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Intramolecularly Catalyzed Dynamic Polyester Networks Using Neighboring Carboxylic and Sulfonic Acid Groups

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ABSTRACT: Dynamic covalent bonds in a polymer network lead to plasticity, reshapability, and potential recyclability at elevated temperatures in combination with solvent-resistance and better dimensional stability at lower temperatures. Here we report a simple one-step procedure for the catalyst-free preparation and intramolecularly catalyzed stress-relaxation of dynamic polyester networks. The procedure is based on the coupling of branched OH-end functional polyesters (functionality ≥ 3) by pyromellitic dianhydride (PMDA) or 2,5-bis(methoxy-carbonyl) benzenesulfonic acid resulting in ester linkages with, respectively, a COOH or a SO_3H group in a position *ortho* to the ester bond. This approach leads to an efficient external catalyst-free dynamic polyester network, in which the topology rearrangements occur via a dissociative mechanism involving anhydrides. The SO_3H-containing network is particularly interesting, as it shows the fastest stress relaxation and does not suffer from unwanted additional transesterification reactions, as was observed in the COOH-containing network.
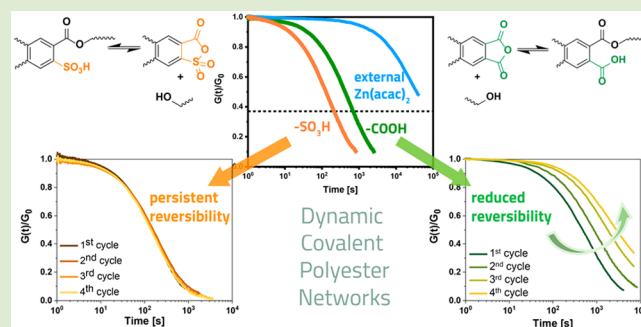
Dynamic covalent bonds endow covalently cross-linked networks with plasticity and recyclability at elevated temperatures without compromising their mechanical properties under operating conditions.[1−5] This advantageous combination of macroscopic properties has resulted in an increasing interest in dynamic covalent networks (DCNs) as promising materials in a range of different applications.[6−14] Among the ever-growing library of DCNs, dynamic polyester networks, pioneered by Leibler and co-workers,[1] have received extensive attention because of their potentially broad applicability.[15−19]

Dynamic polyester networks based on transesterification often require additional catalysts, such as Zn(II) salts, triazacyclodecene, and Brønsted acids.[15,16,19,20] In such systems, potential catalyst leaching may affect the dynamic properties of the materials and be harmful to the end-users or the environment.[21] Systems without catalysts or with immobilized catalysts would not suffer these drawbacks, and the aim of the current work is to develop such a system. Catalyst-free dynamic polyester networks have been reported previously but either required a great excess of hydroxyl functionality in the network[17,22] or in the hyperbranched building blocks,[23] and relatively restricted efficiencies of the bond exchange were observed. Inspired by mechanisms in enzyme catalysis and neighboring group participation (including in DCNs),[11,12] we investigated the effect of neighboring carboxylic and sulfonic acid groups on transesterification reactions. A very similar approach (but not involving sulfonic

acid groups) was recently reported by Du Prez and co-workers.[24] Prompted by this disclosure, we here compare the properties of dynamic polyester networks with neighboring group participation of carboxylic and sulfonic acid groups and demonstrate the sulfonic acid groups to be more effective and less susceptible to potential further cross-linking.

Our approach is a simple one-pot and catalyst-free synthesis involving the coupling of polyester chains with three or more hydroxyl end groups by difunctional chain extenders. Two different OH-endfunctional polyesters were used in this study: a "soft" aliphatic triarm polycaprolactone star polymer (PCL, functionality = 3, M_n = 1930 g/mol, and T_g = −63 °C) and a "hard" amorphous copolymer of neopentyl glycol, hexanediol, terephthalic, and isophthalic acid (PNHTI, average functionality = 3, M_n = 4035 g/mol, and T_g = 40 °C). Networks containing pendent neighboring carboxylic acid groups were prepared from the polyesters by reaction with pyromellitic dianhydride (PMDA, also used by Du Prez and co-workers[13]) as the coupling agent (see Figure 1, reaction A); gelation occurred within 1 h of the reaction in toluene at 100 °C (without the use of any additional catalyst). Networks
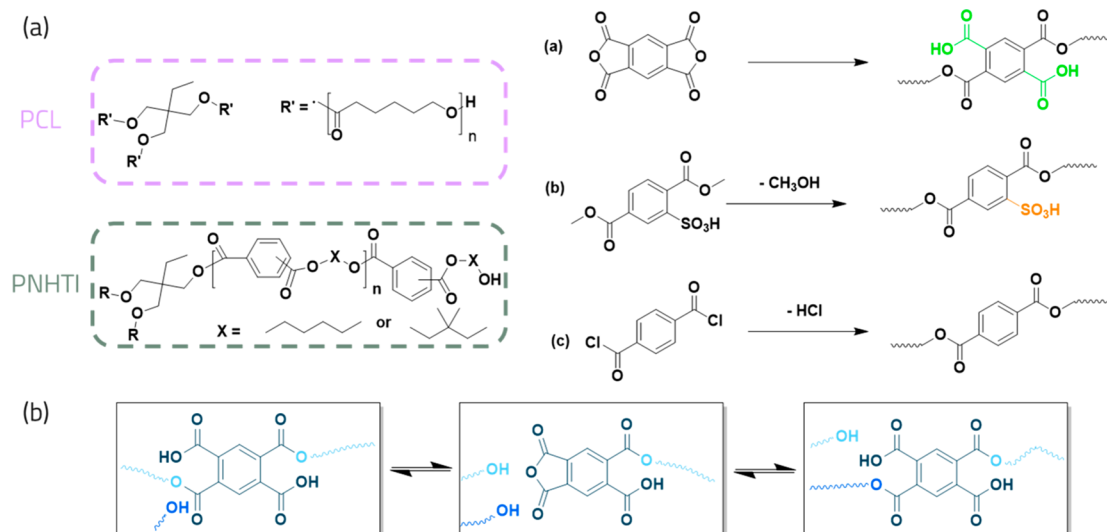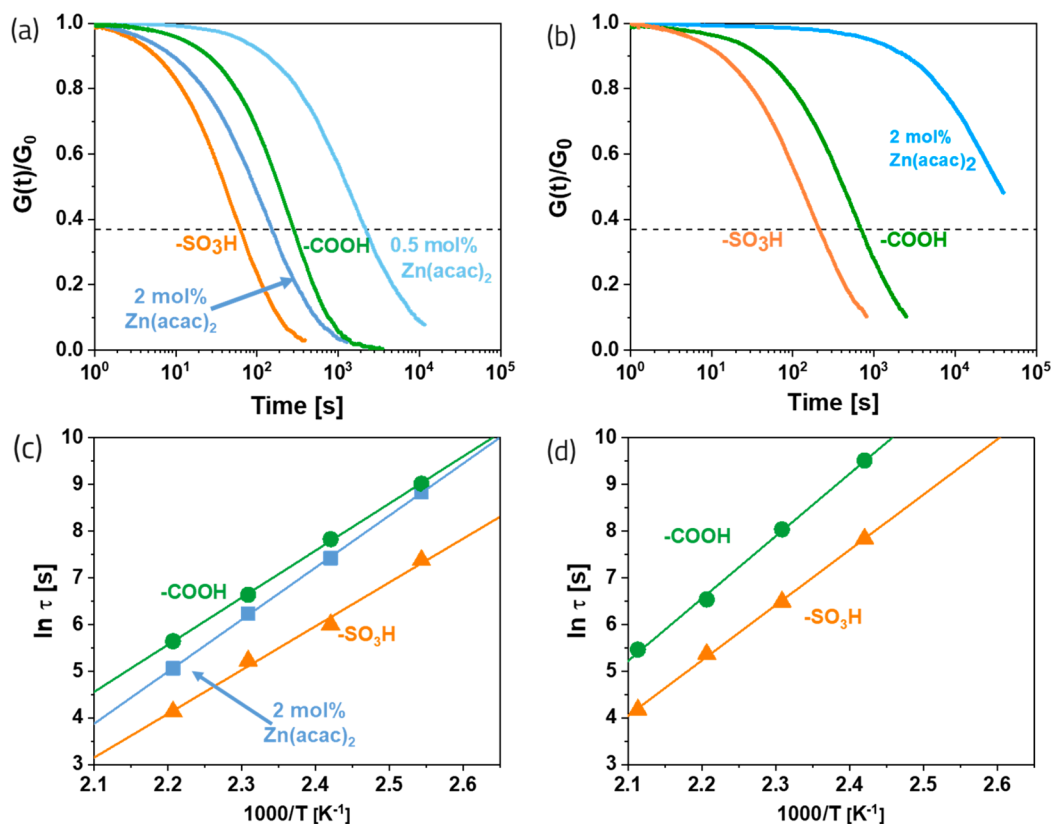
Figure 1. (a) Reactions of network formation with highlighted functional internal acid groups and (b) schematic presentation of the bond rearrangement in networks with neighboring carboxylic acid groups.

Figure 2. Oscillatory rheology stress relaxation experiments (1% step strain) on polyester networks with $r = n_{OH}/n_{linker} = 2.4$ at 180 °C on (a) PCL- and (b) PNHTI-based networks and the corresponding Arrhenius plots of (c) PCL- and (d) PNHTI-based networks. The intersections of the horizontal dotted lines with the stress relaxation curves indicate the points where $G(t)/G_0 = 1/e$ and $t = \tau^*$.

containing neigboring sulfonic acid groups were prepared from the polyesters by a condensation reaction with 2,5-bis-(methoxy-carbonyl) benzenesulfonic acid (see Figure 1, reaction B); this transesterification was carried out overnight in toluene at 100 °C and required effective removal of methanol. After removal of the solvent under reduced pressure, the dry products of reactions A and B were compression molded at 160−180 °C for oscillatory rheology and Dynamic Mechanical Analysis (DMA) measurements. The gel fractions

(>90 wt %, Table S1) of all samples were estimated by extraction with tetrahydrofuran at room temperature; these high gel fractions confirm the near full completion of the cross-linking reactions. A reference network without any neighboring acid groups was prepared by a reaction of the polyesters with terephthaloyl chloride in toluene at 100 °C overnight (see Figure 1, reaction C), isolated, and soaked for 24 h in a chloroform solution containing $Zn(acac)_2$ to obtain samples

with 2 and 0.5 mol % (w.r.t. the ester groups) of a transesterification catalyst in the (dynamic) polyester network.

Stress relaxation experiments revealed the dynamic nature of these polyester networks. The relaxation modulus $G(t)$ was normalized against its value at $t = 1$ s, which was taken to be the apparent plateau value (G_0) after applying a step strain of 1% (Figure S2).

Normalized relaxation moduli for both −COOH- and −SO$_3$H-containing networks are shown in Figure 2, and it can be seen that full stress relaxation takes place. Although stretched exponentials fit the data better than a single exponential (Maxwell model), the "stretching exponent" is in all cases greater than 0.7 (see SI for more details). Therefore, we still used as the characteristic stress relaxation time (τ^*) the point in time at which the normalized relaxation modulus ($G(t)/G_0$) reaches e^{-1} (or ~37%). Remarkably, the results shown in Figure 2a show that, at 180 °C, the PCL-based network with −SO$_3$H groups showed a much faster stress relaxation (with $\tau^* \approx 60$ s) than the PCL-based network with −COOH groups (with $\tau^* \approx 300$ s). Both (external catalyst-free) networks also show a significantly faster stress relaxation than the conventional reference system with 0.5 mol % of Zn(acac)$_2$ catalyst. Increasing the catalyst content in the reference system from 0.5 to 2 mol % results in a value for τ^* that lies between those of the −COOH- and −SO$_3$H-containing networks. The observed stress relaxation times of these systems are also significantly faster than those observed in other dynamic polyester networks,[16,18,19] but significantly slower than those reported for, for example, boroxine[25] and dioxoborolane[26] based dynamic networks (see also SI).

Comparing the stress relaxation behavior at 180 °C of the PCL-based network (Figure 2a) to that of the PNHTI-based network (Figure 2b), the first thing one notices is that the stress relaxation in the PNHTI-based network is slower for all systems. The −SO$_3$H-containing network again is characterized by the lowest τ^*, now followed by the −COOH-containing network, and this time, the conventional reference system is significantly slower than the other two (even with 2 mol % of Zn(acac)$_2$ transesterification catalyst).

All these results show that the ester exchange rate depends on the nature of acid groups, with the −SO$_3$H-containing networks showing the fastest relaxation, despite its concentration being only half that of the COOH groups in the −COOH-containing networks with the same amount of linking agent. The temperature dependence of the stress relaxation was investigated in the temperature range of 140−200 °C (Figure S4), and the resulting relaxation times (τ^*) are shown in the Arrhenius plots in Figure 2c and d for the PCL- and PNHTI-based networks, respectively. The resulting Arrhenius parameters are summarized in Table 1.

In general, the results in Table 1 show lower activation energies for the PCL-based networks and the networks containing the −SO$_3$H neighboring acid groups. The former observation suggests an important role of the intrinsic chain dynamics in the stress relaxation, with the backbone in the PNHTI-based network being much less flexible than that in the PCL-based network; this also affects the reactivity of the hydroxyl groups in the dangling chain ends. The lower activation energies in the −SO$_3$H networks as compared to those in the −COOH networks are not in line with the results of a recent study that showed that stronger acids lead to higher activation energies.[19] This study dealt with "classical" transesterification reactions, that is, an acid-catalyzed nucleophilic attack of an alcohol on an ester. It was shown[24] by Du Prez and co-workers, however, that the mechanism in the −COOH systems (produced by linking branched polyesters with PMDA) is different and involves an anhydride intermediate. In order to investigate whether a similar mechanism is at play in the −SO$_3$H-containing networks, we studied the following model unimolecular decomposition reaction:
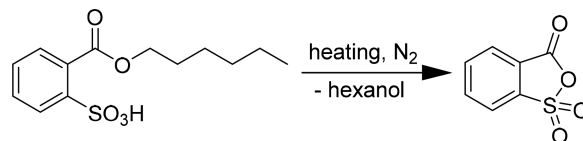
Variable temperature infrared spectra of 2-sulfo hexyl phthalate were collected from 40 to 200 °C under N$_2$ at a heating rate of 5 °C/min and are shown in Figure 3. The
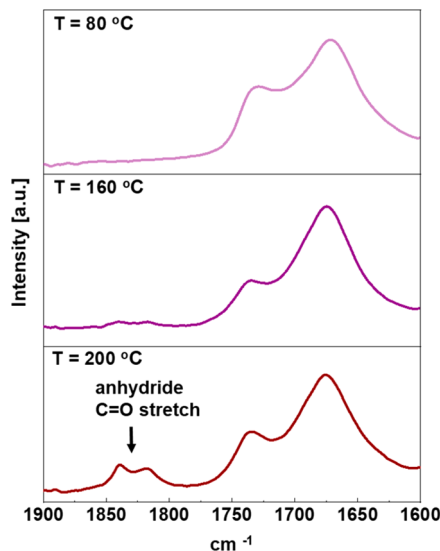
Figure 3. Variable temperature infrared spectra of 2-sulfo hexyl phthalate. .

emerging double absorption band at around 1840 cm^{-1}, which can be assigned to the asymmetric carbonyl stretch in a carboxylate anhydride[27] becomes evident at temperatures above 160 °C (the boiling point of hexanol is 157 °C). Since the leaving OH-end groups in the polyester networks are nonvolatile, this reaction is reversible in the network.

The results of stress relaxation experiments on networks with different cross-link densities, prepared using different OH to linker ratios ($r = n_{OH}/n_{linker}$) are shown in Figure 4a. It is clear from this figure that the relaxation times do not depend on the excess of free OH groups, and this result is also

Table 1. Arrhenius Parameters for Stress Relaxation[a]

network	τ_0 (10^{-9} s)	E_a (kJ·mol^{-1})
PCL/COOH	62 ± 20	84 ± 1
PCL/SO$_3$H	68 ± 54	78 ± 5
PCL/ref (2% Zn^{2+})	3.4 ± 0.9	93 ± 1
PNHTI/COOH	0.03 ± 0.04	116 ± 5
PNHTI/SO$_3$H	0.93 ± 1.54	98 ± 2

[a]The characteristic relaxation times were fitted to the following equation: $\tau^* = \tau_0 e^{E_a/RT}$.
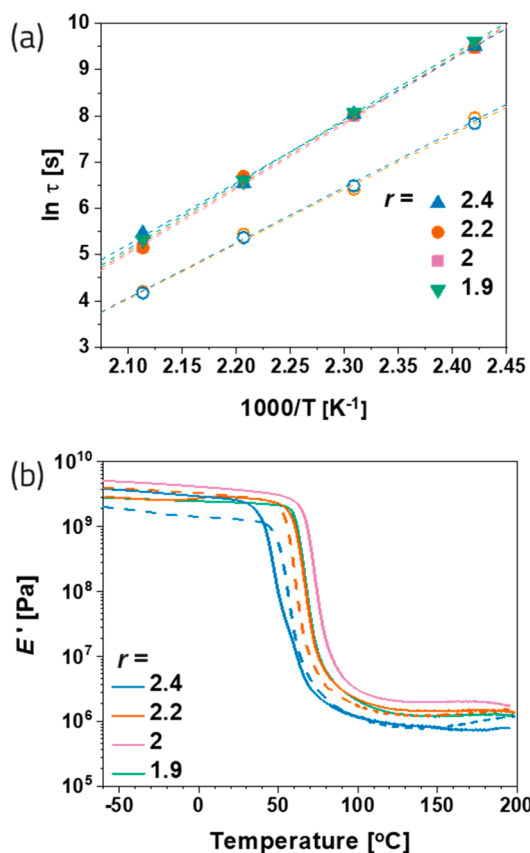
Figure 4. (a) Arrhenius plots of PNHTI-based networks with different feeding ratios $r = n_{OH}/n_{linker}$: (closed symbols) −COOH network, (open symbols) −SO$_3$H network. (b) Corresponding DMA curves: (solid lines) −COOH networks, (dashed lines) −SO$_3$H networks.
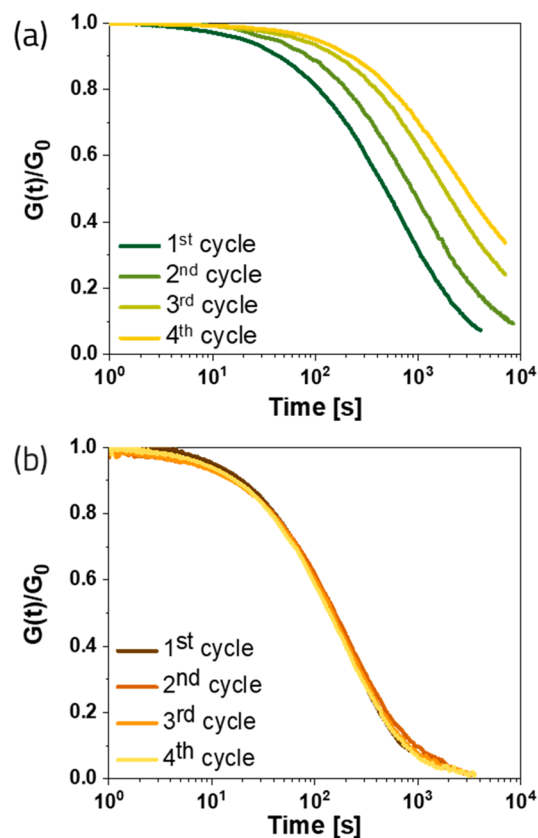

Figure 5. Multiple cycles of oscillatory rheology step−strain stress relaxation experiments at 180 °C on PNHTI-based networks with $r = n_{OH}/n_{linker} = 2.4$ with (a) neighboring −COOH and (b) −SO$_3$H groups.

consistent with a dissociative mechanism in both the −COOH- and −SO$_3$H-containing networks. Even in the absence of an excess of OH groups (i.e., r = 1.9), efficient stress relaxation takes place.

Although different cross-link densities do not result in different relaxation rates, they do lead to different thermomechanical properties, as is clear from the results in Figure 4b. This figure contains the DMA results for networks prepared using different ratios r of the number of OH groups to the number of linkers. The first thing to note is that in all cases the rubbery plateau extends up to temperatures higher than T_g + 150 °C; the PCL-based network starts to display viscous behavior at $T = T_g + 140$ °C at an angular frequency of ∼10^{-1} rad/s (see Figure S8 in the SI). Furthermore, as the ratio r decreases from 2.4 (i.e., an excess of free OH groups) to a stoichiometric ratio of 2, the glass transition temperatures (T_g) and the rubbery plateau moduli increase, as expected. When r further decreases (resulting in an excess of linker), the T_g and rubbery plateau decrease again. Networks with the same r (and theoretical cross-link density), but different acid groups, have similar rubbery plateaus and T_g values.

Finally, we investigated the "persistence" of the reversibility of the networks by subjecting them to four stress relaxation cycles at 180 °C, and the results for the PNHTI-based −COOH- and −SO$_3$H-containing networks are shown in Figure 5a and b, respectively.

From these results it is immediately clear that stress relaxation becomes slower with an increasing number of cycles

in the case of the −COOH-containing networks, but remains the same in the −SO$_3$H-containing networks. The most likely reason for this difference in behavior is the fact that the free COOH groups from the PMDA linker can undergo esterification reactions, effectively transforming the diesters from the reversible 1,4- and 1,3-diesters to form the irreversible 1,2-diesters, (or, to some extent, even further esterification reactions to triesters with one acid group or tetra-esters, see SI, Table S3), while in the case of the SO$_3$H groups, such transesterifications cannot take place. Since the dynamics of the network in the absence of a transesterification catalyst depend on the ability to form anhydrides, reactions resulting in a reduction in the number of neighboring acid groups lead to a reduction in dynamic bonds and a subsequent slower relaxation rate.

In conclusion, we have demonstrated that the strategy to prepare dynamic polyester networks through intramolecular catalysis by neighboring group participation in phthalic monoesters, reported by Du Prez and co-workers, is even more effective with sulfonic acid neighboring groups. The dissociative mechanism involving intermediate anhydrides allows for full stress relaxation and is a useful principle in dynamic covalent networks, because it obviates the need for added low molecular weight catalysts with associated issues of leaching. Intramolecular catalysis by sulfonic acids leads to significantly faster stress relaxation than with intramolecular carboxylic acids. Moreover, while the carboxylic acid neighboring groups are prone to inactivation by ester formation, this reaction is suppressed in sulfonic acid

neighboring groups because their esterification is unfavorable. As a result, the sulfonic acid containing systems maintain the same stress relaxation rates after multiple stress relaxation experiments at higher temperature, while relaxation of the phthalic monoester network is slowing down under these conditions. Intramolecular catalysis promises to be a general strategy in dynamic polymers, and its application beyond transesterification reactions will be the subject of further research.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.9b01023.

Full experimental details and additional results (PDF)

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