Anilinium Salts in Polymer Networks for Materials with Mechanical Stability and Mild Thermally Induced Dynamic Properties

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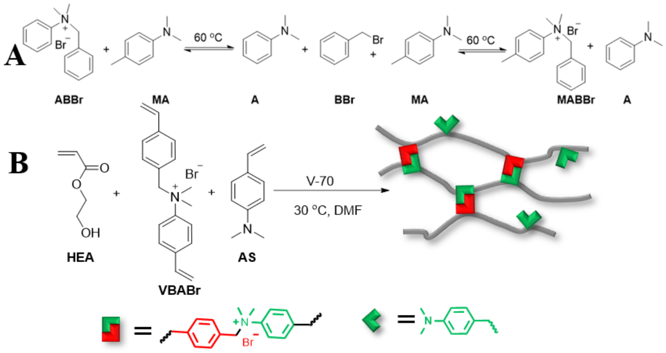
ABSTRACT: Dynamic nucleophilic exchange of quaternary anilinium salts has been incorporated into re-healable and malleable polymeric materials that can be activated under mild (60 °C) thermal stimulus. The mechanism of Dynamic exchange between quaternary anilinium salt and free aniline was assessed in small molecule model experiments. The dynamic exchange was found to be dissociative in nature, due to the indirect S_N2 mechanism, where initially the bromide anion attacks the anilinium salt to generate an alkyl bromide which undergoes subsequent attack by a free aniline group. A quaternary anilinium based crosslinker was synthesized to act as dynamic linkages in the polymer network. Crosslinked polymeric materials showed thermoresponsive re-healing and malleability properties at 60 °C along with being resistant to irreversible creep under ambient conditions. The use of anilinium salts enables dynamic exchange to occur with significantly milder thermal stimulus than other comparable materials, while maintaining mechanical stability.

Introduction. Dynamic polymers are materials that contain dynamic non-covalent interactions and exchangeable bonds. Dynamic materials can have properties such as self-healing ability, recyclability, re-process ability, malleability, degradability and shape-memory, among others.[1-8] These materials are usually based on rapidly exchanging dynamic supramolecular bonds[9-14] or stimulus responsive dynamic covalent bonds[15-25]. Polymer networks with dynamic covalent bonds have been called covalent adaptable networks (CANs). CANs are usually slow exchanging, through either '*dissociative*' or '*associative*' exchange mechanism.[6] In a *dissociative* mechanism, dynamic covalent bonds completely dissociate and reform again, but in an *associative* mechanism, when one bond breaks another forms simultaneously. CANs usually only activate under stimuli like temperature, light, pH and as a result are mechanically stable under ambient conditions, as highlighted in recent reviews.[1, 5, 26] Although there are multiple reports of incorporating convenient dynamic covalent chemistry (DCC) into polymeric materials[3], the use of simple DCCs, especially those which respond to mild stimuli, can bring new possibilities, since many existing DCCs require temperatures above 100 °C or UV to activate exchange.

Quaternary ammonium salts are often used as ionic liquids[27-28], phase transfer catalysts[29-30], surfactants[31], and anti-microbials.[32] Recently, Kulchat and Lehn have reported an extensive study on the dynamic characteristics of different small molecule quaternary ammonium salts.[33] Also, Obadia et. al. reported vitrimer-like materials based on an exchange reaction between 1,2,3-triazolium salts and alkyl halides via a proposed *dissociative* mechanism.[34-35] Du Prez and coworkers reported vitrimeric materials using associative type exchange between thioether and trialkyl sulfonium salts.[36] The dynamic exchange in these reports however occur only at high temperatures over 100 °C. Also, in those reports, dynamic properties like self-healing, i.e. healing in the absence of significant pressures, have also not been explored.



Scheme 1. A) Dynamic exchange between anilinium adducts and free aniline. B) Synthesis of polyHEA material with dynamic anilinium crosslinkers.

This work reports an intrinsically healable dynamic polymeric material, which uses the reversible nature of quaternary anilinium salt formation, and which is shown to occur via a *dissociative* mechanism. The development of these materials and the assessment of their dynamic behavior was carried out based on a series of small molecule kinetic studies. These materials showed dynamic properties under mild thermal stimulus of 60 °C, which is significantly more accessible than other related systems. Despite this mild thermoresponsive dynamic character, all materials are mechanically stable under ambient conditions, making them candidates for applications, which could include antimicrobial surfaces or other coatings.

Results and Discussion. In 2015, Kulchat and Lehn reported dynamic exchange of quaternary benzyl anilinium salts with tertiary amines in presence of different counter anions and concluded the mechanism is mainly indirect S_N2 exchange.[33] Here, both the kinetics of the dissociation of anilinium salts and composite systems i.e. the dynamic exchange between anilinium salts and free amines were studied to evaluate the overall exchange mechanism. Small molecule kinetic experiments initially studied the dissociation of anilinium salts (N-Benzyl-N,N-dimethylbenzenaminium bromide (ABBr) and N-Benzyl-N,N,4-trimethylbenzenaminium bromide (MABBr)) to benzyl bromide and the corresponding aromatic tertiary amines at 60 °C in acetonitrile. The details of the kinetic study are available in the supporting information. The kinetic study found that the bromide anion undergoes nucleophilic attack at the benzylic carbon of the anilinium salts, which then dissociates into benzyl bromide and aromatic tertiary amines. This is apparent by the formation of benzyl bromide (BBr) during the dissociation of ABBr and MABBr adducts as seen in the stacked ^{1}H-NMR plots (Figure S1 and S2). Figure 1A and 1B show the kinetic curves of experimental data (E series) and theoretical fits (T series) of kinetic model. The exchange between quaternary anilinium salts and aromatic tertiary amines are also studied in small molecule model experiments (Scheme 1A). The kinetic study showed that the dynamic exchange between anilinium salts (N-Benzyl-N,N-dimethylbenzenaminium bromide (ABBr) and N-Benzyl-N,N,4-trimethylbenzenaminium bromide (MABBr)) and aromatic tertiary amines (N,N-dimethylaniline (A) and N,N-dimethyl-p-toluidine (MA)) occurs at 60 °C and reaches common equilibrium in 4h in both directions as seen in Figure 1C and 1D.

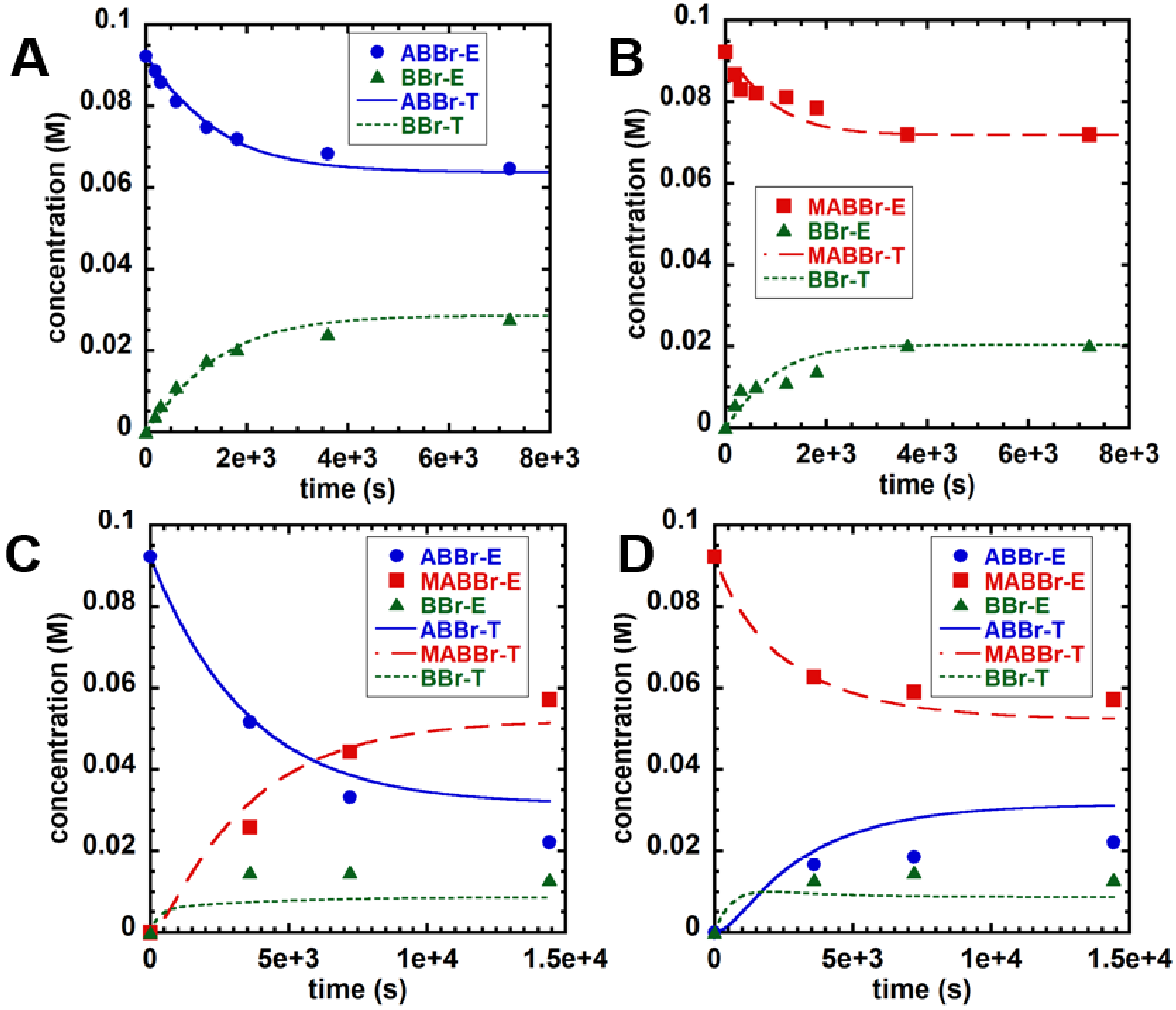


Figure 1. A) Equilibration of ABBr with A and BBr at 60 °C B) Equilibration of MABBr with MA and BBr at 60 °C. C) Kinetics of the exchange of ABBr with a 1 mole equivalent of MA at 60 °C. D) Kinetics of the exchange of MABBr with a 1 mole equivalent of A at 60 °C. The experimental points are labeled E, and simulated fitted curves are labeled T. The parameters $k_{\text{Br-AB+}} = k_{\text{Br-MAB+}} = 2.1 \times 10^{-3}\ \text{M}^{-1}\text{s}^{-1}$, $k_{\text{A-BBr}} = 1.05 \times 10^{-2}\ \text{M}^{-1}\text{s}^{-1}$, $k_{\text{MA-BBr}} = 2.63 \times 10^{-2}\ \text{M}^{-1}\text{s}^{-1}$ were used to fit all experiments. Details of the NMR kinetic experiment and model are in supporting information.

Table 1: Properties of materials – peak stress, strain at break, Young's modulus, T_g, and healing efficiency at 60 °C

polymeric materials	peak stress (kPa)	strain at break (mm/mm)	Young's Modulus (kPa)	T_g (°C)	healing efficiency	
					stress recovered (%)	strain recovered (%)
PHEA-1.5%VBABr	250 ± 20	4.0 ± 0.2	255 ± 20	12	84±3	80± 4
PHEA-3%VBABr	340 ± 30	2.3 ± 0.2	380 ± 40	15	61±5	60± 4
PHEA-1.5%DVB	370 ± 10	4.5 ± 0.3	225 ± 20	11	20± 5	18± 2

Figure 1C and 1D shows the experiment data from ^{1}H-NMR kinetic studies (E series) and the fitted theoretical curves (T series) using a kinetic model for dynamic exchange of anilinium adducts and free aromatic amines. This kinetic model is outlined in the SI. In both overall exchange reactions, formation of benzyl bromide is also observed. The composite systems i.e. the dynamic exchange between anilinium salts and free amines (Figures 1 C and D) can be described by the parameters estimated from the equilibration of benzyl bromide and anilinium salts from the kinetics of the dissociation of anilinium salts (Figures 1 A and B). This rules out significant contribution from direct S_N2, which would be an associative mechanism, and suggests mainly an indirect S_N2 mechanism, or dissociative mechanism. This is because a direct S_N2, where the tertiary amine attacks the anilinium salt, would increase the rate of exchange, beyond that measured in the single component systems in Figures 1A and B.

In this indirect S_N2 mechanism, the first S_N2 process has the bromide attacking the benzylic carbon of the anilinium salt, to give a benzyl bromide followed by attack of the second aniline at the benzylbromide. Characteristic aliphatic protons are assigned in Figure S3. Stacked 1H-NMR plots of the exchanges between anilinium salts and free aromatic amines at 60 °C can be found in Figure S4 and S5. Additionally, significantly slower exchange was observed by using a less nucleophilic counter anion (TsO^-)[37], as shown in Figure S6 .These results are consistent with the report of Kulchat and Lehn, although with other less nucleophilic counter anions.[33] In all the kinetic experiments, the reaction progress was observed by the relative ratio of the benzylic protons (2 protons in 4.2 to 5.3 ppm region) to other aliphatic protons of different components. The ability to undergo dynamic exchange at 60 °C is presumably due to the aniline group being a better leaving group than others used in the literature, such as triazolium, presumably due to the greater stability of the aniline due to its lone pair's interaction with the aromatic ring. Guided by the small molecule study, a quaternary anilinium salts based crosslinker N,N-dimethyl-4-vinyl-N-(4-vinylbenzyl)benzenaminium bromide (VBABr) was synthesized, as a potentially dynamic linker.

Polymeric materials of 2-hydroxyethyl acrylate (HEA), crosslinked with 1.5 wt% and 3 wt% VBABr crosslinkers, along with equal molar 4-(N,N-Dimethylamino)styrene (AS) were synthesized using conventional free radical polymerization (Scheme 1B). A control material with 1.5 wt% DVB was also synthesized following the same procedure. All materials were properly dried to remove excess solvent and unreacted monomer, which was confirmed by ^{1}H-NMR (Figure S7). Differential scanning calorimetry (DSC), infrared spectroscopy (IR), tensile testing, swelling ratio, and rheology were used to characterize the properties of the materials. The IR spectrum of PHEA-1.5%VBABr is given in Figure S8 and the key characteristic peaks are assigned in Table S1. PHEA-3%VBABr had a comparable IR spectrum. Both materials showed similar IR spectra to other HEA based materials.[18, 38] DSC curves of glass transition temperature (T_g) of all the materials are given in Figure S9-11. T_g values of PHEA-1.5%VBABr, PHEA-3%VBABr, and PHEA-1.5%DVB materials were 12 °C, 15 °C, and 11 °C respectively. These values are higher than the T_g = -15 °C of HEA homopolymer[39], as a result of greater chain rigidity and the presence of crosslinkers in the networks. The T_g values of the PHEA-VBABr materials also show that the materials are soft at ambient conditions. DSC data also showed no discernable features, other than a T_g, until at least 160 °C. PHEA-VBABr materials had highest swelling ratio in water, slight swelling in dichloromethane (DCM), and no swelling in hexanes (Table S2). These results are typical of hydrogel forming materials.[18, 38] Swelling ratio data also proved that both materials are fully crosslinked. Additionally, thermogravimetric analysis (TGA) data shows PHEA-1.5%VBABr materials have very limited hygroscopic properties as only 5% weight loss was observed (Figure S12). PHEA-3%VBABr materials also showed similar hygroscopic properties.

Stress-strain curves of uncut PHEA-1.5%VBABr and PHEA-3%VBABr materials are given in Figure S13 and S14, respectively. The stress-strain curves show PHEA-3%VBABr has higher peak stress and Young's modulus but lower strain at break than PHEA-1.5%VBABr. Properties of the PHEA-3%VBABr and PHEA-1.5%DVB materials are given in Table 1. Young's modulus values were calculated using Ogden hyper elastic constitutive law[40] as described in supplemental information. Typical fits of model and experimental data can be found in Figure S15.

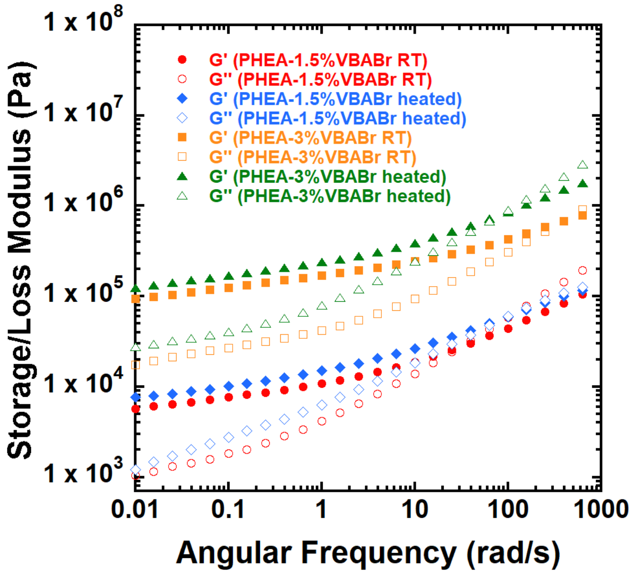


Figure 2. Rheology frequency sweep data of PHEA-VBABr materials at room temperature (RT) and after heating at 60 °C for 24 h.

In addition, rheological frequency sweep experiments were carried out to determine the storage (G') and loss (G") moduli of the PHEA-VBABr materials. Both PHEA-VBABr materials showed faster increase of loss modulus compared to the storage modulus at higher frequency, as seen in Figure 2. Both materials also formed rubbery plateau of G' at lower frequency. These types of rheological behavior are common to slightly-crosslinked material.[18, 41-43] Importantly, after heating at 60 °C for 24 h, both materials preserved similar storage modulus properties as shown in Figure 2. This suggests minimal degradation and no significant loss of mechanical properties or crosslink density upon heating at 60 °C. In addition, strain sweep experiment of PHEA-3%VBABr material showed that the applied 1% strain was in linear viscoelastic region of the PHEA-VBABr materials (Figure S16).

Dynamic properties of PHEA-VBABr materials were assessed by "re-healing" or "self-healing" and malleability experiments. Self-healing properties of the materials were assessed by tensile testing after the materials were cut and healed. Figure 3A compares the stress-strain curve of uncut PHEA-1.5%VBABr to materials which were healed at 60 °C for different time periods. As shown in Figure 3A, after 16 h of healing, the best performing material showed significant healing efficiency with peak stress of 85% and peak strain of 80% compared to the uncut sample. PHEA-1.5%VBABr material also showed good healing efficiency at 4h healing time with recovery of 68% stress and 64% strain of the uncut material as shown in Figure 3A. Interestingly, full healing of the materials could be achieved after heating the cut materials at 80 °C for 16 h (Figure 3A Inset). Additionally, networks were synthesized with 1 mole equivalent of tetrabutylammonium bromide (TBABr) embedded in the material. These PHEA-1.5%VBABr-TBABr materials also showed quantitative healing, requiring only 16 h of healing time at 60 °C (Figure 3B). The improved healing upon the addition of TBABr highlights the critical role of bromide in dynamic exchange. The PHEA-3%VBABr material on the other hand, showed moderate healing with peak stress of 61% and peak strain of 60% compared to uncut materials in 16 h (Figure S17). This could be due to a decrease chain mobility in PHEA-3%VBABr polymer networks compared to PHEA-1.5%VBABr. This decrease in healing behavior as the crosslink density increases is consistent with previously reported dynamic materials.[38, 44-45]

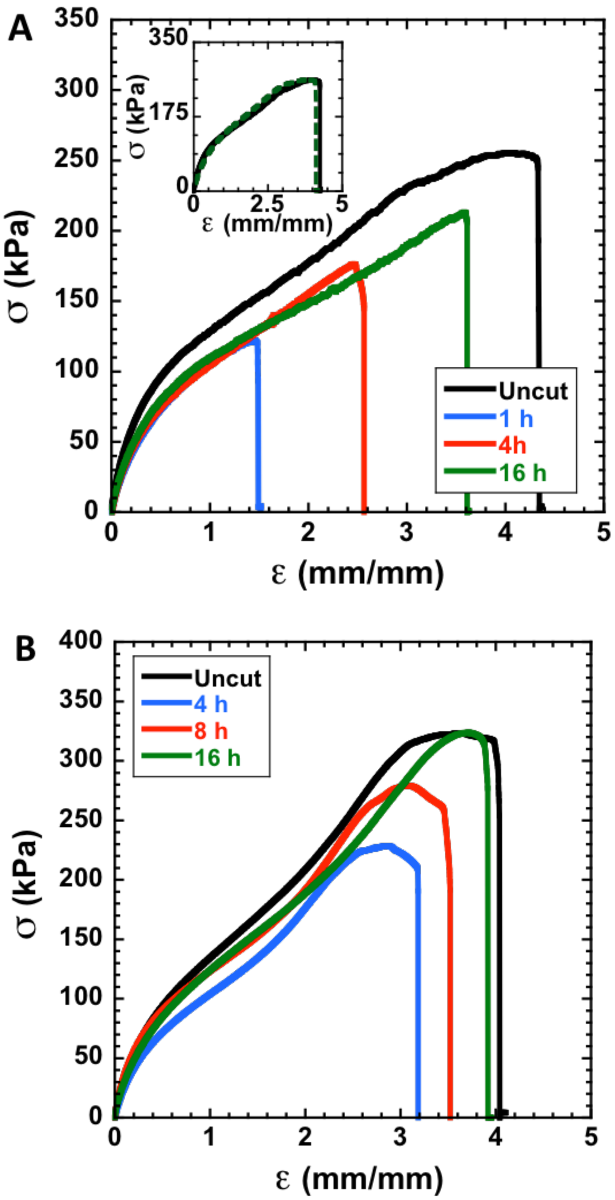


Figure 3. A) Main: stress-strain curves of uncut and representative healed PHEA-1.5%VBABr materials after heating at 60 °C for different time period. Inset: healing after 16h (green dashed) at 80 °C compared to uncut sample (black). B) Stress-strain curves of uncut and representative healed PHEA-1.5%VBABr-TBABr materials after heating at 60 °C for different time period.

In comparison to PHEA-VBABr materials, statically crosslinked PHEA-1.5%DVB materials showed very limited healing efficiency of 20% in 16 h healing period (Figure S18). The 20% recovery of stress and strain could be due to hydrogen bonds involving hydroxyl and carbonyl groups in the PHEA network. This proves that the superior healing of PHEA-VBABr compared to PHEA-DVB materials is due to the dynamic anilinum salts in the polymer matrix of PHEA-VBABr. In all self-healing experiments, at least four samples were replicated for each data point. The PHEA-1.5%VBABr-TBABr materials showed faster healing than PHEA-1.5%VBABr (Figure 3). This is due to the presence of excess bromide anions in PHEA-1.5%VBABr-TBABr, which implies that the dynamic exchange is primarily dissociative. Also, the reactivity of ABBr to ethanol was studied at 60 °C. No nucleophilic attack of ethanol was observed after 24h at 60 °C by NMR (Figure S19). This suggests that the anilinium salts are not susceptible to nucleophilic attack by hydroxyl groups at 60 °C. Healing efficiencies are within 5% error.

In addition to healing properties, the malleability of the PHEA-VBABr materials were also investigated, to observe whether the materials can be molded to new permanent shapes under thermal stimulus. Figure 4A shows the new shapes of the PHEA-1.5%VBABr materials after heating in 360° twisted configuration at 60 °C for different times, and after allowing to fully relax for 2 days. A control malleability experiment of PHEA- 1.5%DVB material was carried out and as shown in Figure 4B. The PHEA-1.5%DVB material showed negligible malleability properties.

As shown in Figure 4C, PHEA-1.5%VBABr materials become increasingly twisted as time increased and ultimately reaching approximately 85% of 360° configuration. This result is consistent with the healing properties of PHEA-1.5%VBABr materials. Also, as shown in Figure 4C, PHEA-3%VBABr materials were less malleable than PHEA-1.5%VBABr, with PHEA-3%VBABr eventually reaching 70% of target 360° configuration. PHEA-1.5%DVB materials on the other hand, reached only 8% of targeted 360° configuration. These new shapes were retained permanently by the PHEA-VBABr materials. This result supports the hypothesis that the dynamic properties of PHEA-VBABr materials are due to dynamic exchange of the anilinium salt linkages, activated by the thermal stimulus. In all the malleability experiments at least two samples were replicated for each data point and reported data are within 10% experimental error.

Dynamic polymeric materials are often susceptible to creep under load due to rapid bond exchange in the crosslinks.[1] This is especially important in this system, since relatively low temperatures of 60 °C could be sufficient to activate dynamic covalent exchange at ambient temperature. Creep deformation, stress relaxation, and creep recovery experiments were carried out to study the mechanical stability of the PHEA-VBABr materials. Figures S20 and S21 shows the stress relaxation experiment at 50% strain and creep deformation under a stress of 50 kPa for PHEA-1.5%VBABr and PHEA-3%VBABr materials respectively at ambient temperature. Both materials showed limited stress relaxation and creep, reaching mechanical equilibrium in 1.5 – 2 h. This is consistent with small molecule kinetic study and dynamic properties of PHEA-VBABr materials, which showed that external thermal stimulus is required to activate the reactive dynamic linkages. In addition to stress relaxation and creep deformation experiments, creep recovery experiments were carried out to assess long-term stability of the PHEA-VBABr materials. As seen in Figure S22 and S23, PHEA-VBABr materials showed complete creep recovery after the samples were kept at 100% strain for 48 h. These results suggest that the VBABr crosslinks have negligible dynamic exchange at room temperature but become dynamic in response to thermal stimulus as seen in healing and malleability experiments.

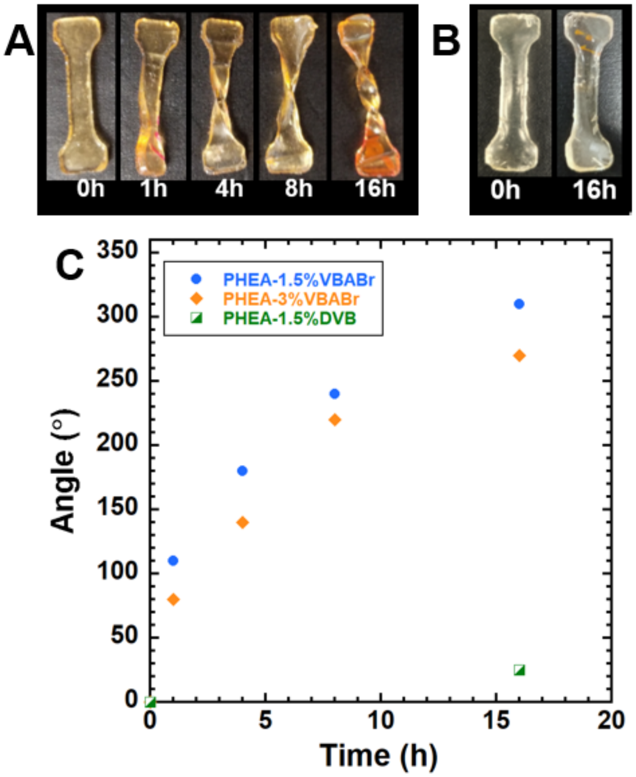


Figure 4. A) Photograph of PHEA-1.5%VBABr materials, and B) Photograph of PHEA-1.5%DVB materials, where samples were twisted at 360° configuration and then heated at 60 °C for different times. C) Malleability of representative PHEA-1.5%VBABr, PHEA-3%VBABr, and PHEA-1.5%DVB materials as a function of time.

Conclusion. Dynamic polymeric materials based on nucleophilic exchange of quaternary anilinium salts have been developed. Small molecule study shows the anilinium salts are dynamic in response to thermal stimulus at 60 °C and the exchange is initiated by nucleophilic attack of the anion of the anilinium salt. This dynamic exchange is overall dissociative in nature. Polymeric materials crosslinked with anilinium salts crosslinks showed significant thermoresponsive dynamic properties like healing and malleability properties compared to statically crosslinked analogue materials. As the anilinium crosslinkers only activate under thermal stimulus, such as 60 °C, these materials are also mechanically stable at room temperature. This work opens the possibilities of utilizing less explored dynamic anilinium salt chemistry for applications such as sealants, surfaces and coatings, especially considering that only a moderate amount of heat is required for exchanges. These materials can also be utilized as solid polymer electrolytes considering the ionic nature of the anilinium crosslinks. A more in-depth study of this chemistry in small molecular scale and polymer networks is currently being pursued in our group.

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Author Contributions

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Conflicts of Interest

The authors declare no conflicts of interest.

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