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Covalent Adaptable Networks Based on Dynamic Alkoxyamine Bonds

*Yixuan Jia, Guillaume Delaittre, and Manuel Tsotsalas**

Covalent adaptable networks (CANs) introduce a new paradigm to polymer science, by making static network polymers dynamic and thereby recyclable, reprocessable, and self-healing. The critical feature in CANs is the presence of dynamic covalent linkages within the network structure. A variety of such linkages are introduced into CANs, making the respective networks responsive to various stimuli, such as light, temperature, or pH. Here, CANs based on alkoxyamines as dynamic covalent bonds are reviewed. Alkoxyamines uniquely combine the ability to dynamically form, break, and reform covalent bonds with the possibility to initiate reversible-deactivation radical polymerization. Polymer networks based on alkoxyamines are therefore both adaptive and quasi-living, able to remodel the network structure by nitroxide-exchange reactions (NER) and extend the network structure by nitroxide-mediated polymerization (NMP). In this review, the concepts behind CANs are first introduced and the properties of nitroxides and derived alkoxyamines are discussed. A special focus is set on the ability to tune the response of alkoxyamines to different stimuli, through alteration of their structure. In addition, possible side reactions during dynamic bond exchange and limitations for polymerization are critically reviewed. Subsequently, examples of alkoxyamine-based CANs responsive to different stimuli, such as temperature, light, or chemical triggers, are discussed. Properties and applications of CANs based on alkoxyamines are then discussed. Finally, an outlook is provided on challenges that need to be addressed as well as opportunities that lie within these "living" CANs.

1. Introduction

Traditionally, polymeric materials were expected to be inert. This led to optimized polymer compositions and the development of additives and stabilizers to avoid or minimize reactivity. The growing interest in smart or dynamic materials, able to self-heal, adapt to changes in their environment, or to change on demand upon specific triggers led to new design concepts in the design of polymer materials. Classical polymeric materials can be categorized into thermoplastics and thermosets, corresponding to their properties and in relation to their macromolecular structure. Below their glass transition temperature (T_g), polymers are hard solids. When heated above the T_g, thermoplastic polymers become viscoelastic liquids. This property is the result of the absence of crosslinks in the macromolecular structure of thermoplastics, which facilitates melting, reshaping, and recycling. As a result, thermoplastics became the most popular material for rapid production of consumer goods.[1] In contrast, thermoset polymers, when heated above their T_g, behave like elastomers[2] and can easily maintain their shape. Even under harsh conditions, thermoset polymers do not melt or dissolve due to their covalently crosslinked macromolecule structure. The density of crosslinks in thermoset polymers determines their mechanical properties, which can be tuned over a wide range.[3–5] Because of their stable structures, thermoset polymers are widely utilized for additive manufacturing, optical, and biomedical applications, or in coatings, adhesives, tires, and others.[4] Despite its benefits, the irreversible covalent nature of the crosslinking bonds in classical thermosets obstruct the possibility of reassembling and altering their structure. Therefore, the recycling of such materials is strongly hindered.[5] In order to provide such features to thermoset polymers, while keeping their favorable properties, Bowman and coworkers introduced the concept of covalent adaptable networks (CANs) in 2010.[6] CANs consist of stimuli-responsive and dynamic covalent crosslinks throughout the network. Depending on the type of dynamic covalent chemistry (DCC) at play,[7] CANs can be activated by stimuli such as light, temperature, or chemical triggers, which allows the material to adapt to its environment.[8] Hence, CANs bridge the attractive features of thermoplastics with the advantages of thermosets.[4] Apart from

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the implementation of DCC as in CANs, other strategies were also developed to dynamically modify the properties of polymer networks and introduce living and dynamic properties. An interesting example is the concept of structurally tailored and engineered macromolecular (STEM) polymers, introduced by Matyjaszewski and co-workers.[9] In STEMs, latent initiator sites are incorporated as side groups in the polymer networks, available for postsynthetic modification. Another such innovative example is the concept of living additive manufacturing, introduced by Johnson and co-workers, where the latent initiator sites are directly incorporated in the network backbone, enabling network, and mesh-size extension.[3,9–11]

1.1. CANs

CANs are usually assembled from discrete molecular building blocks, which can reversibly assemble and disassemble, in analogy to supramolecular polymers.[12,13] However, unlike the noncovalent interactions at play in the latter case, the reversible covalent bonds in CANs maintain a stable, insoluble structure in the absence of external stimuli, similar to conventional covalent polymer networks.[14] Applying external stimuli to CANs initiates dynamic processes that allow the exchange of the molecular components, enabling CANs to enter a new thermodynamic equilibrium or even to be driven out of equilibrium.[15,16] The covalent nature of the bonds enables CANs to acquire outstanding chemical stability and mechanical strength, while the dynamic attribute of the bonds provides diverse opportunities such as self-healing, recycling, and numerous possibilities of post-modification. According to the process of bond exchange in the employed DCC,[7] CANs can be divided into two subclasses.[17,18] The first subclass is based on associative DCCs, in which the crosslink density remains unchanged because the covalent bond at the crosslinking point is only cleaved when another covalent bond is formed. This subclass of CANs is known as vitrimers, introduced by Leibler and co-workers in 2011.[19] The second subclass of CANs is based on dissociative DCCs, where covalent bonds are first cleaved into individual reactive parts and then reformed.[6] The most prominent reversible covalent bonds employed in CANs are boronic esters, trithiocarbonates, imines, hydrazones, siloxanes, Diels–Alder (DA) adducts, and disulfides.[20–23] Here we focus on dissociative CANs with dynamic alkoxyamine bonds. For an in-depth description of other types of CANs, we refer to some excellent reviews.[8,20,22,24]

1.2. Alkoxyamines

Alkoxyamines can be reversibly cleaved into a persistent nitroxide radical and a transient carbon-centered radical. These two radical species can either recombine with one another, exchange with other nitroxide radicals (known as nitroxide-exchange reaction, NER), or initiate a controlled polymerization (known as nitroxide-mediated polymerization, NMP) by monomer addition (see **Figure 1**). The stability or reactivity of alkoxyamines can be tuned through the molecular structure design, particularly of the nitroxide.[25–30] **Scheme 1** depicts some important nitroxides for NMP.

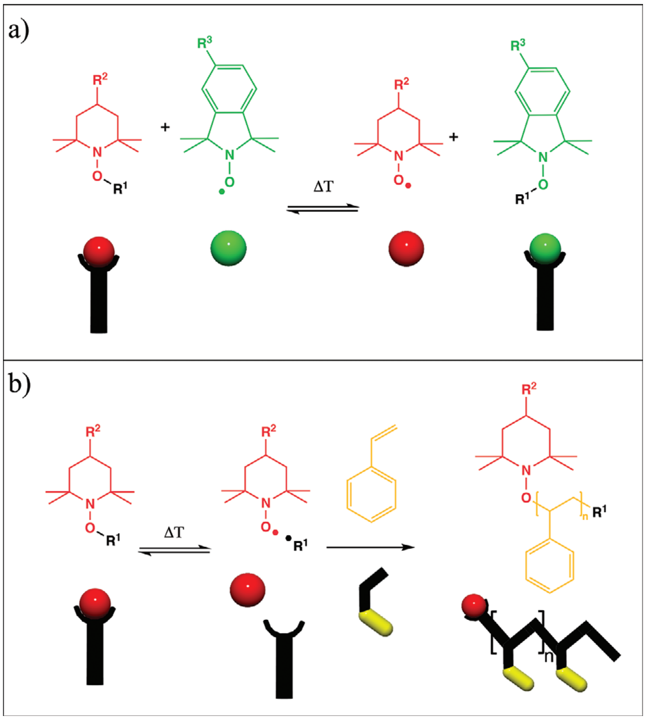
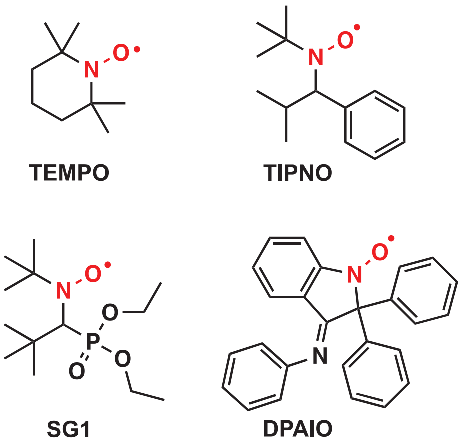


Figure 1. a) Nitroxide-exchange reaction: thermal homolysis of an alkoxyamine leads to a nitroxide and a carbon centered radical. In presence of an additional nitroxide, dynamic exchange will occur between the two nitroxide species. b) Nitroxide-mediated polymerization: the alkoxyamine initiates a controlled polymerization after thermal bond homolysis, in presence of monomer (e.g., styrene).



Scheme 1. Structure of the most common nitroxides employed in NMP.

1.2.1. Stability and Possible Side Reactions of Alkoxyamines

ON covalent bond, that is essential for NMP and NER.[14,34,35] Thus, the effects governing reversible homolysis of alkoxyamines are crucial and widely investigated.[33,36–38] Understanding the reactivity of C–ON bond is essential to design alkoxyamines for applications in various fields such as controlled polymerization, the development of novel crosslinkers for networks, or the design of smart materials such as CANs.

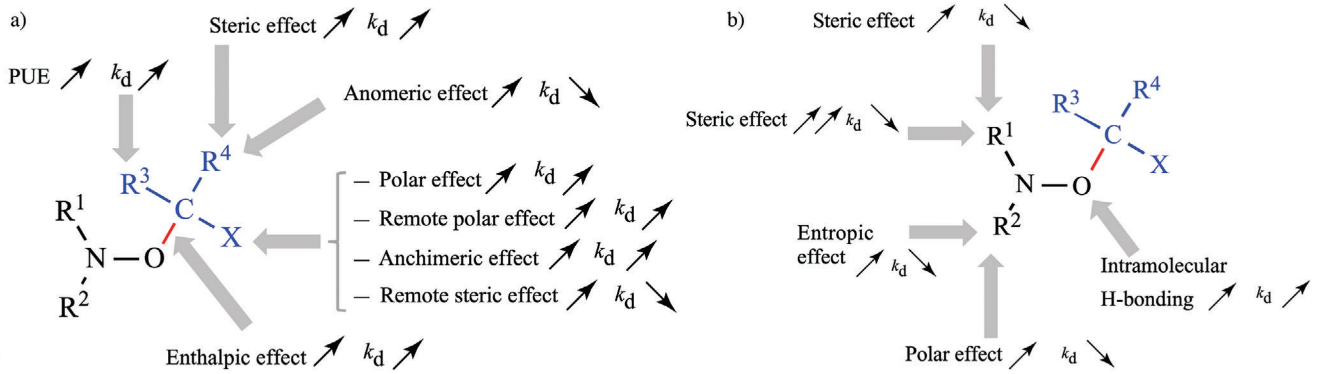


Figure 2. Various effects of the alkyl a) and nitroxyl b) fragments on the C–ON bond homolysis of alkoxyamines. Reproduced with permission.[39] Copyright 2011, Royal Society of Chemistry.

The homolysis of alkoxyamines is mainly triggered by temperature. The main structural effects on the homolysis of the alkoxyamine bond are displayed in **Figure 2**,[39] k_d is the rate constant for the homolysis of the alkoxyamine bond into nitroxide and alkyl radicals.

An increased k_d value represents a faster cleavage of an alkoxyamine bond. In parallel, a slower reformation may originate from a decreased recombination rate constant k_c. There is no simple relation between k_d and k_c (such as "a high k_d would imply a low k_c"), because their variations with the structure of the nitroxide and alkyl radicals can be largely different.[40–42] The involved structural effects in the C–ON bond homolysis are either additive or synergistic, and the main effects are the polarity (electron withdrawing groups) of both radical species, the enthalpic effect (stabilization) of the alkyl radical, the steric effect around the alkyl radical center, the polarity of the solvent, and the intramolecular proton binding. For alkyl fragments (R_3R_4XC–), an increase in these effects leads to higher k_d values, implying a weakening of the C–ON bond and hence preferential homolysis. The nitroxyl moiety ($R_1R_2NO\bullet$), on the other hand, is affected by the polar aspects in the opposite way. Furthermore, the bulkiness around the nitrogen atom, which is described as a leveled steric effect,[43] does not always weaken the C–ON bond further. Additionally, more limited effects can affect the rate constant of alkoxyamine bond homolysis, such as the influence of substituents across several bonds, intramolecular hydrogen bonding (IHB), or anomeric and anchimeric effects.[29,39] As documented for NMP, aside from the desired C–ON bond homolysis, CO–N bond dissociation can appear as a side reaction during alkoxyamine homolysis. CO–N bond dissociation is commonly observed when the bond dissociation energy (BDE) of C–ON is larger than 140 kJ mol^{-1}.[33,44,45] This unwanted CO–N bond dissociation generates an aminyl radical and a highly reactive alkoxyl radical, which will compromise the NMP reaction and obviously any recombination in the context of NER and CANs. The group of Coote investigated the competition between these two types of bond scissions in various alkoxyamines, computationally as well as experimentally.[46] They found that the C–ON free energies bond is mostly related to the structure of the alkyl fragment, whereas the free energy of the CO–N bond largely depends on the properties of aminyl fragment. For instance, in the piperidine-, pyrrolidine-, and isoindoline-derived cyclic alkoxyamines, CO–N bond homolysis only predominates when a heteroatom in alpha position to the alkoxyamine carbon center stabilizes the C–ON bond or when the released alkyl radical is not adequately stabilized. Acyclic and indoline-based alkoxyamines possess lower free energies of CO–N bond homolysis than other cyclic alkoxyamines because of a higher stabilization of the aminyl radical species. Aside from the CO–N homolysis, there are various side reactions in alkoxyamines such as bimolecular self-termination, disproportionation, H-transfer or cross termination, and chain transfer (**Figure 3**).[39,47–49] To limit or even eliminate these side reactions, selecting suitable alkoxyamines and optimizing the experimental conditions are essential.[50] These side reactions are detrimental to the control of the polymerization features in NMP and typically result in increased dispersity and loss of "livingness" (that is, inability to restart a polymerization or ultimately carry out chain-end transformations such as NER).[51] For instance, the back H-transfer from hydroxylamines, themselves formed through a propagating radical-annihilating side reaction, can lead to another dead polymer chain (side-reaction (5) in Figure 3).[52,53]

A more detailed investigation on side reactions of NMP was discussed by Gryn'ova et al. in 2013.[47] They performed kinetic modeling for diverse scenarios utilizing five NMP systems: three successful polymerization systems (TEMPO–styrene, SG1–butyl acrylate, and DPAIO–methyl methacrylate (MMA)) and two failing systems (TEMPO–MMA and SG1–MMA) (**Figure 4**).[47] They found that intramolecular alkoxyamine decomposition via a Cope-type elimination (side reaction (3b) in Figure 4) was an issue for both failing systems, while for the SG1 system, the failure of polymerization originates from an unfavorable equilibrium constant of alkoxyamine bond homolysis. This issue was originally reported in a paper from Guillaneuf et al. in 2006,[30] in which the NMP of MMA using an SG1-based alkoxyamine could be performed at 45 °C, thanks to the low decomposition temperature of this alkoxyamine. At this temperature, partial control and livingness of MMA polymerization should be attainable. A penultimate effect, however, accelerated the dissociation rate constant while decreasing the recombination rate constant. The resulting large equilibrium constant led to uncontrolled polymerization. Sulzer and Bihlmeier computationally investigated the substituent and solvent effects on the Gibbs free energy of the nitroxide-exchange reaction.[54] They quantified the substitution

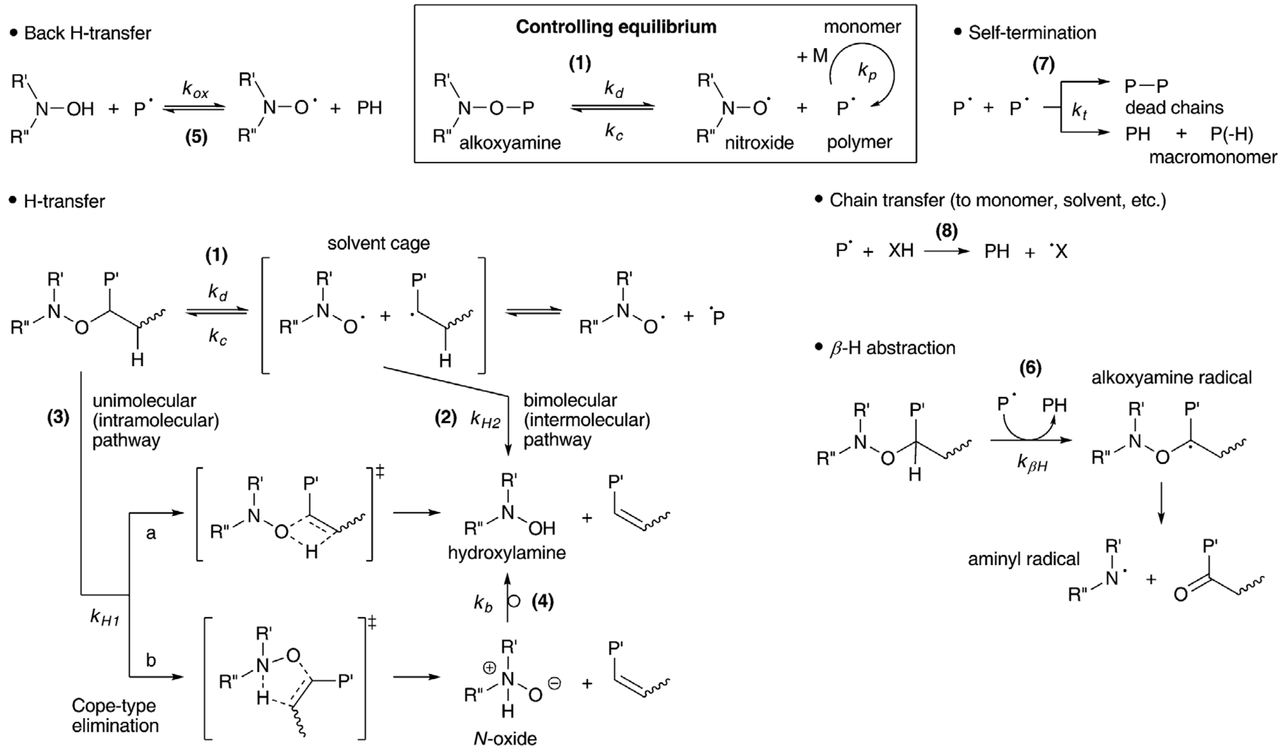


Figure 3. Nitroxide-mediated polymerization and its competing side reactions; k_c and k_d are rate constants of combination and decomposition, k_p – propagation, k_t – termination, k_{H1} and k_{H2} – uni- and bimolecular H-transfer, k_b – rearrangement of N-oxide into hydroxylamine, k_{ox} – oxidation of hydroxylamine into nitroxide $k_{\beta H}$ – β-H-abstraction from alkoxyamine. Reproduced with permission.[47] Copyright 2013, Royal Society of Chemistry.

effect in a series of structurally modified TEMPO radicals on the exchange reaction with an isoindoline-derived nitroxide. These results should be considered to improve product formation in CANs synthesized via the nitroxide-exchange reaction.

1.2.2. Alkoxyamines in Materials Science

The most prominent usage of alkoxyamine bonds in materials science is the NMP reaction. For a long time styrenics were the only monomers which could be polymerized in a controlled manner in NMP. In the early 2000s, nitroxides were specifically developed for NMP of acrylates (and styrenes) such as 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy (TIPNO) and *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1). However, only a copolymerization approach involving a small fraction of comonomer (e.g., styrenics, acrylonitrile) allowed SG1 to control the NMP of methacrylates.[56–59]

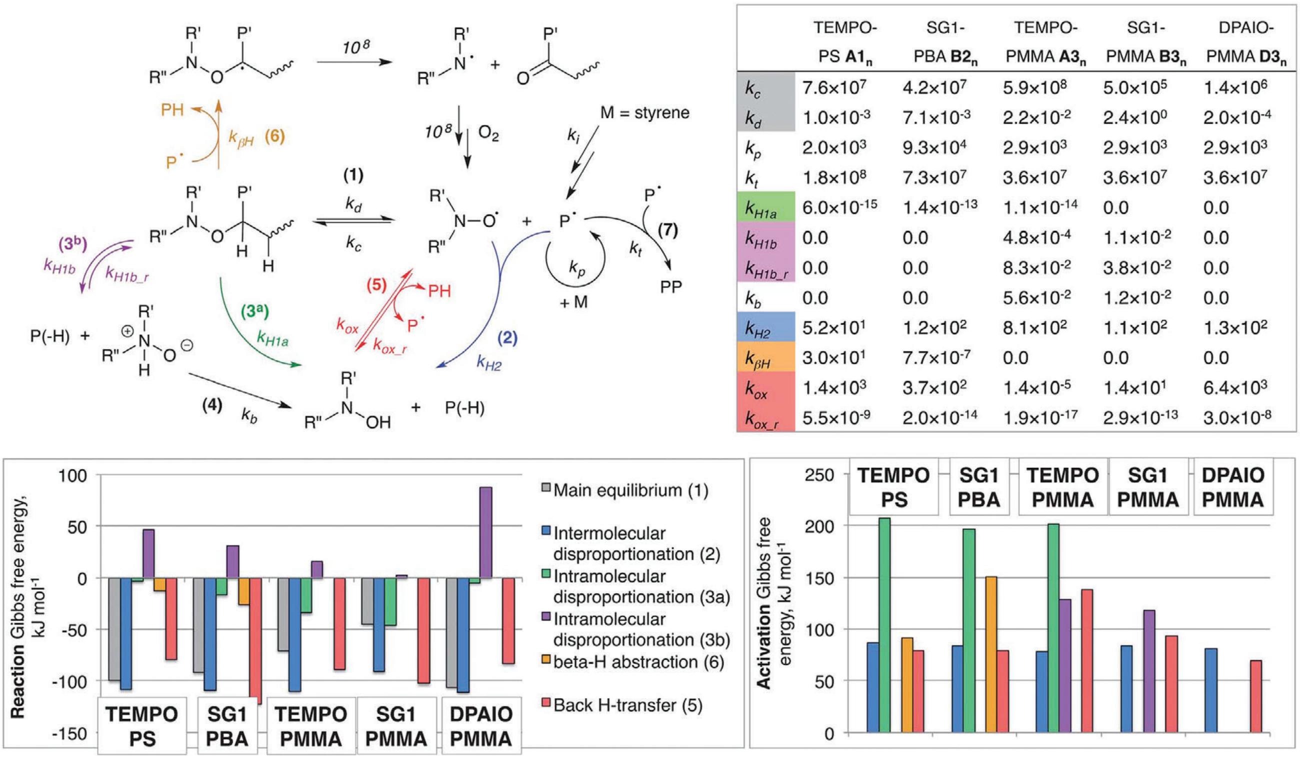
While a few nitroxides were designed to gain control over the pure homopolymerization of methyl methacrylate,[60] they were usually inadequate for other monomers. For instance, Guillaneuf showed that DPAIO (Scheme 1) was efficient for methacrylate polymerization, yet not for other monomers.[61] Derivatives of DPAIO were later developed to additionally impart control over styrene polymerizations.[62] Very recently, Asua, van Es, Leiza, and co-workers reported a series of new nitroxides and corresponding alkoxyamines (particularly the so-called Dispolreg 007) allowing the controlled polymerization of both methacrylates and styrenics.[63–65]

Other than NMP, the reversible nature of the alkoxyamine bond was also exploited for NER. Employing alkoxyamines in the design of macromolecular systems, by combining NMP with NER, was pioneered by Otsuka and co-workers,[14,66] who introduced the usage of alkoxyamines to the design of dynamic polymeric materials. Details on the NMP and NER reactions will not be treated further here. For a comprehensive discussion we refer the reader to several excellent reviews.[29,34,48,67–69]

2. CANs Based on Dynamic Alkoxyamine Bonds

The first example of polymer networks incorporating dynamic alkoxyamine to harness NMP and NER was from Otsuka, Takahara, and co-workers.[14,66] These networks were synthesized by free-radical copolymerization of styrene and a bifunctional monomer with an alkoxyamine bridge. Taking advantage of the dynamic alkoxyamine bond, the networks could be decrosslinked in the presence of an excess amount of alkoxyamine derivatives. The insertion of additional styrene units at crosslinking points, via nitroxide-mediated polymerization, led to network extension, i.e., an increase in mesh size (**Figure 5**a).[66]

In 2016, Torkelson and co-workers introduced a straightforward one-step strategy to synthesize recyclable crosslinked polymer networks through alkoxyamine dynamic bonds.[70] They used a TEMPO-functionalized methacrylate acting as both a monomer and reversible radical scavenger. As a result, the final crosslinked polymer network contains TEMPO-based alkoxyamine units, which can be reversibly exchanged (Figure 5b). Moreover, thanks to the reversible crosslinking of nitrox-



	TEMPO-PS **A1**$_n$	SG1-PBA **B2**$_n$	TEMPO-PMMA **A3**$_n$	SG1-PMMA **B3**$_n$	DPAIO-PMMA **D3**$_n$
k_c	7.6×10^{7}	4.2×10^{7}	5.9×10^{8}	5.0×10^{5}	1.4×10^{6}
k_d	1.0×10^{-3}	7.1×10^{-3}	2.2×10^{-2}	2.4×10^{0}	2.0×10^{-4}
k_p	2.0×10^{3}	9.3×10^{4}	2.9×10^{3}	2.9×10^{3}	2.9×10^{3}
k_t	1.8×10^{8}	7.3×10^{7}	3.6×10^{7}	3.6×10^{7}	3.6×10^{7}
k_{H1a}	6.0×10^{-15}	1.4×10^{-13}	1.1×10^{-14}	0.0	0.0
k_{H1b}	0.0	0.0	4.8×10^{-4}	1.1×10^{-2}	0.0
k_{H1b_r}	0.0	0.0	8.3×10^{-2}	3.8×10^{-2}	0.0
k_b	0.0	0.0	5.6×10^{-2}	1.2×10^{-2}	0.0
k_{H2}	5.2×10^{1}	1.2×10^{2}	8.1×10^{2}	1.1×10^{2}	1.3×10^{2}
$k_{\beta H}$	3.0×10^{1}	7.7×10^{-7}	0.0	0.0	0.0
k_{ox}	1.4×10^{3}	3.7×10^{2}	1.4×10^{-5}	1.4×10^{1}	6.4×10^{3}
k_{ox_r}	5.5×10^{-9}	2.0×10^{-14}	1.9×10^{-17}	2.9×10^{-13}	3.0×10^{-8}

Figure 4. Scheme of model NMP and table of experimental (k_c, k_d, k_p, and k_t) and calculated (all other side reactions) rate constants, used in PREDICI kinetic modeling,[55] as well as column diagrams of calculated Gibbs free energies of reaction and activation for main equilibrium and interfering side-reactions (1)–(6) in NMP of five investigated polymerization systems. All data correspond to bulk monomer solution at 120 °C, all energies are in kJ mol^{-1}, all rate constants are in s^{-1} (unimolecular reactions) and L mol^{-1} s^{-1}(bimolecular reactions). Reproduced with permission.[47] Copyright 2013, Royal Society of Chemistry.

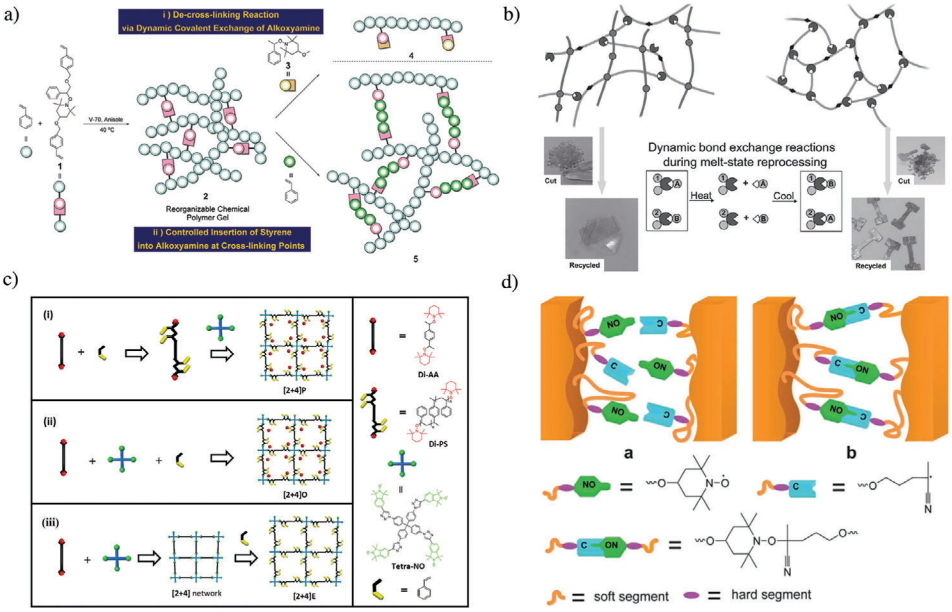


Figure 5. a) A model of the decrosslinking reaction via a radical crossover reaction of alkoxyamine units and insertion of styrene into the alkoxyamine units at crosslinking points. Reproduced with permission.[66] Copyright 2009, American Chemical Society. b) Network reprocessing through rearrangements of dynamic alkoxyamine covalent bonds. Reproduced with permission.[70] Copyright 2016, Wiley-VCH GmbH. c) Different approaches for the synthesis of CANs with alkoxyamine labile bonds: i) regular nitroxide-mediated polymerization of styrene using a dialkoxyamine with the subsequent addition of a multitopic nitroxide, ii) styrene NMP and network formation using a one-pot approach, and iii) network formation followed by network expansion via the in situ NMP of styrene.[10] d) Illustration of the dissociation/association of CTPO-based polyurethane-polyethylene glycol CANs. Reproduced with permission.[25] Copyright 2013, Royal Society of Chemistry.

ide groups, their dynamic polymer networks preserve the elastomeric response and dynamic mechanical properties after multiple melt-reprocessing cycles.

We extended this concept in the development of network structures based on discrete molecular building blocks with tunable crosslinking degrees and mechanical properties ranging from soft and gel-like to rigid and highly porous.[71–73] In such nitroxide exchange networks, the dynamic nature of the NER allows the modulation of properties by shifting the equilibrium state of the reaction and imparts self-healing characteristics and recyclability (sol–gel–sol phase) to the networks.[71] Besides, the connecting alkoxyamine moieties within the networks not only serve as a dynamic bond, providing recyclability, but can also be utilized as NMP initiators, in analogy to the work of Otsuka, Takahara, and co-workers, enabling network expansion with precisely controlled molecular weight. Combining NER with network expansion via NMP (Figure 5c),[10] we demonstrated a versatile approach for the preparation of dynamic polymer networks with controlled microstructure (i.e., mesh size), adjustable at any time (i.e., before, during, or after network formation) by incorporation of additional monomer units and reactivation of the polymerization reaction.

2.1. Stimuli-Responsiveness of CANs with Alkoxyamine Labile Bonds

In alkoxyamine-based CANs, activation of the dynamic bond exchange is typically achieved by an increase in temperature. Depending on the type of alkoxyamine, the dynamic exchange can alternatively be stimulated by photoirradiation, by the introduction of chemical triggers, or using plasmons. During the activation, the dissociation or exchange of the alkoxyamine bonds can change the flexibility of polymer chains and tune the crosslink density of the networks. The formation of new bonds leads to desired material states such as altered mechanical properties, stress relaxation, restoration of a cracked unit, modified pore/mesh size, etc. After removing the stimulus or trigger, the altered network material returns to an inert state. However, due to the dynamic nature of the alkoxyamine bonds, the network can be repeatedly modified upon stimulation. Moreover, one given network can also be stimulated by multiple triggers independently. In the following, some insights into these stimuli in the context of CANs is provided, as a potential base for material design optimization in view of specific applications.

2.1.1. Thermal Stimulus

Temperature is the most common stimulus to activate CANs with dynamic alkoxyamine bonds. In general, the homolysis temperature of alkoxyamine bonds is in the range of 60–120 °C.[74]

An early example of thermally controlled self-healing polymers with integrated alkoxyamine bonds was introduced by the group of Yuan and co-workers.[26] They employed a dimethacrylic ester alkoxyamine as crosslinker in the polymerization of styrene. When exposed to temperatures ranging from 125 to 200 °C, their polystyrene networks could repeatedly self-heal cracks due to the unique properties of alkoxyamine linkages. Meanwhile, the network maintained its high mechanical and thermal stability. In an attempt to lower the bond fission temperature, which would be attractive for self-healing properties at room temperature, the same group altered the molecular structure of the alkoxyamines.[25,75] They particularly introduced 5-hydroxy-2-(4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy)-2-methyl pentanenitrile (CTPO),[25] an alkoxyamine, which once incorporated in a polyurethane, provided self-healing features at ambient temperature. A similar concept of thermally reversible alkoxyamines as crosslinks in polymer materials was also utilized in polyurethane copolymers[76] and epoxy-based polymer materials.[77] Furthermore, alkoxyamine bonds are typically sensitive to air, as oxygen acts as a scavenger for transient carbon radicals. Zhang and co-workers conducted thiol-ene chemistry to synthesize crosslinked polymethacrylates with an embedded alkoxyamine moiety.[78] Because of the electron-withdrawing group around the alkyl radical center, the integrated reversible alkoxyamine bonds in these polymer networks allow the homolysis of C–ON bonds to occur in air and within a moderate temperature range of 20–80 °C. Besides, it is also important that over multiple cycles of thermal actuation, e.g., breaking and reforming the networks, the materials maintain their mechanical properties. For example, the previously mentioned polymer networks from the Torkelson group,[70] presented a crosslinked PB/S (polybutadiene/styrene) network containing thermally reversible alkoxyamine bonds. The PB/S network was cut into small pieces and remerged at 140 °C under pressure (**Figure 6**a).

Moreover, by altering the composition at the synthesis stage by stoichiometric variation, the characteristics of the network, e.g., crosslink density and T_g, can easily be tuned without considerably affecting the reprocessability of the networks. Apart from using alkoxyamine-based as crosslinkers, specifically designed multifold alkoxyamines and nitroxides can be utilized directly to generate the dynamic crosslinked polymer networks.[71] The resulting polymer networks possess a defined structure that can self-heal and easily be recycled through controlling of reaction equilibrium. Additionally, the networks also have a thermally tunable crosslinking degree that can be modulated by varying the concentration of mono-nitroxide units (Figure 6b). We developed a more precisely thermally controlled CAN, utilizing the alkoxyamine functional groups not only as a dynamic bond providing recyclability but also to act as an NMP initiator enabling network expansion.[10] The thermal actuation can stimulate both types of reactions either synchronously or step-wise, depending on the combination sequences of these two reactions.

2.1.2. Photochemical Stimulus

Although photoresponsive alkoxyamines are not as common as thermally activatable ones in CANs, harnessing light is still very promising for building and manipulating dynamic networks. Initial research on the photocleavage of the C–ON bond was performed by Scaiano et al. in 1997.[79] A decade later, Guillaneuf et al. and Yoshida et al. introduced NMP based on photoactivatable alkoxyamines (**Figure 7**a).[80,81]

They used TEMPO-based alkoxyamines to initiate the photopolymerization of *n*-butyl acrylate, resulting in polymers of low dispersity. The photosensitive alkoxyamine contains a

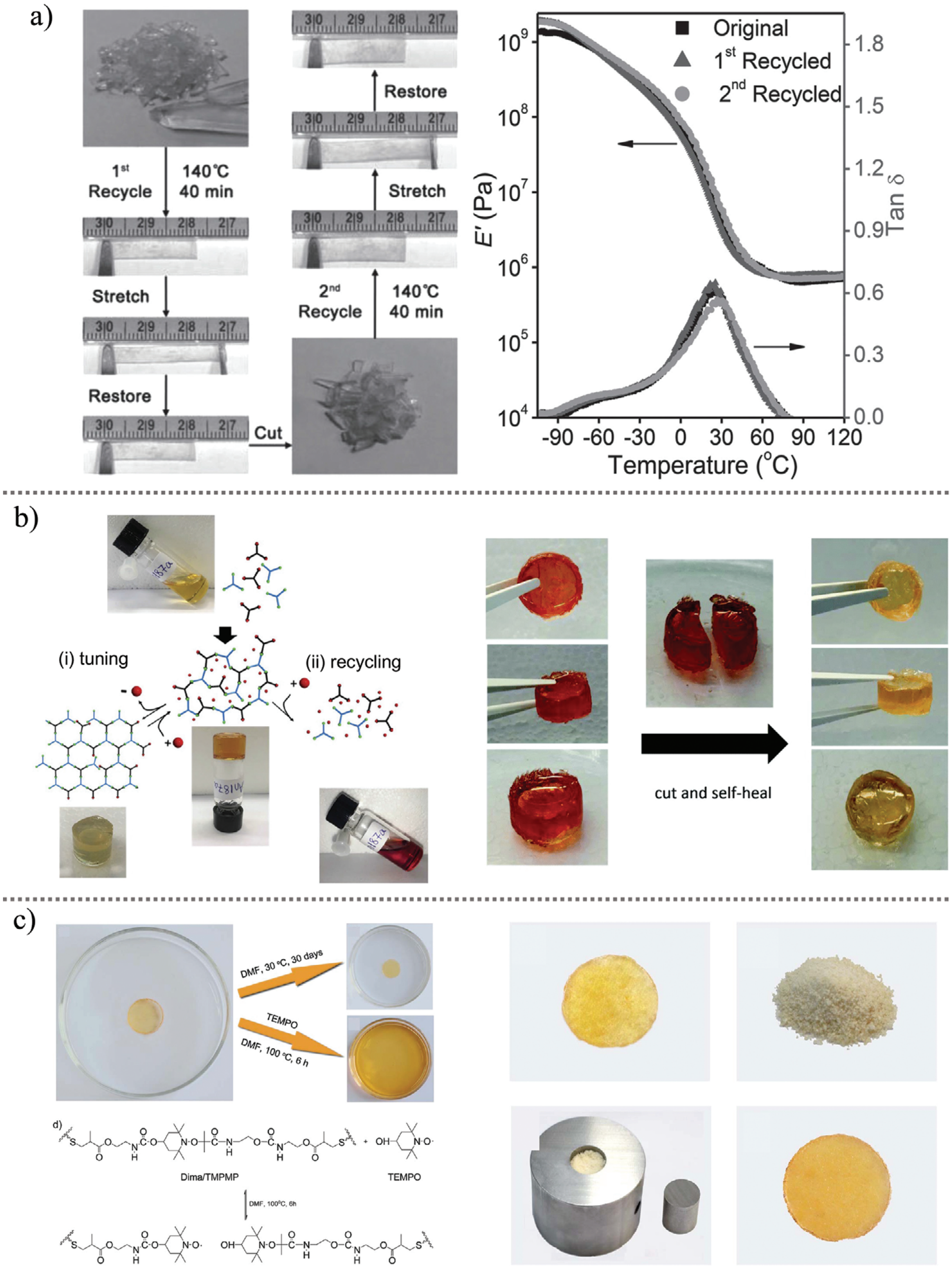


Figure 6. a) Demonstration of elastomeric characteristics of 43/57 wt% PB/S networks containing TEMPO-based alkoxyamine crosslinks (left) and their dynamic mechanical responses of CANs shown (right), *E′* (solid symbols) and tan *δ* (open symbols) as functions of temperature for original (squares), once recycled (triangles), and twice recycled (circles) samples. (One recycling process corresponds to reprocessing at 140 °C for 40 min). Reproduced with permission.[70] Copyright 2016, Wiley-VCH GmbH. b) Equilibrium control of the nitroxide-exchange reaction when using multitopic alkoxyamines and nitroxides (left), where the crosslinking degree of the polymer network is tuned by adding or removing TEMPO radicals i) or its complete decrosslinking is induced by adding an excess amount of TEMPO radicals ii). On the right-hand half, the self-healing of this polymer network is shown, with from left to right the polymer network after synthesis, then cut in two pieces, and finally after self-healing. Reproduced with permission.[71] Copyright 2018, Royal Society of Chemistry. c) Optical images of Dima/TMPMP immersed in *N*,*N*-dimethylformamide (DMF) and dissolved in DMF with an excess amount of 4-OH-TEMPO (20 equiv. alkoxyamine unit) due to decrosslinking (left). On the right-hand half, recycling and reprocessing of a film of Dima/TMPMP (top left) is shown, by frozen pulverization (top right), and remolding (bottom right) using a metal mold (bottom left). Conditions of reprocessing: 80 °C, 2.5 h, and 3 MPa. Reproduced with permission.[78] Copyright 2016, Royal Society of Chemistry.

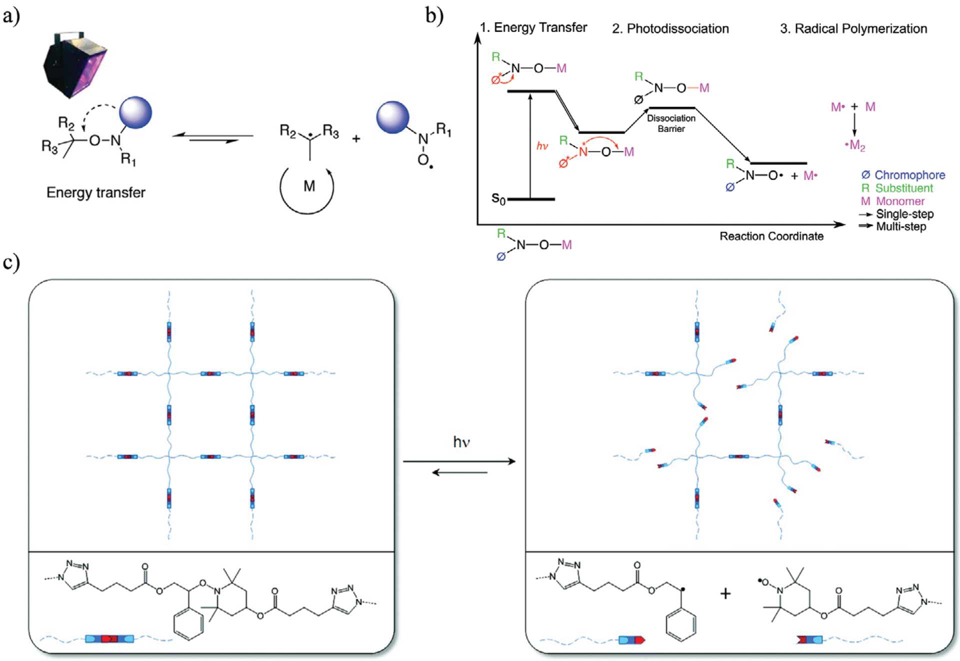


Figure 7. a) Principles of nitroxide-mediated photopolymerization (NMP^2). Reproduced with permission.[80] Copyright 2010, American Chemical Society. b) General scheme of the photochemically induced (NMP^2) initiation mechanism. The red part of the structure indicates the localization of the excitation energy in the structure. Reproduced with permission.[83] Copyright 2014, American Chemical Society. c) Representation of the photodissociation of the alkoxyamine junctions resulting in the cleavage of the network structure. Reproduced with permission.[85] Copyright 2013, Royal Society of Chemistry.

chromophoric group that is directly linked to the nitroxyl moieties.[80,82] According to the results of Huix–Rotllant et al., the homolysis rate constant is related to the structure of the alkoxyamine—including the nature of the chromophore group—the irradiation wavelength, and the initial light intensity.[83,84] Homolysis of photo-alkoxyamines typically occurs in three steps: i) light absorption and subsequent singlet-to-triplet conversion localized in the chromophore fragment; ii) triplet energy transfer, in which the delocalized excitation energy is transferred to the alkoxyamine moiety; and iii) cleavage of the alkoxyamine C–ON bond (Figure 7b).[83] In CANs, photosensitive alkoxyamine bonds as responsive reversible crosslinks provide access to self-healing networks by applying photoirradiation. For instance, Telitel et al. prepared networks from azido-end-functionalized poly(*n*-butyl acrylate) star-like oligomers and dialkynylated alkoxyamines by copper-catalyzed 1,3-dipolar cycloaddition.[85] The homolysis of incorporated alkoxyamine linkages under UV irradiation led to cleavage of the connections between the star-like precursors in the network despite the absence of a specific chromophore. The resulting radical species could progressively recombine after irradiation, followed by the network reformation (Figure 7c), which resulted in self-healing. The combination of thermally and photochemically induced polymerization is also intriguing for polymer materials.[86] The dual control (UV and thermal initiation(s)) of the polymerization using light-sensitive alkoxyamine was applied to the postmodification of polymer coatings for patterning and polymer grafting. This combination and its applications demonstrate the promising perspective of photostimulated alkoxyamines, even capable to shift reaction networks out of equilibrium as shown by Lehn and co-workers for molecular reaction systems (**Figure 8**).[87] Aside from thermal and photochemical stimuli, there are also other interesting concepts such as chemical and plasmon activation of alkoxyamines, which will be briefly discussed in Section 2.1.3.

2.1.3. Other Stimuli

Chemical,[88–90] biological,[91,92] or plasmonic[93,94] stimuli are relatively new as triggers for dynamic alkoxyamine bond dissociation. Although these stimuli have not been exploited in alkoxyamine-based CANs, they were already successfully utilized in NMP or as smart alkoxyamines.[91–93,95] Marx et al. introduced the possibility of chemical activation of alkoxyamine bonds in 2009.[96] They synthesized a new versatile TIPNO-type alkoxyamine based on pyridine. Through protonation or alkylation of a pyridyl substituent in the alkoxyamine, the steric hindrance and polarity around the nitroxide O atom of the alkoxyamine can be modulated. This pyridyl TIPNO alkoxyamine can more effectively initiate the NMP of styrene and *n*-butyl acrylate than TIPNO due to its increased polarity. Later in 2011, Marque and co-workers demonstrated a proton triggered alkoxyamine bond homolysis.[97] This new alkoxyamine was prepared from SG1 nitroxide and 4-pyridyl-1-ethyl radical following protonation with trifluoroacetic acid. Compared to the non-protonated homologue alkoxyamine, this novel alkoxyamine has a 20-fold increase in k_d and exhibits C–ON bond homolysis driven by protonation of the alkyl fragment. In the same year, Bagyanskaya and colleagues reported a pH-sensitive C–ON bond homolysis of alkoxyamine as a tool for controlling NMP.[98] The NMP was mediated by imidazoline alkoxyamines with functional groups including multiple ionizable centers. These pH-

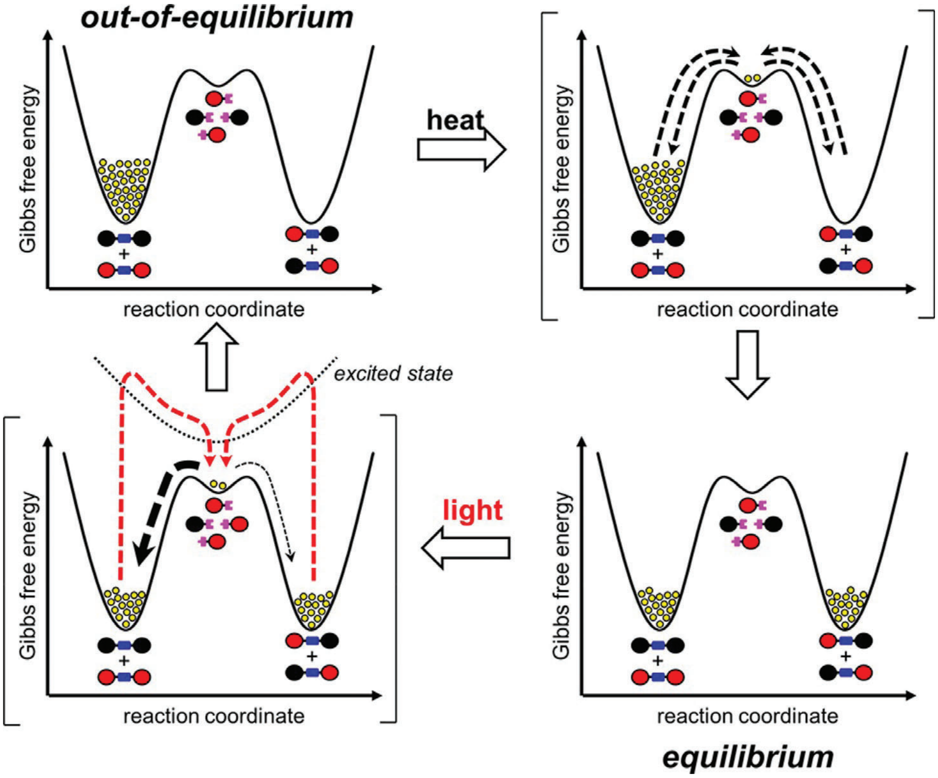


Figure 8. Thermodynamic picture of the photodynamic reaction network showing the generation of an out-of-equilibrium state under irradiation (bottom). Black arrows indicate the probability of thermal dissociation and recombination reactions while red arrows indicate the probability of photoexcitation from either side of the equilibrium. As photoexcitation is selective for constituents possessing a sensitizer (depicted in red) the amount of nonsensitized building blocks reaching the intermediate high-energy region depletes over time leading to a higher probability for the formation of homo-substituted constituents and thus a net flow of material from the right to the left side of the equilibrium under irradiation. Reproduced with permission.[87] Copyright 2018, American Chemical Society.

switchable alkoxyamines have several basic groups that can undergo successive protonation when the pH varies. Using the same alkoxyamine and varying the pH value, a controlled NMP of different hydrophilic monomers (styrene, acrylamide, and styrene sulfonate) in aqueous solution under mild conditions (90 °C) could be obtained. The length of polymer chains is regulated by the pH during the polymerization. In 2014, Marque and colleagues proposed the use of alkoxyamines as drugs or pro-drugs for theranostics, based on their radical reactivity.[92] The alkoxyamine should be stable enough to be handled at room temperature while still having the ability to perform rapid C–ON homolysis under mild conditions (35–40 °C). Thus, they proposed a concept of smart alkoxyamines, which have a BDE > 140 kJ mol^{-1} at ambient temperature and a BDE < 100 kJ mol^{-1} after the activation. Later in 2019, they synthesized a peptide-labeled alkoxyamine that can be enzymatically hydrolyzed by chymotrypsin and subtilisin A to release a protonated alkoxyamine at pH = 7.2.[99] This protonated alkoxyamine can then spontaneously dissociate into an alkyl radical and nitroxide SG1. The energy of plasmons can significantly enhance reaction rates. It provides a new way to activate chemical transformations, which can be used for instance in surface-assisted polymerization at ambient temperature.[100] The group of Baumberg presented an example of employing plasmon energy for polymerization in 2018.[94] Polymer brushes were grown via plasmon-induced polymerization with nanoscale precision. Plasmon actuation was utilized in the context of reversible addition-fragmentation transfer (RAFT) polymerization,[101] before Guselnikova et al. introduced it to induce NMP.[93] The plasmon-induced homolysis of alkoxyamine C–ON bonds was activated upon laser irradiation (785 nm) at room temperature and controlled by the plasmon effect. With surface-grafted SG1-based alkoxyamine, block copolymer brushes of *N*-isopropylacrylamide (and 4-vinylboronic acid) could be grown, apparently in a controlled manner.[93]

2.2. Methods of Characterization

The unique characteristic of nitroxide radicals is their paramagnetic behavior due to their single unpaired electron. Conventional organic compounds are diamagnetic, i.e., contain fully filled orbitals with paired electrons. The unpaired electrons of nitroxide radicals enable their detection with electron paramagnetic resonance (EPR) spectroscopy. Thus, the reversible dissociation of alkoxyamine bonds within the CANs thereby generating paramagnetic nitroxide radicals can be detected and characterized by EPR spectroscopy. EPR spectra can be exploited in this case to detect the radical concentration in the materials, and accordingly explore the fission behavior or the healing performance of crosslinked materials respectively.[25,26] Moreover, the course of

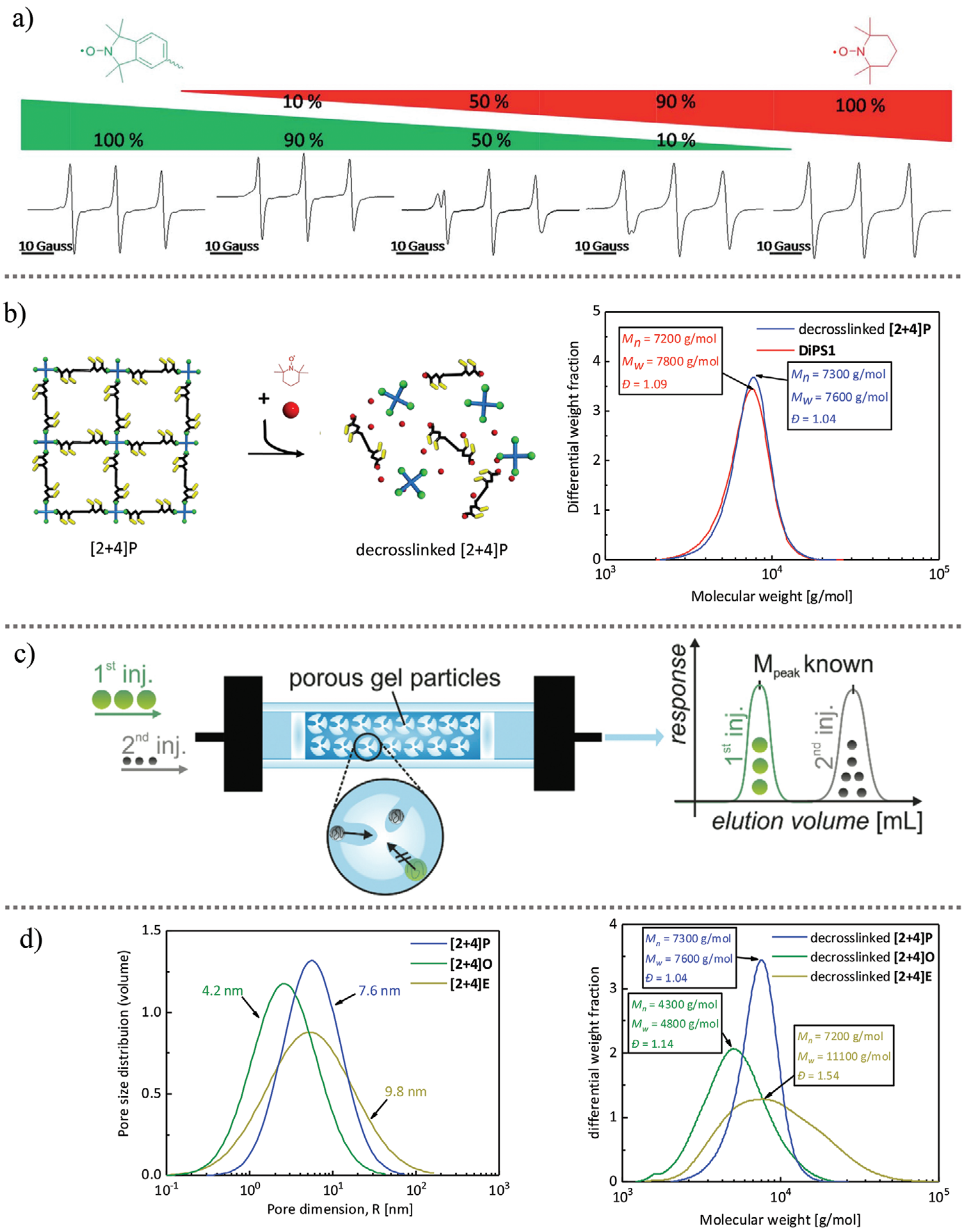


Figure 9. a) Continuous-wave EPR spectra of tetraphenylmethane nitroxide (TPM-NO, green) and TEMPO (red), and mixture of TPM-NO/TEMPO with molar ratio 9/1, 1/1, and 1/9. Reproduced with permission.[72] Copyright 2016, Royal Society of Chemistry. b) Left: The addition of TEMPO in excess dissolves the crosslinked polymer network formed by the 2 + 4-combination (dialkoxyamine + tetranitroxide) network and styrene monomer;[10] right: Comparison of SEC results of the decrosslinked [2+4]P polymeric network, and the prepolymer DiPS1.[10] c) Schematic representation of the ISEC setup. A series of polymer standards with known molecular weights were passed through the porous materials stationary phase made of CAN. Reproduced with permission.[107] Copyright 2020, Wiley-VCH GmbH. d) Left: Mesh size distribution of three different [2 + 4]-combination networks determined from ISEC investigations; right: SEC results of the decrosslinked polystyrene from different [2 + 4]-combination networks.

a nitroxide-exchange manipulation of the network, which corresponds to the presence of two different nitroxide moieties (illustrated as red and green in **Figure 9**a), can be precisely monitored in situ with high sensitivity via EPR spectroscopy due to the distinct hyperfine coupling constants of the two nitroxides.[10,71,72] Accordingly, the radical nature of the nitroxide-exchange reaction enables the precise monitoring of crosslink density in the networks in a straightforward manner.[10,71]

Besides EPR spectroscopy, nitroxides generated by alkoxyamine dissociation can also be detected and quantified by fluorescence spectroscopy, due to their fluorescence quenching property. Indeed the intercalation of their single-occupied molecular orbital centered on the nitroxide radical in between the frontier molecular orbitals of a neighboring fluorophore results in nonradiative relaxation of the excited fluorophore.[102] This phenomenon is for instance advantageously exploited in the case of profluorescent nitroxide molecular probes which are turned on by radical generation and oxidation processes, such as occurring in materials degradation events or biological processes.[103,104] Thus, fluorescence spectroscopy of fluorophore-containing nitroxide moieties additionally allows to evaluate the crosslinking density of the networks and offers complementary information to EPR spectroscopy for the characterization of the networks.[71]

Moreover, differential scanning calorimetry (DSC) is a common technique for determining the T_g of polymers, including crosslinked polymer networks. Fox and Loshaek introduced several models demonstrating that in crosslinked materials T_g is a function of the crosslink density and increases with increased crosslink density.[105,106] Obviously, the alkoxyamine homolysis events will have an impact on the network dynamics only if the network segments are intrinsically soft at the cleavage temperature. The dynamic nature of the nitroxide exchange reactions in the CANs additionally allows full decrosslinking of the networks.[10] In the presence of a large excess of nitroxide or low-molecular-weight alkoxyamine, the initial alkoxyamine moieties forming the crosslinks can be dissociated at elevated temperature and turned into pendant alkoxyamine moieties. The latter may even be more stable, if a suitable nitroxide leading to lower K constant is introduced. This deconstruction of the networks allows the application of classic size-exclusion chromatography (SEC) to determine the length of the polymer segments between crosslinks. For instance, the reversibility of NER enables the original components of the [2+4]P network seen in Figure 9b to be recovered by introducing an excess of monomeric TEMPO nitroxide radicals. The resulting solution comprises the tetranitroxide crosslinker as well as TEMPO-capped polystyrene segments that can be investigated by SEC (Figure 9b,c).[10] In the inverse mode, namely inverse size-exclusion chromatography (ISEC), it is possible to determine the mesh-size distributions of the networks. In this technique, a range of well-defined polymer standards with known number-average molecular weights flow through a column constituent of networks of unknown mesh sizes as stationary phase (Figure 9d)[107] The resulting standard elution volumes are plotted against the molecular weights of polymer standards, which allows for the calculation of the mesh sizes in the examined networks.[10] For instance, the mesh-size radius of the three networks similar to what is seen in Figure 9b were determined to be 7.6 ± 1.7 nm ([2+4]P), 4.2 ± 1.1 nm ([2+4]O, and 9.8 ± 2.3 nm ([2+4]E), respectively (Figure 9d). The molecular weights of the polystyrene segments determined by SEC were compared to these results. [2+4]O had the smallest mesh size following deconstruction, with the lowest number-average molecular weight, $M\bar{M}_n$, of 4300 g mol^{-1}. [2+4]P and [2+4]E had a similar $M\bar{M}_n$ of roughly 7200 g mol^{-1}, but [2+4]E had a larger weight-average molecular weight, $M\bar{M}_w$, of 11 100 g mol^{-1} compared to $M\bar{M}_w$ of [2+4]P of 7800 g mol^{-1}. M_w is particularly sensitive to the presence of higher-molecular-weight molecules $\bar{M}$, whereas M_n is relatively sensitive to the presence of lower-molecular-weight molecules. As a consequence, its decrosslinked version having a similar M_n but a larger M_w than the analogue of [2+4]P, the network [2+4]E incorporated more long polystyrene segments $\bar{M}$ $\bar{M}$ and exhibited a larger mesh size, as determined by ISEC analysis (Figure 9d). Thus, the combination of SEC and ISEC in the characterization of alkoxyamine-based CANs provides insights in both mesh size and polymer chain length, and their relationship.

To determine the pore size distribution and the specific surface area of permanently porous polymer materials, the gas adsorption method is most suited. The technique is based on determining the adsorption performance of an inert gas, typically nitrogen, argon, or krypton on a solid surface at low temperature—which goes well with alkoxyamine thermal (in)stability—and under varying pressure.[108,109] This method is typically applied for materials with pore size in the range of micropores (<2 nm) and mesopores (2–50 nm).[108]

Investigation of mechanical properties of CANs is typically achieved through dynamic mechanical analysis (DMA).[8,110] A sinusoidal oscillating stress with predefined amplitude is applied to the sample, and the resulting phase displacement and deformation strain data is subsequently recorded. In conventional DMA measurements, the stress is performed at a constant frequency and the sample is given a stimulus such as temperature with a constant heating rate. The output from DMA are characteristic mechanical properties such as storage modulus, loss modulus, and corresponding loss tangent. As the DMA technique developed, more features were included such as the possibility of sample measurement in various physical states (e.g., solid, fluid, viscous oil), different geometries (tension, compression, bending, torsion), and under different environments (e.g., humidity, solvent vapors).[110] This technique is very sensitive to the dynamics of the polymer chains. It thus is an effective tool for investigating transitions in polymer materials such as measuring the crosslink density, which is a fluctuating parameter in alkoxyamine-based CANs.[26,70] Furthermore, DMA measurements can be used to determine the T_g of the polymer materials. Compared to DSC, the accuracy of DMA in determining T_g is higher and it can additionally resolve secondary transitions such as side chain movements, which have a considerable impact on the properties of polymer materials.[111] **Figure 10** gives an overview of the most important characterization methods for CANs based on dynamic alkoxyamine bonds. For more detailed information on polymer network characterization methods, we refer the reader to the excellent review of Danielsen et al.[112]

3. Properties and Applications of CANs Based on Dynamic Alkoxyamine Bonds

3.1. Recyclability and Reprocessability

Classical thermosets consist of covalently crosslinked structures that provide them with mechanical and thermal stability, which is a prerequisite for high-quality plastics and high-performance applications. Reversible alkoxyamine bonds offer dynamic covalent exchanges in thermosets and thus provide reprocessability and recyclability, yet may not be suitable for high-temperature operation. Alkoxyamine-based CANs are dynamic covalent networks that are possibly—depending on their exact structure—fully recyclable to monomers or oligomers/polymers and can retain the dynamic exchange during the reaction. The recycling of CANs with alkoxyamine labile bonds is performed either by direct reprocessing of damaged materials, which results in qualitatively identical and mechanically retained networks after restoration,[70,78] or by

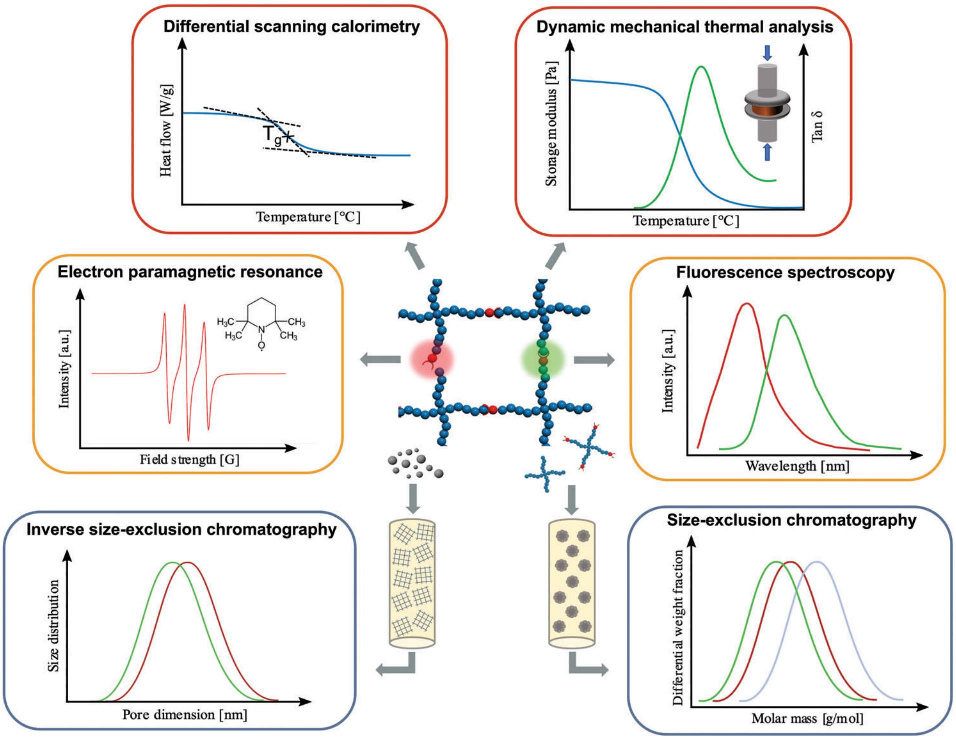


Figure 10. Schematic representation of the main methods for characterization of CANs with alkoxyamine labile bonds.

decrosslinking in the presence of excess nitroxide radicals in a controlled manner.[10,71] Examples of reprocessability and recyclability are illustrated in Figure 6.

Torkelson and co-workers prepared PB/S copolymer network by grafting through copolymerization of styrene and a polymerizable nitroxide radical (TEMPO methacrylate), initiated by bifunctional initiator 1,1-bis(*tert*-butylperoxy)cyclohexane (BI) in the presence of a low-molar-mass polybutadiene (3 kg mol^{-1}).[70] At a reaction temperature of 120 °C, the initiator being difunctional leads to bidirectional propagation and crosslinking of PB chains. The presence of the polymerizable nitroxide leads to additional reversible crosslinks. After cutting the material, it could be reprocessed by compression molding at 140 °C. This process could be repeated several times, with the dynamic mechanical properties of the original crosslinked PB/S networks remaining constant after two recycling rounds (Figure 6a). Tuning of the polymer network properties such as the glass transition temperature was possible via copolymerization of styrene (S) and *n*-butyl acrylate (N) at various molar ratios. Furthermore, even after extremely long reprocessing times, the dynamic nature of the crosslinked material was preserved. For example, the initial 50/50 wt% S/N network without sol fraction remained crosslinked after 13 h of annealing at 130 °C. The same group recently refined their system, employing the same one-step NMP strategies to build reprocessable networks and network composites with alkoxyamine dynamic bonds.[113] The resulting networks exhibit full crosslink density recovery and creep arrest at 80 °C after multiple molding cycles at 140/160 °C (networks/network composites).

Our group combined NER and NMP to produce networks with varying polymer chain lengths and mesh sizes (Figure 5c).[10] To this aim, we developed isoindoline and TEMPO-based multifold nitroxides (e.g., tetranitroxide) and (polymeric) alkoxyamine building blocks, that can be directly utilized for the construction of CANs with alkoxyamine bonds through the dynamic nitroxide-exchange reaction.[72,73] The dynamic equilibrium in the NER allows for adjustment of the crosslinking degree or complete dissolution of the networks by adding an excess amount of mononitroxide. After decrosslinking, linear polymers, and tetranitroxide building blocks remain and can be fully recycled. The recycled PS-based polymeric alkoxyamines exhibited unaltered chain length and dispersity compared to those involved in the first instance of crosslinking (Figure 9c). These results are highly attractive for the recycling of the network structure. Aside from the ability of recycling and reprocessing, the possibility to disassemble the network at the crosslinking points greatly facilitates the characterization of the networks, e.g., determining the strand length by SEC, which is usually a great challenge in polymer network formation.[114]

A reversibly crosslinked poly(urethaneamide) system consisting of a novel alkoxyamine with moderate homolysis temperature and air insensitivity was obtained by room-temperature thiol-ene polymerization by Zhang et al. in 2016.[78] In this study, two networks based on Dima/TMPMP (Dima = dimethacrylate-functionalized alkoxyamine; TMPMP = trimethylol-propane tri(3-mercaptopropionate)) and Dima/PETMP (PETMP = pentaerythritol tetra(3-mercaptopropionate)) were prepared. The original Dima/TMPMP networks swell in *N*,*N*-dimethylformamide (DMF) and can be dissolved by adding an excess amount of nitroxides such as 4-OH-TEMPO (20 equiv./alkoxyamine unit) within 6 h at 100 °C (Figure 6c). These results prove that these crosslinked networks can be thermally degraded, and provide a controllable approach of decrosslinking, recycling, and reprocessing by varying the amounts of added nitroxide in the system. After pulverization of disk-shaped specimens, a simple molding step at 80 °C provided CAN disks akin to initial ones (Figure 6c). Mechanical testing indicated that the tensile strength and failure strain of the recycled Dima/TMPMP network only slightly decreased by about 20–30% compared to the original network, while the tensile strength of recycled Dima/PETMP had also decreased by about 30% yet with no reduction in failure strain. Due to the dynamic nature of the alkoxyamine bonds, these crosslinked networks can be easily disassembled into oligomers/polymers which can be dissolved in solvents or reprocessed directly in solid state.

3.2. Smart Materials and Self-Healing

Alkoxyamines were also put to use in the development of crosslinked smart materials (e.g., polymers with self-healing properties or self-assembled hybrid materials).[14,26,27] The construction of smart materials requests building blocks, whose properties or structures can be altered upon external stimuli such as temperature or light. Related to reprocessability and recyclability, the self-healing property of CANs is also a prominent research interest for the plastics industry (e.g., toward extension of lifetime).[115,116] Due to the dynamic reversible alkoxyamine bonds, alkoxyamine-based CANs are represented through several examples in self-healing materials.

An early example of self-healing materials was proposed by Yuan et al. in 2011.[26] They simply utilized an alkoxyamine, containing two methacrylic ester groups at both ends, as a crosslinker and copolymerized it with styrene. This crosslinked polystyrene network exhibited reversible bond dissociation and recombination, which enabled the repeated self-healing of the polymer materials. The material did not show any deformation caused by chain scission and retained its mechanical properties before and after the thermal process. Since the alkoxyamine moiety can easily be attached to monomers as a crosslinking group, analogous self-healing crosslinked polymer networks with an alkoxyamine as the crosslinking linkage were investigated, such as polyurethane elastomer or epoxy material.[76,77] In these cases, both initial and healed networks exhibited similar mechanical properties. As mentioned before, through structural variations the homolysis temperature of the alkoxyamine bond can be tuned.[75] This is how Zhang et al. introduced a self-healing material with lowered homolysis temperature.[25] Accordingly, a self-healing covalent network of stiff polyurethane was prepared by incorporating a specifically designed dihydroxylated alkoxyamine moiety, CTPO, and soft segments of polyethylene glycol (PEG) with subambient T_g. In order to maintain the strength and stiffness of the materials, CTPO was copolymerized with 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate. The CTPO alkoxyamine contains an electron-withdrawing nitrile group in alpha position to the radical formed by homolysis of alkoxyamine bonds (Figure 5d), which is well known to stabilize carbon radicals, such as in typical azoinitiators or RAFT agents. CTPO enters a dynamic reversible equilibrium at ambient temperature with 4-OH-TEMPO and the cyano-based radical. The subsequent healing investigation indicated that the polyurethane can be repeatedly mended at ambient temperature without external stimuli (Figure 5d). The homolysis and recombination of alkoxyamine bonds in CTPO rapidly proceed, and the dissociated cyano-substituted radical is more stable than the typical methyl radicals,[117] leading to a lesser oxygen sensitivity.

By employing custom-designed multifold nitroxide and alkoxyamine building blocks, alkoxyamine-based CANs could be synthesized in one step via a nitroxide-exchange reaction.[71] The resulting material is an intrinsically self-healable dynamic network, since all polymer-forming bonds are based on alkoxyamines. To investigate its self-healing properties, the polymer network was cut into two pieces. Subsequently, the two pieces were placed in contact and heated at 100 °C to mend. Figure 6b shows the state of the polymer networks before cutting and after self-healing. The direct coupling of multifold alkoxyamines and multifold nitroxides allows the precise monitoring of the reaction process via EPR spectroscopy in case the utilized nitroxides possess different hyperfine coupling constants, as in the case of isoindoline and TEMPO nitroxides. Additionally, through design of rigid building blocks, dynamic porous organic polymers with tunable crosslinking degree and porosity can be obtained (**Figure 11**a).[118] These polymer materials consist of a series of multitopic alkoxyamines combined with tetratropic nitroxides. EPR spectroscopy monitoring enables dynamic tuning of the porosity as well as the crosslinking degree by adding or removing nitroxide moieties.

3.3. Living Additive Manufacturing

Light-initiated additive manufacturing techniques, also known as a type of 3D printing, typically relies on layer-by-layer addition or continuous extraction of polymers.[119] The additive manufacturing techniques enable printing of sophisticated 3D architectures, leading to highly customizable design.[120] However, in classic 3D printing the final printed materials are static ("dead") and cannot be reactivated and postmodified, e.g., by reactivation of latent initiator sites for further insertion of monomers.[11] In 2017, Johnson and co-workers proposed a novel concept of living additive manufacturing, where photocontrolled living radical polymerization is employed to include monomers into dormant "parent" materials under high spatiotemporal control, to generate "daughter" materials with more complex and diverse functionality (Figure 11b).[11] This living additive manufacturing enables the postmodification of the parent materials to control polymer strand length, change the crosslink density, and vary the composition of the polymer networks. In contrast to conventional photoradical polymerization induced via photoinitiator, this investigation utilized a photocatalyst to activate the incorporated trithiocarbonate iniferters in the polymers through a single-electron transfer.

In 2020, we introduced the synthesis of living dynamic polymer networks with a controlled network structure and molecular composition via NER and NMP.[10] As previously mentioned regulation of the crosslink density and dissolution of the networks can be achieved by modulating the NER equilibrium. Moreover, the described system allows manipulating the network properties via NMP, either by using different types of monomers or by varying the mesh size of the polymer networks, thereby

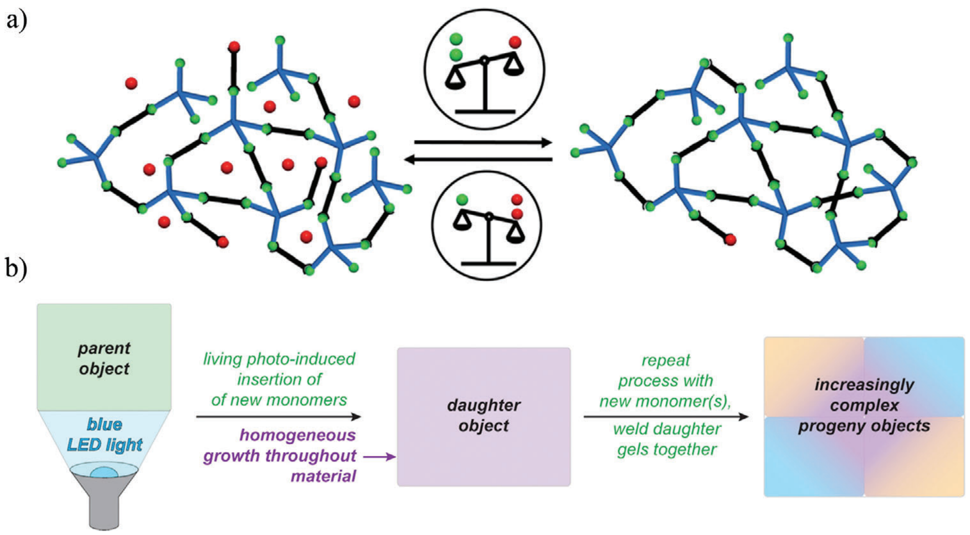


Figure 11. a) Tuning of crosslinking degree via equilibrium control in the reversible multifold nitroxide exchange reaction. Reproduced with permission.[118] Copyright 2021, Royal Society of Chemistry. b) Living additive manufacturing approach wherein parent objects comprised of dynamic covalent polymer networks are reactivated via a photoinduced living radical polymerization to generate daughter objects with homogeneous network modifications. These daughter objects of varying composition can be welded together to form increasingly complex progeny with spatially defined stimuli-responsive behaviors. Reproduced with permission.[11] Copyright 2017, American Chemical Society.

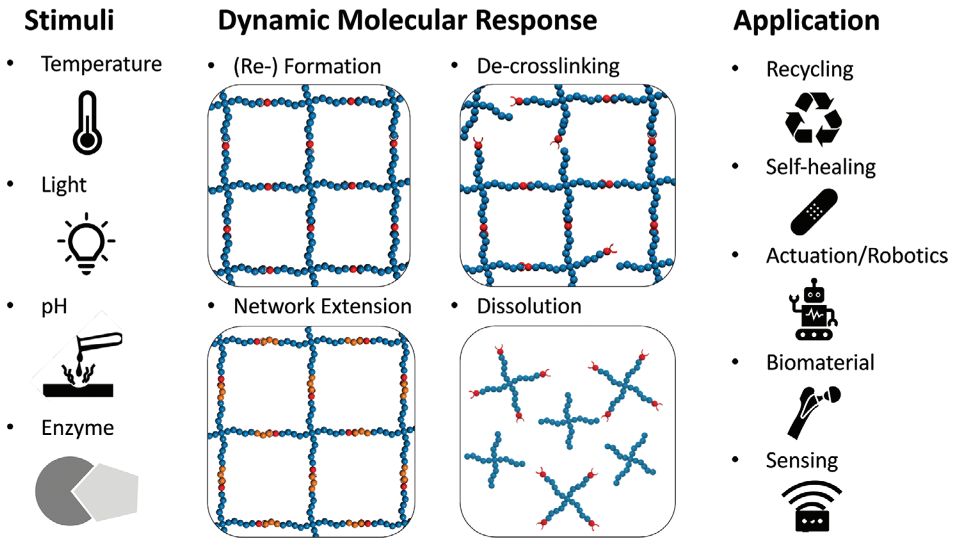


Figure 12. Summary of potential stimuli, dynamic molecular responses, and applications for CANs based on alkoxyamine bonds.

generating dynamic and postfunctionalizable polymer networks. Though the modification of this system operated through temperature variation, there are multiple examples of photosensitive alkoxyamines used in photopolymerization.[80,87,121] We therefore see great promise in the use of alkoxyamine bonds in living additive manufacturing.

4. Summary and Outlook

CANs have evolved as a new class of polymer network materials. A wide variety of reversible covalent bonds, based on different mechanistic principles and with tunable molecular reactivity, are available to optimize CAN properties. Here, we reviewed CANs based on alkoxyamine bonds as reversible covalent chemistry. Alkoxyamines feature several properties, that make them attractive in CAN design: 1) the stability of the alkoxyamine bond can be altered by its molecular structure; 2) the activation of alkoxyamine bonds can be performed thermally, photochemically, through pH variation, by plasmon induction, or through enzyme reactions; 3) the alkoxyamine functional group can additionally be used as initiators for nitroxide-mediated polymerization. The design of CANs based on alkoxyamines, as well as the processing conditions, need to be carefully adjusted to reduce the impact of potential side reactions and different characterization methods should be combined to follow their dynamic modifications. **Figure 12** provides an overview of the different stimuli and the dynamic changes in the molecular structure of CANs based on alkoxyamines, as well as their potential applications.

Especially promising is the development of multistimuli-responsive CANs.[122] Recent investigations into this direction have already demonstrated that alkoxyamines can be employed in forming various complex polymers by combining light and other stimuli.[87,121,123] In addition, the hybridization of CANs with nanoparticles, or their hierarchical structuring can further extend the scope of properties and applications.[124,125] Preparation of alkoxyamine-containing CANs via additive manufacturing will further extend the possibility of generating well-defined adaptive and “living” 3D microstructures.[126]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

alkoxyamine, covalent adaptable networks, nitroxide exchange, nitroxide-mediated polymerization

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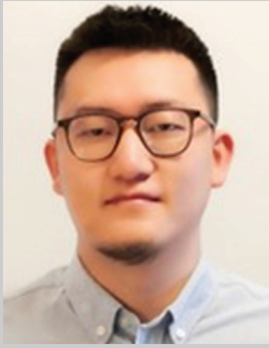

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