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Dynamic photopolymer networks that take advantage of the thermodynamically controlled reversibility of thiol-succinic anhydride adducts were synthesized from commercial substrates and investigated as a new class of covalent adaptable networks (CANs). Through systematic studies of the catalyst and stoichiometry effects on the exchange dynamics two distinctive exchange mechanisms were found, and then demonstrated to contribute to the overall dynamic characteristics. By varying the catalyst activity, i.e. basicity and/or nucleophilicity, control over the dynamic responsiveness through changes in the type of dynamic covalent chemistry mode (reversible addition vs. reversible exchange) was achieved in otherwise compositionally analogous materials. More specifically, the participation of the associative mechanism (thiol-thioester exchange) in the otherwise dissociative networks, and its relevance on materials properties was demonstrated by dielectric analysis (DEA) and dynamic mechanical analysis (DMA). The activation energies (E_a) for viscous flow obtained from DMA stress relaxation experiments and from dielectric modulus and loss crossover points shown to match well between the two techniques. The E_a in stoichiometric systems was found to be 110-120 kJ/mol, whereas 50% excess thiol systems were characterized by E_a ranging 95-105 kJ/mol. The thermodynamic equilibrium conversion, estimated in the temperature controlled FTIR, for a stoichiometric 3-mercaptopropionate-succinic anhydride combination was determined at 92 ±1 % at ambient temperature, and decreased to 67 ±1 % at 120°C within one hour of equilibration time ($\Delta H^0 = -46 \pm 5$ kJ/mol). Such high potential for reversibility of the thioester anhydride linkages resembles maleimide-furan Diels-Alder networks but has many other attributes that make these CANs of unprecedented value in fundamental research on dynamic materials.

Introduction

Covalent Adaptable Networks (CANs) are thermosets with a “latent” ability to flow which is a typical property of thermoplastics. As such CANs combine the attributes of thermoplastics such as pliability and facile end-of-life processability, with thermosets’ thermomechanical and dimensional stability[1-3]. As a result, CANs can be reprocessed like thermoplastics, and having a three-dimensional network structure, they also retain the high performance characteristics of thermosets. As such, CANs are situated at the intersection of thermoplastics and thermosets, even existing as their own distinct type of polymer. As hybrids at the border between thermoplastics and thermosets, they are envisioned to enable new, previously unattainable applications in shape memory, dynamic composite, smart materials and 3D printing fields[4].

Generally, dynamic networks are composed of covalently crosslinked polymer chains with labile covalent bonds that change their dynamic character in response to the application of a specific stimulus, e.g., temperature or light. Two distinctive types of covalent bond exchange pathways have been repeatedly incorporated to date. Specifically, bond exchange occurs through either a dissociative or associative mechanism[1, 5]. Dissociative networks, based for example on reversible additions of Diels-Alder adducts[6, 7], when activated gradually reduce the time-averaged network crosslinking by cleaving the covalent bonds until depolymerization and fluidization of the original material is achieved. On the other hand, associative networks, such as vitrimers[8-10] operate through a reversible exchange mechanism, and enable covalent bond rearrangement without any significant reductions in the time-averaged crosslink density, thus preventing depolymerization. Both types of covalent bond rearrangement have been amply exemplified in the relevant literature on CANs[11]. However, there exist several dynamic covalent exchange reactions that could potentially operate through multiple exchange routes sometimes preventing unambiguous distinguishment between reversible exchange and reversible addition. For instance, the urethane (and urea)

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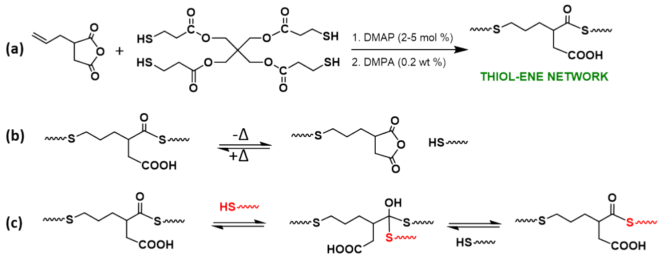
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See dissociative cleavage and associative transcarbamoylation with excessive hydroxyls (and amines) are both proposed as possible mechanisms in polyurethane and polyurea dynamic networks[12-15]. To distinguish between the two mechanisms, Dichtel and coworkers devised a methylated polyurethane network where a N-centered hydrogen was substituted with a methylene group, thus preventing reversions of such "blocked" urethane bonds[14]. In the presence of pendent hydroxyls only transcarbamoylation was possible, and it was confirmed that the networks remained dynamic through a clean, associative pathway. Interestingly, a stoichiometric amount of hydroxyls in hydrogen-bearing urethanes resulted in similar activation energies from stress relaxation experiments as in methylene-bearing urethanes pointing towards transcarbamoylation as the dominant exchange pathway in either type of material. On the other hand, hydroxyl-free polyurethanes were demonstrated to be dynamic in the presence of a Lewis acid and assumed to undergo bond reversion-formation through an associative route[10, 16]. A dual mode of exchange involving dissociative and associative processes was also proved in disulfide-based networks[17-19]. Homolytically cleaved disulfides easily recombine or engage through associative intermediates with other disulfides resulting in rapid exchange at generally benign reaction conditions. Moreover, anionic as well as radical pathways are possible depending on the type of disulphide links and inclusion of catalysts and/or reductants[20]. Finally, a change in the exchange mechanism mode was recently observed in vinylogous urethane vitrimers, where the transition occurred after a particular temperature threshold was overstepped[21]. Namely, the reversible exchange of vinylogous urethane crosslinks with excessive amines (5 and 10 mol%) was shown to exhibit a significant change in activation energy (around 60 kJ/mol) depending on whether the stress relaxation experiments were performed below or above 140°C. It was argued that at temperatures below 140°C, a transamination via an iminium exchange pathway dominates the overall exchange kinetics with lower activation barrier, whereas at higher temperatures Michael-type pathway proceeding through an enamine intermediate association prevails and is characterized by significantly higher E_a. This last example illustrates the possible change in and also control of the mechanism of exchange between two associative yet different pathways by temperature modulation.

In the current work, an attempt was made to establish the extent of possible control over two distinctly different mechanisms of exchange primarily in the thiol-succinic anhydride covalent adaptable networks (Scheme 1b and c). Recently, thiol-anhydride-based CANs were reported to exhibit an extraordinary reversibility of the thioester-anhydride linkages which markedly depended on the cyclic anhydride structures[22]. Maleic, succinic and phthalic anhydrides were characterized by different propensities for thioester anhydride reversion, thus dictating the dynamic properties of materials based on these anhydrides. For example, the thiol-phthalic anhydride networks exhibited rapid depolymerization rates as exemplified by close to 70% thioester anhydride ring closing (reversion) at 80°C. On the other hand, the thioesters of maleic anhydride required over 100°C to achieve any discernible reversion and dynamic exchange. Since the ring opening reaction of the anhydride results in a thioester product, it is hypothesized that such thioesters would exchange through an associative pathway but with a necessary condition that free thiol functionalities and proper catalysts are present. The thiol-thioester exchange (transthioesterifiaction) has already been demonstrated as a potent dynamic chemistry offering tremendous choice of suitable substrates, temperature conditions, and a broad array of catalytic species that could be used to control the exchange dynamics[23]. Therefore, a photopolymer network of allyl succinic anhydride and tetrathiol pentaerythritol tetrakis (3-mercaptopropionate) – PETMP was selected for exchange dynamics studies (Scheme 1a). To monitor the extent of possible reversible exchange and reversible addition reactions in the networks, various catalyst types, catalyst loadings and excess thiol levels were all considered in a systematic manner. Changes in the dynamic character of the thiol-anhydride CANs were monitored as a function of temperature in DMA stress relaxation experiments, DMA rubbery moduli measurements, and dielectric modulus and loss profile changes collected over a broad frequency range.



Scheme 1. (a) Allyl succinic anhydride (ASA) and tetrathiol ring opening reactions coupled with the thiol-ene polymerization, (b) reversible addition of a thioester anhydride network link, and (c) reversible exchange of thioester anhydride network link with a free thiol.

Experimental

Materials and methods. All chemicals were purchased from common suppliers (Sigma Aldrich, Fisher Scientific, Bruno Bock) and used as received. Radical photoinitiator: 2,2-dimethoxy-2-phenylacetophenone (DMPA). Reactants and monomers: allyl succinic anhydride (98%), n-buthyl 3-mercaptopropionate (99%) (BMP), methyl 3-mercaptopropionate (99%) (MMP), pentaerythritol tetrakis (3-mercaptopropionate) (PETMP). Organic catalysts: 4-dimethylaminopyridine (DMAP), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

Sample casting. Anhydride and thiol reactants were mixed at ambient conditions and the catalyst/photoinitiator mixture was added in a DCM solution. After 10-30 min of initial reaction the solvent was removed *in vacuo*, and the mixture casted between glass slides separated by spacers (typically 250 µm thick). After 0.5-1 h of the thiol-anhydride reaction at ambient temperature the mixtures were exposed to UV irradiation at 10 mW/cm^2 (365nm) in the presence of DMPA (0.2 wt%) to form crosslinked dynamic networks. Generally, the anhydride was reacted for an extended time prior to UV curing to allow for quantitative thioester formation in initially off-stoichiometric mixtures. In the case of DMAP, and DBU-catalysed reactions, a 5% anhydride excess was used in stoichiometric systems to enforce quantitative thiol conversion, and to bias the initial thiol-free equilibrium in repeatedly post-processed CANs. No solvent was used in the case of TEMPO catalysis which was directly dissolved in neat monomers and cured thermally between glass slides at 80-100°C for 1h. The extent of curing was monitored by ATR and transmission IR spectroscopy. Typical sample dimensions were: 5mm/15mm/0.25mm. All network polymerizations yielded clear and colorless samples. Interestingly, in initial characterization the succinic anhydride dynamic networks were found quite resistant to water swelling. When assessed for the impact of prolonged moisture exposure, they resulted in less than 5 wt % of water uptake over the course of one week (Figure S1).

Fourier Transform Infrared Spectroscopy. Sample conversions were analyzed using an FT-IR spectrometer (Nicolet 8700). Monomer mixtures were sandwiched between glass slides (near-IR) or salt plates (mid-IR) with or without 250 µm spacers, and placed into a horizontal transmission apparatus where they were analyzed before and after photocuring with UV light at 10 mW/cm^2 (365nm). The final double bond conversions were calculated from the absorbance peak area of the vinyl functional group, around 6150 cm^{-1} in the near-infrared spectrum. Anhydride ring conversions were analyzed in the ATR-IR. Uncured resin mixtures and thermally cured or photocured samples of fixed geometries (5mm/15mm/0.25mm) were surface-analyzed in ATR-IR where the highest peak absorbance was set to 0.9-1.

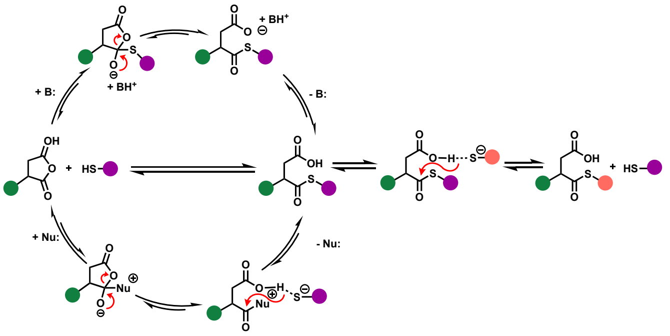
Dynamic Mechanical Analysis (DMA) and Stress Relaxation. The glass transition temperature (T_g), storage modulus (E’), loss modulus (E”) and tangent δ were determined on a Q800 DMA (TA Instruments) using a ramp rate of 3°C/min and a frequency of 1 Hz, with a fixed oscillatory strain of 0.01% and a preload force of 0.002 N. Stress relaxation experiments were performed in tensile elongation mode using a Q800 DMA instrument. The built-in stress relaxation DMA settings were used, with a 5-10% maximal strain and an initial strain rate of 1%/min at a fixed temperature. Rectangular samples of the dimensions 10/5/0.25 were used.

Dielectric Spectroscopy. Broadband dielectric spectra of thiol-anhydride CANs were recorded using a ModuLab XM Material Test System (AMETEK Scientific Instruments, U.K.) at various temperatures (20-120°C) over a frequency range from 10^{-3} to 10^{6} Hz under an applied sinusoidal voltage of 5000 mV in amplitude to determine the dielectric properties of the dynamic materials including changes in polarization characteristics as expected to occur when/if the dynamic reaction exchange modes were changing. The photocured samples were sandwiched between two indium-tin oxide (ITO) coated glass plates (supplied by Instec, Inc.) so that the CAN film and the conducting faces were in intimate contact, forming a parallel plate capacitor. The ITO layer thickness was 0.023 ± 5 µm over 256 mm^2 active surface area. CAN films of 1.0-1.2 cm^2 surface area and 250 µm in thickness were analysed. Thiol-ene films of 1.6-1.8 cm^2 surface area and 20-30 µm in thickness were analysed for comparison of relative permittivity The samples were mounted in a hot/cold stage equipped with Instec mK2000 temperature controller whose temperature was controlled between 20 and 120 °C.

Results and discussion

In this report, contributions of two possible dynamic exchange mechanisms were investigated as was their effect on the dielectric and mechanical properties for thiol-anhydride photopolymers. This work was undertaken by incorporating different exchange promoting catalysts as well as a varying level of thiol excess in the network constituents. The rubbery moduli and the stress relaxation rates were analysed systematically for a series of dynamic thiol-anhydride networks. By combining these distinctive measurements, it is possible to assess the relative contributions from the reversible exchange and reversible addition reactions.

Reaction Reversibility. Two types of photopolymer networks were primarily discussed throughout this report. Allyl succinic anhydride (ASA) was reacted with tetrathiol PETMP at two molar ratios. A stoichiometric system was created by combining 2 moles of ASA with 1 mole of PETMP (ASA/PETMP) and an off-stoichiometric system was composed of 2 moles of ASA and 1.5 moles of PETMP (ASA/PETMP-50), leading to the presence of residual thiol functional groups. The reason for including an off-stoichiometric system abundant in free thiols was to increase the likelihood and rate of the associative thiol-thioester exchange. On the other hand, the stoichiometric system, reacted stoichiometrically or with slight anhydride excess (5 %), would be characterized by residual thiols due to the incomplete equilibrium conversions as discussed further in the text. In theory, such a system should also be able to revert to reactants to a greater extent since the networks formed with excess thiols will be shifted towards higher conversion to the thioester as compared to a 1-to-1 functional group ratio. Although the thiol-anhydride addition was previously demonstrated to proceed without any added catalyst, here, catalysts were employed to increase the rates toward equilibrium conversions. Moreover, the kinetically controlled reversible exchange depends on the strength of the catalyst which brings another possible means of control over the extent of this exchange pathway. The mechanism of the thiol-thioester reversible exchange catalyzed by bases and nucleophiles was previously proposed, and the reaction itself greatly depended on the basicity and nucleophilicity of a variety of tested catalysts. Herein, a similar mechanism is proposed for the catalyzed thiol-anhydride addition/reversion (Scheme 2).



Scheme 2. A proposed mechanism for the reversible addition between a thiol and an anhydride (left part of the scheme). The reaction rates toward equilibrium are increased in the presence of bases (B:) and nucleophiles (Nu:). The thiol-thioester reversible addition is included in the scheme (right part).

In the presence of a base, a thiolate anion is generated that then adds to a carbonyl group of the anhydride ring. The subsequent ring opening event results in a thioester product with carboxylate/protonated base ion pair. When a nucleophile is used as a catalyst, its nucleophilic attack on a carbonyl anhydride facilitates thiol approach and thiolate generation which can then replace the nucleophilic catalyst leading to the thioester acid product. Either type of catalyst enhances the rates of ring opening/closing and thus shortens the time required to reach the equilibrium. In an attempt to shift, in a controllable way, between the possible modes of dynamic behavior, each of the two compositional network variations underwent thiol-anhydride ring opening reactions in the presence of three catalysts of various catalytic strengths (and loadings). TEMPO was used as the weakest catalyst (a latent base) at the lowest loading of 2 mol% with respect to the thioester anhydride units. When exposed to thiols TEMPO (pK_a = 5.5) undergoes reduction to 2,2,6,6-tetramethylpiperidine (TMP, pK_a = 11.4) which is a generated base of potential catalytic value for exchange[24]. DMAP (pK_a = 9.6), although a weaker base is considered here as a moderate strength catalyst because of its nucleophilic character. The activation of thioester carbonyls by a nucleophilic catalyst is assumed to affect the rates of both reversible exchange and reversible addition. Finally, DBU (pK_a = 13.5) a non-nucleophilic base used at 5 mol% was considered as the strongest catalyst for exchange. To increase any expected differences in catalytic activities more significantly, DMAP and DBU were both used at higher loadings than TEMPO (5 mol%). According to the proposed mechanisms for thiol-anhydride reversible addition and thiol-thioester reversible exchange in the presence of catalytic species, the excess thiols in off-stoichimetric systems favor thiol-thioester exchange and hinder thiol-anhydride reversible addition due to the off-stoichiometry driven product formation. On the other hand, increasing the strength of the catalyst (nucleophilicity and basicity) would be expected to enhance the rates of both exchange pathways. Conversely, reducing the catalyst strength would be assumed to bias the reversible addition over the reversible exchange. In previous studies, both TEMPO and DMAP were used for thiol-anhydride ring opening/closing, and proved efficient catalysts even when considering the possible acid-base equilibria in a system containing a high concentration of carboxylic groups[22]. Being trapped in an acid-base pair, bases such as TMP or DBU are assumed to remain non-volatile and active at the temperatures of the experiments (≤ 120 °C). Moreover, at the time of stimulus activation, any events of thermoreversible protolysis would be expected to temporarily generate higher concentrations of an active catalyst. Indeed, no significant reduction in dynamic response, and thus catalytic activity, was noticeable after repeated heating-cooling cycles in the formulated CANs. Before discussing the possible dynamic reaction's interplay in crosslinked materials, model reversibility studies were carried out using a non-crosslinking system composed of ASA and BMP at one-to-one molar ratios (ASA/BMP). A neat ASA/BMP mixture was equilibrated overnight with 5 mol% DMAP reaching around 92 % anhydride conversion. This outcome suggests that the stoichiometric systems require excess anhydrides to shift the reaction equilibrium to complete thiol elimination, particularly in these mobility-restricted crosslinked networks. The reversibility studies were performed in an IR spectrometer equipped with a heating stage at temperatures ranging from 20-120°C. The anhydride ring peaks with maxima at 1790 cm^{-1} and 1870 cm^{-1} were monitored and integrated to extract the ambient temperature conversion at equilibrium as well as the extent of reversion at elevated temperatures (Figure 1a).

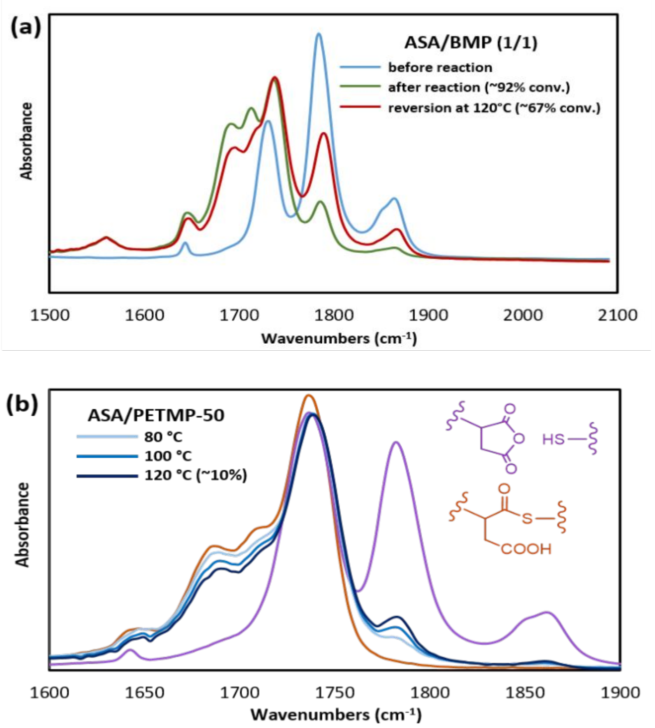


Figure 1. FT-IR reversibility studies for (a) a ASA/BMP stoichiometric mixture and (b) a ASA/PETMP-50 crosslinked network. In both cases DMAP was used as the exchange catalyst with a 5 mol% loading. Evident is a higher propensity for reversion in the stoichiometric system (~33% reversion at 120°C) as compared to ~10% for ASA/PETMP-50.

A stoichiometric mixture of thiol and succinic anhydride does not reach full conversion at ambient temperature after overnight reaction in these mobility-unrestricted conditions. On the other hand, the ASA/PETMP-50 crosslinking mixture reaches 100 % anhydride ring opening in 30 min followed by UV curing as detailed in the Experimental section and shown in Figure 2b. Because of excess thiols, the crosslinked system exhibits hindered thioester anhydride reversion of only 10% at 120 °C after 1h equilibration. The stoichiometric mixture amounts to around 33 % of anhydride ring regeneration at 120 °C which is consistent with previous NMR results demonstrating 38% thermal reversion of methyl succinic anhydride and methyl 3-mercaptopropionate adducts[22]. The IR data for the model, nonpolymer mixture (ASA/BMP) was then used to calculate the standard free energy change (ΔG^0) as well as the heat (ΔH^0) and entropy (ΔS^0) of the reaction. Using monofunctional reactants for such thermodynamic characterization was justified by facilitated IR conversion analysis in liquid mixtures as well as shortened substrate-product equilibration times (1 h). No thermodynamic characterization or equilibration was attempted on any of the crosslinked systems discussed throughout this study. Initially, the conversions were extracted after 15 min equilibration time (Figure S2). However, such time length was not sufficient to drive the reaction to the desired equilibrium conversion. Considering the initial fitting discrepancies, a 1 h equilibration time was chosen to more accurately determine the reaction equilibrium constants (K_{eq}) (Figure 2).

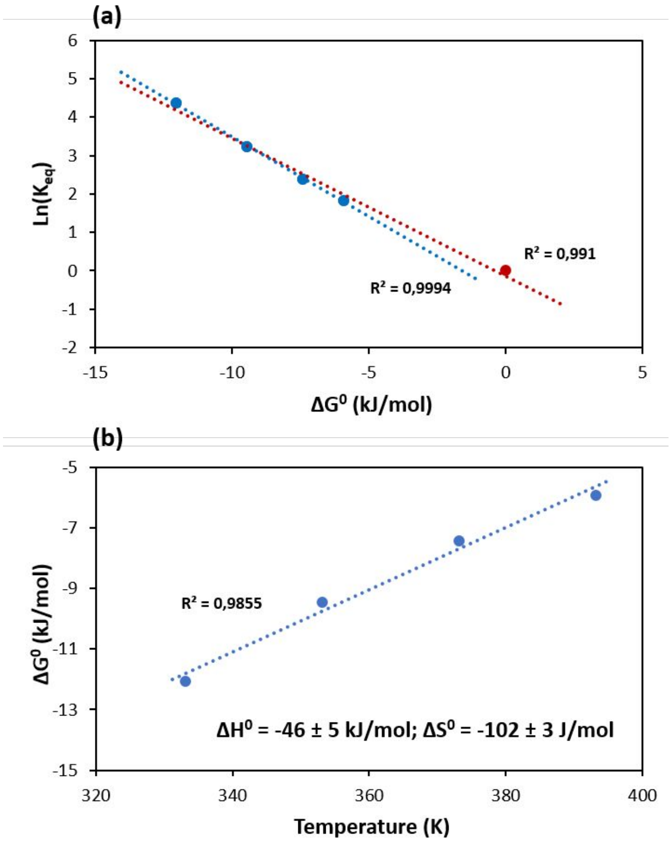


Figure 2. Standard free energy change (ΔG^0) in the function of $\ln(K_{eq})$ for ASA/BMP model reaction (a). The estimated enthalpy and entropy of the reaction are included in the figure (b) where $\Delta G^0 = f(T)$. R square values indicate good accuracy at 1 h equilibration times. The experimental points diverge slightly when fitted on their own and when combined with the theoretical point $\Delta G^0 = 0$ at $K_{eq} = 1$ (a).

The longer temperature equilibration may lead to side reactions as the allyl groups present within the system, and any thermally induced thiol-ene reactions, would deplete the thiols and shift the equilibrium more towards the substrates. Indeed, side products were detected and overestimated conversion values were obtained in the NMR equilibration studies carried out for 2 h at elevated temperatures (Figures S3-5). From the data in Figure 2 it is evident that after one hour of equilibration at each experimental temperature (60, 80 100 and 120°C) the reaction equilibria were not achieved, and the conversions produced underrepresented the equilibrium conversion. However, the R^2 (0.991) value implies a good fit after the experimentally acquired data points were grouped together with the theoretical point of $\Delta G^0 = 0 - \ln(K_{eq}) = 0$. Even though the extracted values of ΔH^0 and ΔS^0 are somewhat overestimated, they bring valuable information on the general reversibility of the process at hand.

Dielectric Analysis (DEA). Dielectric spectroscopy (DS) can be used to exploit the presence of permanent and induced dipoles in the chemical structure of the polymeric materials and as such delivers important information on molecular or segmental mobility which result in complex molecular conformations[25-27]. Polymers that exhibit dipole moments are termed to be “dielectrically active”. Measuring the polarization induced in polymers due to an applied electric field is a useful method for probing polymer structure and properties. It is hypothesized here, that dynamic exchange in CANs would enhance the capacity for network polarization as the dipole alignment will be facilitated in a dynamic system where bond-breaking and bond-forming events are intrinsic and provide for mobility in the polymer network. DEA provides significant insight into the mechanism of dynamic exchange, or the overall exchange dynamics in CANs where the exchange phenomena depend substantially on temperature. In other words, any variations in the mechanism of exchange would be expected to differentiate the dielectric response of the thiol-anhydride CANs. Moreover, it is crucial to investigate how the possible exchange reactions affect the dielectric properties of dynamic networks, particularly the relative permittivity (RP) (or dielectric constant) which is an important parameter in characterizing the electric energy density of dielectric materials[27]. Dielectric constants are known and DEA is a common technique for many polymeric materials, but the relevant literature lacks reports on CANs.

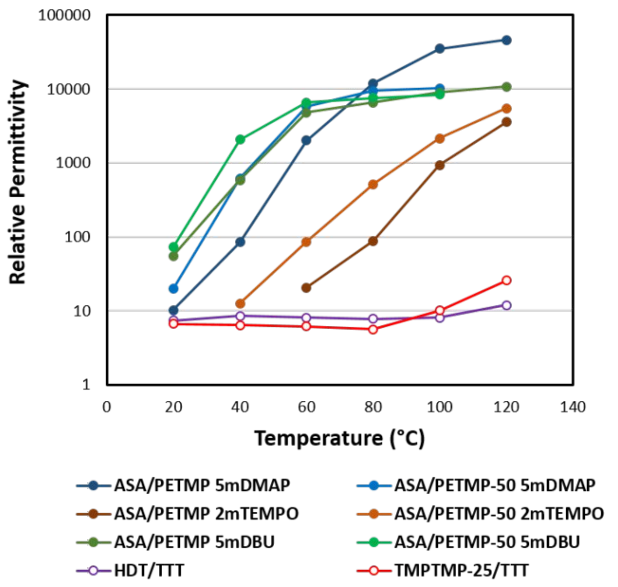
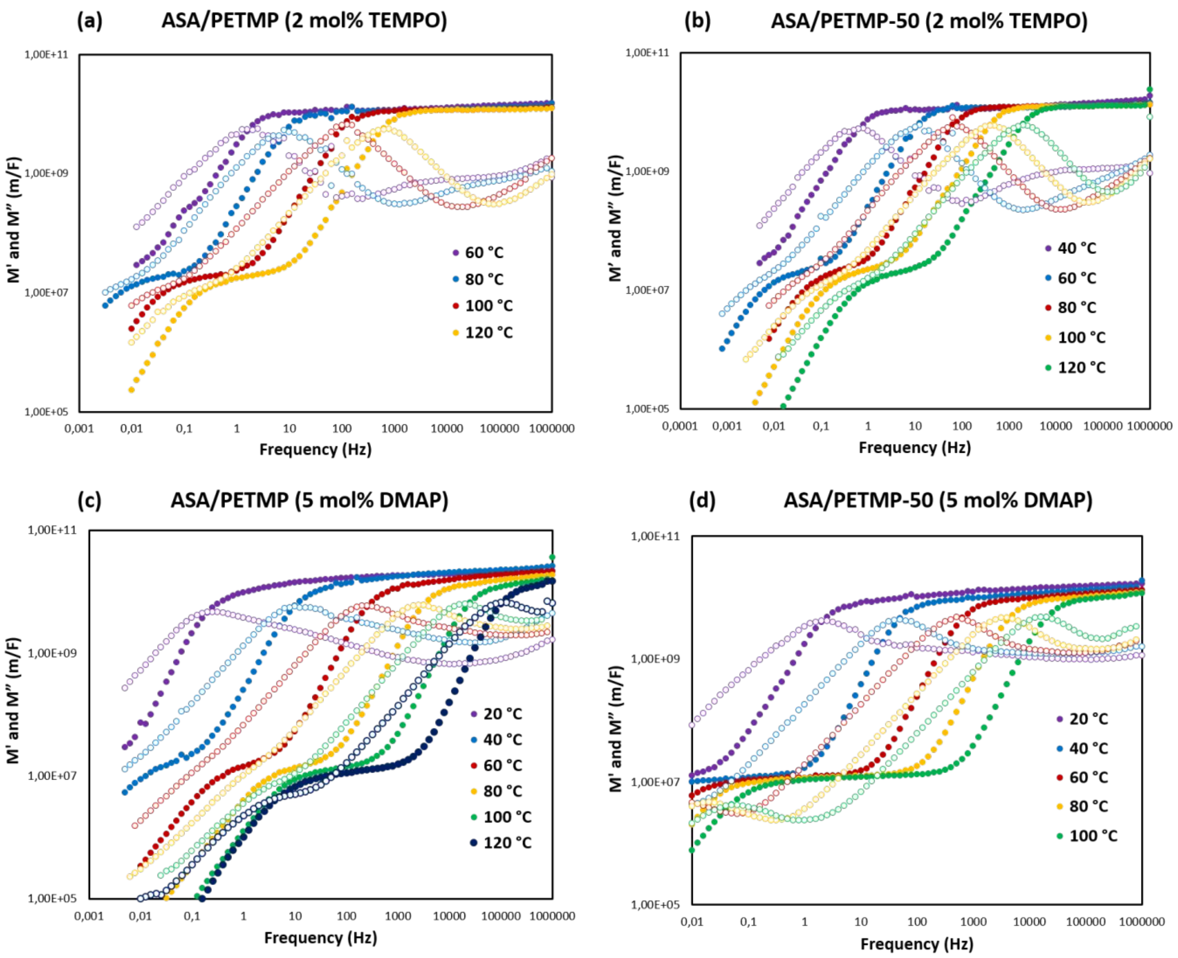


Figure 3. Relative permittivity at 1 Hz in the function of temperature for two types of CANs (filled circles) and two thiol-ene non-dynamic networks (open circles).

Consequently, relative permittivities of the two types of CANs activated by three catalysts each were measured at 1 Hz and compared with two non-dynamic thiol-ene networks of similar crosslinking and T_g. Hence, as a type of control sample, a dithiol (HDT) was polymerized with a triene (TTT), and a tritiol (TMPTMP) was polymerized with TTT. The HDT/TTT system[28] (T_g = 23 ±1 °C) was prepared at stoichiometric thiol-to-ene ratios, whereas in the TMPTMP/TTT system[28] TMPTMP was used in 25% excess to further reduce its T_g (42 ±1 °C) as well as to observe the effect of having free pendant thiols in a non-dynamic network. In Figure 3, the relative permittivities are plotted over a range of temperatures (20 - 120 °C).

From the data in Figure 3, drastic differences can be observed between the tested materials. It is typical that dielectric constant increases with temperature to a varied extent[27]. However, the CANs show a gigantic increase in RP of three orders in magnitude within the scanned temperature range. In contrast, the thiol-ene reference materials increase their RPs only minimally from 6 (at 20 °C) to 12-25 (at 120 °C). The 25 RP value for TMPTMP-25/TTT at 120 °C is attributed to the facilitated polarization of the network chains with pendent mercaptopropionates. Clearly, these huge enhancements observed in CANs originate in covalent exchange reactions which increase in rate with the increase in temperature. All three ASA/PETMP-50 samples have larger RPs than their stoichiometric relatives at corresponding temperatures, likely due a higher potential for polarization and dipole orientation resulting from faster bond exchange rates. Further, the same materials behave differently depending on the exchange catalyst used. TEMPO-catalysed CANs exhibit initially smaller PRs which gradually increase with temperature, whereas DBU-catalyzed exchange results in rapid initial RP increase which plateaus at 60 °C. On the other hand, the stoichiometric CAN with DMAP shows a gradual RP increase whereas the off-stoichiometric system is characterized with a plateau just like the DBU-based CANs. The data also suggest an exchange reaction proceeding at ambient temperatures in DBU-infused CANs, as these have relatively large ambient RPs of 55 and 75, respectively. Overall, this initial dielectric results show some promise of a new practical application for CAN materials as dielectric capacitors with high electric energy density that are used in electronic devices[29, 30]. To gain insight into the possible modes of exchange in the thiol-anhydride dynamic photopolymer networks dielectric modulus and loss were measured as a function of frequency for a range of temperatures. In Figure 4 dielectric modulus and dielectric loss functions are plotted for the new CAN systems. As illustrated, there is a typical frequency shift visible with temperature in all analysed materials. Further, the plots in Figs a, b, and c show similar trends where the dielectric modulus, constant at high frequencies regardless of the temperature, drops down rapidly at progressively lower frequencies with an inflection region at intermediate frequencies followed by a further drop at yet lower frequencies. The initial dielectric modulus drop is associated with a transition region typically attributed to a glass transition. The intermediate frequency shoulder visible in modulus in TEMPO-based materials becomes progressively broader in the DMAP-based stoichiometric system (Figure 4c). At 120°C it is plateauing over a broad frequency range. This evident plateau is even wider for dynamic networks shown in Figs. 4d, e and f where it spans a frequency range of up to five orders of magnitude (Figure 4d). Interestingly, for samples in Figs. 4d-f, the plateau in dielectric modulus is of constant value at some frequencies regardless of the temperature of the experiment. For example, in Figure 4d at 1 Hz frequency, the dielectric modulus has the same value for four runs at temperatures between 40 and 100°C. Similar intermediate frequency ranges where the dielectric moduli have constant values can be seen in Figures 4e and f. The plateau dielectric modulus exceeds the dielectric loss at corresponding frequencies, except for the 120 °C DMAP run, as is not otherwise seen in Figs. 4a-c. The first three dielectric data sets in Fig. 4 are two CANs with poor exchange catalysts at low loadings and a stoichiometric thiol-free network though with a better exchange catalyst. Notably, the DEA profiles of the TEMPO networks very much resemble those of the nondynamic thiol-ene networks (Figures S6-8) although the crossover points are shifted in frequencies for the corresponding temperatures. Considering the findings from IR reversibility studies as discussed earlier, it is assumed that the thiol-anhydride reversion is the primary exchange mode responsible for the dynamic behavior observed. However, a secondary exchange mode appears apparent in off-stoichiometric systems or in systems with more potent catalysts. For instance, the dielectric data in Figure 4c, clearly shows a change in shape of dielectric moduli profiles with increasing temperatures which is progressively more resembling the off-stoichiometric system, i.e. where the reversible exchange could be facilitated because of abundant thiols and the stronger catalyst. Knowing that the stoichiometric systems have approximately 30% of reversed thioesters at 120°C, there will be substantial thiol concentration to affect the relaxation mode at that point and increase the contribution of the reversible exchange. As an associative exchange mechanism, the reversible exchange, when active, would not promote network depolymerization, keeping the modulus-frequency response constant. For instance, the dielectric modulus for the ASA/PETMP 5 mol% DMAP system is lower at 1Hz at temperatures 80-120C than in the initially less crosslinked off-stoichiometric system where the reversible exchange is assumed to “postpone” the modulus decrease (or the timescales for relaxation are long enough to reorient all polarized chains and segments). In other words, the increasing contribution of reversible exchange affects the mobility of the network segments as it is not causing crosslinking density reduction, and a constant number of polar groups are oriented in a broad range of time scales, or frequencies. The same trend is obvious when comparing off-stoichiometric CANs with TEMPO and DMAP, or even DBU. A dominant reversible exchange would hold the dielectric modulus constant over a broader frequency range, even though its primary transition occurs at higher frequencies. Moreover, at intermediate frequencies where the dielectric modulus remains constant, the loss factor is continually lower until the second crossover is reached.



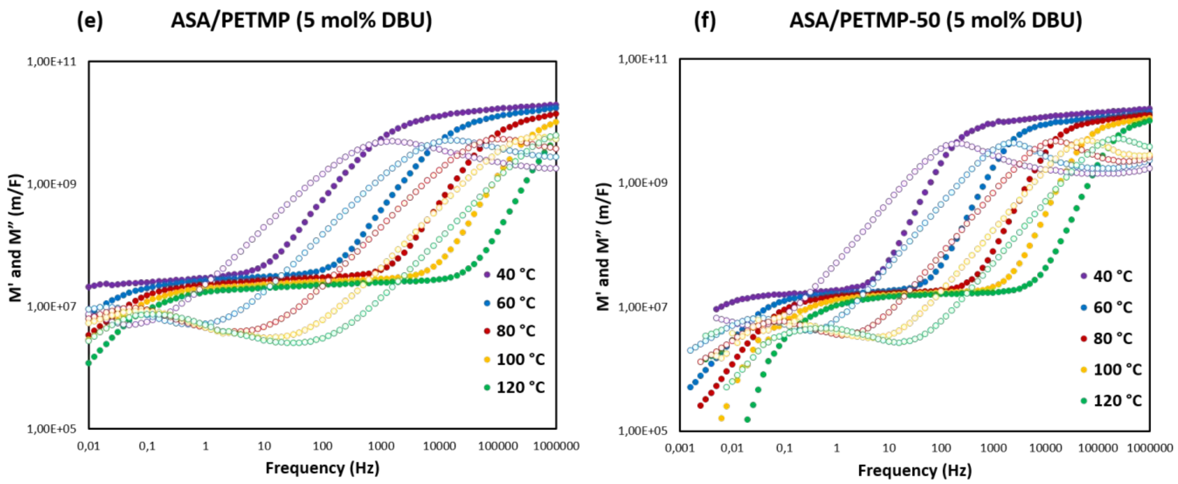


Figure 4. Dielectric modulus (filled circles) and dielectric loss (open circles) as a function of frequency for thiol-anhydride CANs.

This behavior is observed for CANs in Figure 4d-f, i.e. the three most dynamic system variations reported in this paper. Particularly, the two DBU containing CANs are both highly dynamic materials. It appears, that reversible exchange is substantial even in the stoichiometric system, probably due to a higher concentration of thiolate species. Its dielectric modulus plateau is the broadest of all tested samples. In DBU-based CANs both mechanisms play an important role in the overall exchange dynamics. The off-stoichiometric systems also exhibit a pronounced plateau which breaks down rapidly at lower frequencies. The timescales for polar relaxations now become long enough at lower frequencies apparently due to the coupling effects of low crosslinking, partial reversion and rapid exchange as their cooperation helps to orient larger in size, polarized segments and network sections. Finally, what is seen as a shoulder in the dielectric loss at intermediate frequencies in Figs 4a-c becomes a secondary peak visible at higher temperatures in Figs. 4d-f. This peak marks a second transition in the dielectric relaxation which overcomes the “inhibitory” effects the reversible exchange has on the alignment of molecular moments at lower frequencies. A steep increase in the tan delta profiles is seen at progressively lower frequencies after the initial peak-marked relaxation which is in accordance

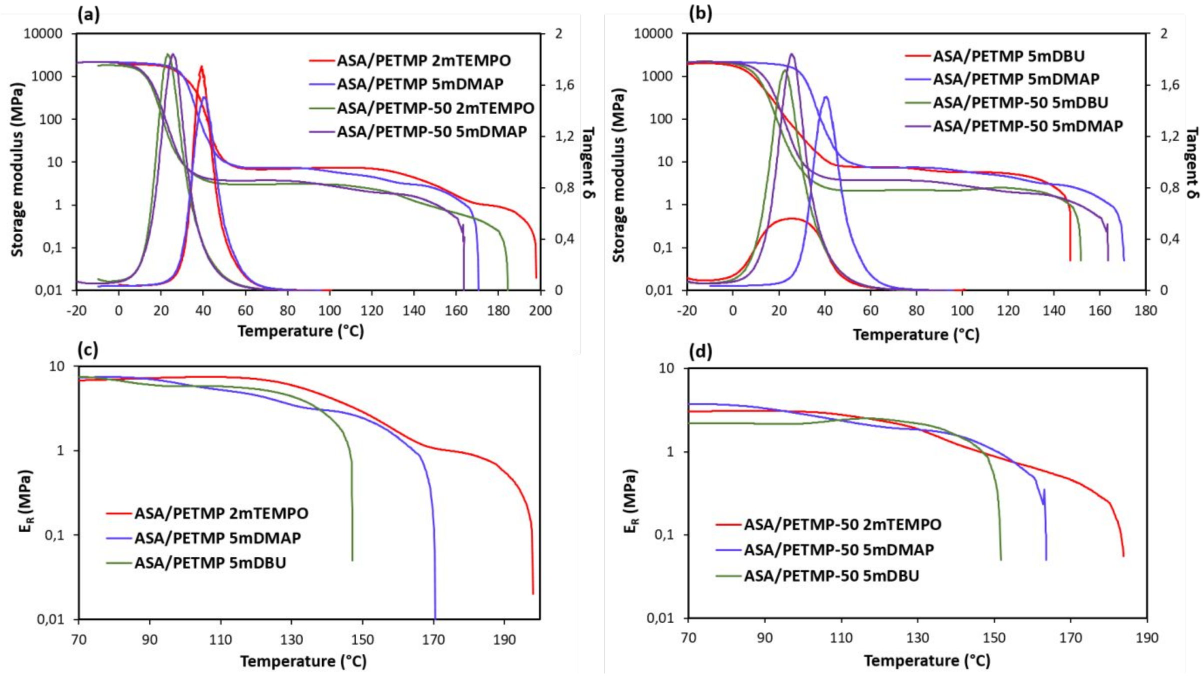


Figure 5. DMA storage moduli and tangent delta values for thiol-anhydride CANs. (a) a comparison of TEMPO-based networks with DMAP-based networks; (b) a comparison of DMAP-based networks with DBU-based networks. Evident are rubbery moduli drop-offs at temperatures ranging from 140 to 200 °C when thee preload force was set to 0.002 N; (c) an enlarged set of E_R for stoichiometric ASA/PETMP CANs, and (d) an enlarged set of E_R for off-stoichiometric ASA/PETMP-50 CANs.

with the observed dielectric inflection range and secondary dielectric loss peak (Figure S5).

Dynamic Mechanical Analysis (DMA). Additional confirmation of the change in the exchange modes in the thiol-anhydride CANs is gleaned from the DMA rubbery moduli drop-offs observed at constant preload forces, and at temperatures nearing or exceeding the gel-point conversions (Figure 5). It is expected that a dynamic material would reach a breaking point when it is gradually heated under constant stress. A breakdown in properties will be seen, for example, when a gel-point conversion is approached under applied stress in a dynamic reversible network. Prior to such an event however, a continuous drop in the rubbery modulus (E_R) would be observed. By comparing the E_R profiles before the drop-offs occur in Figure 5a, it is evident that above 90-120°C the rubbery moduli decrease gradually until the materials yield abruptly under the applied stress. The TEMPO-catalyzed networks exhibit more rapid modulus decrease than their DMAP analogues, although the thermomechanical data, i.e. the T_g and the initial rubbery moduli values, are practically identical in both types of CANs. Moreover, as seen in Figure 5b, where DBU and DMAP-based CANs are compared, the differences in the moduli profiles are more pronounced, i.e. the decrease in the rubbery moduli in DBU-based samples is less significant until the drop-off point. The ASA/PETMP-50 DBU sample which has the highest potential for reversible exchange is even characterized by an increase in E_R occurring above 100 °C until 140 °C followed by a breakdown (Figure 5d). Such an increase in E_R is typically observed in nondynamic networks at temperatures above T_g.

In theory, nondynamic networks will have the rubbery modulus proportional to the absolute temperature while dynamic networks will only have a decrease in rubbery modulus when the exchange process becomes rapid relative to the timescale of the measurement or until reversible addition becomes significantly temperature dependent. Poor catalysis of the reversible exchange would thus favor reversible addition. Accordingly, the rubbery moduli are affected by the continually decreasing crosslinking densities, hence the observed decline. Further, the materials differ in the temperatures of their dramatic modulus decrease. The three different catalysts employed in the networks would not affect the reaction equilibria, but clearly they affect the rates at which these equilibria are approached. A poor catalyst implies a slow reversion rate, and the breaking point is reached at higher temperatures as exemplified by the ASA/PETMP and TEMPO combination. Assuming that DBU would facilitate faster rates of reversion towards equilibrium conversion, then the drop-off would occur earlier, as it did. Although, the associative exchange could also be expected to reveal plasticity in a dynamic material even at relatively short timescales provided that the exchange is rapid enough as demonstrated previously

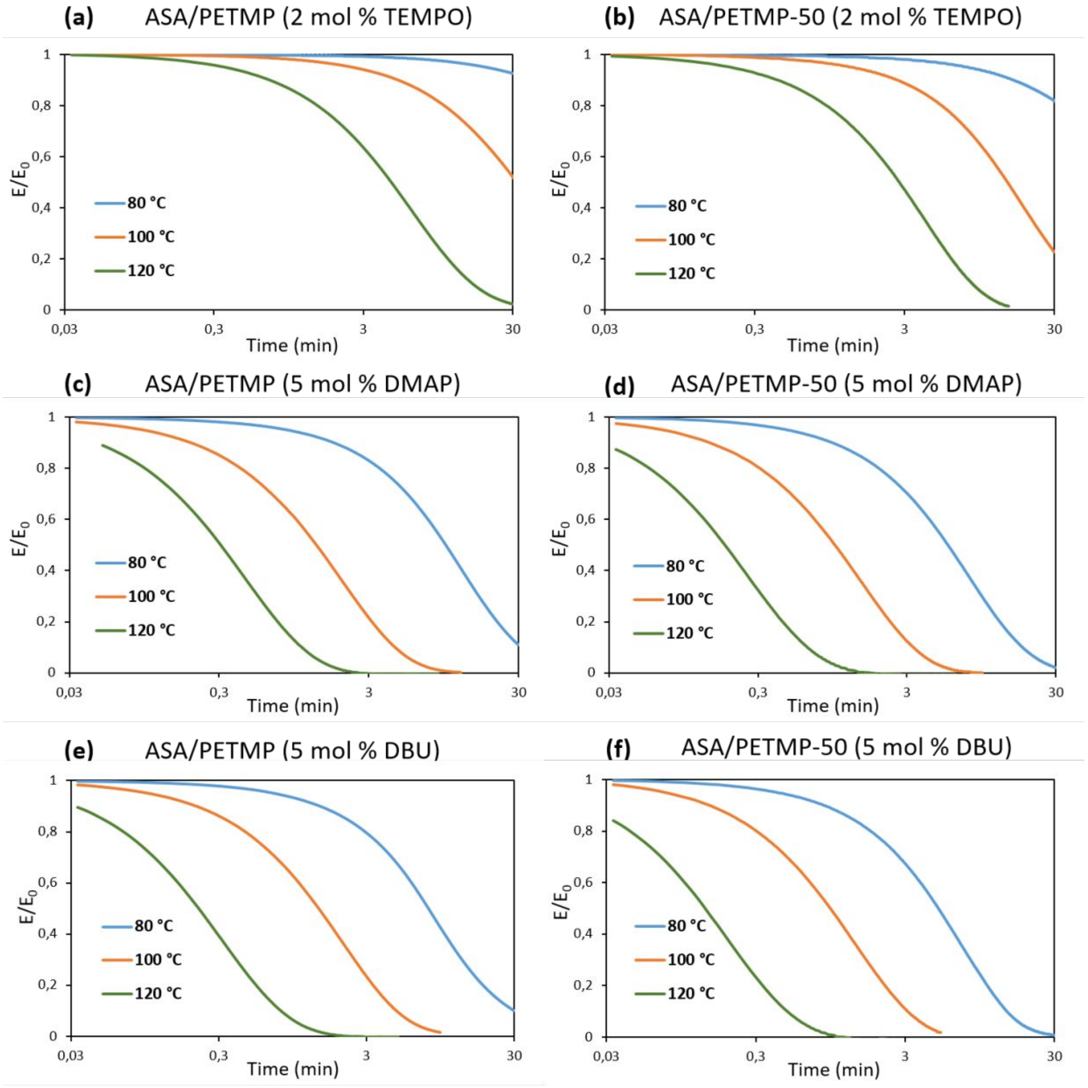


Figure 6. Representative stress relaxation data of the thiol-anhydride CANs. TEMPO-catalyzed relaxation in insets (a) and (b). DMAP-catalyzed relaxation in insets (c) and (d). BDU-catalyzed relaxation in insets (e) and (f).

in thiol-thioester networks[31]. Overall, the DMA data confirms the findings from dielectric spectroscopy that the mode of exchange in thiol-anhydride CANs is easily controlled depending on how potent the catalyst is, and even in off-stoichiometric systems, the reversible exchange may be hindered in favor of reversible addition, and vice versa.

DMA Stress Relaxation. The stress relaxation data was obtained from the DMA experiments carried out at constant temperatures and strains (10 %) in tensile modes. Also, dielectric modulus and loss crossover points occurring during the first high frequency transitions were used to calculate the activation energies and compare with those extracted for viscous flow from the DMA. In light of the DEA data discussed earlier, the crossover points at a given temperature become shifted toward higher frequencies when the systems become increasingly more dynamic as is the case when catalyst strength (loading) is increased. This trend is also evident in less dynamic materials formed from maleic anhydride (MAn) and PETMP, where a catalyst-free MAn/PETMP-50 system is contrasted in DEA against a DMAP-catalyzed analogue (Figure S10). Moreover, the DEA data of the nondynamic thiol-ene materials very much resemble the MAn-based dynamic network which exhibits significantly reduced reversibility in the range of temperatures tested[22]. The stress relaxation trends for all ASA-based CANs at three temperatures are depicted in Figure 6. The characteristic takeaway points are: the rates of stress relaxation increase in off-stoichiometric CANs regardless of the catalyst type, with the slowest rates found for TEMPO-catalyzed dynamic networks. Even though the mechanism of exchange was previously argued to be changing between the DMAP and DBU CANs, both types of materials are characterized by comparable rates of stress relaxation in stoichiometric as well as in off-stoichiometric systems. Further, the activation energies extracted from DMA and DEA match well, and show little dependence on the catalyst type (Table 1). This data suggest that the dominant exchange mechanism is the reversible addition. On the other hand, each dynamic mechanism may be characterized by a similar activation threshold which would hinder any differentiation between the mechanisms, especially in stress relaxation experiments that produce erratic data in a single exponential decay scenario.

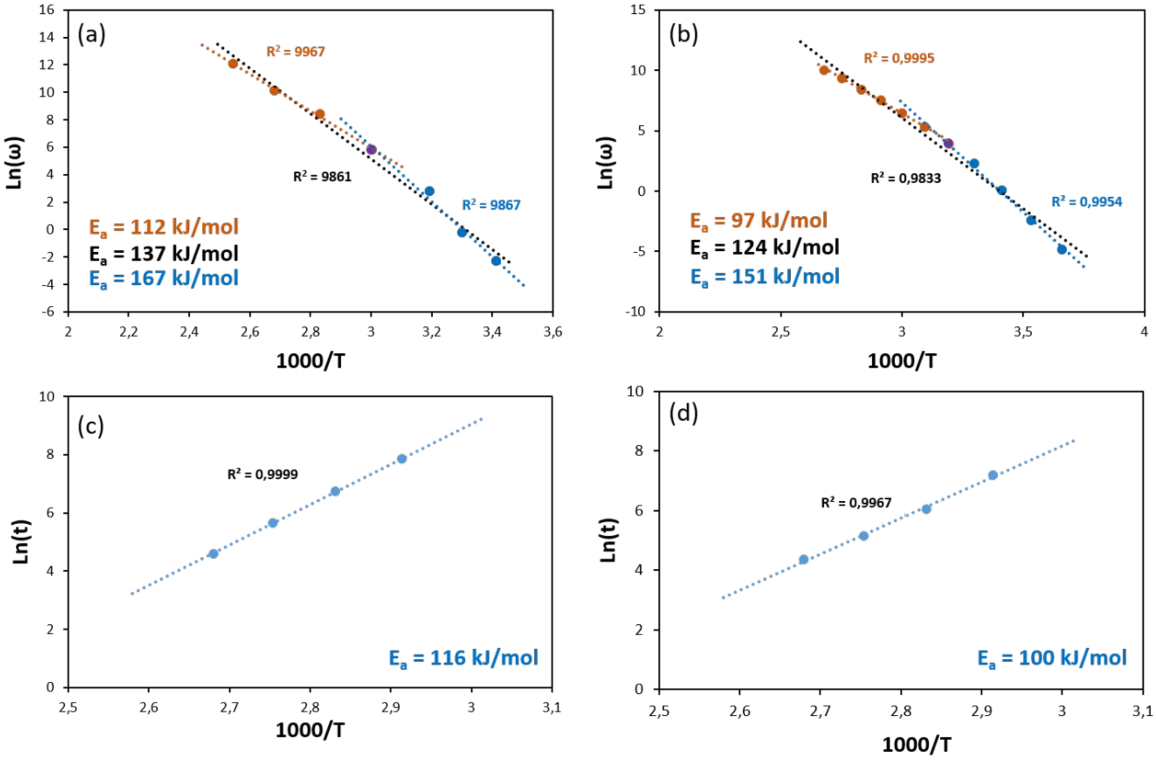


Figure 7. Representative Arrhenius fits of the dielectric data and DMA stress relaxation data for the ASA/PETMP CANs with DMAP catalyst. Logarithmic crossover frequencies in the function of T^{-1} for ASA/PETMP materials: stoichiometric syatems (a) and off–stoichiometric (b). Logarithmic relaxation times at e^{-1} in the function of T^{-1} for stoichiometric (c) and off–stoichiometric (d) DMAP-catalyzed dynamic networks. Activation energies (E_a) are included in the figures.

Table 1. Activation energies (E_a) for thiol-anhydride CANs extracted from DMA stress relaxation experiments and Dielectric Spectroscopy.

CAN composition (catalyst)	E_a from DMA stress relaxation (kJ/mol)	E_a from dielectric spectroscopy (kJ/mol)
ASA/PETMP (2mTEMPO)	120 (2)	112 (-)
ASA/PETMP-50 (2mTEMPO)	105 (-)	102 (-)
ASA/PETMP (5mDMAP)	116 (3)	112 (4)
ASA/PETMP-50 (5mDMAP)	100 (3)	97 (5)
ASA/PETMP (5mDBU)	111 (4)	101 (-)
ASA/PETMP-50 (5mDBU)	106 (7)	97 (-)

The stoichiometric systems all have higher activation energies as compared to the off-stoichiometric ones which would suggest an involvement of reversible exchange in the overall exchange mechanism in samples abundant in free thiols, the more so that the off-stoichiometry would also hinder the reversible addition by pushing the thermodynamic equilibrium towards product formation. The energies of activation from DMA and DEA (Table 1) were all calculated using data points gathered between 60 and 120 °C. Interestingly, if additional data points at lower temperatures are included in the Arrhenius fits from dielectric analysis, further deviation is observed (Figure 7). This deviation implies other, non-reaction related phenomena may be of significance at lower temperatures. For instance, hindered segmental orientation of polarized network chains that at low temperature conditions behave more as typical non-dynamic materials.

Conclusions

In this work we studied the dynamic properties of two compositionally distinct thiol-succinic anhydride photopolymer CANs. Stoichiometric and thiol-abundant off-stoichiometric networks were facilely fabricated by premixing the monomers with a catalyst (base or nucleophile) followed by subsequent UV-photopolymerization. The reversibility of the thiol-anhydride ring opening reactions in both types of CANs was extensively characterized. It was demonstrated that the new CAN-containing materials are highly dynamic, and their dynamic response is controlled depending on the catalyst type and the initial monomer feed ratios. Depending on the compositional differences between the CANs, it was argued that a second, associative exchange mechanism (thiol-thioester exchange) is contributing in the overall exchange dynamics. IR reversibility studies, dielectric spectroscopy, and DMA stress relaxation and rubbery moduli vs. temperature dependencies were used as the characterization techniques. Further it was argued that based on the acquired data the exchange is likely switching in modes from primary (dominant) reversible addition to increasing contributions of reversible exchange, although the reversible addition is assumed predominant in all materials. However, there is a drop in activation barriers in thiol rich networks, which together with the dielectric data suggest an associative mechanism of exchange to be involved as well. Extensive as it is, although not exhaustive, this study proves that there exist two reaction mechanisms in thiol-anhydride CANs which both contribute to their dynamic behavior. Apparently diverse dynamic behaviors were shown to result in similar stress relaxation profiles. Also this study demonstrates that dielectric analysis is an insightful characterization method of dynamic materials, not only those discussed herein. The current examples represent only a small fraction of the potential dynamic materials that are possible from thiol-anhydride functionalities. For instance, other commercial anhydrides such as those with strained anhydride rings would likely produce less reversible thioester products. Further, the reaction reversibility would be expected to further diversify by employing thiols differing in their basicity.

Conflict of interest

The authors declare no potential conflict of interest.

Acknowledgements

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TOC graphic

Thiol-succinic anhydride dynamic photopolymer networks were fabricated and their dynamic behaviour characterized. The thioester anhydride reversible addition and thiol-thioester reversible exchange are discussed as two competing mechanisms dictating the overall dynamic response.