Macromolecules

Room-Temperature Self-Healing Polymers Based on Dynamic-Covalent Boronic Esters

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Supporting Information

ABSTRACT: Cross-linked polymers constructed with dynamic-covalent boronic esters were synthesized via photoinitiated radical thiol—ene click chemistry. Because the reversibility of the boronic ester cross-links was readily accessible, the resulting materials were capable of undergoing bond exchange to covalently mend after failure. The reversible bonds of the boronic esters were shown to shift their exchange equilibrium at room temperature when exposed to water. Nevertheless, the materials were observed to be stable and hydrophobic and absorbed only minor amounts of water over extended periods of time when submerged in water or exposed



to humid environments. The facile reversibility of the networks allowed intrinsic self-healing under ambient conditions. Highly efficient self-healing of these bulk materials was confirmed by mechanical testing, even after subjecting a single site to multiple cut-repair cycles. Several variables were considered for their effect on materials properties and healing, including cross-link density, humidity, and healing time.

INTRODUCTION

Polymeric materials constructed via dynamic-covalent bonds with sufficient chain mobility have the capacity to demonstrate reversible equilibria^{1,2} in the solid state, which may have broad implications for the design and development of smart materials.³ Many recent reports in the literature detail the exploitation of dynamic-covalent bonds to effect self-healing behavior.⁴⁻⁹ Progress in this arena fundamentally expands the macromolecular hypothesis as stated by Flory¹⁰ and originally published by Staudinger.¹¹ Indeed, as the field of dynamic polymers expands, the covalent structure of polymers is no longer solely responsible for the unique characteristics and properties of novel polymers. Rather, the additive effects of reversible bonds can lead to new properties and structurally dynamic polymers,3 which are defined by Rowan and coworkers to be macromolecules with macroscopic responses to changes at a molecular level due to reversible chemistry.³ With these new capabilities, novel functions and applications, such as reconfigurable surfaces,¹² robust recyclable materials, and selfhealing coatings, are attainable.¹³

Self-healing based on reversible bonds can occur via two pathways, depending on the end condition and time scale of the damage. Macroscopic failure can often be prevented by the preemptive healing of microscopic damage as it forms.^{14–16} On the other hand, healing of macroscopic damage can be either externally triggered to heal or internally induced via shape memory^{17–20} by placing the edges of the damaged interfaces in close proximity to allow bond exchange. Both routes can prolong material lifetime and may allow repeated healing.

Although there have been recent reports of gels that undergo healing by exchange of dynamic-covalent bonds,²¹⁻²⁵ there are relatively few examples of dynamic-covalent chemistry being applied toward materials that can self-heal in the bulk. Healing of macromolecular materials in the bulk state is arguably the most important area of self-healing, given that many polymers are typically utilized in a solventless environment. Given the diversity of dynamic-covalent bonds and the wide variety of conditions under which their exchange can be triggered, there remain many opportunities for improvement and expansion in this area. Most previous examples of bulk self-healing have relied on bond exchange externally triggered by heat or light. The earliest thermally responsive systems, prepared by Wudl and co-workers, were based on furan-maleimide Diels-Alder chemistry with temperatures greater than 115 °C needed for healing.^{26,27} However, exposure to high temperatures is often not feasible or desirable for many applications, which has led to other approaches being explored to induce healing. For example, Klumperman and co-workers developed a healing process based on a thiol-disulfide exchange mechanism at 60 °C.^{28,29} Although this approach proved highly successful for the preparation of healable materials, the concentration of thiols was observed to decrease over time under an ambient atmosphere because of continuous oxidization of thiols to disulfides. Alkoxyamines have also been considered as

Received: January 30, 2015 Revised: March 10, 2015 thermoreversible dynamic-covalent bonds that can bring about self-healing behavior. However, the radical products of alkoxyamine dissociation are also sensitive to oxygen and high temperatures (90–130 °C), which are typically required to induce dissociation of the labile O-C bond.^{30,31} There have been only limited reports of healing via photoirradiation of alkoxyamines at room temperature.³² Like thiol-disulfide exchange, the efficiency of alkoxyamine healing is expected to decrease with time, in this case, due to the inevitable irreversible combination of carbon-centered radicals. Alternatively, in one of the earliest reports that relied on a light trigger, Chung and co-workers achieved covalent healing by the photoinduced [2 + 2] cycloaddition of cinnamoyl groups to reversibly form a cyclobutane derivative.³³ More recently, trithiocarbonate moieties were employed by Matyjaszewski and co-workers in the first example of macroscopic fusion from UVinduced healing.34

While photo- and heat-induced dynamic-covalent chemistries have proven valuable in many self-healing systems, autonomous healing with no external trigger is often desirable. Fewer examples exist of bulk systems being healed with no significant outside stimulus being necessary. In most of these cases, such healing typically occurs as a result of the stimuli being present under ambient conditions (i.e., ambient light or heat). For example, the relatively stable radicals from thiuram disulfide have been employed for visible-light self-healing over a 24 h period, which succeeded efficiently in air as long the damaged pieces had not been separated for an extended time.³⁵ Ghosh and Urban developed a UV self-repairing polyurethane based on oxetane rings capable of scratch healing within an hour, only needing power densities similar to sunlight.^{36,37} Other previously reported materials rely on the heat present at room temperature to induce healing. However, some of these systems require the presence of catalysts in the bulk matrix. For example, Lehn and co-workers designed a double dynamic bisimino carbohydrazide polymer infused with acid catalyst that healed at room temperature in bulk.³⁸ Similarly, disulfide metathesis can also cause healing at room temperature with the aid of an aliphatic phosphine catalyst.³⁹ Catalyst-free approaches comprise an even smaller subset of strategies to achieve bulk healing at room temperature. Preliminary investigations qualitatively suggest room-temperature selfhealing can occur through tailor-made Diels-Alder moieties.⁴⁰ Furthermore, Odriozola and co-workers have demonstrated a compelling example of room-temperature intrinsic self-healing in the solid state due to aromatic disulfide metathesis;⁴ however, this material relies largely on reversible supramolecular hydrogen bonds for healing instead of reversible covalent bonds. We are interested in exploiting new dynamiccovalent chemistries for intrinsic self-healing in bulk under ambient conditions.

For this purpose, we were interested in boronic acids, which are known to form a variety of dynamic-covalent bonds.^{42–44} For example, the dehydration of boronic acids to form boroxines is readily reversible by hydrolysis. Boroxine formation has been employed to prepare a number of dynamic-covalent assemblies.^{45–47} The direction of the boroxine/boronic acid equilibrium can be readily controlled by temperature, the addition of Lewis bases, or the addition of water. Boronic acids are also capable of forming dynamiccovalent bonds by reacting with diols, typically either in basic aqueous media or in anhydrous organic solutions to form boronate esters or boronic esters, respectively. Our group has demonstrated that boronic ester-based macromolecular stars can be rendered dynamic in organic solutions.⁴⁸ Boronate esters have also been employed to prepare self-healing hydrogels, wherein covalent healing can be effected by formation of new boronate ester bonds along the interface of damage.^{21,49–54} Esterification of boronic acids can also be exploited to bring about mending in the absence of water. Lavigne and co-workers have prepared dynamic-covalent linear polymer chains by polymerization of low molecular weight bisdiols with diboronic acids.⁴³ The resulting polymers were hydrolyzed in organic solution, isolated by drying, and restored back to the original molecular weight under vacuum.

As compared to these previous reports, we were interested in using boronic esters for self-healing of networks in the bulk, reasoning that these linkages may be ideal for self-healing because they can be rendered dynamic at room temperature under ambient conditions. We reasoned that hydrolysis of surface-exposed boronic esters in a bulk material could occur by intentionally wetting the surface at the site of damage (or from water present in the atmosphere under ambient humidity) to induce exchange of boronic esters to heal the material by covalent bridge formation across the damage interface. Accordingly, a boronic ester diene was synthesized and incorporated into a network by a radical-based thiol-ene process. The bulk behavior of these networks was investigated for their self-healing properties that arise from the dynamiccovalent nature of their boronic ester cross-links. The polymeric networks were capable of bulk-state healing at room temperature, suggesting they may hold promise for various applications, including being used as coatings, composites, and biological materials.

EXPERIMENTAL SECTION

Materials. Divinylbenzene (Sigma-Aldrich, 80%) was passed through a column of basic alumina. Dimethyl sulfoxide- d_6 (*d*-DMSO, Cambridge Isotope, 99.9% D) was dried overnight over 4 Å molecular sieves. Dichloromethane (DCM, Sigma-Aldrich) was dried using an anhydrous solvent system (Innovative technologies). 4-Vinylphenylboronic acid (VPBA, Combi-blocks, 98%), 3-allyloxy-1,2-propanediol (Acros Organics, 98%), pentaerythritol tetrakis(3-mercaptopropionate) (PTMP, Sigma-Aldrich, 95%), 3,6-dioxa-1,8-octanedithiol (DODT, TCI America, 95%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Sigma-Aldrich, 99%), potassium chloride (BDH, 99%), sodium chloride (Fisher, 99%), potassium acetate (Macron Chemicals, 99%), deuterium oxide (D₂O, Cambridge Isotope, 99.9% D), and molecular sieves (4 Å, Mallinckrodt) were used as received.

Instrumentation and Analysis. ¹H NMR (500 MHz), ¹³C NMR (125 MHz), and ¹¹B NMR (160 MHz) spectra were recorded using an Inova 500 spectrometer. For ¹¹B NMR spectroscopy, 5 mm thinwalled quartz NMR tubes were used. Chemical shifts are reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm). Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High-resolution mass spectrometry (HRMS) was conducted with an Agilent 6220 TOF-MS mass spectrometer in the Direct Analysis in Real Time (DART) mode with the IonSense DART source. Infrared spectra were collected on a Thermo Nicolet 5700 FTIR spectrometer equipped with a single bounce diamond stage attenuated total reflectance (ATR) accessory. Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q1000 equipped with a liquid nitrogen cooling accessory and calibrated using sapphire and high-purity indium metal. All samples were prepared in hermetically sealed pans (4-7 mg/sample) and were referenced to an empty pan. A scan rate of 10 °C/min was used. Glass transition temperatures were evaluated as the midpoint of a step change in heat



Figure 1. (a) Dynamic equilibrium of the boronic ester diene. (b) 1 H NMR spectrum of a solution of the boronic ester in *d*-DMSO before and after the addition of D₂O.

capacity. Thermal experiments were conducted as follows: samples were heated through 50 °C, followed by cooling at 10 °C/min to -80 °C, and then heated through 50 °C at 10 °C/min. Data reported reflects the average of the second and third heating scans. Stress/strain properties of all network compositions were measured on a standard Instron testing machine (No. 4204) using test specimens in the form of dog bones according to ASTM standard and procedure (D 638). The gauge length was 50.0 mm, and the crosshead speed was 10 mm/ min at 25 °C and 50% humidity. The data reported are the averages of five measurements. The UV lamp used for photocuring was a UVP Blak-Ray Model B100AP at 365 nm with 8.9 mW/cm².

Synthesis of 4-((Allyloxy)methyl)-2-(4-vinylphenyl)-1,3,2-dioxaborolane (VPBE). 4-Vinylphenylboronic acid (24.4 g, 165 mmol) and 3-allyloxy-1,2-propanediol (19.8 g, 150 mmol) were stirred in dry DCM (200 mL) with molecular sieves (4 Å, ca. 20 g) at room temperature. The progress of the reaction was monitored by ¹H NMR spectroscopy, and additional molecular sieves were added as needed to drive the reaction to completion. After confirming reaction completion, VPBE was purified by filtering, centrifuging, filtering again, and concentrating to give the final colorless-to-pale yellow liquid (30.4 g, 125 mmol, 83%). The product was characterized by ¹H NMR and 13 C NMR spectroscopy. ¹H NMR (500 MHz, *d*-DMSO): δ (ppm) 7.68 (d, 2H), 7.50 (d, 2H), 6.76 (dd, 1H), 5.92 (d, 1H), 5.87 (m, 1H), 5.34 (d, 1H), 5.24 (d, 1H), 5.13 (d, 1H), 4.73 (m, 1H), 4.37 (dd, 1H), 4.08 (t, 1H), 4.01 (m, 2H), 3.56 (m, 2H). The boron-bound carbon was not observed due to quadrupolar relaxation. ¹³C NMR (125 MHz, *d*-DMSO): δ (ppm) 140.0, 136.5, 135.0, 134.8, 125.7, 116.5, 115.7, 75.9, 71.4, 71.4, and 67.5. 11B NMR (160 MHz, d-DMSO): δ (ppm) 35.2. ESI-HRMS: Calcd for [M + Na⁺]: 266.1199. Found: 266.1187. Elemental analysis: Calcd for C14H17BO3: C, 68.89%; H, 7.02%. Found: C, 68.82%; H, 7.08%.

Model Degradation of VPBE. VPBE (40.0 mg, 0.164 mmol) was dissolved in dry *d*-DMSO (0.7 mL). After the ¹H and ¹³C NMR spectra were obtained, D_2O (0.050 mL, 2.5 mmol) was added to the NMR tube, and ¹H and ¹³C NMR spectra were recorded again after the solution was mixed well.

Synthesis of Thiol–Ene Networks. Ratios of VPBE, DODT, PTMP, and DMPA at targeted ratios were mixed and then sonicated for several minutes until a homogeneous solution was formed. Reaction size scale was typically 1–5 g total with vinyl to thiol

functionalities being maintained in a 1:1 ratio. Networks with different ratios of DODT and PTMP were prepared. The samples had either 25:75, 50:50, or 75:25 of the thiol equivalence coming from DODT:PTMP. All reactions used 1 wt % DMPA. The same procedure was followed for the reference material made with divinylbenzene in the place of VPBA. The solution was then transferred to pre-formed molds and cured for 30 min while being irradiated at 365 nm, rotating periodically to ensure uniform curing from the top and bottom of the samples. This same procedure was followed for all networks. ATR-FTIR spectroscopy was used to monitor thiol conversion using the S–H absorption peak at 2590 cm⁻¹. Thermal characterization of the final materials was performed by DSC.

Water Absorption of Networks. Three samples with compositions of 75:25 DODT:PTMP were weighed and placed in vials of water at room temperature. At 24 h intervals, samples were removed, patted dry, and weighed.

Humidity Chamber Preparation. Constant humidity environments were prepared as previously reported.⁵⁵ Briefly, 23, 75, and 85% humidity atmospheres were made by filling the bottom of sealed containers with saturated salt solutions with potassium acetate, sodium chloride, and potassium chloride, respectively. These salts were selected to minimize humidity variation within our typical laboratory temperature ranges, thereby optimizing the environments for use in controlled healing experiments.

Water Contact Angle Measurements. Three samples with compositions of 75:25 DODT:PTMP were kept for 21 days in 23, 75, and 85% humidities. The samples were then removed, and the water contact angle was immediately measured with a goniometer using high-resolution video. A minimum of 5 drops was recorded per composition. Still images were isolated from the video at 0, 10, and 20 s. Mathematical fitting software (Low-Bond Axi-symmetric Drop Shape Analysis (LBADSA) Plugin for ImageJ) was used to determine the water contact angles, which are reported as averages of 5–7 measurements.

Network Healing. To evaluate healing, cured samples of all compositions were healed for varying times under ambient conditions after dabbing the cut interfaces with water and reconnecting the two individual pieces along their freshly exposed interface. Likewise, divinylbenzene control networks were cut, dabbed or immersed in



Figure 2. Synthesis of boronic ester network materials via photoinitiated thiol-ene curing.



Figure 3. FTIR spectra of the boronic ester diene, tetrathiol (PTMP), the solution prior to cross-linking, and the final cross-linked network.

water, and reconnected for more than 3 days. Healing was also attempted for all boronic ester samples over several days under ambient conditions without wetting the damaged samples prior to reconnecting. The 75:25 DODT:PTMP composition was additionally tested for healing with heat in the absence of water at 50 °C for 30 min. To assess healing quantitatively, dog-bone-shaped samples were cured in silicone molds, cut, dabbed with water, reconnected, returned to the mold, and placed in 85% humidity chambers for up to 3 days. After removal from the chambers, the samples were vacuum-dried for over 18 h and with consistent intermittent storage in a desiccator until their final weights were within 0.3 wt % of their weights before humidity exposure. For repeat damage and healing studies, samples were cut, healed, and dried for approximately 6 h before being cut and healed in the same place for several cycles. All samples were characterized by tensile testing.

RESULTS AND DISCUSSION

Monomer Synthesis and Reversibility. To demonstrate boronic esters can be used for macroscopic healing in the bulk state and to examine simple variations in the network composition, the polymer formation reaction needed to possess a few key characteristics, such as tailorability, an absence of side products, and easy processability to facilitate sample preparation. All these features can be found in reactions categorized as click chemistry.^{56–58} Specifically, we chose radical photoinitiated thiol—ene chemistry because of the readily available monomers, the potential to conduct the reaction without solvent, and mild reaction conditions that allow for ambient temperatures and the tolerance of oxygen.⁵⁹ To enable subsequent thiol—ene chemistry, we used commercially available thiols and a novel boronic ester diene.

The boronic ester diene was formed in good yields from the corresponding boronic acid and diol in dry organic media. The resulting boronic ester diene was a liquid at room temperature and miscible with common thiol—ene reagents, DODT and PTMP, and the photoinitiator. Furthermore, the diene was stable at room temperature when stored in a dry environment. Because the healing behavior of the polymeric networks was designed to exploit the reversibility of boronic esters, the monomer was evaluated in a model experiment by ¹H NMR spectroscopy under both dry and wet conditions to show the extreme shifts in equilibrium. The dry sample demonstrated clear downfield shifts of the protons near the oxygen atoms of the boronic ester and a narrowing of the distance between the two aromatic peaks relative to the starting materials. After

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adding a small amount of water and waiting for 30 s, 97% of the boronic ester was observed to have hydrolyzed to its constituent boronic acid and diol components (Figure 1), clearly demonstrating the hydrolytic reversibility of the boronic ester bonds.

Network Formation. The diene boronic ester was reacted with readily available di- (DODT) and tetrathiols (PTMP) and a photoinitiator to produce networks with boronic ester linkages between all cross-linking points (Figure 2). The cross-link density was varied by altering the ratio of the di- to tetrathiol while maintaining a 1:1 ratio of thiol to ene. The T_g of all the samples was below room temperature, suggesting the samples would have sufficient chain mobility under ambient conditions to allow efficient healing (Table S1).

Complete consumption of thiols was verified for all monomer compositions by ATR-FTIR spectroscopy.²⁸ Confirmation of the absence of excess thiols was essential to verify that healing of the resulting materials was due to boronic ester exchange and not the result of thiol-disulfide or disulfide-disulfide exchange reactions (*vide infra*), which have previously been shown to allow healing.^{28,29} Figure 3 shows the FTIR spectrum for the boronic ester, the tetrathiol, the pre-cross-linked solution, and the network after curing. The S-H absorbance peak completely disappeared after curing, suggesting the thiol-ene cross-linking reaction was essentially quantitative and that the network-forming monomers completely reacted to give a highly cross-linked product.

Network Characterization. The cured samples were insoluble in dry DMSO, THF, and acetone-all solvents that were previously demonstrated to be good for the precursor monomer components. This transition in solubility offered further evidence of the cross-linked network structure. Because the reversibility of the boronic ester functionality is hydrolytically driven, we examined the network stability and interaction with water. Despite the lability of the boronic ester cross-links, samples completely immersed in water were stable and did not degrade over a period of 60 days, though prolonged immersion did result in more significant creep. The samples also absorbed a small amount (<10%) of water during this time (Figure 4), and while this amount was greater than would be theoretically necessary to hydrolyze all of the boronic esters, the persistent stability of the samples suggests the relative hydrophobicity of the networks was sufficient to retard infiltration of water to



Figure 4. Water absorption of disk-shaped samples of boronic estercross-linked network materials (DODT:PTMP = 75:25) completely submerged in water as a function of time.

preserve the boronic ester cross-links and prevent overall material degradation.

To more thoroughly assess the response of the material to aqueous environments, a series of water contact angle measurements were performed on samples equilibrated for 21 days at three different humidities (Figure 5). These samples were then removed to ambient conditions and immediately tested. The initial contact angles $(95^{\circ}-103^{\circ})$ revealed the hydrophobicity of the networks. Interestingly, the measured contact angles decreased with time, a behavior often associated with surface rearrangement. However, given the expected uniform distribution of polar groups within the network and the results of the water absorption experiments, we attribute the reduction in contact angle to be at least partly the result of droplet absorption during the measurement. This hypothesis was supported by the fact that the samples aged in the most humid environment (85% humidity) prior to analysis demonstrated the least change in contact angle over time, as the outer surface of the material already had sufficient opportunity to absorb water from the humid atmosphere in which it was previously stored. On the other hand, the sample aged at 23% humidity demonstrated the most significant change in contact angle, which is consistent with it being initially drier. The drier samples also demonstrated lower initial contact angles, which we attribute to water absorption occurring immediately upon contact with water thereby complicating the absolute measurement of contact angle. If the change in contact angle was the result of increased polarity due to surface rearrangement, the samples aged at higher humidity would be expected to be the most hydrophilic initially.

Self-Healing. Given the reversibility and exchange of boronic esters in the presence of water, we reasoned the networks might be capable of self-healing when damaged. In this case, the envisioned healing behavior would arise from boronic esters present at the interface of a cut exchanging with those on the adjacent surface to span the divide at the site of damage. Healing was first explored qualitatively (Figure 6). Disklike samples were cut and separated, and their newly revealed cut surfaces were dabbed with 2-3 drops of water before being placed back in contact with one another. We expected the addition of water to the freshly cleaved surfaces could shift the equilibrium of surface-exposed boronic ester groups toward the disassociated state so that the resulting free boronic acid and diol groups on each surface could more readily form bridges via bond formation across the fracture interface.⁶⁰ Additionally, because of the increased propensity for creeping when wet, moistening the surfaces prior to healing should also facilitate more intimate contact and increased chain mobility along the cut surfaces, which may help healing to occur through a "zipping-up" process starting from areas in contact.¹⁵ Interestingly, the samples were not particularly tacky when dry, so self-healing behavior would be distinct from selfadhesion in which two surfaces with reversible bonds at equilibrium are brought in contact. In this case, the bridges would only be allowed to grow slowly because of low concentrations of reactive groups present at their equilibrated surfaces.⁶⁰ It was envisioned that self-healing of these boronic ester materials would be achieved by cutting a sample and wetting its surface to create a situation far from the bulk equilibrium, with many pairs of boronic acids and diols being available to induce healing by bridge formation. Also, given that there could be preexisting finite concentration of free diol

Macromolecules

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Figure 5. Water contact angles as a function of time for a boronic ester-cross-linked network (DODT:PTMP = 75:25) equilibrated at 85, 75, or 23% humidity measured at a series of times after removal from their respective humidity chambers.



Figure 6. Self-healing of boronic ester network materials. (a) Proposed mechanism of healing. (Note that while the middle image suggests complete hydrolysis of the boronic esters at the damage interface, there may also be intact boronic esters that participate in the healing process by transesterification.) (b) Photos of the healing process for a boronic ester sample with 75:25 DODT:PTMP. (c) Control experiment demonstrating attempted healing of a network with 75:25 DODT:PTMP cross-linked via divinylbenzene, an irreversible diene.

groups within the matrix and at the cut interface, we cannot entirely exclude the possibility of healing via transesterification.

Adhesion of the two separate pieces was noticeable within several minutes, and after 3.5 days, the sample had healed to such an extent that the original scar had nearly disappeared. At the end of 4 days, the materials could be manually stretched to more than twice the original length without fracturing. The relatively long time required for healing is consistent with the theory proposed by Rubinstein and co-workers in that recovery of bonds across the fracture is the result of exchange of reactive components (i.e., boronic acids and diols) between different bonded partners.⁶⁰ The materials were also evaluated for their ability to heal without the direct addition of water to the cut surfaces under ambient conditions and in high-humidity environments (85%). While the networks healed in both cases, healing appeared to be faster and more efficient with the



Figure 7. Self-healing of boronic ester network materials as evaluated by tensile testing. (a) Representative stress-strain plot for a network with 25:75 DODT:PTMP healed for 3 days at 85% humidity. (b) Maximum stress and (c) elongation at break as a function of the relative amount of dithiol (i.e., DODT:PTMP) and healing time.



Figure 8. (a) Maximum stress and (b) elongation at break of boronic ester network materials with 75:25 DODT:PTMP after multiple cycles of damage and repair (repair conditions: 3 days at 85% humidity).

minor addition of water. As previously reported, careful realignment when contacting the cleaved pieces along the damaged interface proved to be critical.²⁸

The increased healing efficiency observed when the two freshly cleaved surfaces were wet prior to healing seemed to support the important role of bridge formation via boronic ester exchange along the surface. Additional evidence was obtained to support the proposed mechanism of healing. First of all, the absence of thiols after curing, as confirmed by FTIR spectroscopy, would seem to exclude healing by thiol disulfide exchange reactions, as has been described in previous publications.^{28,29} Additionally, when the networks were cut, adjoined without water, and heated in a dry environment, no healing was observed, further suggesting the mending process was likely not due to exchange of a small amount of disulfides or transesterification of boronic esters. Furthermore, control samples were prepared with the same thiol components but with divinylbenzene, instead of the boronic ester, as the ene component (Figure 6c). In this case, no healing was observed with or without the addition of water, even after 4 days. As compared to the networks formed with the boronic ester crosslinker, there was no stickiness along the failure interface when

the two cut pieces were placed in contact, implying that chain entanglement likely has very little role in the healing process.

Tensile testing experiments were conducted to quantify the efficiency of healing.²⁸ Three different compositions were considered (75:25, 50:50, and 25:75 DODT:PTMP), with particular attention being paid to the effect of healing time on the recovery of tensile strength and elongation at break (Figure 7). The tensile properties of the healed samples were compared to those of the original uncut material. After healing for 3 days at 85% humidity, good recovery of peak stress and strain at break was observed for all three compositions. When samples were healed for only 3 min, efficient healing was observed only for the 25:75 samples, while the 50:50 and 75:25 samples showed only partial recovery.

The samples were also investigated for their ability to heal after multiple cycles of damage and repair at the same site. These experiments were particularly important, as the ability of repeated recovery is a primary advantage of healing through a mechanism of reversible bond exchange. The material with a composition of 75:25 DODT:PTMP composition demonstrated excellent healing in up to three cycles, with nearly full

Macromolecules

recovery of tensile strength and elongation at break being observed after each cycle of repair (Figure 8).

CONCLUSION

These results indicate it is possible to achieve bulk-state selfhealing via boronic ester exchange. Repair was demonstrated to take place under ambient conditions, in the presence of air, at room temperature, and in the absence of solvent, although application of a thin layer of water to the freshly cleaved surfaces facilitated bond exchange and increased the efficiency of healing. Despite being composed of hydrolytically labile boronic esters, the materials were stable in humid environments and even when completely submerged in water. The dynamiccovalent nature of the bonds allowed healing to occur over multiple cycles, though the reversibility of all cross-links did lead to creep. Future studies will involve the incorporation of both reversible and permanent cross-links to investigate the effect on creep and healing efficiency. Beyond this work, boronic ester incorporation could be expanded to networks made by a variety of chemistries that go beyond the thiol-ene approach employed here. The reversibility of the boronic ester linkages in the bulk state also suggests this functionality may have applicability beyond self-healing, in other types of materials that rely on structurally dynamic polymers.

ASSOCIATED CONTENT

S Supporting Information

Additional DSC results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Article

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