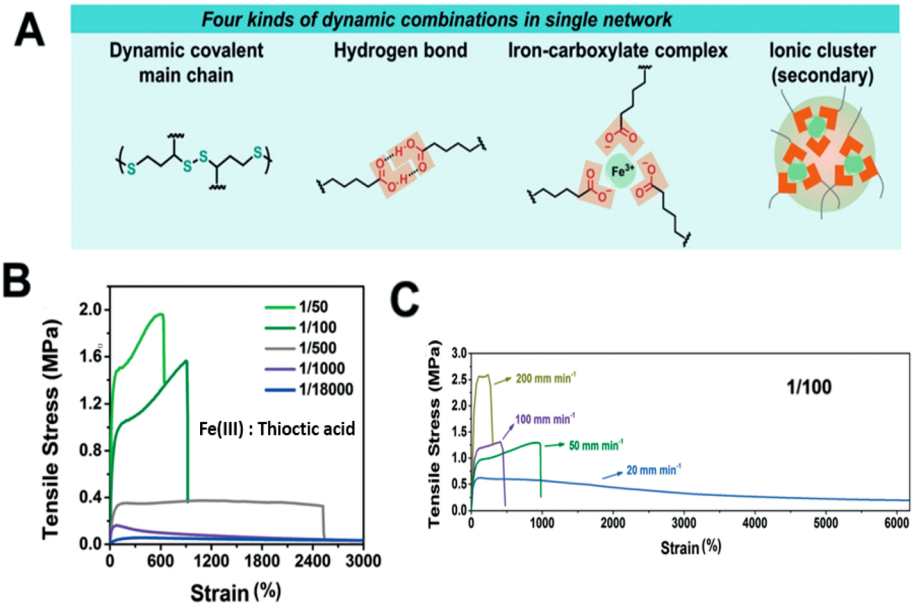

Figure 7. (A) Cartoon representation of four types of dynamic interactions introduced in the network. (B) Stress−strain curves of the copolymer with different iron(III) concentrations at a loading rate of 50 mm min^{-1}. Increasing the Fe(III) concentration promotes ionic cluster formation and significant enhancement of tensile strength and Young's modulus. (C) Rate dependent tensile curves indicate stretchability of the polymer up to 6500% of its original length. Reprinted with permission from ref 65. Copyright 2020 Wiley-VCH.

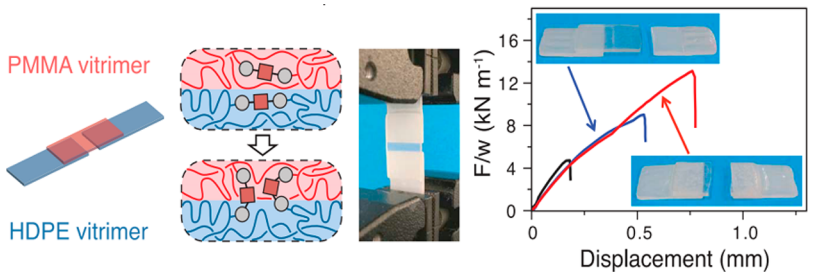

Figure 8. Enhanced adhesion of PMMA and HDPE vitrimers: (left) schematic representation, (middle) photo, and (right) force−displacement plot of lap-shear testing of double lap joints of PMMA/HDPE dioxaborolane thermoplastic precursors (black, contact time 10 min, adhesive failure) and PMMA/HDPE vitrimers for 10 min (blue, adhesive failure) and 20 min (red, bulk failure in PMMA). Reprinted with permission from ref 79. Copyright 2017 American Association for the Advancement of Science.

during deformation, and their ability to break/reform bonds keeps the system intact, providing a much larger extension before the break.[71,72] For example, utilization of dynamic H-bonds or metal-coordination bonds within a polymer network in many cases provides the material with superstretchability and toughness.[9,12,67,73] In this aspect, characteristic exchange times of the dynamic bonds play an important role. If the polymer chains are stretched much faster than the rate of the dynamic bond exchange time, they will behave as permanent bonds, and improvements in toughness will be lost. Even more interesting mechanical properties can be achieved using a combination of dynamic bonds with different E_a within a single system, e.g., using hydrogen and dynamic covalent bonds in the same polymer. Recently, Deng et al. introduced four kinds of dynamic interactions in a single network, which include dynamic covalent disulfide bonds, H-bonding, ionic interactions, and nanophase clustering of ionic complexes. The presence of these clusters imparts high mechanical strength to the network, while noncovalent H-bonds help energy dissipation and bestow superstretchability and self-healability to the network (Figure 7).[65] It is also notable that a bioinspired reversible dynamic bond such as the mussel-inspired iron−catechol coordination cross-link was utilized to simultaneously enhance the stiffness, strength, and toughness of a dry cross-linked epoxy network.[74]

Additional time for structural rearrangements introduced by dynamic bonds also enables properties of the material to be time-dependent (programmable). This might happen on the time scale faster than the longest time of dynamic bond rearrangements, providing shape-memory materials, and materials with mechanical properties reversibly changing on the time scale of bond rearrangements. Yan et al. has developed a shape-memory polymer with enhanced mechanical property utilizing the bond rearrangement of dynamic disulfide bonds.[75] The disulfide bonds enable a shape-memory effect via temperature control for permanent deformation by dynamic bond exchange above the topology freezing temperature ($T > T_v$), and temporary deformation−recovery by softening ($T_g < T < T_v$)−freezing ($T < T_g$) cycles. The metal-coordination is another supramolecular dynamic bond mechanism that is utilized for inducing the self-healing, recyclability, and shape-memory properties.[67,76−78] For example, a shape-memory polymer was prepared from biomass material cellulose, grafted with imidazole moieties coordinating

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divalent Cu ions.[77] The dynamic Cu−imidazole bonds provided the polymer network with controllable mechanical properties by simply tuning the fraction of Cu^{2+}. In addition, the metal−ligand clusters tended to phase separate from the soft copolymer to serve as reinforcing components.

The incorporation of dynamic covalent bonds can be utilized in developing reprocessable cross-linked adhesives.[17,79,80] For example, Röttger et al. showcased a strong adhesion between incompatible polymer layers of PMMA and PE via dioxaborolane transesterification metathesis reaction (Figure 8).[79] The PMMA and PE, which are incompatible with each other without modification, showed an adhesion strength of 400 N/m by using a grafted copolymer compatibilizer.[81] Remarkably, the adhesion strength could be enhanced to over 4000 and up to ∼12000 N/m in the dioxaborolane-modified PMMA and PE vitrimers. These results demonstrate that the dynamic exchange reactions to form covalent bridges between the two vitrimers led to strong interfacial bonding, significantly enhancing the adhesion strength. Rowan and co-workers developed strong, rebondable cellulose nanocrystal composite adhesive films utilizing dynamic disulfide bonds.[80] Torkelson and co-workers have also exploited dynamic disulfide bonds to develop adaptive thermoset adhesives that can be reshaped, resulting in improved wettability to the surface, in contrast to the traditional thermoset adhesives that cannot be reshaped after curing.[17]

The transient, reversible nature of dynamic bonds is actively applied in developing recyclable thermosets and composite structural materials.[82−87] Use of vitrimers as the polymer matrix in composite materials takes advantage of the reversibility of the dynamic covalent bonds that enables the reprocessability and change of shape, while their chemically cross-linked thermoset aspect is offering thermal, mechanical, and chemical stability to the material. This has provided an attractive platform to hybridize with carbon or glass fibers to further reinforce the mechanical properties of the material with simpler and milder processing conditions.[82−84] Finally, we note that the dynamic bonds have been applied in extrusion-based additive manufacturing (e.g., fused deposition modeling, direct ink writing) to enhance shape fidelity, printability, and thermomechanical properties of the printed materials.[88−90] In particular, the capability of supramolecular polymers to produce well-defined parts, hierarchical structures, and scaffolds with tunable surface and gradient properties are expected to serve as promising materials for biomedical, tissue-engineering applications.[91,92]

V. CONCLUSIONS

Modern polymer chemistry provides various ways to introduce dynamic (reversible) bonds in polymeric materials. Moreover, the number of discovered dynamic covalent bonds increases every year, and this enables novel chemistries and applications of the dynamic bonds. The introduction of dynamic bonds in polymers offers new dimensions to manipulate their viscoelastic properties and relaxation behavior. They strongly improve toughness and adhesive properties by enabling structural rearrangements and strong energy dissipation. They also enable unique properties, such as self-healing, shape-memory, and time-programmable properties, and they strongly improve the recyclability of the polymeric materials. Although numerous application-based research is being carried out using the materials with dynamic bonds, a deep fundamental molecular-level understanding of the underlying phenomena is still lacking. The interplay of thermodynamics, multiple dynamic components, and morphology of the systems with dynamic bonds remains to be disentangled. This basic understanding will provide more flexibility in designing new functional materials by employing dynamic bonds. Beyond the simple binary interactions among the stickers, a novel engineering approach to design the complex hierarchical structures in phase-separated supramolecular networks will pave new avenues to control the properties of materials (from mechanical strength and viscosity to self-healing and adhesion) and to design advanced materials with unprecedented properties. Moreover, improved recyclability will provide better sustainability for polymer-based materials. We expect that polymers with dynamic bonds will replace traditional polymers in most of the current and future applications, and they probably will find many new applications that we cannot envision now.

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Notes

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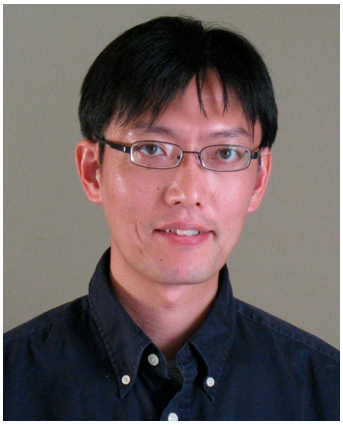

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