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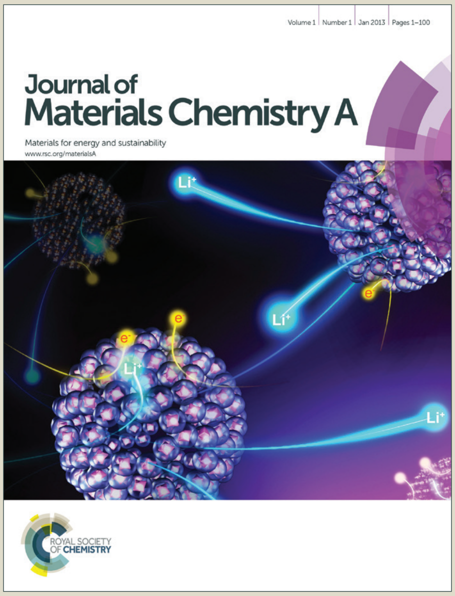

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COMMUNICATION

Catalyst-free dynamic exchange of aromatic Schiff base bonds and its application to self-healing and remolding of crosslinked polymer†

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The present work reveals that catalyst-free dynamic reversible exchange of aromatic Schiff base bonds is enabled at room temperature. Attachment of aryl groups to both nitrogen and carbon atoms of the carbon–nitrogen double bonds is a critical structural factor that contributes to the dynamic characteristics and complete reaction between aromatic aldehyde and aromatic amine. The exchange mechanism is studied by model compounds, and free radicals intermediates are found to be involved in the non-equilibrium stage of the exchange reaction. By taking advantage of dynamic equilibrium of aromatic Schiff base bonds, infusible and insoluble crosslinked polyacrylate is self-healed and reprocessed through rearrangement of the macromolecular networks. The reprocessed polymer is still self-healable. Either the self-healing or reprocessing is completed in air without heating. Considering that Schiff base polymers have shown diverse properties and stimulus-response behaviors, activation of dynamic exchange of the inherent Schiff base bonds would result in a series of novel functionalities. More interestingly, traditional crosslinked polymers might thus be provided with a facile way of being smarter.

Introduction

Self-healing polymers have been substantially studied in recent years to autonomically recover the cracks created during manufacturing and/or usage.[1-3] Unlike extrinsic self-healing that requires incorporation of healing agent-loaded microcapsules[4] or micropipelines,[5,6] intrinsic self-healing takes effect by means of intramolecular interaction. So far, the available functioning units of the latter strategy include reversible non-covalent and covalent bonds.[7] The former involves hydrogen bonding,[8] π-π stacking,[9] ionic interaction,[10] host-guest interaction,[11] metal-ligand coordination,[12] and supramolecular interaction,[13] while the latter deals with Diels-Alder (DA) reaction,[14] imine bonds,[15-22] trithiocarbonate,[23] thiuram disulfide units,[24] disulfide-thiol exchange reactions,[25] disulfide metathesis,[26] coumarin derivatives,[27] alkoxyamine moieties,[28] siloxane equilibration,[29] transesterification,[30,31] diarylbibenzofuranone links,[32] Ru-catalyzed olefin metathesis,[33,34] urea bonds,[35] transalkylation exchanges of C–N bonds,[36] and boronic ester linkages.[37,38]

Comparatively, reversible covalent bonds are more suitable for constructing self-healing polymers towards structural application owing to their stronger nature. In addition, dynamic reversible reaction, during which the reversible processes synchronically occur, is preferentially favored for self-healing, because the healing can be completed in a single-step fashion,[24-26,28,30-37] rather than the two-step mode required by conventional reversible reaction like DA reaction.[14] In a polymer built up by dynamic reversible covalent bonds, although a great deal of the covalent bonds are disconnected at any time in the course of crack healing, meanwhile the rest covalent bonds keep on being connected. Accordingly, the possible collapse of the material due to fission of all reversible bonds[39] is prevented and the material can maintain its integrity and load-bearing capability.

Herein, for the first time, we report that catalyst-free dynamic reversible exchange is able to operate at room temperature between single type of aromatic Schiff base bonds, i.e. specific imines containing carbon–nitrogen double bond with the nitrogen and carbon atoms connected to aryl groups. On the basis of this finding, a simple self-healing chemistry is developed, which takes advantage of both reversible C=N covalent bonds and their dynamic reaction. Although Zhang et al. have introduced Schiff base bond into self-healing gels,[17] it does not carry aryl groups on both nitrogen and carbon atoms, as the aromatic Schiff base bond defined above. They actually made use of reversible reaction between Schiff base bond products and aldehyde and amine reactants, rather than reversible exchange between Schiff base bonds themselves. The forward and reverse reactions took place under different conditions (e.g., pH) in their gels. In

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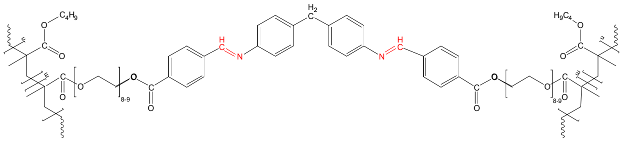
contrast, dynamic reversible exchange of Schiff base bonds should allow for efficient shuffling of the carbon-nitrogen double bonds at a constant condition (e.g. room temperature for the present case), so that fractured surfaces of the polymer containing Schiff base bonds as inter-chain linkages can be covalently re-bonded without manual intervention soon after damaging. Chow et al. synthesized several dynamic imine polymers displaying constitutional dynamics by reorganization and exchange of the monomers in the polymer chains through bond recombination between their dialdehyde and diamine components under solvent/heating stimuli.[40] Aromatic imine was included in two polymers, but reshuffling of the chains were only revealed among different imine polymers rather than in single aromatic imine polymer.

In this work, polyacrylate is modified to bring in aromatic aldehyde group (Fig. S1 and S2, ESI†), and then reacts with 4,4'-diaminodiphenyl methane, forming aromatic Schiff base bonds crosslinked networks (Scheme 1 and Fig. S3, ESI†). The condensation reaction between aromatic aldehyde and amine is completely forward under suitable conditions, producing stable networks without reverse reactions. Meanwhile, the exchange reaction between aromatic Schiff base bonds can be activated at room temperature. Based on the dynamic reversible exchange of aromatic Schiff base bonds, the polymer has acquired the ability of self-healing and reprocessing. Compared with conventional covalent bonds, Schiff base bonds are created in mild reaction condition without by-products. Molecular assembly based on Schiff base bonds exhibits interesting stimulus-response behavior.[41] By exploring the mechanism involved in the dynamic reversible exchange of aromatic Schiff base bonds and its application in self-healing and reprocessing of crosslinked polymer, a new platform for constructing smart responsive and adaptive materials is hoped to be established.



Scheme 1. Crosslinked aldehyde-functionalized polyacrylate (PA-SH).

Results and discussion

Schiff base can be synthesized from an aliphatic or aromatic amine and a carbonyl compound by nucleophilic addition reaction. When the carbon or nitrogen atom of C=N double bonds is attached to a phenyl or a substituted phenyl group, the Schiff base becomes a stable imine. This is true especially for the nitrogen atom carrying an aromatic chain. Imine has been known for its reversible reaction feature: bond formation and hydrolysis, where an equilibrium is established between imine/water and aldehyde (or ketone)/amine. However, no reports show that (i) dynamic reversible exchange reaction can proceed among individual aromatic Schiff bases and (ii) polymer containing single type of aromatic Schiff base unit behaves like dynamic materials, to the best of our knowledge.

To reveal the dynamic exchange feature between aromatic Schiff base bonds, a model mixture of small molecules (i.e., benzylideneaniline and N-(4-methylbenzy-lidene)-3-chloroaniline) is investigated. As shown by the high-performance liquid chromatography (HPLC) chromatograms in Fig. 1, the exchange products emerge quickly at room temperature. With a rise in time, the molar fractions of benzylideneaniline and N-(4-methylbenzy-lidene)-3-chloroaniline continuously decrease, while the fractions of the exchange products increase. The reaction approaches to equilibrium after 8 h, when the relative intensities of all peaks nearly no longer change. The exchange products lead to two peaks, which correspond to N-(4-methylbenzylidene)aniline and N-benzylidene-3-chloroaniline, respectively, as revealed by mass spectroscopy analysis (Fig. S4, ESI†). Clearly, the exchange reaction takes place without the aid of catalyst or heating.

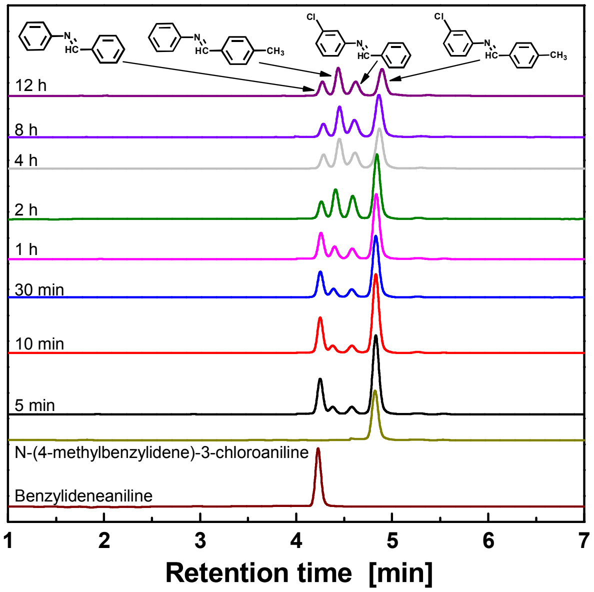


Fig. 1 HLPC chromatograms of the mixture containing equivalent amount (0.005 mol/L) of benzylideneaniline and N-(4-methylbenzy-lidene)-3-chloroaniline in methanol as a function of reaction time at 25 °C.

Owing to the lone pair electrons of its N atom, Schiff base possesses specific properties and has been used to synthesize flame retardant.[42] Additionally, the condensation product of aldehyde and amine is one of the oldest antioxidants, mainly serving as rubber stabilizer (e.g., antiager 3-hydroxybutyraldehydenaphthylamine). Since either flame retardant or antioxidant works by acting as free radical scavenger in the gas or solid phase, we assume free radicals might be involved in the above exchange reaction. Accordingly, (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) was added to the reaction system as radical trap to ascertain the underlying mechanism by means of electron spin resonance (ESR) spectroscopy.[43] If radicals existed in the system, the detected ESR signal intensity would be lower than that of neat TEMPO.

It is seen from Fig. 2 that free radicals indeed appear during the exchange reaction between single type of aromatic Schiff base compounds (i.e. N-(4-methylbenzy-lidene)-3-chloroaniline, refer to Fig. 2c) as well as between different aromatic Schiff base compounds (i.e. benzylideneaniline and N-(4-methylbenzy-lidene)-3-chloroaniline, refer to Fig. 2a and Fig. 2b). It is worth noting that radicals were not found in benzylideneaniline by the same experimental method. Because benzylideneaniline is liquid at room temperature, this phenomenon suggests that the exchange equilibrium must have been already reached and the exchange reaction is able to proceed at the equilibrium state in the absence of free radicals. The decline trend of radicals amount with time as revealed in Fig. 2 offers support to the deduction. Based on the above discussion, the possible reaction mechanism is plotted in Fig. 3.

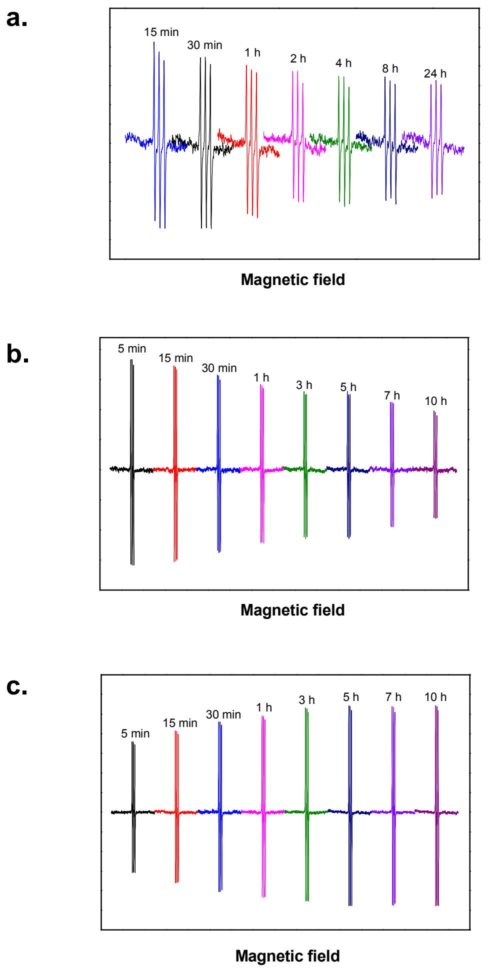


Fig. 2 Time dependences of ESR spectra of (a) mixture of TEMPO solution (0.02 wt.%) and equimolar solutions of benzylideneaniline and N-(4-methylbenzy-lidene)-3-chloroaniline in methanol (0.2 mol/L); (b) and (c) mixture of TEMPO solution (0.01 wt.%) and N-(4-methylbenzy-lidene)-3-chloroaniline solution in methanol (0.2 mol/L). For (a), TEMPO solution and solutions of benzylideneaniline and N-(4-methylbenzy-lidene)-3-chloroaniline were mixed at the same time. Afterwards, ESR spectra were acquired at certain time intervals. The plots show that signal intensity of residual TEMPO decreases with time. It means that when the reaction approaches to the equilibrium, the total amount of the free radicals generated during the exchange reaction are gradually reduced. In the case of (b), the scenario resembles (a) except that only single type of aromatic Schiff base compound is included, so that similar trend is perceived because of the exchange reaction between the same aromatic Schiff base compounds. With respect to (c), the solution of aromatic Schiff base compound in methanol was prepared in advance, allowing the exchange reaction to occur. After certain reaction time, methanol solution of TEMPO was added and ESR spectrum was immediately recorded. That is, for each data point in Fig. 2c, TEMPO solution was freshly incorporated. The detected signal intensity of the residual TEMPO is thus inversely proportional to real-time radical concentration in the system. Therefore, the increase of signal intensity of TEMPO with a rise in reaction time also reflects the decline trend of the radicals produced by the exchange reaction and confirms the conclusion drawn from Fig. 2a and Fig. 2b. Temperature: 25 °C.

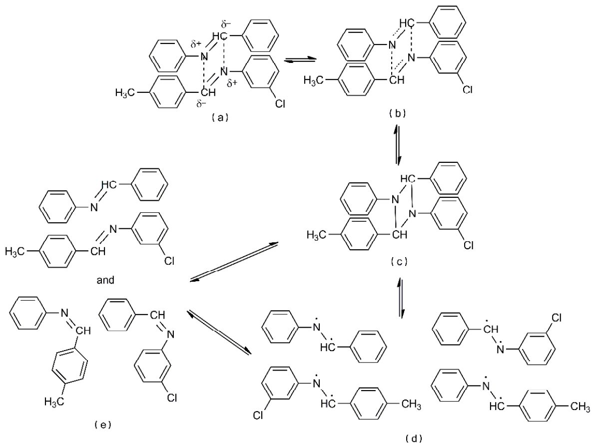
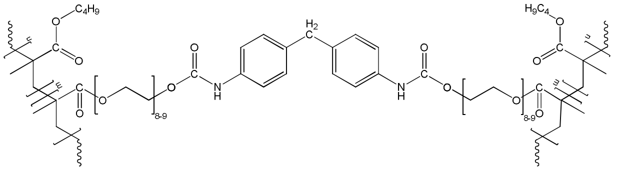


Fig. 3 Radical mediated dynamic exchange of aromatic Schiff base bonds of benzylideneaniline and N-(4-methylbenzy-lidene)-3-chloroaniline. Prior to the equilibrium, the reaction pathway consists of the following steps: (a), (b), (c), (d) and (e). After the equilibrium is reached, the reaction pathway becomes (a), (b), (c) and (e).

Actually, the two aromatic Schiff base compounds used in this work belong to conjugated system, in which π electrons are delocalized across all the adjacent aligned p-orbitals. The electronic absorption effect of chlorine atom and the lone pair electrons on the nitrogen atom of C=N double bonds lead to uneven distribution of electronic clouds. When aromatic Schiff base compounds approach one another, the p-orbitals of C=N double bonds and the delocalized electrons would overlap, creating a transition state (Fig. 3a) and its resonance form (Fig. 3b). Afterwards, a four-member-ring structure (i.e. the transition state) is built up between aromatic Schiff base compounds (Fig. 3c), which is then split into double-radical intermediates (Fig. 3d). Finally, two exchange products are obtained (Fig. 3e). According to the ESR results, it is known that the free radicals only appear in the early stage of the exchange reaction. When the reaction is equilibrated, no free radicals can be detected. The radical intermediates must be quite unstable and quickly transformed to the exchange products. It is thus reasonable to deduce that the high reaction speed at the beginning of the reaction originates from the concentration-driven effect. When the equilibrium state is approached, the reaction slows down. As a result, the high energy barrier radical intermediates are skipped, while the four-member-ring structure is directly converted to the exchange products.

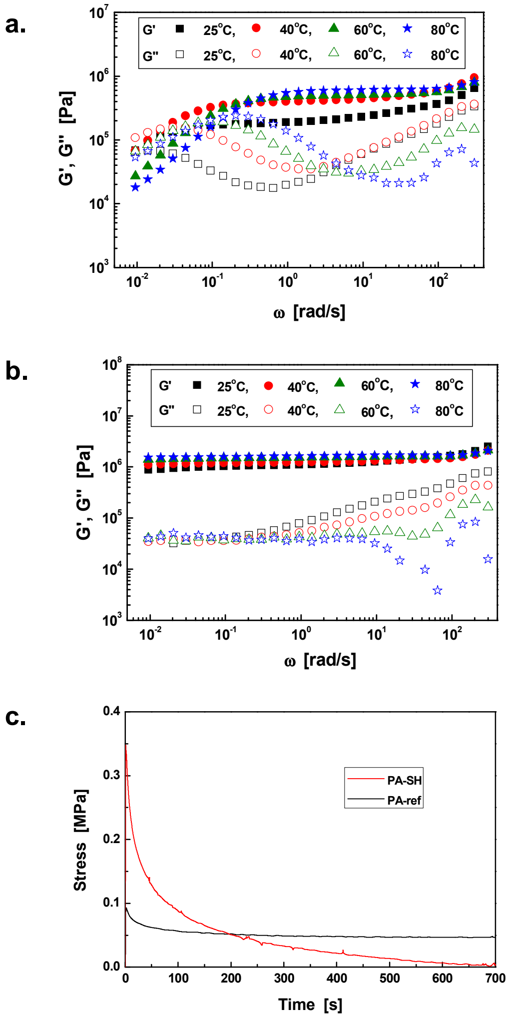
Since the dynamic exchange habit of aromatic Schiff base bonds in the absence of catalyst has been confirmed by the small molecule model study, we proceed to the study of the aromatic Schiff base bonds crosslinked polyarylate, PA-SH (Scheme 1). Fig. S5, ESI†, plots dynamic mechanical performance of the polymer in comparison with that of the control, PA-ref (Scheme 2 and Fig. S6, ESI†). Clearly, both the temperature dependences of storage modulus and tan δ keep unchanged during the cyclic tests. It means that (i) the polymer has been fully cured and the yield of imine bonds is almost 100 %, and (ii) all ruptured aromatic Schiff base bonds can be rapidly recovered due to the dynamic reversible equilibrium between random disconnections and reconnections. As a result, the polymer would not be liquidized, and PA-SH behaves like PA-ref without reversible bonds. On the other hand, the molecular weight between the crosslinks of PA-SH, M_c, is estimated to be 2.1 × 10^3, which is slightly lower than the value of PA-ref, 2.7 × 10^3. The higher crosslinking density of PA-SH than PA-ref coincides with the higher peak position of tan δ (i.e. T_g) of the former (-21.2 °C) than that of the latter (-29.6 °C), but is inconsistent with their tan δ peak heights. As shown in Fig. S5, ESI†, tan δ peak of PA-SH is obviously higher than that of PA-ref. This discrepancy should originate from the transient response of the temporary dangling chains carrying disconnected aromatic Schiff base bonds in the course of synchronous dissociation/recombination of aromatic Schiff base bonds.

One thing needs to be mentioned is that PA-SH is a soft material especially because of introduction of butyl acrylate. This would help to improve molecular mobility for crack healing with high efficiency. Besides, the lower T_g of PA-ref than PA-SH is appropriate, as it means that PA-ref has higher mobility than PA-SH. Accordingly, when comparing room temperature self-healability of the two materials hereinafter, one should not correlate the lower healing efficiency of PA-ref with its chain mobility.



Scheme 2. Structure of the control polymer PA-ref.

To have deeper understanding of the material's response to the dynamic exchange of Schiff base bonds, rheological measurements were carried out as a function of angular frequency. Fig. 4a indicates that storage shear modulus, *G'*, of PA-SH is nearly independent of frequency at higher frequency regime like conventional thermosetting polymers. The insignificant decline at lower frequency regime implies that (i) the rates of disconnection and reconnection of aromatic Schiff base bonds start to synchronize with the testing frequency and (ii) the polymer partly loses elasticity due to the transient dissociation of a certain amount of aromatic Schiff base bonds. Meanwhile, loss shear modulus, *G"*, of PA-SH firstly decreases with decreasing frequency and then increases. At frequency lower than the crossing point of the *G'* ~ T and *G"* ~ T curves, *G'* < *G"*, meaning the crosslinked networks of PA-SH are changed from elastic-like to viscous-like solid. It means that it has to take longer time for the disconnected networks to be reconstructed through dynamic exchange of aromatic Schiff base bonds under low angular frequency. Consequently, viscous-like behavior plays the leading role.



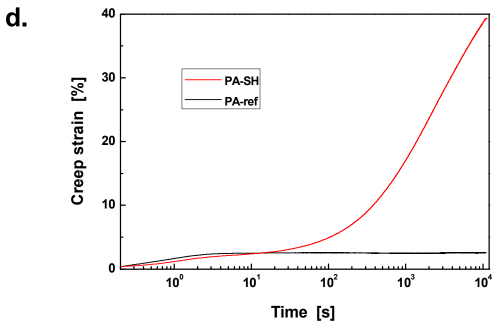


Fig. 4 Storage shear modulus, *G′*, and loss shear modulus, *G″*, as a function of angular frequency, *ω*, for (a) PA-SH and (b) PA-ref. (c) Stress relaxation and (d) creep behaviors of PA-SH and PA-ref.

A careful survey of Fig. 4a reveals that the crossing frequency of *G′* = *G″* increases with a rise in temperature. Higher temperature favors appearance of the viscous characteristics. This is reasonable as the crossing frequency of *G′* = *G″* is related to the dissociation rate constant of reversible networks.[44] The exchange reaction among aromatic Schiff base bonds is always accelerated at elevated temperature, so that the crosslinked polymer becomes viscous-like at higher frequency under higher temperature.

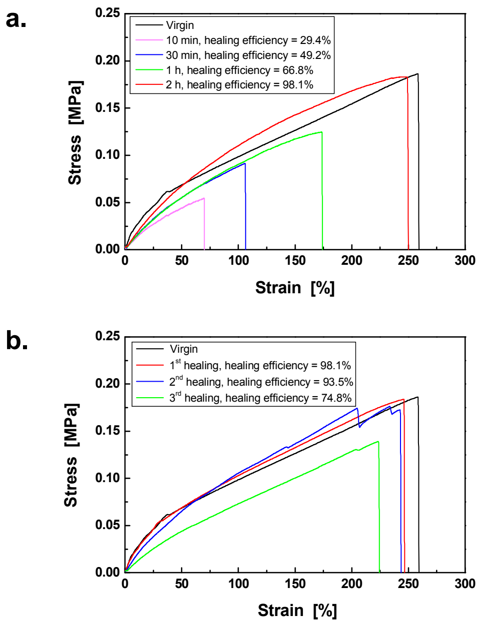
The rheological performance of the control material, PA-ref, which does not contain any reversible bond, forms sharp contrast to that of PA-SH. As exhibited in Fig. 4b, *G′* of PA-ref is almost constant within the entire frequency range of interest. No matter how *G″* changes with frequency, it is always lower than *G*′. These habits are peculiar to polymers with permanent covalent bonds, and further reflect the importance of dynamic exchange of aromatic Schiff base bonds in the time and temperature dependent mechanical properties of PA-SH.

The results of Fig. 4a demonstrate the variation in mechanical performance of PA-SH as a result of network rearrangement under dynamic shear loading. If such a network rearrangement induced by exchange of aromatic Schiff base bonds does exist, the polymer should also respond to long term static loading. The stress relaxation and creep behaviors illustrated in Fig. 4c and 4d prove that it is true. As shown in Fig. 4c, there is complete stress relaxation after about 800 s (i.e. the stress relaxes to 0) in the case of PA-SH. The crosslinked networks in the polymer must have been rearranged to reach a less stretched state during stress relaxation.[26] Comparatively, PA-ref lacks this mechanism and can only conduct limited stress relaxation through conformation change. The material is allowed to bear certain equilibrium stress for long time.

Similarly, the result of creep test of PA-SH (Fig. 4d) exhibits that the creep rate gradually decreases with time at the beginning and then increases rapidly, entering unstable development phase. With respect to PA-ref, however, its creep strain remains unchanged within the most time range of the experiment, except for the initial deformation arising from movement of crosslinks and chain segments. It is evident that the crosslinked networks of PA-SH keep on managing to accommodate the applied force in terms of rearrangement through exchange of aromatic Schiff base bonds. When a few disconnected aromatic Schiff base bonds fail to be reconnected due to reduced collision probability at larger deformation, stress concentration would inevitably occur and lead to irreversible failure of the polymer. As for PA-ref, the permanent crosslinked networks prohibit plastic flow at room temperature. Therefore, its creep rate and creep strain are far lower than those of PA-SH.

The above results and discussion reveal the effect of aromatic Schiff base bonds exchange in intact crosslinked polymer, which is also supposed to function in damaged material for re-bonding cracks. The simple qualitative examination in Fig. S7, ESI† shows this is the case. Here the PA-SH specimen was cut, recombined and healed. Eventually, it can still bear load like the original version. It is thus known that PA-SH can be self-healed at room temperature in air.

The curves in Fig. 5 further quantify the self-healability of PA-SH. With a rise in healing time, tensile strength of healed specimen approaches to that of the virgin one (Fig. 5a). After 2 h, strength of the healed version almost reaches the equilibrium value. According to the results of Fig. 5a, 24 h is set as the constant healing time for the subsequent tests to ensure complete healing. Fig. 5b verifies the multiple healability of PA-SH. The specimen can be repeatedly self-healed as other intrinsic self-healing polymers. The decline of healing efficiency for the 3rd healing event is due to the fact that the distorted fracture surfaces fail to be perfectly aligned and recombined. The smaller effective contact area would certainly reduce the number of reconnected bonds at the interface, and hence the healing efficiency decreases.



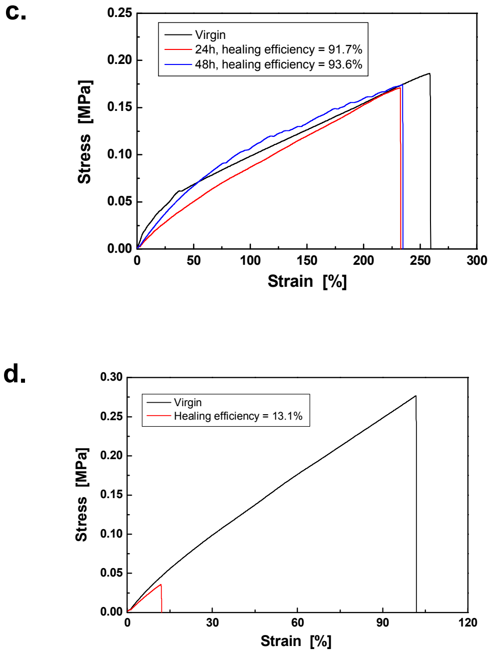


Fig. 5 Typical tensile stress-strain curves of virgin and healed PA-SH: (a) effect of healing time, (b) effect of repeated repair (Because tensile strength of the virgin specimen was not fully restored, the reconnected interface became the weakest part, and had to break again during the subsequent tensile tests. This ensured that the second and third tensile failures happened to the same healed portion), and (c) effect of waiting time taken for intentionally separating the broken specimens before recombination. (d) Typical tensile stress-strain curves of virgin and healed PA-ref. Healing conditions: 25 °C in air. Healing times for (b), (c) and (d): 24 h.

To identify the predominant healing mechanism, two control healing tests were made. First, the specimen of PA-SH was cut and recombined for healing after waiting times of 24 and 48 h, respectively. If hydrogen bonding governed the crack healing, the measured healing efficiency would be rather low in this case, as the neighboring free hydrogen bonds on the same fracture surface should have been preferentially combined with each other.[8] Fig. 5c shows that it is not true. The healing efficiencies are not affected by the waiting time and are close to the values reported in Fig. 5b, where the broken specimens were immediately rejoined for healing. Secondly, the specimen of PA-ref was also cut and healed like PA-SH under the same circumstances. The healing efficiency is only 13 % (Fig. 5d), which should primarily contributed by both dangling chains and hydrogen bonding. Based on these findings, we know that the dynamic exchange of aromatic Schiff base bonds is mainly responsible for the self-healing capability of PA-SH.

In fact, Fig. 5c demonstrates an important feature of dynamic exchange of aromatic Schiff base bonds. That is, the exchange reaction is always in dynamic equilibrium so that the number of aromatic Schiff base bonds available for healing does not change whether the cut surfaces are in contact with each other or not. In this context, rearrangement of the aromatic Schiff base bonds crosslinked networks is carried out throughout PA-SH all the time at room temperature. So long as the surfaces of different PA-SH specimens come into contact, the exchange reaction of aromatic Schiff base bonds would take place not only in the bulk but also across the interface forming new interaction. This habit would thus enable reprocessing of the crosslinked polymer without the need of depolymerization.

Under the guidance of the analysis, PA-SH specimens were cut into small pieces (Fig. 6a), which were then compression molded in air at room temperature under 4.5 MPa for 12 h. Eventually, an intact sheet was recovered (Fig. 6b). The recovered PA-SH possesses almost the same mechanical properties as the original one (cf. Fig. 6c and Fig. 5a). In addition, the recovered PA-SH also has repeated room temperature remendability (Fig. 6c). The results well agree with the prediction based on the principle of dynamic reversible bonding. Similar room temperature reprocessability is also available for cross-linked epoxidized polysulfide via disulfide metathesis.[26]

Reclaiming of traditional crosslinked polymer used to break down the irreversible covalent bonds. The decomposed products are hard to be converted into their original version. Here the solid state reprocessing by means of reshuffling of the dynamic crosslinks provides a facile and energy-saving solution with attractive application potential.[45] Therefore, thermosetting polymer might thus be born with both self-healabiliy and recyclability.

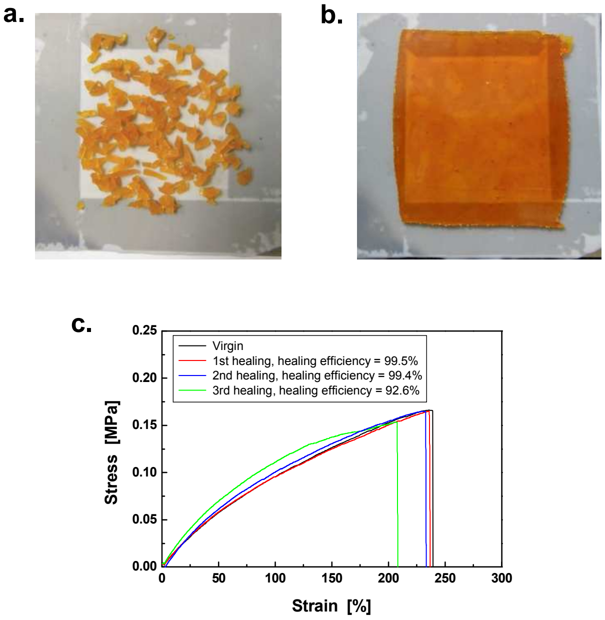


Fig. 6 (a) Fragments of PA-SH. (b) PA-SH sheet remolded from (a) at room temperature. (c) Typical tensile stress-strain curves of recycled PA-SH subjected to successive breakage and healing events. Healing temperature = 25 °C; healing time = 24 h.

Conclusions

Dynamic exchange of aromatic Schiff base bonds is allowed to proceed in air at room temperature in the absence of catalyst. Free radicals prove to be involved in the exchange reaction. By incorporating aromatic Schiff base bonds into polyacrylate as intermolecular linkages, dynamically reversible crosslinked networks are built up. Accordingly, the polymer acquires catalyst-free self-healability and reprocessability without the need of manual intervention through rearrangement of the crosslinked networks as a result of dynamic exchange of the Schiff base bonds. Although the synthesis and structure of the aromatic Schiff base bonds crosslinked polymer have not yet been optimized, the results of the present work evidence the feasibility of the concept.

Schiff base polymers (or polyazomethines) have been known for their ability to form metal chelates and supramolecular interactions with electrophyles, fiber-forming ability, good thermal stability, semiconductivity, photoelectric properties, and liquid crystal performance, etc.[46-49] Moreover, Schiff base bond has successfully acted as stimuli-responsive group in various polymers, and Schiff base compound is an epoxy curing agent used for underwater and damp environment. Exchange of aromatic Schiff base bonds would be inevitably accompanied by changes in the conjugated molecular chains and energy state. When the present free radical mediated dynamic exchange reaction is activated in these polymers, a wide variety of novel functionality would be aroused due to hybrid effect, in addition to the self-healability and reprocessability. In this context, the outcomes of the present work offer a general platform for developing a family of new smart materials.

Acknowledgements

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Catalyst-free dynamic exchange of aromatic Schiff base bonds and its application to self-healing and remolding of crosslinked polymer

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Crosslinked polyacrylate is self-healed and reprocessed through rearrangement of the networks based on catalyst-free dynamic exchange of aromatic Schiff base bonds.