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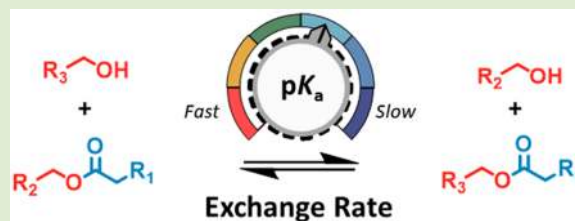
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Brønsted-Acid-Catalyzed Exchange in Polyester Dynamic Covalent Networks

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Supporting Information

ABSTRACT: The effect of catalyst strength on polyester–alcohol dynamic covalent exchange was systematically studied using Brønsted acids and a low- T_g poly(4-methylcaprolactone) vitrimer formulation. Relaxation times, activation energies, and Arrhenius prefactors are correlated with pK_a . Strong protic acids induce facile network relaxation at 25 °C on the order of 10^4 – 10^5 s, significantly faster than Lewis acid alternatives that function only above 100 °C. Activation energies span 49–67 kJ/mol and increase as pK_a decreases. The opposite trend is observed with the Arrhenius prefactor. We anticipate that the quantitative understanding of Brønsted acid effects disclosed herein will be of utility in future studies that exploit acid-catalyzed dynamic covalent bond exchange.



Dynamic covalent bonds imbue polymer networks with unique properties, for example, self-healing¹ and reconfigurability² in response to heat³ or light.^{4,5} The macroscopic behavior of these so-called covalent adaptable networks⁶ (CANs) crucially depends on the mechanism of exchange between pendant, reactive functional groups and cross-links.³ Both dissociative and associative mechanisms are possible, but only the latter occurs without a transient change in cross-link density, producing thermosets (sometimes referred to as “vitrimer”⁷) that exhibit the unusual combination of solvent resistance and plasticity. Consequently, significant effort has been invested to develop different types of chemistries that undergo associative exchange, culminating in a diverse array of options including allyl sulfides,⁸ esters,⁷ alkenes,⁹ carbonates,¹⁰ (vinylogous¹¹) urethanes,¹² boronate esters,¹³ and Meldrum’s acid derivatives.¹⁴ Many vitrimers require catalysts to stimulate bond rearrangement, for example Lewis acids that promote transesterification,¹⁵ Grubbs-type complexes for metathesis,⁹ and photoinitiators that generate radicals.⁵ Despite the success of these systems, a quantitative connection between catalyst strength and exchange kinetics remains poorly developed; catalysts—when necessary—are often selected merely to establish the efficacy of a new associative dynamic covalent bond. Here, we describe Brønsted acids as a new platform to systematically study the influence of catalyst strength on polyester vitrimer exchange (Figure 1) via correlation with the established scale that describes their acidity (pK_a). The results reveal how relaxation times, activation energies, and Arrhenius prefactors track with Brønsted acidity.

CANs comprising main-chain esters and pendant alcohols were selected as a model vitrimer system to study with

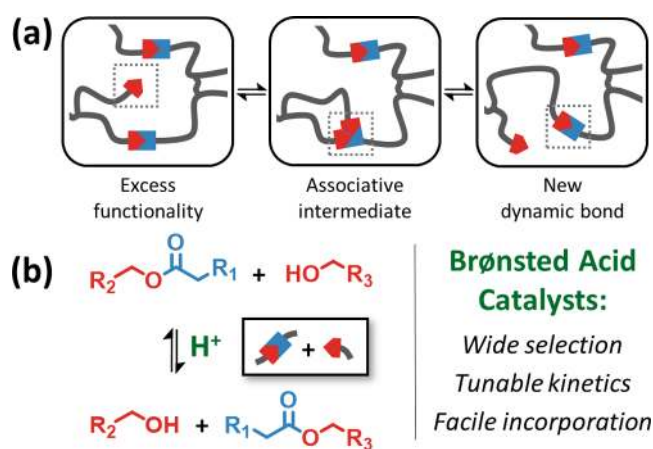


Figure 1. Brønsted acids promote exchange reactions in polyester vitrimers. The kinetics and thermodynamics are correlated with acid strength (pK_a).

Brønsted acid catalysts. This choice was motivated by considerations related to both the dynamic covalent bond and catalyst chemistry. Polyesters are a versatile material platform that is synthetically accessible (via condensation¹⁶ or ring-opening¹⁷ polymerization) with a wide range of possible mechanical properties. Leibler⁷ and Hillmyer¹⁸ have pioneered the development of polyester vitrimers using Lewis acids to promote transesterification at elevated temperatures (≥ 100 °C), and we reasoned that Brønsted acids might broaden the

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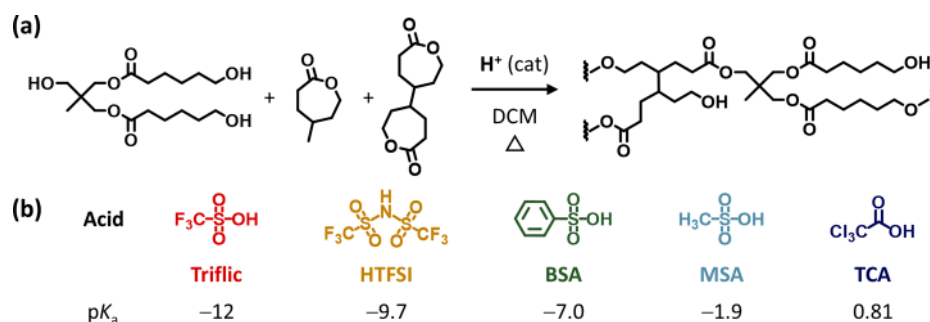


Figure 2. (a) Schematic describing the ROP synthesis of low- T_g polyester vitrimers. (b) Brønsted acid catalysts used to promote ROP and subsequent exchange reactions via transesterification. pK_a values are referenced in H_2O .

scope of available relaxation times in addition to facilitating the quantification of catalyst strength effects. Since Brønsted acids catalyze the (trans)esterification of small molecules¹⁹ and vinylogous urethane CANs,¹¹ it seems reasonable to anticipate they should also trigger polyester vitrimer exchange.

We developed a one-pot synthesis of polyester vitrimers (Figure S1) using ring-opening polymerization catalyzed by a range of Brønsted acids (Figure 2, Table S1) to cleanly form the networks of interest. This approach, inspired by recent work,¹⁸ exhibits two notable differences. First, use of the bis-lactone cross-linker (4,4'-bioxepane-7,7'-dione)²⁰ enables *in situ* cross-linking instead of necessitating postpolymerization reaction with diisocyanates.¹⁸ Our networks are thus exclusively composed of ester linkages, which avoids other cross-links (e.g., urethanes) that can undergo competitive exchange reactions.¹² Second, the monomer 4-methylcaprolactone produces an amorphous polymer with a low glass transition temperature²¹ ($T_g \approx -55^\circ\text{C}$) (Table S2) that facilitates the analysis of vitrimer exchange at room temperature. Such rubbery mechanical properties complement the glassy and semicrystalline variants previously reported with poly(lactide)¹⁸ and poly(caprolactone)²² vitrimers. An additional advantage of this process is that introducing a Brønsted acid catalyst into the network during synthesis avoids any subsequent swelling/deswelling manipulations, which would complicate processing.

Figure 2b illustrates five Brønsted acid catalysts spanning a wide range of pK_a values (-12–0.81) that we embedded in low- T_g polyester vitrimers. All samples were formulated with a 1:25:3 ratio of initiator:monomer:cross-linker to produce reasonably stiff materials (shear moduli ca. 0.5 MPa) with a sufficient density of free chain ends to facilitate bond exchange. One equivalent of acid was added to each formulation, which catalyzes both network curing and subsequent transesterifications. Qualitatively, gel time was inversely proportional to acid strength, but to verify near-complete conversion of both the monomer and cross-linker, solid-state ^{13}C NMR spectra were collected for TCA and MSA—the two weakest acids tested (Figures S2–S5). Solvent (dichloromethane) was removed during processing (see Supporting Information for experimental details), and samples were subsequently analyzed by oscillatory rheology. Step-strain stress relaxation experiments indicate these materials indeed behave as dynamic networks, with a characteristic relaxation time (τ^*) that depends on both temperature (Figure 3a) and acid chemistry (Figure 3b). Additional data for each acid sample are provided in the Supporting Information. Note that τ^* is typically identified as the point in time when the normalized relaxation modulus $G'(t)/G'(0)$ reaches a value of e^{-1} (≈ 0.37), but these data do

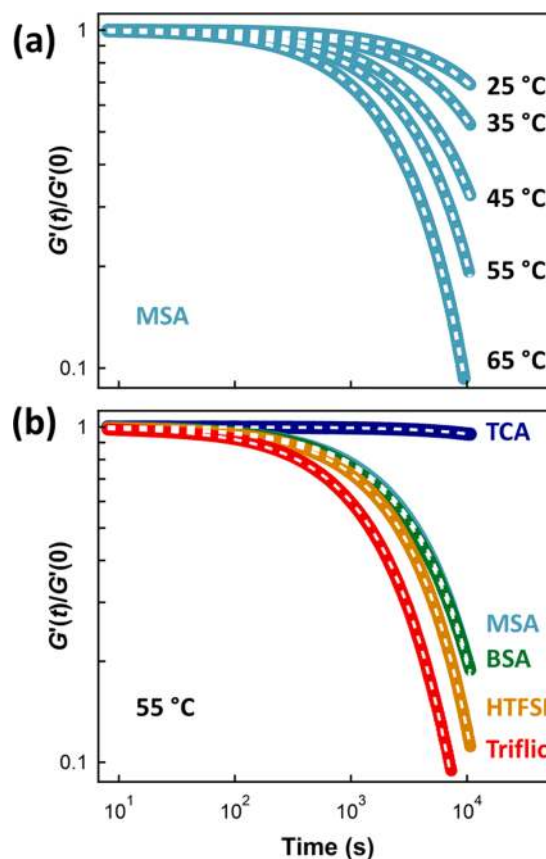


Figure 3. Oscillatory rheology step-strain stress relaxation experiments on low- T_g polyester vitrimer formulations containing Brønsted acid catalysts. (a) Methanesulfonic acid measured at different temperatures. (b) Various acids compared at 55°C . White dashed lines are fits to eq 1.

not perfectly adhere to a simple exponential decay. Instead, the dashed lines in Figure 3 depict a fit to the stretched exponential (eq 1):

$$\frac{G'(t)}{G'(0)} = e^{-\left(\frac{t}{\tau^*}\right)^a} \quad (1)$$

This function is commonly used to model stress-relaxation data²³ when there is a distribution of relaxation rates,²⁴ which seems reasonable herein since primary alcohols and esters are surrounded by different chemical environments depending on the exact network connectivity. Fits are in excellent agreement at all of the temperatures studied for each acid (25 – 75°C , see Figures S6–S10, Tables S3–S7), and eq 1 permits the

extraction of τ^* even for samples that do not fully relax past $G'(t)/G'(0) = e^{-1}$ (Figure S11, Table S8).

Figure 4a plots the temperature-dependent relaxation time $\tau^*(T)$ extracted using eq 1 for each acid versus $(RT)^{-1}$, where

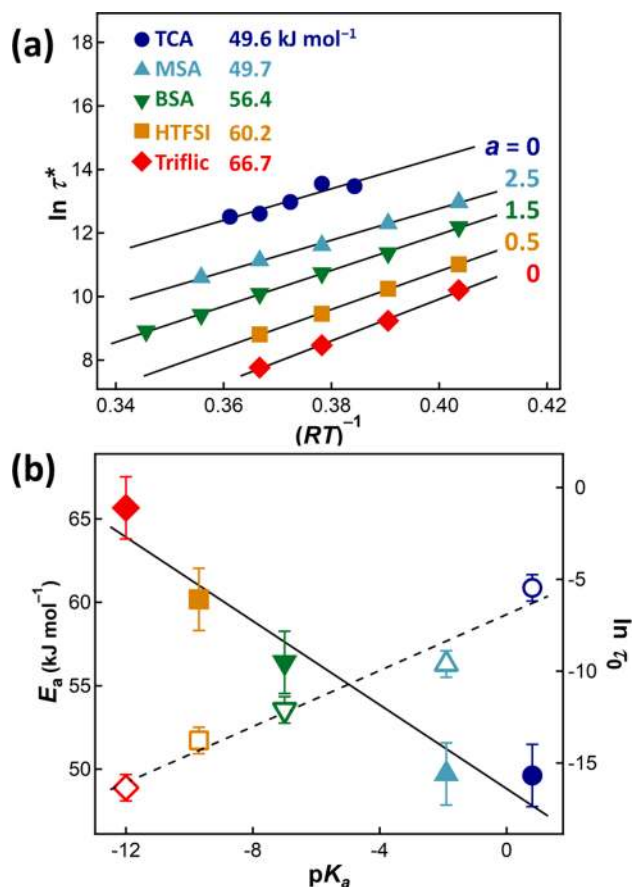


Figure 4. (a) Characteristic relaxation time (τ^*) exhibits an Arrhenius temperature dependence for all five Brønsted acids. Solid lines are fits to eq 2. Arbitrary vertical shifts a were applied to improve the clarity of presentation; Figure S13 provides the same data without offsets. (b) Activation energy (E_a , filled symbols) and Arrhenius prefactor (τ_0 , open symbols) are strongly correlated with Brønsted acidity (pK_a). Error bars are taken as the standard deviations determined from Figure S14.

R is the gas constant and T is absolute temperature. Solid lines are fits to the inverse Arrhenius rate equation

$$\tau^* = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (2)$$

with activation energy (E_a) and front factor (τ_0) treated as fit parameters. The linear trend observed for each acid (on a semilog scale) is a hallmark of associative network rearrangement, one distinctive trait of all vitrimeric materials.³ Both E_a and τ_0 are monotonic functions of Brønsted acid pK_a (Figure 4b). Stronger acids have higher activation energies, implying the characteristic relaxation time will depend more strongly on temperature than that of weaker analogues. τ_0 can be interpreted as the characteristic relaxation time at infinite temperature, when the exponential asymptotes to 1. We find this trend to be inversely related to that of the activation energy, with weaker acids exhibiting larger τ_0 values.

Brønsted acid strength is clearly correlated with vitrimer exchange kinetics and thermodynamics as evidenced by Figures 3 and 4. Consequently, relaxation times and their temperature dependence are tunable over a relatively broad range by the choice of Brønsted acid. While we have selected five that span fairly disparate pK_a values, many other options are commercially available and presumably follow similar trends. In contrast, no studies to date have established firm quantitative relationships using traditional Lewis acid catalysts. Such a correlation is in principle possible, for example using Gutmann–Beckett acceptor numbers that assess Lewis acid strength via reference chemical shifts in nuclear magnetic resonance spectra.²⁵ Nevertheless, Lewis acid catalysts exhibit important qualitative and quantitative differences with the Brønsted acids described above. Liu et al.²⁶ reported a systematic study of different tin-based catalysts and found that activation energy and characteristic relaxation time increase concurrently. Brønsted acids yield the opposite trend; stronger acids relax faster (smaller τ^* , Figure 3b) but have higher activation energies (Figure 4b) than weaker analogues. The underlying cause for this behavior is not yet understood. Moreover, typical Lewis acids tend to activate transesterification only at elevated temperatures ≥ 100 °C, with essentially no exchange at room temperature. Brønsted acids clearly promote transesterification at much lower temperatures (Figure 3). Even though the activation energies we measure for Brønsted acids (ca. 55 kJ/mol) are roughly half that of Lewis acids (100–150 kJ/mol^{7,18,26}), extrapolation of the Arrhenius fits from Figure 4 indicates some Brønsted acids would still relax stress at comparable rates to Lewis acids at elevated temperatures. For example, triflic acid at 140 °C is predicted to have $\tau^* = 16$ s, in contrast to Zn(acetate)₂ ($\tau^* \approx 10^4$ s) and Sn(2-ethylhexanoate)₂ ($\tau^* \approx 10^1$ s). Parallels with Grubbs-catalyzed olefin metathesis vitrimers that exchange at room temperature⁹ are also interesting. The activation energies reported herein are again about two times smaller, yet the Brønsted acid τ^* values are around ten times larger at 25 °C (Tables S3–S7). These comparisons are not entirely fair since the backbone chemistry and catalyst loading vary across literature reports, but in an approximate sense, order-of-magnitude differences or similarities in the kinetics and thermodynamics likely reflect at least in part the effect(s) of catalyst chemistry.

Factors other than pK_a could theoretically account for the trends in relaxation behavior (Figure 3) and Arrhenius parameters (Figure 4) calculated for different Brønsted acids. Both cross-link density²⁷ and catalyst loading^{18,26} are known to influence relaxation times and Arrhenius parameters. To circumvent these potential concerns, all samples were prepared with identical constituent molar ratios in an attempt to maintain constant cross-link density. However, as noted above, weaker acids require longer reaction times to form a gel. To understand if this resulted in a higher sol fraction and incomplete network formation that would accelerate exchange, solid-state ¹³C NMR experiments were conducted. These results indicate even the weakest acids reach >95% conversion of both monomer and cross-linker after processing (Figures S2–S5). Moreover, the modest variability observed in the initial storage modulus across samples (Figure S12) likely cannot account for the orders-of-magnitude changes in stress relaxation behavior as a function of acid chemistry. All processing conditions (see Supporting Information) and rheology analysis were performed at temperatures (25–75

°C) below the boiling point of each catalyst to minimize evaporative changes in acid concentration (as that affects calculated Arrhenius parameters, Figure S15). The only borderline case is HTFSI, which has a reported boiling point of 91 °C (Table S1). Note also that there is no correlation between acid strength and boiling point with the acids used herein, which might otherwise explain the monotonic dependence of E_a , τ_0 , and τ^* on pK_a . There is some sensitivity of the Arrhenius parameters to recycling, but an MSA sample that experienced two additional iterations of grinding/remolding can still undergo stress relaxation at room temperature (Figure S16). Finally, replicate samples of MSA demonstrate reasonable reproducibility and activation energies in agreement within 4% relative standard error (Figure S14).

The logarithmic acid dissociation constant (pK_a) reflects the thermodynamic equilibrium between a given Brønsted acid and its conjugate base plus a proton. However, released H^+ in general binds to solvent molecules, and its concentration thus depends on the medium in which it is embedded.²⁸ Figure 2 lists pK_a values for the five acids under study as reported in water: triflic acid²⁹ (−12), bis(trifluoromethane)sulfonimide³⁰ (−9.7), benzenesulfonic acid³¹ (−7.0), methanesulfonic acid³² (−1.9), and trichloroacetic acid³³ (0.81). While these absolute values probably change when the acids are incorporated into poly(4-methylcaprolactone) vitrimers, the trend should still hold. The measurement of pK_a within our materials is difficult, but two factors are of anticipated importance to understand any differences. Pendant network alcohol functionality is slightly less basic than water (as measured in H_2O ³⁴), which would decrease the donating power of the surroundings and also the apparent Brønsted acidity of a catalyst.²⁸ This effect is amplified by a significant reduction in dielectric constant (as a reference: water ≈ 80 and isopropanol ≈ 18) that would destabilize ionic species, thereby pushing the equilibrium back toward conjugate acid. Thus, we propose that the monotonic trend plotted in Figure 4b would still persist if the matrix-induced difference in pK_a for every acid was similar, simply with a corresponding shift along the x -axis.

One of the most striking features of Figure 3b is that MSA and BSA exhibit nearly indistinguishable stress relaxation traces at 55 °C, yet evidently different Arrhenius parameters (Figure 4). Figure S17 plots their temperature-dependent data sets together as $\ln \tau^*$ vs $(RT)^{-1}$. A crossover point exists near room temperature, which explains this apparent paradox. We have opted to report the behavior of both acids for this reason.

Brønsted acids catalyze polyester–alcohol dynamic covalent bond exchange. Reaction kinetics are significantly accelerated at lower temperatures compared to Lewis acid analogues, and exchange at 25 °C is facile in materials with sufficiently low T_g . Relaxation times, activation energies, and Arrhenius prefactors are all correlated with Brønsted acid pK_a . Stronger acids tend to relax stress faster, exhibit higher activation energies, and asymptote to shorter relaxation times as $T \rightarrow \infty$. Expanding the scope of catalysts used to induce vitrimer plasticity, in conjunction with a quantitative understanding of the associated kinetics and thermodynamics, should prove useful in the future design of materials with tailored properties, for example, shape memory polymers,^{22,35} particles with controlled topology,³⁶ and high-performance composites.^{37,38}

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.8b00370.

Experimental details, solid-state ^{13}C NMR spectra, stress relaxation data and fits for each catalyst at different temperatures, and additional comparisons between data sets (PDF)

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Author Contributions

The manuscript was written by CMB and JLS. Experiments were designed by CMB, JRdA, JLS, NDD, and MSZ. JLS, NDD, and MSZ performed the experiments. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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