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Dynamic Composites

Thiol–Anhydride Dynamic Reversible Networks

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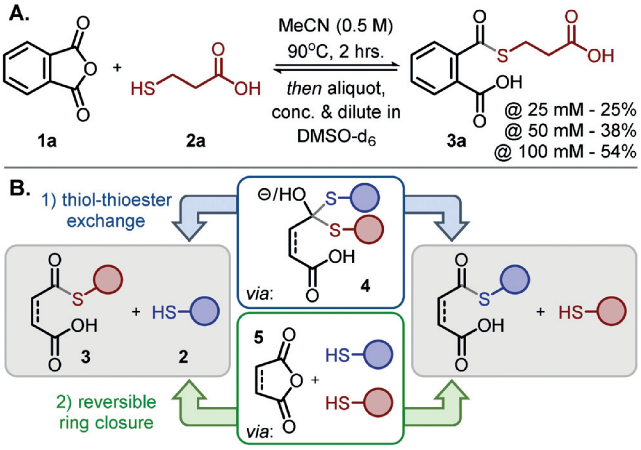
Abstract: *The reaction of thiols and anhydrides to form ring opened thioester/acids is shown to be highly reversible and it is accordingly employed in the fabrication of covalent adaptable networks (CANs) that possess tunable dynamic covalent chemistry. Maleic, succinic, and phthalic anhydride derivatives were used as bifunctional reactants in systems with varied stoichiometries, catalyst, and loadings. Dynamic characteristics such as temperature-dependent stress relaxation, direct reprocessing and recycling abilities of a range of thiol–anhydride elastomers, glasses, composites and photopolymers are discussed. Depending on the catalyst strength, 100 % of externally imposed stresses were relaxed in the order of minutes to 2 hours at mild temperatures (80–120 °C). Pristine properties of the original materials were recovered following up to five cycles of a hot-press reprocessing technique (1 h/100 °C).*

Covalent adaptable networks (CANs) are a subset of thermosetting polymer networks that exhibit covalent bond reshuffling capabilities while retaining typical thermoset end-use properties and solvent insolubility.[1] Unlike conventional thermosets, CANs[1b,2] can be reshaped or repurposed by application of an external stimulus, such as temperature,[3] light,[4] or changes in pH,[5] which activates the internal dynamic covalent chemistry (DCC). Consequently, there exist a considerable number of DCCs available for implementation into CANs,[6] although many of these reactions, with some notable exclusions (such as urethanes,[7] thiourethanes,[8] or siloxanes[9]), require multistep monomer synthesis and complex methods for implementation. Herein, a previously unreported dynamic chemistry based on the reversible ring-opening reaction of anhydrides with thiols is studied. It is shown here that different commercial anhydrides efficiently act as tunable dynamic crosslinks at different temperatures, opening the possibility for broad application of this chemistry in material science and polymer chemistry (Scheme 1).



Scheme 1. A) The unexpected concentration dependent reversion of the thiol–anhydride reaction in polar media as evidenced by ^{1}H NMR spectroscopy; B) proposed mechanisms of the reversible exchange of thiols to anhydrides via thiol-thioester exchange (1) or reversible anhydride ring closure (2).

Previous reports regarding the room temperature dynamic exchange of thiols and thioesters within network polymers[10] were largely based on monomers derived from the ring-opening of succinic anhydride with 3-mercaptopropionic acid to form functional thioesters. While further exploring the scope of this ring-opening, it was observed that the reaction of phthalic anhydride (**1a**) with 3-mercaptopropionic acid (**2a**) gave highly variable yields of the product, and attempts to further functionalize the diacid (**3a**) through esterification resulted in an intractable mixture of products. Accordingly, model studies were performed whereby phthalic anhydride (**1a**) was reacted with thiol **2a** in acetonitrile at 90 °C for 2 h in the absence of a base or catalyst. Aliquots of various volumes were extracted, concentrated, and dissolved in [D$_6$]DMSO to give three homogeneous samples at different concentrations (25, 50, and 100 mM); ^{1}H NMR spectroscopy of these samples revealed different conversions to the product (25, 38, and 54 %, respectively). This simple experiment demonstrated that the ring-opening reaction was spontaneous, highly reversible, and likely proceeding through a reversible ring opening/closing mechanism. This effective reversibility was attributed to the planar structure of the phthalic anhydride, which after ring opening enforces close vicinity between the aromatic thioester anhydride and the neighboring carboxylic group. A similar ester–anhydride reversion was recently shown in polyester networks designed from multi-functional alcohols and phthalic anhydride derivatives.[11]

To determine the reversibility of the thiol–anhydride adducts derived from aliphatic anhydrides, methyl succinic anhydride (MSA) was reacted in another model reaction with methyl 3-mercaptopropionate (MMP; Supporting Information, Figure S1). The combination of equimolar concentrations of MMP and MSA, this time with inclusion of 5 mol %

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DMAP catalyst (4-(dimethylamino)pyridine), resulted in two regioisomers whose thermal reversibility was investigated by NMR (Supporting Information, Figure S2). Though devoid of the structural planarity of the aromatic anhydrides, the aliphatic thioester anhydrides were also found to be highly reversible, resulting in close to 40 % substrate regeneration at 120 °C. Both model experiments clearly demonstrated the general reversibility and fidelity of the thiol–anhydride adducts in structurally diverse anhydrides.

Following discovery of this highly reversible and spontaneous reaction, application was sought in material science, specifically with interest in utilizing inexpensive multifunctional anhydrides as dynamic crosslinks. Accordingly, maleic anhydride (MAn) was reacted with a tetrathiol PETMP (pentaerythritol tetrakis(3-mercaptopropionate)) at various stoichiometries, in the presence of DMAP (5 mol %) and DCM (monomers/solvent 50:50 vol %). After solvent evaporation and drying, the concomitant thiol-Michael and thiol–anhydride reactions resulted in the formation of thioether/thioester-based networks with side-chain carboxylic groups (Supporting Information, Figure S3). Because the thiol-Michael reaction of the MAn generated a substituted (thioether) analogue of the succinic anhydride, this provided justification for the expected dynamic behavior of such two-component thiol–anhydride systems. The thermomechanical properties of MAn/PETMP networks of varied stoichiometries are illustrated by DMA results (Figure 1 A; Supporting Information, Figure S4). As expected, increasing the thiol concentration leads to less crosslinked networks with progressively lower glass transition temperatures and rubbery storage moduli (E_R). As opposed to our previous reports on thioester containing CANs,[10] here, thiol–anhydride polymerizations form thioesters in situ without any need for involved monomer synthesis. Further exploration of these materials is seen in Figures 1 B,C, which illustrate exemplary DMA stress relaxation curves, showing these networks to behave dynamically in response to increased temperature. It is evident that rapid stress relaxation occurs at relatively low temperatures, and even in the absence of free thiols (Figure 1 B). By taking into consideration the thermal reversibility of the model thioester anhydride compounds, the reversible addition is proposed as the main dynamic exchange mechanism. However, in this instance such dynamic behavior may also be related to thiol–thioester exchange, as illustrated in Scheme 1, as an auxiliary exchange mechanism, especially when abundant thiols are present. Indeed, increasing the thiol excess increases the stress relaxation rate, although such behavior is concomitant with the reductions in crosslinking densities, and therefore prevents any efficient decoupling of either effect.[12] It would be expected that the off-stoichiometry in a thermodynamically driven process would favor the product (thioester) formation, thus imposing an obvious constraint on the reversibility. Such an effect cannot be ruled out in the network where the anhydride is in excess (no free thiols and reduced crosslinking), which exhibits longer relaxation times than the more crosslinked, but also a more reversible, stoichiometric system (Figure 1 B). Conversely, free thiols allowing for associative thiol–thioester exchange and reduced crosslinking could effectively counter the reduced reversibility and result in networks with a higher propensity for stress reduction.

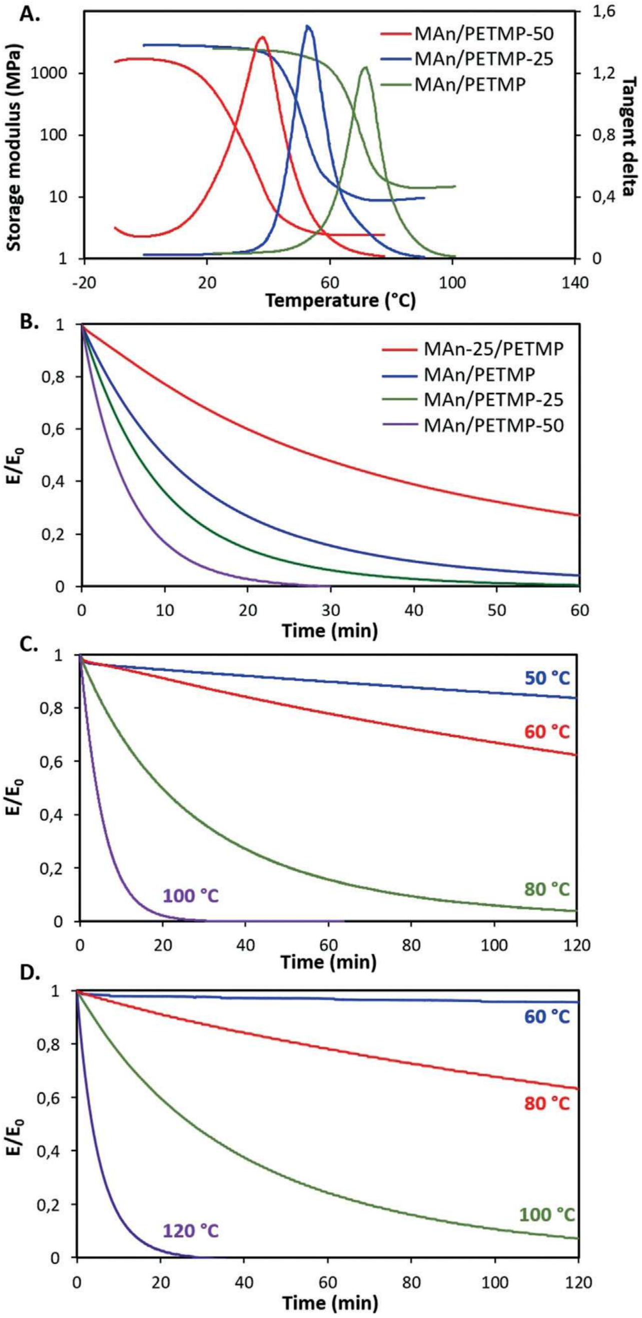

Figure 1. A) Storage modulus and tangent delta results of MAn/PETMP dynamic networks of varied thiol–anhydride stoichiometries (the number after the monomer acronym indicates % monomer excess). B) DMA stress relaxation profiles for MAn/PETMP CANs at 100 °C. C) Temperature-dependent stress relaxation for MAn/PETMP-50 formulations with 5 mol % DMAP, and D) 5 mol % TEMPO.

Furthermore, the rates of stress relaxation also vary for compositionally analogous networks with catalyst types (Figure 1 C,D). The Arrhenius activation energies (E_a) were estimated at around 100–115 kJ mol^{-1} when DMAP or TEMPO were used (Supporting Information, Table S2). As seen from comparison of Figure 1 C and D, in a 50 % thiol excess system 5 mol% of a nucleophile (DMAP) is a more efficient catalyst, in this implementation, than 5 mol% of a base generator such as TEMPO.[13] The mechanisms of catalytic activation are clearly different for either type of catalyst. Here, the nucleophile ($pK_a = 9.4$) performs better than the base, a product of TEMPO reduction (tetrametylpiperidine, $pK_a = 11.4$). Even though less efficient than DMAP, using TEMPO, a source of a thermally latent base,[13] facilitates casting of the resin as solvent is no longer necessary. Here, TEMPO-based samples were cast in thin films and cured thermally at 80–100 °C for 1 h. Interestingly, even catalyst free samples exhibit dynamic characteristics (Supporting Information, Figure S5), further supporting the reversible addition mechanism as outlined above.

Overall, having excess thiol (rather than anhydride) in combination with a catalytic species clearly accelerates the relaxation (exchange) rates which is suggestive of an associative pathway (Scheme 1 B, bottom). Although a more detailed mechanistic study would be required to distinguish the differences between these mechanisms, especially in systems of defined crosslinking densities, it seems that both pathways are active and play a role in the overall dynamic characteristics of thiol–anhydride materials. Because of the enhanced dynamic performance of systems with free pendant thiols and nucleophilic catalysts, a 50% excess thiol composition (MAn/PETMP-50, 5 mol% DMAP) was selected to further demonstrate self-healing and reprocessability properties of these materials (Figure 2; Supporting Information, Figure S6). As presented in Figure 2 A, direct reprocessing by hot press molding was conveniently achieved at 100 °C for 1 h. The same material was assessed for its tensile properties after multiple reprocessing cycles (Figure 2 B). A slight decline in the stress–strain profiles was observed initially (up to the third cycle), but it was attributed to a possible off-equilibrium of the system with a number of cleaved bonds still present. When re-equilibrated by time-extended slow cooling (30 min), the properties of the pristine CAN were recovered. Further, a dynamic composite was readily prepared by thermal curing of a MAn/PETMP stoichiometric resin with 50 wt% thiolated silica microparticles (av. $d = 0.4\ \mu m$) and 2 mol% TEMPO. This resulted in a composite glass that was characterized by an impressive 7.6(± 0.7) GPa Young's Modulus and 130(± 9) MPa peak stress from a three-point bending test (Supporting Information, Figure S7). As demonstrated in Figure 2 C, this dynamic composite was thermally reshaped through several intermediate and permanent functional shapes eventually returning the material to its original flat rectangular shape. Each of the shapes in Figure 2 C were found to be permanent and stable at elevated temperatures in unconstrained configurations.

This new thiol–anhydride dynamic chemistry was further implemented in the fabrication of dynamic thiol–ene photopolymers. Three examples of dynamic thiol–ene networks based on three anhydride derivatives (**1b–d**) and HDT or PETMP were readily synthesized (Figure 3 A–C). Each of the photopolymer resins was formulated using solventless conditions and cured by exposure to UV irradiation ($10\ mW\,cm^{-2}$, 365 nm) in the presence of DMAP (5 mol%) and DMPA photoinitiator (0.2 wt%). Structurally distinctive anhydrides were found to influence the thermodynamic equilibria and thus gave rise to variations in the temperature-dependent thioester–anhydride adduct formation and reversibility. A stoichiometric and more crosslinked ASA/PETMP system ($T_g = 42$ °C; $E_R \approx 8$ MPa) was characterized by significantly accelerated rates of stress relaxation when compared with the loosely crosslinked MAn/PETMP-50 composition ($T_g = 39$ °C; $E_R \approx 2$ MPa; Supporting Information, Table S2). Furthermore, the off-stoichiometric, thiol-abundant systems have apparently lower activation energies than their stoichiometric analogues but the differences seem minimal (around $10\ kJ\,mol^{-1}$). Because of its planar structure, the phthalic anhydride derived thiol–ene network exhibits the

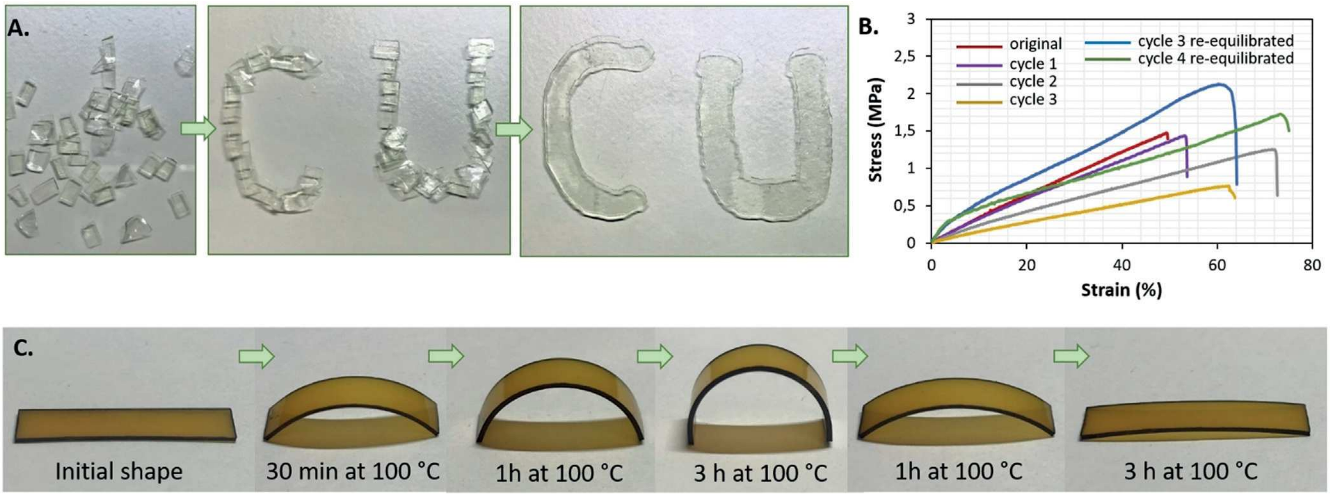

Figure 2. A) Direct reprocessing of MAn/PETMP-50 by hot press molding at 100 °C for 1 h. B) Stress–strain dependence of pristine and recycled MAn/PETMP-50 dynamic elastomers. C) Permanent shape reconfiguration of a MAn/PETMP-sillica particle filled composite. The composite was initially deformed around a cylinder at 100 °C for a prescribed amount of time (up to 3 h). After each time interval the constraints were removed and the resulting shape at temperature of the experiment photographed. The shape retention ratio after 3 h at 100 °C was 94%. The material was then returned to its flat shape by deformation (flattening) and heating for 3 h.

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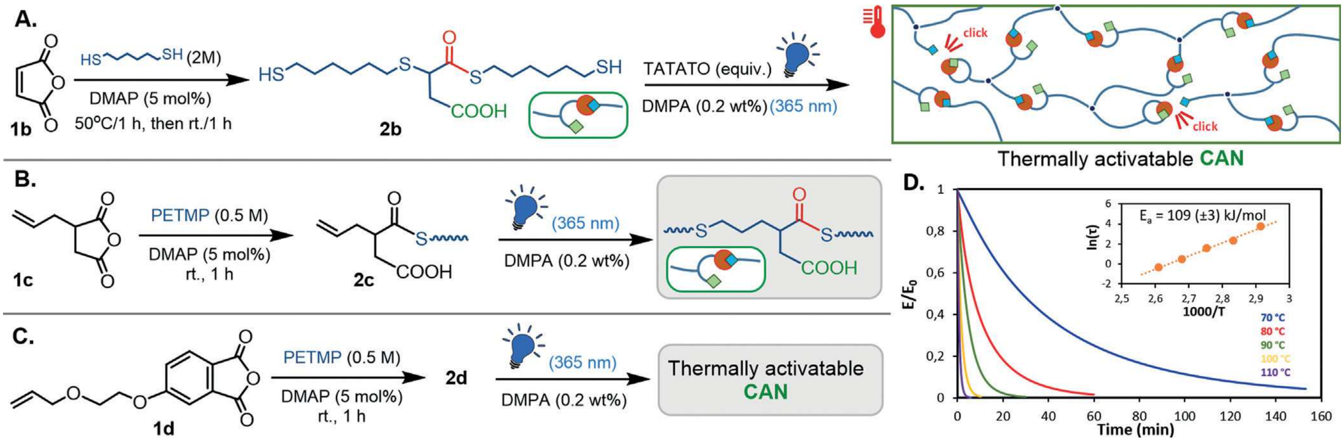

Figure 3. Dynamic thiol–ene photopolymer fabrication based on A) MAn (**1b**), B) ASA (**1c**), and C) APA (**1d**). In (D), the DMA stress relaxation curves are shown for ASA/PETMP stoichiometric system at temperatures ranging from 70 to 110 °C. The inset in (D) shows an Arrhenius fit of the relaxation times at e^{-1} and the respective activation energy (E_a).

highest reversibility at ambient-to-moderate temperatures. Small molecule model studies indicate a 55–60 % thiol–anhydride conversion at ambient conditions when such mixtures are left to equilibrate for an extended time (Supporting Information, Figure S8). The thiol–phthalic anhydride mixture requires extended reaction times in the presence of DMAP before UV exposure to achieve equilibrium conversion; only then subsequent UV exposure in the presence of DMPA results in thiol–ene crosslinking.

Once de-gelled at elevated temperatures, the oligomers must be re-equilibrated at 30 °C for up to 9 h to repolymerize back to a crosslinked network. The depolymerization was monitored in the DMA. For example, at a 0.01 N preload force, the drop-off in the rubbery modulus occurs at around 80 °C for the phthalic anhydride thiol–ene network whereas at the same preload force the MAn/PETMP-50 network breaks down at 160 °C (Supporting Information, Figure S9). Because of low reversibility threshold the phthalic anhydride-based thioester systems are not practical for many high-performance applications, although they could have excellent utility in soft materials or organogels where increased chain mobility would facilitate required reaction yields and reversibility.

Finally, the retro-Michael reaction, which was previously reported in the construction of dynamic thiol-Michael[14] and thiol–yne[15] networks, was also considered as a possible contributing mechanism in the MAn-based dynamic system reported here. To compare the potential for the reversibility of thiol-Michael derived thioethers and anhydride-based thioesters, a control ester only system was prepared by anhydride ring-opening with ethylene glycol and subsequent thiol-Michael crosslinking with PETMP (Supporting Information, Figure S10). Here, stress relaxation profiles were generated at elevated temperatures and stress relaxation solely attributed to the retro-Michael reaction is noted. However, significantly higher temperatures (160 °C) are required to achieve comparable bond exchange rates and match those of the anhydride thioester CANs.

In summary, it has been demonstrated here that the thiol–anhydride dynamic chemistry has a great potential for application in CANs. This conclusion is supported by the ease of use in materials fabrication with no necessity for monomer synthesis. Impressive tunability of bond exchange dynamics was achieved by judicious monomer and catalyst selection and loadings as well as variations in monomer stoichiometries. This new dynamic chemistry was shown to be applicable in diverse types of thermosetting CANs including elastomers, high T_g glasses and composites as well as a broad range of dynamic thiol–ene photopolymers. The latter is particularly appealing considering recent developments in 3D printable technologies. Aside from the versatility in thermomechanical responsiveness, the thiol–anhydride CANs show impressive ability to self-heal, reshape and recycle. No discoloration nor any other property deterioration is observed after repeatable reprocessing cycles. Such dissociative CANs are characterized by rapid dynamic response at elevated temperatures, and little to no dynamic response at temperatures below or nearing glass transitions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: covalent adaptable networks · dynamic composites · photopolymers · recycling · stress relaxation

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