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Photoactivated Healable Vitrimeric Copolymers

Taylor Wright,[†] Tanja Tomkovic,[‡] Savvas G. Hatzikiriakos,[‡] and Michael O. Wolf^{*,†}

[†]Department of Chemistry, 2036 Main Mall, University of British Columbia, Vancouver, BC V6T 1Z1, Canada

[‡]Department of Chemical and Biological Engineering, 2360 East Mall, University of British Columbia, Vancouver, BC V6T 1Z3, Canada

Supporting Information

ABSTRACT: A composite polymer based on vinylogous urethane vitrimer bonding with both photodimerizable and thermally exchangeable functionalities is described. Polymers containing various ratios of photodimerizable diaminoanthracene monomers and thermally exchangeable diaminoalkyl monomers linked by a common bisacetoacetate group are studied. It is demonstrated that alkyl amines undergo the necessary thermal exchange reactions for vinylogous urethane vitrimers, while aromatic amines do not. UV-induced dimerization of the anthracene units results in changes to the rheological properties



and the glass transition temperature due to polymer cross-linking. Rapid and near-complete scratch healing upon heating is demonstrated, with a tunable onset temperature for healing controlled by UV irradiation. The viability of a composite vitrimeric system, wherein vitrimeric monomers are combined with non-vitrimeric, stimuli-responsive monomers to generate random copolymers with new properties, is demonstrated.

INTRODUCTION

Vitrimers are an emerging class of polymers characterized by the presence of thermally exchangeable bonds.¹⁻³ This network rearrangement imparts high mechanical recyclability, an ability to undergo thermal healing, and rapid stress relaxation not found in conventional cross-linked systems.^{2,4,5} These systems can also exhibit shape memory effects allowing for the autonomous arrangement into complex shapes.⁶, Vitrimeric systems have been modified using additives that respond to a variety of stimuli including IR light, pH, redox conditions, electrical current, and solvent.⁸ The kinetics of the exchange reaction have also been shown to be controllable using low amounts of a variety of small molecule additives.⁹ The incorporation of functional molecular groups integrated directly into the polymeric backbone of these systems may allow for the development of multifunctional and responsive materials, but this has not been explored extensively to date. The relatively high temperature (>100 °C) at which these systems are cured in the presence of the amine, ester, and ketone functional groups that comprise vinylogous urethane vitrimers means careful consideration for functional group tolerance is required to incorporate new responsive molecules into the polymeric chain.

Polymeric systems containing anthracene units have been reported to undergo self-healing through a reversible 4 + 4 photocycloaddition reaction, allowing monomers and polymer chains to be linked and unlinked.¹⁰⁻¹³ The viscoelastic properties of hydrogels have also been dynamically altered using UV-induced dimerization of coumarin groups.¹⁴ Tunable stress relaxation in these hydrogel materials has been demonstrated to be beneficial for roles as extracellular

matrices.^{15,16} Here, we integrate photodimerizable anthracene units into a polymer system based on vinylogous urethane vitrimers, enabling phototuning of a thermally healable system. This approach opens alternative routes to control the properties of vitrimeric materials. Irradiation of the polymer permits tuning of the glass transition temperature, rheological behavior, and scratch-healing dynamics without the need for compositional modification.

In our approach, a linear vitrimeric system is cross-linked post-synthetically through the dimerization of anthracene units in the backbone of the polymer chain. The inclusion of aromatic anthracenes and aliphatic alkyl chains results in a composite polymer system with anthracenes responding to UV irradiation and the alkyl monomers undergoing vinylogous urethane exchange.

EXPERIMENTAL SECTION

Materials. All chemical reagents were purchased from commercial sources and used without further purification. 1,12-Dodecanediol (99%), 1,12-dodecanediamine (98+%), 2,2,6-trimethyl-1,3-dioxin-4one (94% containing up to 6% acetone), ethyl acetoacetate (99+%), and 1,5-diaminoanthraquinone (90+%) were all purchased from Alfa Aesar. 2-Aminoanthracene (96%) and ammonium cerium nitrate (≥98.5%) were purchased from Sigma-Aldrich.

Analytical Methods. Spectroscopy. ¹H NMR spectroscopic data were collected on a 400 MHz Bruker Avance 400dir spectrometer at 25 °C. Residual protosolvent peaks were used to reference the ¹H NMR spectra. Absorption spectra were collected on a Varian Cary

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5000 UV-vis-NIR spectrophotometer. FT-IR measurements were conducted on a PerkinElmer Frontier FT-IR instrument equipped with an attenuated total reflectance (ATR) crystal. UV irradiation of samples was performed using either a Rayonet photochemical reactor equipped with four 365 nm light sources (35 W each) or an Entela 365 nm hand lamp (6 W). Visible light irradiation of samples was performed using a commercial CFL bulb (13 W) in tandem with a Xe arc lamp (150 W).

Mass Spectrometry and Differential Scanning Calorimetry. Mass spectrometry measurements were conducted on a Waters ZQ instrument equipped with an ESCI source. Differential scanning calorimetry (DSC) experiments were performed using a TA Instruments DSC Q2000 instrument equipped with a TA Instruments RCS90 refrigerated cooling system at a ramp rate of 10 °C/min.

Compression Molding and Rheology. Compression molding of samples was performed using a Carver Laboratory Press, pressing the samples at 9 psi between two stainless steel plates at 130 °C for 15 min. Parallel plate rheology was performed on an Anton-Parr MCR 501 instrument under open-air conditions. An 8 mm top plate was used, and the gap was set at ~1 mm for all measurements. Temperatures ranged from 70 to 150 °C. Frequency sweep experiments were conducted at 0.1% strain, measuring from 0.1 to 100 Hz. Strain sweep experiments were conducted at 0.1 Hz, measuring from 0.001 to 10% strain. Stress relaxation experiments were conducted at an instantaneous initial strain of 0.5%.

Optical Images. Optical microscope images were collected on either an Olympus BX41 microscope with a CCD camera using a $\times 10$ objective lens and equipped with an INSTEC heating stage or on a Senterra Raman microscope and CCD camera capable of stitching multiple images together using a $\times 10$ objective lens. Samples were mounted on glass slides and scratched on the top surface using a razor blade.

Synthesis and Characterization. 1,12-Dodecanebisacetoacetate (2). 1,12-Dodecanediol (1.7 g, 8.4 mmol) and *m*-xylene (4.7 mL) were combined in an open vial and brought to reflux while stirring. 2,2,6-Trimethyl-1,3-dioxin-4-one (2.6 mL, 18.5 mmol) was added dropwise, and the solution was stirred at 130 °C for 35 min. The mixture was cooled to room temperature and then dried under vacuum to afford a crude oil. The oil was purified using column chromatography on silica gel with 7:3 ethyl acetate to hexanes as the mobile phase. $R_{\rm f} = 0.72$. Yield: 2.40 g (77%) of a pale yellow solid. ESCI MS: 371.3 (M–H)⁺, 393.2 (M–Na)⁺. ¹H NMR (400 MHz, (CD₃)₂SO, RT): δ 4.03 (t, J = 6.6 Hz, 4H), δ 3.58 (s, 4H), δ 2.17 (s, 6H), δ 1.54 (p, J = 6.7 Hz, 4H), δ 1.27 (m, 16H).

Compound **1a.** 2-Aminoanthracene (0.24 g, 1.2 mmol), ethyl acetoacetate (0.8 g, 6.1 mmol), and ammonium cerium nitrate (0.034 g, 0.06 mmol) were dissolved in CH₂Cl₂ (2.4 mL) and DMSO (0.8 mL). The mixture was stirred at room temperature for 2.5 h, and the CH₂Cl₂ was then removed under vacuum. Deionized water (50 mL) was added, and the mixture was sonicated for 10 min. The crude solid was vacuum filtered and rinsed with deionized water. The product was purified using flash column chromatography on silica gel with hexanes as the mobile phase. Yield: 0.128 g (34%) of a bright yellow solid. APCI MS: 306.2 (M–H)⁺, 328.1 (M–Na)⁺. ¹H NMR (400 MHz, CD₂Cl₂, RT): δ 10.66 (s, 1H), δ 8.40 (s, 1H), δ 8.34 (s, 1H), δ 7.99 (m, 3H), δ 7.64 (m, 1H), δ 7.47 (m, 2H), δ 7.25 (dd, *J* = 9.2, 2.1 Hz, 1H), δ 4.77 (d, *J* = 0.6, 1H), δ 4.16 (q, *J* = 7.0 Hz, 2H), δ 2.18 (s, 3H), δ 1.29 (t, *J* = 7.0 Hz, 3H).

Compound 1b. Compound 1a (0.056 g) was dissolved in 250 mL of 1:1 ethanol and ethyl acetate. The solution was degassed using three freeze-pump-thaw cycles and then stirred at room temperature under nitrogen for 24 h while irradiating with a 365 nm hand lamp. The solvent was then removed under vacuum to afford a dark brown solid.

Polymer Synthesis. *P1a* and *P2a*. 1,12-Dodecanediamine, 1,12dodecanebisacetoacetate, and 1,5-diaminoanthracene were combined in the indicated molar ratios (Table 1) and dissolved in a minimum amount of hot ethyl acetate and ethanol (1:1). The solution was heated at reflux for 1 h and then reduced to a minimum volume under vacuum. The solution was transferred to a silicone mold in a beaker Table 1. Relative Molar Ratios of Monomers for Polymers P1a and P2a



and heated to 70 $^{\circ}$ C in an oil bath until the solvent had evaporated. The temperature was then raised to 90 $^{\circ}$ C for 18 h and then to 130 $^{\circ}$ C for 60 min. The resulting black polymer sheets were removed intact as one piece from the warm molds.

P1c. 1,5-Diaminoanthracene (0.1 g) was dissolved in 300 mL of ethanol and ethyl acetate (1:1) and degassed using three freeze– pump–thaw cycles, followed by irradiation in the same manner as for **1b** over 3 days using a Xe arc lamp in conjunction with a CFL bulb. 1,12-Dodecanediamine (0.097 g) and 1,12-dodecanebisacetoacetate (0.34 g) were then added, and the solution volume was reduced to a minimum under vacuum. The solution was polymerized in the same manner as for **P1a** and **P2a**.

P1b and **P2b**. Samples of **P1a** and **P2a** were suspended in the middle of a Rayonet photochemical reactor using clips and irradiated on all sides for 18 h.

RESULTS AND DISCUSSION

To examine the effects of anthracene photodimerization on the β -keto enamine systems that comprise vinylogous urethane vitrimers, a model compound (1a) was synthesized via the condensation of 2-aminoanthracene with ethyl acetoacetate.

Irradiation of 1a in 1:1 ethanol:ethyl acetate to form 1b (Scheme 1) was followed using UV-vis spectroscopy (Figure

Scheme 1. Irradiation of Compound 1a (Enamine) To Give 1b (Imine)



S1). A decrease in the absorbance in the 300–450 nm region was observed with an isosbestic point at 290 nm when the sample was irradiated with 365 nm light. Compound 1a in solution and solid state strongly emitted blue light under 365 nm irradiation while 1b was nonemissive (Figure S2). These observations are consistent with 4 + 4 photocycloaddition of the anthracene units resulting in a break in the π -conjugation.¹⁷

FT-IR analysis of solid 1a and 1b showed a shift to higher wavenumber of the ester C=O stretch after irradiation (1649 to 1725 cm^{-1}) (Figure 1). This indicates a decrease in



Figure 1. Comparison of the FT-IR spectra of 1a, 1b, and ethyl acetoacetate.

conjugation with the ester, bringing it closer to the C=O stretching frequency in ethyl acetoacetate (1739 cm⁻¹). These spectral changes are in good agreement with literature values for enamine–imine tautomerization observed in quinoxalinone and pyridopyrazinone systems.¹⁸ It is proposed that the photodimerization of **1a** results in a change from the enamine to imine tautomer.

The ¹H NMR spectrum of **1a** in CD_2Cl_2 contains peaks due to the alkene proton (δ 4.77 ppm) and N–H proton (δ 10.66 ppm) that are consistent with only the enamine tautomer being present at room temperature. The spectrum of **1b** under the same conditions did not show any peaks in these two regions, and two singlets near δ 2.6 ppm are assigned to the methylene protons of the imine tautomer (Figure S3). Further analysis of the spectrum of **1b** was not performed due to the complexity resulting from the high number of possible stereoisomers.

Liebler et al. have previously examined the kinetics of the exchange reaction between aliphatic amines and β -keto enamines.² The exchange reaction between aromatic amines and β -keto enamines was examined here using a similar approach (Scheme 2).

Scheme 2. Kinetic Exchange Experiment for Aromatic Vinylogous Urethanes



Compound 1a was heated at 120 °C in d_6 -DMSO in the presence of 5 equiv of *p*-toluidine and the exchange reaction followed by ¹H NMR spectroscopy (Figure S4). Peaks matching the expected exchange product were observed, but no 2-aminoanthracene was present. In addition, the reaction stopped after only ~25% of the 1a present had reacted. Heating the sample at higher temperatures did not result in

further **1a** reacting. This result demonstrates that aromatic amines of this type do not undergo the thermal exchange reaction necessary for vitrimeric behavior and that inclusion of anthracenes in vitrimers may result in the introduction of nonexchangeable cross-links into the system after dimerization. Composite systems containing vitrimeric and non-vitrimeric portions have been reported and exhibit similar properties to systems composed entirely of exchangeable monomers.¹⁹ Composite vinylogous urethane systems containing both exchangeable alkyl diamines and nonexchangeable, photoactive anthracene diamines linked by a common bis-acetoacetate monomer were consequently prepared. Exchangeable crosslinking monomers were omitted to ensure only cross-links resulting from anthracene dimerization were present.

Polymer Synthesis. The synthesis of solid polymer sheets was performed via the thermal condensation of acetoacetate and amine monomers in different ratios, and the effects of UV irradiation on the polymer samples were studied using FT-IR spectroscopy as well as thermal and rheological measurements. 1,12-Dodecanebisacetoacetate (2) was synthesized from 1,12-dodecanediol and 2,2,6-trimethyl-1,3-dioxin-4-one,²⁰ and 1,5-diaminoanthracene (3) was synthesized by reducing 1,5-diaminoanthraquinone using Zn/Cu.²¹ Polymers containing differing amounts of anthracene were prepared by using a fixed amount of 2 and altering the ratio of 3 to 4 while maintaining a 5% molar excess of amine functional groups shown to be beneficial for vitrimeric exchange (Table 1).²

Polymers were synthesized by heating the monomer mixtures to reflux in 1:1 ethanol:ethyl acetate followed by transferring the solutions to a silicone mold. After evaporation of the solvent, the molds were heated at 90 °C overnight and then cured at 130 °C for 1 h, resulting in nearly black polymer sheets largely free of surface defects (Figure S5). Thinner samples from compression molding were seen to be red in color, consistent with the deep red color of monomer **3** in solution.

P1a was irradiated and the IR spectrum monitored as a function of irradiation time (Figure 2). After 5.5 h of irradiation no further changes were observed, and this remained the case upon continued UV irradiation up to 18 h. An isosbestic point was observed at 1665 cm⁻¹, and the peak assigned to the ester C=O stretch shifted to higher energy after irradiation (1648 to 1725 cm⁻¹). The peak at 1602 cm⁻¹ was assigned as the enamine C=C stretch and decreased in



Figure 2. IR spectra of P1a after different irradiation times at 365 nm and sample P1c containing fully dimerized anthracene units.

intensity with irradiation. A sample with the same monomer ratios as in P1a was prepared by fully dimerizing 3 prior to polymerization, and the IR spectrum of the resulting sample P1c was collected. When compared against P1c in which all anthracene units are dimerized, the FT-IR spectrum of P1b shows nondimerized anthracene units that are attributed to poor spatial overlap of some of the anthracene units preventing dimerization. The spectral changes between P1a and P1b closely match those seen in the model compounds 1a and 1b (Figure S6), and consequently enol to keto tautomerization is also proposed for the polymeric systems upon irradiation. Similar changes were observed for irradiation of P2a to P2b, with no further changes after 12.5 h of UV irradiation. The higher concentration of anthracene units in P2a requires longer UV irradiation.

Samples of P1a and P2a were compression molded to a thickness of 200 μ m to ensure full UV light penetration and then irradiated overnight. The resulting samples were characterized using differential scanning calorimetry (Figure 3).



Figure 3. DSC traces of polymer samples before and after irradiation, measured on the second heating cycle at 10 °C/min. Solid circles indicate T_{o} .

The glass transition temperature (T_g) increases from 30 °C for **P1a** to 35 °C for **P1b**, consistent with the UV irradiation resulting in cross-linking of the polymer chains. A 25 °C increase in T_g was observed between **P2a** and **P2b**, consistent with a higher concentration of anthracene units in **P2b** and therefore a greater concentration of cross-links after irradiation than in **P1a**. No decrease in T_g was observed for **P1b** and **P2b** when heated to higher temperatures, suggesting that the photodimerization is irreversible. Samples containing <0.5

relative molar ratio of anthracene were not tested as the change in T_g was expected to be negligible in these cases, given there is only a 5 °C increase in T_g from **P1a** to **P1b**.

Rheology. Parallel plate rheological studies were performed on samples before and after irradiation to probe the effect of anthracene dimerization on the flow characteristics. Experimental temperatures were adjusted between samples in accordance with the increase in T_g associated with irradiation.

As discussed above, frequency sweep experiments were conducted using a constant strain of 0.1% over a frequency range from 0.01 to 100 rad/s (Figure 4). From the low frequency region, P2a was observed to behave as a typical viscoelastic polymer (G'' > G'), consistent with its linear nature and exchangeable bonds. Although the terminal zone has not been attained, the tendency of reaching its Newtonian plateau is evident. After irradiation, the storage modulus, G', increased to above the loss modulus, G'' (G'' < G'), indicating a transition from a viscoelastic fluid to solid-like behavior, consistent with the formation of anthracene-based cross-links. Similar results were observed for P1a and P2a (Figure S7).

Previously reported vitrimeric systems exhibited rapid stress relaxation attributed to the thermal exchange of urethane bonds.^{2,9} A sudden deformation of 0.5% was applied to P2a and P2b, and their relaxation moduli were monitored as a function of time (Figure 5). Two stages in their stress



Figure 5. Stress relaxation curves for P2a and P2b under a 0.5% initial strain.

relaxation were observed for both P1 (Figure S9) and P2. Rapid relaxation occurred for the initial 300 s, during which approximately 50% (P2a) and 60% (P2b) of the applied stress



Figure 4. G', G", and η for P2a (left, 60 °C) and P2b (right, 85 °C) measured at 0.1% strain.

were relaxed nearly reaching a plateau that represents an initial elastomeric plateau modulus of the anthracene portion that initially showed solid-like behavior. After this, a slower relaxation period was observed; however, the remaining stress did not fully relax during the duration of the experimental period. The two-stage relaxation is attributed to mixed polymerization of the flexible, thermally exchangeable diaminoalkyl along with the rigid, nonexchangeable diaminoanthracene monomer. The alkyl portion of the polymer initially relaxed, followed by the slow stress relaxation of the anthracene component. This two-stage relaxation process is also evident from Figure 4 (right) where G' tends to attain a plateau before the second mode of relaxation begins. Stress relaxation at higher temperatures (>150 °C) was not pursued as the polymers became too fluid to load properly into the parallel-plate rheometer.

To test the proposal that the two-stage relaxation arises from the mixed polymerization of two different amine monomers, a polymer (P3) composed only of monomers 4 and 2 was prepared ($T_g = -15$ °C). This sample exhibited rapid stress relaxation between 120 and 150 °C, relaxing fully after 36.5 min at 120 °C and 10 min at 150 °C (Figure 6). The 120 °C



Figure 6. Stress relaxation curves and Arrhenius plot for P3 containing no anthracene units.

stress relaxation for P3 at 100 s is comparable to the amount P2b relaxes over the same time interval. The stress relaxation of vitrimers can be described by the Maxwell law (eq 1).

$$G(t)/G_0 = \exp(-t/\tau) \tag{1}$$

Relaxation times at 37% (1/e) relaxation were fit to an Arrhenius plot for P3, and the activation energy was found to be 47 kJ/mol. The reported activation energy for cross-linked vitrimers is typically ~60 kJ/mol.² The lower value for P3 is attributed to the linear nature of the polymer in conjunction with thermal bond exchange. The rapid relaxation of P3 in comparison with P1 and P2 demonstrates that the anthracene units are responsible for deviations from expected vitrimeric stress relaxation profiles.

Polymer Healing. UV penetration depth is a limiting factor for potential applications of the polymers studied here. Modification of surface properties was examined wherein the degree of anthracene dimerization can be considered consistent as a function of depth. Scratch healing experiments were conducted to demonstrate the photocontrol of vitrimeric properties. Polymer samples before and after irradiation were mounted on glass slides and scratched with a razor blade.

Samples were observed using an optical microscope and heated in 5 °C increments using a heating stage until the scratch ($\approx 100 \ \mu m$ wide initially) was observed to begin healing (Table 2). By use of optical microscopy, scratches were initially

Table 2. Composition, Glass Transition Temperature, and Scratch Healing Onset Temperature of Polymers with and without Anthracene Incorporated

sample	mol % anthracene	T_{g} (°C)	healing onset (°C)
P1a	25	30	45
P1b	25	34	50
P2a	50	23	60
P2b	50	49	80
P3	0	-15	35

observed as dark lines crossing the sample, which were seen to decrease in width during healing through a series of expansions and contractions of the material (Video S1). This behavior is consistent with previously reported examples of visually observed scratch healing.^{3,22,23}

The onset of scratch healing was observed to be a slow expansion and contraction of the polymer sample, gradually resulting in closing of the scratch (Video S2). Below the healing onset temperature (Table 2), no significant changes in scratch width or sample volume were observed. At higher temperatures (\sim 70 °C above T_{σ}) scratches in all tested polymers healed to a width of $< 5 \ \mu m$ in under 5 min with no changes in width observed on cooling. An increase in healing onset temperature is consistent with the increase in T_{σ} caused by UV irradiation. Despite the low T_g for P3, the onset of healing did not begin until ~35 °C, close to the healing onset of polymers with a much higher T_{g} . The topological freezing point transition (T_v) for vitrimers is the temperature at which network rearrangement begins to occur and is commonly in the range 30-70 °C for rigid vitrimers.^{2,24,25} Scratch healing necessitates heating to both above the T_{g} , to enable mobility of the polymer chains and above the T_{v} , to allow for network rearrangement to heal the scratch. In the case of P3, T_g is below room temperature and the healing onset above room temperature; thus, $T_{\rm v}$ can be estimated at between 25 and 35 °C.

To demonstrate the overall effect of UV irradiation on scratch healing, samples of P2a and P2b were scratched and heated on a hot plate at 60 °C (the healing onset for P2a but below that for P2b) for 10 min followed by heating at 80 °C (the healing onset for P2b) for 10 min (Figure 7).

The scratch in polymer **P2a** had an initial width of 135 μ m and healed 93% to a width of 9 μ m after treatment at 60 °C. Polymer **P2b** had an initial scratch width of 118 μ m and healed 10% to a width of 106 $\mu \rm m$ after treatment at 60 $^{\circ}\rm C$ and healed 98% (2 μ m) after treatment at 80 °C. A decrease in the darkened area of the scratch for P2b after treatment at 60 °C was observed (Figure 7d), but the width of the scratch measured from the onset of deformation does not decrease significantly. This suggests that closing of the scratch is likely occurring slowly at this temperature for the irradiated sample and from the bottom of the scratch. Depending on the depth of the scratch, this may be consistent with a reduced amount of anthracene photodimer present at the bottom of the scratch, resulting in a lower scratch healing temperature compared to the photodimerized surface. Near complete rapid healing of the scratch in P2b at elevated temperatures (Figure 7e) is

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a) 🛔 c) (135 µm) (118 µm) 60 °C 60 °C 10 min 10 min b) d) (106 µm) (9 µm) 80 °C 10 min e) (2 µm) P2a (no irradiation) P2b (irradiated)

Figure 7. Optical microscope image of (a) sample P2a initial scratch, (b) P2a after 60 °C 10 min, (c) sample P2b initial scratch, (d) P2b after 60 °C 10 min, and (e) P2b after 80 °C 10 min. Black scale bar is 300 μ m. Value in parentheses indicates approximate scratch width. Images were assembled from individual photos focused at each position.

consistent with the thermal healing of the nonirradiated sample **P2a** and demonstrated that the introduction of nonexchangeable cross-links does not disable the thermal healing of these vitrimer copolymers.

CONCLUSIONS

Composite materials based on vitrimeric bonds containing photoresponsive aromatic diamines and thermally exchangeable aliphatic diamines have been prepared. UV irradiation causes dimerization of the anthracene units, resulting in crosslinking of the material and an increase in glass transition temperature. Thermal scratch healing was observed, and the healing onset temperature was tunable using both UV irradiation and changes in composition. It was seen that aromatic amines do not undergo vinylogous urethane exchange reactions, and as such alkyl amines must be present to retain the desired vitrimeric properties. We believe that this work will lead to further integration of functional and responsive molecules into the polymeric backbone of vitrimeric materials.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b01898.

Spectral details and rheological data (PDF) Video S1 (AVI) Video S2 (AVI)

AUTHOR INFORMATION

Corresponding Author *E-mail: mwolf@chem.ubc.ca.

ORCID

Taylor Wright: 0000-0002-7224-6574 Tanja Tomkovic: 0000-0002-1144-2723 Savvas G. Hatzikiriakos: 0000-0002-1456-7927 Michael O. Wolf: 0000-0003-3076-790X

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-Like Malleable Materials from Permanent Organic Networks. *Science* **2011**, *334*, 965–968.

(2) Denissen, W.; Rivero, G.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Vinylogous urethane vitrimers. *Adv. Funct. Mater.* **2015**, 25, 2451–2457.

(3) Cho, S. H.; White, S. R.; Braun, P. V. Self-healing polymer coatings. *Adv. Mater.* **2009**, *21*, 645–649.

(4) Azcune, I.; Odriozola, I. Aromatic disulfide crosslinks in polymer systems: Self-healing, reprocessability, recyclability and more. *Eur. Polym. J.* **2016**, *84*, 147–160.

(5) Denissen, W.; De Baere, I.; Van Paepegem, W.; Leibler, L.; Winne, J.; Du Prez, F. E. Vinylogous Urea Vitrimers and Their Application in Fiber Reinforced Composites. *Macromolecules* **2018**, *51*, 2054–2064.

(6) Pei, Z.; Yang, Y.; Chen, Q.; Wei, Y.; Ji, Y. Regional Shape Control of Strategically Assembled Multishape Memory Vitrimers. *Adv. Mater.* **2016**, *28*, 156–160.

(7) Zheng, N.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Thermoset Shape-Memory Polyurethane with Intrinsic Plasticity Enabled by Transcarbamoylation. *Angew. Chem., Int. Ed.* 2016, *55*, 11421–11425.
(8) Chen, Q.; Yu, X.; Pei, Z.; Yang, Y.; Wei, Y.; Ji, Y. Multi-stimuli responsive and multi-functional oligoaniline-modified vitrimers. *Chem. Sci.* 2017, *8*, 724–733.

(9) Denissen, W.; Droesbeke, M.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Chemical control of the viscoelastic properties of vinylogous urethane vitrimers. *Nat. Commun.* **2017**, *8*, 14857.

(10) Froimowicz, P.; Frey, H.; Landfester, K. Towards the generation of self-healing materials by means of a reversible photo-induced approach. *Macromol. Rapid Commun.* **2011**, *32*, 468–473.

(11) Xu, J. F.; Chen, Y. Z.; Wu, L. Z.; Tung, C. H.; Yang, Q. Z. Dynamic covalent bond based on reversible photo [4 + 4] cycloaddition of anthracene for construction of double-dynamic polymers. *Org. Lett.* **2013**, *15*, 6148–6151.

(12) Radl, S.; Kreimer, M.; Griesser, T.; Oesterreicher, A.; Moser, A.; Kern, W.; Schlögl, S. New strategies towards reversible and mendable epoxy based materials employing $[4\pi s + 4\pi s]$ photocycloaddition and thermal cycloreversion of pendant anthracene groups. *Polymer* **2015**, *80*, 76–87.

(13) Van Damme, J.; Van Den Berg, O.; Brancart, J.; Vlaminck, L.; Huyck, C.; Van Assche, G.; Van Mele, B.; Du Prez, F. Anthracene-Based Thiol-Ene Networks with Thermo-Degradable and Photo-Reversible Properties. *Macromolecules* **2017**, *50*, 1930–1938.

(14) Tamate, R.; Ueki, T.; Kitazawa, Y.; Kuzunuki, M.; Watanabe, M.; Akimoto, A. M.; Yoshida, R. Photo-Dimerization Induced Dynamic Viscoelastic Changes in ABA Triblock Copolymer-Based Hydrogels for 3D Cell Culture. *Chem. Mater.* 2016, 28, 6401–6408.
(15) Chaudhuri, O.; Gu, L.; Klumpers, D.; Darnell, M.; Bencherif, S. A.; Weaver, J. C.; Huebsch, N.; Lee, H. P.; Lippens, E.; Duda, G. N.;

DOI: 10.1021/acs.macromol.8b01898 Macromolecules XXXX, XXX, XXX–XXX

Macromolecules

Mooney, D. J. Hydrogels with tunable stress relaxation regulate stem cell fate and activity. *Nat. Mater.* **2016**, *15*, 326–334.

(16) Lou, J.; Stowers, R.; Nam, S.; Xia, Y.; Chaudhuri, O. Stress relaxing hyaluronic acid-collagen hydrogels promote cell spreading, fiber remodeling, and focal adhesion formation in 3D cell culture. *Biomaterials* **2018**, *154*, 213–222.

(17) Chandross, E. A.; Ferguson, J.; McRae, E. G. Absorption and emission spectra of anthracene dimers. *J. Chem. Phys.* **1966**, 45, 3546–3553.

(18) Seki, T.; Iwanami, Y.; Kuwatani, Y.; Iyoda, M. Heterocycles Structurally Influenced by a Side Chain. X. Effect of Temperature and Side Chain on the Imine-Enamine Tautomerism in the Quinoxalinone and Pyridopyrazinone Systems. *J. Heterocycl. Chem.* **1997**, *34*, 773– 780.

(19) Stukenbroeker, T.; Wang, W.; Winne, J. M.; Du Prez, F. E.; Nicolaÿ, R.; Leibler, L. Polydimethylsiloxane quenchable vitrimers. *Polym. Chem.* **2017**, *8*, 6590–6593.

(20) Clemens, R. J.; Hyatt, J. A. Acetoacetylation with 2,2,6-trimethyl-4H-1,3-dioxin-4-one: a convenient alternative to diketene. *J. Org. Chem.* **1985**, *50*, 2431–2435.

(21) Kuster, S.; Geiger, T. Coupled π -conjugated chromophores: Squaraine dye dimers as two connected pendulums. *Dyes Pigm.* 2015, 113, 110–116.

(22) Wu, D. Y.; Meure, S.; Solomon, D. Self-healing polymeric materials: A review of recent developments. *Prog. Polym. Sci.* 2008, 33, 479–522.

(23) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A thermally re-mendable cross-linked polymeric material. *Science (Washington, DC, U. S.)* **2002**, *295*, 1698–1702.

(24) Capelot, M.; Unterlass, M. M.; Tournilhac, F.; Leibler, L. Catalytic control of the vitrimer glass transition. ACS Macro Lett. **2012**, *1*, 789–792.

(25) Brutman, J. P.; Delgado, P. A.; Hillmyer, M. A. Polylactide vitrimers. ACS Macro Lett. 2014, 3, 607–610.