Dynamic covalent exchange in poly(thioether anhydrides)†

Kelly R. Tillman, Rebecca Meacham, Anne N. Rolsma, Mikenzie Barankovich, Ana M. Witkowski, Patrick T. Mather, Tyler Graf and Devon A. Shipp*

Dynamic covalent exchange (DCE) of anhydride moieties is examined in both model compounds and network polymers. In addition, the polyanhydrides are shown to be capable of self-healing and recycling. Specifically, thermodynamic and kinetic analysis of the exchange process in symmetric model compounds methacryl anhydride and 4-pentenoic anhydride, which produce an asymmetric anhydride upon exchange, was undertaken using 13C NMR spectroscopy. The equilibrium constant ($K_{eq}$) was determined to be approximately 2–3, and the activation energy ($E_a$) for the production of the asymmetric anhydride was 178 kJ mol$^{-1}$. The rate of exchange was shown to be increased catalytically in the presence of carboxylic acid. Poly(thioether anhydrides) were made using 4-pentenoic anhydride and mixtures of dithiol (1,6-hexanediol) and tetra thiol (pentaerythritol tetrakis(3-mercaptopropionate)) via radical-mediated thiol–ene polymerizations, and network relaxation rates studied using dynamic mechanical analysis. The activation energy and stress relaxation times for various polymer compositions were correlated to crosslink density and polymer composition. It was determined that cross-link density of the polymer system does not significantly impact $E_a$; however, relaxation time ($\tau$) nearly quadrupled from the least cross-linked system to the most cross-linked system. The network polymers exhibited self-healing and facile recycling behavior, which we attributed to the anhydride DCE process that occurs readily in these materials at elevated temperatures. Using the composition with the fastest relaxation, we observed complete visible recovery of damage (notch) within a 4 hours duration at 90 °C. Recycling under compression molding for 15 minutes using 76 MPa hydrostatic pressure at 90 °C was successful. Both healed and recycled samples were successful in recovering or surpassing their original mechanical properties.

Introduction

There has recently been much focus on integrating dynamic functionality into polymer networks to produce new polymer-based materials with recycling, reconfiguring, and self-healing capabilities. Of particular interest are covalently adaptable networks (CANs), which contain reversible covalent structures throughout their network that can be triggered by external stimuli (i.e. light, heat, addition of a catalyst, etc.). Reversible hydrogen bonds, metal–ligand complexes, and covalent interactions are types of dynamic exchanges that have been studied in polymeric networks. CANs are classified based on their exchange mechanism, whether it is dissociative or associative. Dissociative CANs undergo exchange by initially breaking chemical bonds and then reforming at another location. The sequence of breaking and reforming bonds causes a decrease in network connectivity throughout the crosslinks, resulting in sudden drop in viscosity. Stress relaxation and flow can be then be achieved, thus the polymer can be reprocessed similarly to a thermoplastic. Diels-Alder, thiol-disulfide, and reversible thiol-Michael addition are common chemistries that are used for dissociative CANs. In contrast, associative network rearrangement undergoes the addition of a new bond before the elimination of the preexisting bond, which maintains the structural integrity throughout the exchange, like a thermoset. Associative CANs originated with Bowman and coworkers in 2005, who used radical addition–fragmentation of allyl sulfides in acrylic networks, followed by Leibler in 2011 with catalytic transesterification of cross-linked polyesters. Since then numerous exchange reactions have been studied including vinylogous urethane vitrimers, thioesters with free thiols, and boronic ester complexes.
While all these chemistries prove successful in dynamic rearrangement, the future application of such materials will rely heavily on the reprocessing conditions needed. For example, majority of CANs require the use of a catalyst, the application of high heat, pressure, or extreme pH changes to achieve rearrangement in a reasonable time frame. As such, the applicability of CANs is dependent on a range of factors and should be defined in the context of an application.

Anhydrides are a reactive functional group that possess the ability to undergo dynamic covalent exchange (DCE) under relatively mild reac tion conditions without the presence of a catalyst. The earliest documented DCE in anhydride systems was published in 1932, regarding the disproportionation of synthesized mixed anhydrides. During subsequent decades, there have been various studies in small organic anhydrides have examined and/or utilized anhydride exchange. Anhydride exchange was also noted in polymers, although not examined in detail nor leveraged for specific applications, such as self-healing. For example, Domb and Langer published a study in 1989 on linear polyanhydride stability in solution, where gel permeation chromatography was used to monitor the decrease in molecular weights over time as a function of concentration and structural composition, and Tarcha et al. showed that exchange occurs in methacrylated asymmetric anhydrides.

Polyanhydrides are of interest for drug delivery applications in the biomedical field due to their ability to undergo surface erosion. Our group developed a new synthetic route for polyanhydrides based on radical-mediated thiol–ene polymerization, which occurs rapidly under mild reaction conditions. In addition, to examine the erosion process and drug delivery potential of these materials, we have also shown that we could successfully use these materials to make shape memory composites based on a low-melting poly(ε-caprolactone)-based polyurethane electrospun fiber mat imbibed with the cross-linked polyanhydride. We noted, however, that the ability of the composite to undergo shape memory was negatively impacted by the presence of anhydride exchange, and that a better understanding of dynamic exchange reaction is needed in order to produce polyanhydrides with optimized thermo-mechanical properties. Therefore, the goal in this paper is three-fold: first, to examine the kinetics of this process in greater detail using model compounds in $^{13}$C NMR spectroscopy; second, to monitor the dynamic exchange in all-polyanhydride polymer matrices using dynamic mechanical analysis (DMA); and third, to test the efficiency of self-healing and recycling using anhydride dynamic covalent exchange.

**Experimental section**

**Materials**

1,6-Hexanediolthiol (HDT), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), 1-hydroxycyclohexyl phenyl ketone (99%) were purchased from Sigma-Aldrich and used as received. Chloroform-D 99.8% atom (CDCl$_3$) was dried with potassium carbonate ($K_2CO_3$) to remove water or acid. 4-Pentenoic anhydride (PNA) was distilled under vacuum (10 torr) at 140 °C to remove any carboxylic acid present. Methacrylic anhydride (MAAn) was run through a basic alumina column to remove inhibitor (topanol A) and distilled under vacuum (10 torr) at 100 °C.

**Exchange reaction between MAAn and PNA**

In a 3 dram vial, the purified anhydride reagents, MAAn (125 mg) and PNA (148 mg), were dissolved in CDCl$_3$ (0.4 mL), along with anhydrous anisole (109 mg) as an internal standard. The mixture was vortexed for 30 seconds and transferred to a tip-off NMR tube to be flame sealed under vacuum. The sample was stored at −60 °C until characterization by NMR. The reaction was monitored as a function of time until an equilibrium was reached.

**Synthesis of cross-linked polyanhydrides**

Six different compositions of cross-linked poly(thioether anhydrides) were used in these studies. The polymerizations occurred through a photo-initiated thiol–ene reaction. In each case, stoichiometric amounts of ene and thiol functionality were used. Compositions are labeled in the following manner: a PNA/HDT/PETMP sample labeled (100 : 80 : 20) has 100% enes from PNA, 80% thiols from HDT, and 20% thiols from PETMP. This particular mixture was made up of PNA (700 mg), HDT (461 mg), and PETMP (187 mg) with 1-hydroxycyclohexyl phenyl ketone (0.6 mg); other compositions were made with the appropriate adjustments to the amounts of each monomer. The mixtures were stirred and transferred to 1 mm thick PDMS molds (see Fig. S1†) that were placed under a LED 365 nm UV lamp (60 mW cm$^{-2}$) for 20 minutes to cure. The samples were then annealed under nitrogen atmosphere at 90 °C for 1 hour and then placed in the freezer overnight. For the specific amounts of PNA, HDT, PETMP in each of the compositions, please refer to Table S1.†

**NMR spectroscopy**

Small molecule studies of the dynamic covalent exchange were monitored with $^{13}$C (100 MHz) NMR spectroscopy using the Bruker Avance 400 with a BBO probe. Each trial was automated with multi-eg programming, using 15-minute intervals (256 scans) until the system reached equilibrium. The integration of the anisole peak in each spectrum was calibrated to 10, enabling changes in the carbonyl peaks to be tracked. The sample remained in the NMR spectrometer throughout the duration of the experiment.

**Dynamic mechanical analysis (DMA)**

A TA Instruments DMA 850 with liquid nitrogen cooling was used to characterize the thermomechanical properties of the six cross-linked polyanhydride compositions, performing a temperature sweep test in a range of −100 to 90 °C. From this data, the tensile storage modulus ($E'$), tensile loss modulus...
(E″), and tan δ (E′″/E′) were determined. To monitor the dynamic covalent exchange, stress relaxation testing was performed on a TA Instruments Q800 analyzer monitoring the iso-strain, time dependent response at a constant temperature. The dependency of composition and temperature on the relaxation rates were tested. Each composition was annealed in the instrument for 15 minutes at 80 °C before testing to remove any residual stress created during the polymerization. The relaxation modulus was monitored at a 1% applied strain over an hour duration at each temperature, starting at 60 °C and working up to 85 °C in 5 °C intervals.

**Self-healing of crosslinked polyanhydrides**

The self-healing process used an as-prepared polyanhydride that was notched with a razor blade 20 mm from the edge of the dog-bone (dimensions can be seen in Fig. S1†). Pictures were then taken of the damaged sample using an Omax oil immersion microscope at 4× and 10× magnification. The polyanhydride was then placed in the healing apparatus also shown in Fig. S1, and then placed in the oven at 90 °C for allotted amount of time. Images were taken over the duration of healing to monitor healing progress. For each time interval the samples were taken out of the oven, purged with nitrogen for 5 minutes and then placed in the freezer for 30 min before imaging.

**Compression mold recycling**

The recycle process used an as-prepared polyanhydride that was finely chopped up, placed in an aluminum square mold (25.4 mm × 25.4 mm × 1.1 mm) and hot pressed at 90 °C with 4.9 × 10⁴ N (76 MPa hydrostatic pressure) for 15 minutes. After compression, the sample was cooled to room temperature, then was purged with nitrogen for 5 minutes and placed in the freezer for 30 min before tensile testing.

**Tensile tests**

Room-temperature tensile properties were used to characterize the self-healing of the cross-linked polyanhydride networks in the three different stages: original, notched, and healed. The original samples were annealed in the oven at 90 °C under nitrogen atmosphere in order to be comparable to the healed samples. The notched samples were annealed similarly and then notched after being in the oven. The healed samples were prepared as aforementioned. Dog-bone shaped samples were evaluated (ASTM D638 standard) with tension pulling at 125 mm min⁻¹ until failure using a Mark-10 ESM301. This method was also used to test the tensile properties of the recycled polyanhydrides.

**Results and discussion**

**Dynamic covalent exchange in model anhydride compounds**

Anhydride DCE kinetics were investigated using small molecule model systems of PNA and MAAn (Fig. 1(a)). This was achieved using ¹³C NMR spectroscopy of equal molar mixtures of distilled and dried PNA and MAAn in CDCl₃, heated in a sealed tube within the spectrometer. Example spectra are shown in Fig. 1(b), where the relevant ¹³C NMR signals are found between 162–169 ppm. Due to the finite amount of time required to collect a spectrum, each spectrum represents an average of 15 min. For the first 5 h of each experiment, proton and carbon NMR spectra were alternately obtained to ensure no measurable formation of carboxylic acids. Hence the first spectrum collected was labeled as 17 min, representing the carbon data collected between 2 and 17 min, as the first proton spectrum required 2 min. The first spectrum collected (17 minutes) shows large signals from MAAn (δ_{MAAn} 162.8 ppm) and PNA (δ_{PNA} 168.4 ppm), and small signals from the asymmetric anhydride (δ_{asymMAAn} 162.7 ppm; δ_{asymPNA} 168.4 ppm).

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Fig. 1  (a) Scheme of the dynamic covalent exchange between methacrylic anhydride (MAAn) and 4-pentenoic anhydride (PNA) resulting in a mixed anhydride. (b) ¹³C NMR spectrum of the carbonyl carbons of the anhydride moieties as a function of time for the equal molar system of PNA and MAAn at 40 °C showing the generation of the asymmetric anhydride.
Over time, the signals from the asymmetric anhydride increase. The peak assignments for the symmetric anhydrides were based on spectra collected from model compounds (Fig. S2†).

Using the obtained spectroscopic data, the integration of the signals from each carbonyl carbon were monitored over time to ascertain the kinetics of the DCE process. Due to the well-known effects of varying relaxation times of $^{13}$C nuclei in NMR spectroscopy, the absolute integration values for the individual curves shown in Fig. 2 are not comparable to each other; however, the rate of change in each curve can be compared. Therefore, we note that for each temperature (35, 40, 45, 50 °C), the integrations of carbonyl signals of the reactants MAAn ($d_{MAAn}$) and PNA ($d_{PNA}$) decrease concomitantly, while the two signals from the asymmetric anhydride ($d_{asymMAAn}$, $d_{asymPNA}$) increase at a similar rate to each other. Eventually, each signal in each reaction plateaus, indicating that each reaction reaches an equilibrium.

Table 1 includes the equilibrium constants ($K_{eq}$) determined from $^{13}$C NMR spectroscopy data at each reaction temperature studied. The concentrations of each species were estimated using the initial PNA concentration and extrapolating the integration $vs.$ time curves to zero time and assuming conservation of mass and no side reactions. There are small variations in the $K_{eq}$ values, but they are all close to unity, indicating that $\Delta G \sim 0$, which is not unexpected for these exchange reactions given the small differences between the symmetric and asymmetric anhydride species. We note that similar small molecule studies of anhydride exchange (based on R–C(O)–O–C(O)–R, where R = –CH$_3$, –CH$_2$CH$_3$, and –CH$_2$CH$_2$CH$_3$) report $K_{eq}$ values$^{47,48}$ with the same order of magnitude as ours, while thiol-Michael dynamic exchange of thiophenol and mercaptoethanol adducts with phenylvinylketone based Michael acceptors by Konkolewicz et al.$^{19}$ also resulted in a mean equilibrium constant close to unity (in this case, $K_{eq} \sim 0.66$).

The activation energy ($E_a$) of the DCE small molecule study was calculated using second order kinetic analysis. Integration of the decreasing PNA concentration ($b_{PNA}$) signal yielded the forward reaction rate constant ($k_f$); these are also listed in Table 1. The rates of the disappearance of PNA and MAAn were essentially identical and were equal to the rates of increase of the asymmetric anhydride. As expected, the rates increase as temperature increases. An Arrhenius analysis (Fig. S3†) of the rate constants gave an activation energy of 178 kJ mol$^{-1}$, indicating that the exchange process in these compounds is sensitive to temperature changes. Unfortunately, there are no publications that have studied carboxylic acid anhydride exchange to provide a direct comparison to our data. The closest is the work by Mironov and Zharkov$^{47,48}$ mentioned above, who in addition to examining the equilibria between simple acetyl-, propyl-, and butyl-based anhydrides, also reported activation energies for the reactions between acids and anhydrides (they did not report $E_a$ values for exchange between anhydrides). The $E_a$ values for these anhydride/acid exchange reactions ranged between 50–67 kJ mol$^{-1}$. It is not surprising that the values for $E_a$ for the acid/anhydride reactions are quite a bit lower than for the anhydride/acid reactions, but it is interesting that the values are in the same range.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k_f$ (M$^{-1}$ s$^{-1}$)</th>
<th>Equilibrium constant$^b$ ($K_{eq}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>$6.92 \times 10^{-7}$</td>
<td>1.78</td>
</tr>
<tr>
<td>40</td>
<td>$1.42 \times 10^{-6}$</td>
<td>3.15</td>
</tr>
<tr>
<td>45</td>
<td>$2.89 \times 10^{-6}$</td>
<td>2.90</td>
</tr>
<tr>
<td>50</td>
<td>$1.77 \times 10^{-5}$</td>
<td>1.78</td>
</tr>
</tbody>
</table>

$^a$Rate determined by second order kinetic analysis. $^b$ $K_{eq} = \frac{[AsymAnhydride]^2}{[SymPNA][SymMAAn]}$, where concentrations are determined by assuming conservation of mass and the extrapolation of initial concentrations.
lower than for the anhydride/anhydride exchange reactions reported in the present work because of the greater nucleophilicity of the free acid as compared to an anhydride. In order to confirm the role of free acid in exchange reactions between MAAn and PNA, a control experiment was performed which involved the addition of 5% carboxylic acid to the PNA/MAAn mixture. The resulting $k_f$ value was approximately an order of magnitude higher than observed in the earlier reactions and the $K_{eq}$ was unaffected (Fig. S4†), indicating the catalytic activity of free acid.

**Dynamic covalent exchange in poly(thioether anhydrides)**

While small molecule studies give an understanding of reaction kinetics, a more practical understanding of the DCE in polymeric systems can be observed when anhydrides are incorporated into a polymer matrix. It is expected that anhydride exchange rates will be more complex, as they are now reliant on the thermal and mechanical properties of the network poly(thioether anhydrides) in addition to the stereo- and regio-chemistry of the exchange. Therefore, to determine how anhydride exchange occurs in network polymers, an understanding how polymer composition influences the exchange dynamics is necessary. To explore this aspect further, six polyanhydride compositions were made using the thiol–ene monomers shown in Scheme 1, and subjected to stress relaxation measurements for a range of temperatures. The polyanhydride samples were all made using a 1 : 1 ratio of ene : thiol functionality, and vary in cross-link density and crystallinity through adjustments in the amounts of 1,6-hexanediithiol (HDT) vs. pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) while keeping the molar ratio of ene : thiol constant. In the discussion that follows, composition written as 100 : 80 : 20 indicates that 4-pentenoic anhydride (PNA) provides 100% of the ene functionality (which is always the case in this work), HDT provides 80% of the thiol functionality, and PETMP provides 20% of thiol functionality; this particular example is the least cross-linked polymer. The crosslinked networks prepared were generally found to be soft, elastomeric solids with notable increase in stiffness with increasing proportion of PETMP relative to HDT.

Initially, the thermomechanical properties of the poly(thioether anhydride) matrices were determined through DMA, which measured the materials’ glass transition temperature ($T_g$), crystalline melt temperature ($T_m$), and temperature-dependent storage ($E'$) and loss ($E''$) moduli of each sample. Knowledge of these parameters is instructive when determine the rates of covalent exchange in these polymers. The temperature dependence of $E'$ and tan $\delta$ are shown in Fig. 3(a) and (b), respectively. Three samples (100 : 80 : 20, 100 : 70 : 30, 100 : 60 : 40) exhibit two transitions ($T_g$ and $T_m$), indicating that they are semi-crystalline; the other three samples show a single, sharp transition ($T_g$ only) and are amorphous (Fig. 3(a)). Crystallinity of these polymers have been previously characterized using powder X-ray diffraction and comply with these results. 40 The maxima of the tan $\delta$ curves shown in Fig. 3(b) were used to determine the $T_g$ values, which are summarized in Table 2.

With various thermomechanical properties and network crosslinking present in these samples because of the range in compositions, it is important to identify a measurable parameter related to prescribed variation in crosslink density to enable quantitative observations of trends in exchange dynamics with composition. In this case, the average molecular weight between cross-links ($M_c$) was used, calculated using eqn (1). For systematic comparison, we assumed that at a temperature = $T_g + 90$ °C, the differences in material density would be negligible so that the ratio $M_c/\rho$ ($\rho$ is density) could be used to discern trends in DCE with changes in composition that were designed to vary crosslink density. The values of

![Scheme 1](image-url) Molecular structures of the thiol–ene monomers used to generate polyanhydrides ranging in crystallinity and crosslinking.
Fig. 3  (a) Storage modulus vs. temperature shows the variance in thermomechanical properties based on polyanhydride composition (b) \( \tan \delta \) curve used to determine \( T_g \) for polyanhydride systems with molar compositions shown (PNA : HDT : PETMP), where (100 : 0 : 100) represents the most crosslinked and (100 : 80 : 20) the least crosslinked.

Table 2 Summary of values generate from DMA experiments using a film tension clamp

<table>
<thead>
<tr>
<th>Composition(^a) (PNA : HDT : PETMP)</th>
<th>( T_g )(^b) (°C)</th>
<th>( E' ) @ ( T_g ) + 90°(^c) (MPa)</th>
<th>( M_c/p )(^d) (L mol(^-))</th>
<th>( E_a )(^e) (kJ mol(^-))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 : 0 : 100</td>
<td>−20</td>
<td>10.2</td>
<td>0.84</td>
<td>77.5</td>
</tr>
<tr>
<td>100 : 20 : 80</td>
<td>−24</td>
<td>9.1</td>
<td>0.92</td>
<td>77.6</td>
</tr>
<tr>
<td>1000 : 50 : 50</td>
<td>−38</td>
<td>6.0</td>
<td>1.36</td>
<td>69.9</td>
</tr>
<tr>
<td>100 : 60 : 40</td>
<td>−40</td>
<td>5.0</td>
<td>1.61</td>
<td>70.0</td>
</tr>
<tr>
<td>100 : 70 : 30</td>
<td>−37</td>
<td>2.7</td>
<td>3.03</td>
<td>61.2</td>
</tr>
<tr>
<td>100 : 80 : 20</td>
<td>−33</td>
<td>3.2</td>
<td>4.33</td>
<td>77.4</td>
</tr>
</tbody>
</table>

\(^a\) Based on moles of functional groups (–SH, C\(\equiv\)C). \(^b\) Determined from \( T_g \) at \( T_g \) + 90 °C. \(^c\) A single storage modulus data point taken at \( T_g \) + 90 °C. \(^d\) Determined from the temperature and storage modulus at \( T_g \) + 90 °C. \(^e\) Determined from the stress relaxation data.

\( M_c/p \) are listed in Table 2 and follow the expected trend in that \( M_c/p \) increases as the amount of PETMP decreases.

\[
E = 3pRT/M_c
\]

where \( E \) is the elastic modulus at \( T_g + 90 \) °C, \( R \) is the gas constant, and \( T \) is the temperature \( T_g + 90 \) °C.

For these poly(thioether anhydrides) to be classified as vitrimers, one quality they must possess is resistance to dissolution in a solvent. To illustrate such solvent resistance, an additional swelling test was conducted on the composition with the lowest \( M_c/p \) studied \( (i.e., 100 : 80 : 20) \), to prove that the lowest cross-linked system still maintained its connectivity at elevated temperatures where DCE would occur. As shown in Fig. S5,‡ the sample did swell but not dissolve, even after heating at a temperature that induces dynamic covalent exchange (90 °C). Thus, in the sense of maintaining sample integrity during solvent exposure (though with swelling) the materials tested in this way are solvent-resistant.

Stress relaxation rates were then measured in order to understand DCE in the poly(thioether anhydrides), shown in Fig. 4. Compositional and temperature dependencies can be observed. Two primary trends are important to note for these data. First, all compositions show a clear increase in relaxation rate as temperature increases. This is consistent with our previous findings.46 From this trend, Arrhenius analysis (Fig. S6†) for each composition resulted in the activation energies summarized in Table 2. There, differences in the activation energy as a function of polymer composition are seen to be negligible; this is likely due to the activation energy being dominated by the chemical processes of the exchange, which are the same for each composition. However, compositional effects on stress relaxation are more noticeable when comparing the relaxation times (\( \tau \)) of the polymer materials at a given temperature. All compositions follow the trend of decreasing relaxation time with increasing temperature, shown in Fig. 5(a). As seen in Fig. 5(b), at every temperature, there is a decrease in relaxation time as \( M_c/p \) values increase. Increasing \( M_c/p \) correlates with an increase in HDT content. This provides higher chain mobility throughout the network, allowing for increased interactions between anhydride moieties and thus increased exchange rates and stress relaxation. From these observations of stress relaxation at elevated temperature, it clear that these materials would exhibit significant creep when stressed at the same temperatures, and this must be taken into account when considering potential applications.

There is a clear difference between the DCE activation energies from our model studies (178 kJ mol\(^-\)) to the polymer network studies (\(~72\) kJ mol\(^-\)). This can be attributed to multiple factors regarding the different chemical and physical environments of the two sets of experiments. The small molecule study involves anhydrides that are structurally different, \( e.g. \) the MAAn has a conjugated \( \pi \)-bond system, where as the PNA does not, are liquids, and thermally limited to the boiling point of CDCl\(_3\). The polymer network system is molecularly more constrained, and because the polymer samples were not prepared and studied under strict anhydrous conditions, there is a strong possibility that carboxylic acid catalysis occurs. If this is indeed the case, then the \( E_a \) for polymer network (\(~72\) kJ mol\(^-\)) is approximately the same as that observed for the acid/anhydride model student of Mironov and
However, it should be cautioned that comparisons of the activation energies determined in the model compound studies with those measured in the polymeric systems may not be appropriate given the several chemical and physical differences between the systems which may lead to different rate-determining steps/mechanisms.

Fig. 4 Stress-relaxation curves for all polyanhydride compositions as a function of temperature. (a) 100 : 0 : 100 (b) 100 : 20 : 80 (c) 100 : 50 : 50 (d) 100 : 60 : 40 (e) 100 : 70 : 30 (f) 100 : 80 : 20.

Fig. 5 (a) Relaxation time ($\tau$) as a function of temperatures for all composition. (b) Relaxation time ($\tau$) as a function of $M_c/\rho$. Dotted lines are to guide the eye only.

Zharkov. However, it should be cautioned that comparisons of the activation energies determined in the model compound studies with those measured in the polymeric systems may not be appropriate given the several chemical and physical differences between the systems which may lead to different rate-determining steps/mechanisms.
Self-healing and recycling in poly(thioether anhydrides)

Cross-linked polymers that are able to undergo DCE typically display the capacity to self-heal and recycle. Self-healing is illustrated using a notched dog-bone film of composition = 100 : 80 : 20 that was returned to its PDMS mold and compressed gently with heat-tolerant rubber bands (Fig. S1†). The sample was imaged hourly using optical microscopy until complete disappearance of the notch, shown in Fig. 6. Tensile testing was performed under ambient conditions comparing original, notched, and healed samples. Healing efficiency was observed through physical properties obtained from these tensile stress–strain curves, shown in Fig. 7. The quantitative data from the tensile tests are summarized in Table 3 (complete data sets are shown in Table S2†). There is some variation in the Young’s modulus, with the modulus of the

Fig. 6 Microscopic images of PNA : HDT : PETMP 100 : 80 : 20 sample monitoring self-healing progress of notched poly(thioether anhydrides) at two magnification levels, 4x and 10x.

Fig. 7 Stress–strain (tensile) plots of poly(thioether anhydrides) samples before notching (blue), after notching (black) and self-healed after being notched (red). “X” symbol indicative of sample break.
notched sample lower than the original and healed samples, as might be expected given the deformation (notch) should affect the measurement. More dramatically, notching the sample severely impacted the polymer’s peak stress, strain at break, and toughness. The process of heating the sample at 90 °C for 4 hours to induce self-healing was not only successful but the healed sample also shows slight improvements compared to the original mechanical properties (peak stress, strain at break, toughness). This is likely to be due to anhydride exchange that occurs while heating such that the network is able to obtain improved molecular ordering through increased crystallinity and higher cross-link density.

Compression molding was used to show the recyclability of the poly(thioether anhydrides). A (100 : 80 : 20) sample was diced into ~1 mm sized cubic pellets using a razor blade, and subjected to 76 MPa of pressure at 90 °C. Within 15 min, the recycled pellets produced a continuous polymer film. This recycled film was subjected to tensile and DMA testing, and the results shown in Fig. 8(a) indicate an improvement in maximum peak stress of the recycled sample. As discussed above, these increases can be attributed to the DCE occurring under high heat and pressure, again resulting in higher crystallinity and increased cross-link density, shown by the increase in storage modulus and shift to a higher $T_m$ displayed in Fig. 8(b).

### Conclusions

We have shown through a thermodynamic and kinetic analysis that anhydride-anhydride DCE occurs in both model compounds and macromolecular network systems. $^{13}$C NMR spectroscopy was used to monitor the exchange between the symmetric anhydrides, PNA and MAAn, which resulted in the formation of a mixed asymmetric anhydride product. The equilibrium constants ($K_{eq}$) over a temperature range of 35–50 °C were determined, and found to be all close to unity, indicating that $\Delta G \sim 0$ for anhydride DCE. Second order kinetic analysis was also performed on the rate data, and resulted in rate constants for exchange ($k_f$) that were used to obtain the activation energy of 178 kJ mol$^{-1}$. The addition of 5 mol% 4-pentenoic acid (PNAcid) to the PNA and MAAn exchange reaction was much faster, indicating an acid catalytic effect.

DMA was used to monitor the DCE process in cross-linked polymers that contain high volume of anhydride moieties throughout the network synthesized from photo-initiated thiol–ene chemistries. Stress relaxation measurements showed that the variance in the modulus did not affect the activation energy of the DCE, while stiffer, more crosslinked polymers showed much longer relaxation times. It therefore appears that greater crosslinking, which decreases chain mobility, slows anhydride exchange, but does not change the activation energy, an indication that the activation energy of this process

### Table 3  Tensile mechanical properties of poly(thioether anhydrides) samples before notching (original), after notching, and after healing

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young’s modulus (MPa)</th>
<th>Peak stress (MPa)</th>
<th>Strain at break</th>
<th>Tensile toughness (MJ m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>42 ± 5</td>
<td>5.5 ± 0.6</td>
<td>0.31 ± 0.03</td>
<td>125 ± 19</td>
</tr>
<tr>
<td>Notched</td>
<td>24 ± 1</td>
<td>1.4 ± 0.1</td>
<td>0.06 ± 0.0</td>
<td>5 ± 0.3</td>
</tr>
<tr>
<td>Healed</td>
<td>38 ± 8</td>
<td>6.6 ± 1.1</td>
<td>0.36 ± 0.07</td>
<td>176 ± 58</td>
</tr>
</tbody>
</table>

Fig. 8  (a) Stress–strain (tensile) and (b) DMA storage modulus vs. temperature plots of poly(thioether anhydrides) samples before (blue) and after (red) recycling.
is driven mainly by chemical rather than physical process. The activation energy of polymer samples was significantly lower than that of the small molecule study could be contributed to the presence of free carboxylic acids in the polymer sample, or possibly to structural differences in the anhydrides studied. Finally, the poly(thioether anhydrides) were shown to successfully undergo self-healing and recycling.

We expect that the outcomes of this research will have a significant impact on the development of new degradable biomaterial devices. For example, polyanydride-based biomaterials can be customizable through compositional adjustments to target desired mechanical properties, erosion rate, and/or rates of DCE (i.e., healing/recycling/reconfiguring). They have the potential to be used in many critical biomedical areas such as tissue engineering, erodible/resorbable adhesives, and scaffolds for cell growth. From a production standpoint, these materials can be produced in bulk and then through DCE reconfiguration be personalized for a specific application.

Conflicts of interest
The authors declare no potential conflicts of interests.

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