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## Internal catalysis in covalent adaptable networks: phthalate monoester transesterification as a versatile dynamic crosslinking chemistry

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#### Abstract

Covalent adaptable networks (CANs) often make use of highly active external catalysts to provide swift exchange of the dynamic chemical bonds. Alternatively, milder species can act as an internal catalyst when covalently attached to the matrix and in close proximity to the dynamic bonds. In this context, we introduce the dynamic exchange of phthalate monoesters as a novel chemistry platform for covalent adaptable networks. A low MW model study shows that these monoesters undergo fast transesterification via a dissociative mechanism, caused by internal catalysis of the free carboxylic acid, which reversibly forms an activated phthalic anhydride intermediate. Using this dynamic chemistry, a wide series of CANs with a broad range of properties have been prepared by simply curing a mixture of diols and triols with bifunctional phthalic anhydrides. The dynamic nature of the networks was confirmed via recycling experiments for multiple cycles and via stress relaxation using rheology. The networks proved to be resistant to deformation but showed a marked temperature response in their rheological behavior, related to the swift exchange reactions that have a high activation energy (120 kJ/mol). While densely crosslinked and hydrolytically stable polyester networks with low soluble fractions can be obtained, we found that by swelling the networks in a hot solvent, a gel-to-sol transition happened, which resulted in the full dissolution of the network.

#### Introduction

Because of their excellent mechanical properties, thermosets are a widely used class of polymers. However, due to their fixed crosslinked nature, thermosets need to be synthesized or 'cured' in their desired final shape, giving a rigid material that cannot be reprocessed or recycled. A compromise between thermoset rigidity and thermoplastic processing abilities can be found in reversibly crosslinked polymer networks. These dynamic polymer networks have been referred to as covalent adaptable networks or CANs, as their molecular architecture is malleable and it can adapt to external stimuli by the rearrangement of network bonds.<sup>1-3</sup>

Based on the mechanism of exchange, CANs are typically subdivided in two classes. The first group makes use of a so-called dissociative mechanism, for example the Diels-Alder reaction between furans and maleimides.<sup>4,5</sup> Here, the dynamic bond is in a thermal equilibrium with its constituent reagents. By heating, this equilibrium should shift toward the reagents and thus a dissociated state. On the level of the material, this dissociation leads to a depolymerization, which can cause an abrupt viscosity drop related to a gel-to-sol transition, or a loss of network integrity, making the polymer not only more liquid but also soluble.<sup>5</sup> In 2011, Leibler and coworkers introduced a second class of CANs that undergo dynamic exchanges without decrosslinking, following a so-called associative mechanism. In fact, these CANs were found to show a highly unusual thermal behavior, not corresponding to that of thermosets or thermoplastics, but to that of materials known as strong glass formers, a category known mainly for inorganic materials. Because of the high resemblance in thermal properties of these remarkable CANs to vitreous silica materials, these materials were called 'vitrimers'.<sup>6</sup> Leibler designed his vitrimers

around the transesterification of polyester-polyol networks, doped with a Lewis acid or strong base to catalyze the addition/elimination of the pendant hydroxyl moiety to ester crosslinks.<sup>7</sup> Since then, a lot of associative covalent exchange chemistries have been explored in the context of vitrimers,<sup>8</sup> such as anhydride exchange,<sup>9</sup> boronic esters<sup>10-12</sup> and silyl ethers<sup>13</sup> in the last couple of years. In our group, the transamination of vinylogous urethanes<sup>14-16</sup> or vinylogous ureas<sup>17</sup> and the transalkylation of sulfonium salts<sup>18</sup> have been developed as chemistry platforms for associative CANs, together with the dissociative triazolinedione chemistry<sup>19,20</sup> and anthracene dimerization.<sup>21</sup>

The unique properties of vitrimers have been related to the peculiarities of the bond exchange mechanism. In an associative mechanism, a new bond is always formed before the original bond is broken and the number of cross-links remains constant, preventing a sol-gel transition at all temperatures (excluding degradation). Because all net molecular motion that results in network rearrangements are controlled by the same chemical exchange reaction, this fixed cross-link density results in a rheological behavior that is controlled solely by a chemical reaction rate. Thus, rheological measurements can be used to determine a chemical activation energy, as the viscosity will show an Arrhenius-type dependence on the temperature. Another important result of the permanently crosslinked architecture, is that vitrimers remain insoluble in any non-reactive solvent at all temperatures.<sup>6</sup> Arrhenius-like properties have also been observed in networks that exchange bonds through dissociative pathways, although at least theoretically such materials should show a gel-to-sol transition, for instance upon heating in the presence of a good solvent. This behavior was observed for CANs using furan-maleimide chemistry,<sup>22</sup> transalkylation of triazolium salts<sup>23</sup> or hindered urea.<sup>24</sup>

To achieve a swift exchange reaction in CANs, in order to allow macroscopic flow at useful temperatures, often a highly active catalyst needs to be included as a material additive such as Lewis acids, Brønsted acids, transition metals, strong bases or nucleophilic catalysts, which can lower the activation energy of the exchange reaction.<sup>6,14,25-28</sup> However, catalytic additives can result in problems with catalyst ageing and thus in a deterioration of material properties over time. As another major strategy to achieve rapid exchange kinetics in CANs, intrinsically reactive linking groups have been introduced in CANs that are reactive even in the absence of a catalyst. However, such reactive moieties are often also sensitive to hydrolysis, oxidation or other degradation reactions. Examples here are networks that incorporate maleimides,<sup>4</sup> phosphines,<sup>29</sup> thiols<sup>30,31</sup> and (di)sulphides,<sup>32</sup> imines<sup>33</sup> or free amines.<sup>15</sup>



Figure 1: In the case of external catalysis (left), the catalyst (orange star) is often a highly active acid, base or transition metal. With NGP (right), the catalyst (green hollow dot) is covalently bound to the network next to the dynamic bond. Because of this proximity effect, less active species can be used as catalyst.

From the outset of this work, we wanted to explore a conceptually novel option to achieve fast exchange reactions in CANs. For this, our plan was to use only robust chemotypes as monomer, polymer or crosslinkers in the design of polymer networks, as commonly found in normal industrially applied polymers, but to combine these simple chemotypes into functional arrays that can undergo more rapid exchange reactions. This would constitute an example of internal catalysis or neighboring group participation (NGP). NGP is a classical principle in organic chemistry and has been studied extensively in bio-organic chemistry, as this is also a mimic or model of enzymatic catalysis.<sup>34-36</sup> In general, NGP is the phenomenon where the relative proximity of functional groups within a compound results in an enhancement of a reaction rate.<sup>37</sup> Explicit applications of this principle in polymer chemistry were reported in synthesis,<sup>38-44</sup> modification<sup>45</sup> or hydrolysis,<sup>46-50</sup> although they have been rare. Significant rate enhancements have also been observed in CANs that could be related to the adventitious placement of neighboring amines<sup>10,13</sup> or hydroxyl groups<sup>51-53</sup> within the polymer backbones. This encouraged us to pursue the use of the NGP principle as a design principle in CANs.

The general principle of internal catalysis or NGP for CANs is schematically depicted in Figure 1. It is important to realize that next to 'catalyst immobilization', NGP first and foremost is a catalytic principle in and of itself, and that in principle much less activated (and thus more robust) species can be used as a 'catalyst' in such a scheme, because the enhancement of the reaction rate is also due to the proximity effect, lowering the activation entropy rather than the activation enthalpy. Mildly acidic, basic, electrophilic or nucleophilic functions can thus have a very pronounced (and mostly temperature-independent) effect on the exchange kinetics.

One well-known example of NGP is the unusually rapid hydrolysis of phthalate monomethylester (PME), in which the cleavage of the ester bond is greatly accelerated by a neighboring carboxylic acid,<sup>54,55</sup> whereas the corresponding benzoate esters, lacking this carboxylic neighbor, require heating and strong (Lewis) acid or base catalysts to achieve swift hydrolysis.<sup>56</sup> For example, the hydrolysis of phthalate monomethylester was reported to be 10 times faster at 109°C<sup>54</sup> than the 'background' hydrolysis of methyl benzoate at 200°C (See Scheme 1).<sup>57</sup> Because of the widespread use of phthalates and polyesters in polymer materials, including high end thermosets, we set out to explore the internally catalyzed transesterification of PMEs as a chemistry platform for the design and synthesis of CANs that would not require catalysts.



Scheme 1: Neighboring group effect in phthalate monoester (PME) hydrolysis.

As no information could be found in the literature, we started our investigations with the study of the PME transesterification exchange mechanism, using low MW model compounds to assess the extent and the nature of the neighboring group effect on transesterification kinetics. This then allowed us to rationally design and optimize dynamic polyester networks based on PME transesterification chemistry.

#### **Results and discussion**

 **Model Study.** While the hydrolysis of phthalate monoesters (PMEs, see Scheme 1) has been studied in great detail more than 60 years ago,<sup>54,55</sup> to the best of our knowledge, the transesterification of PMEs has not been studied explicitly. Thus, we set out to prepare some low MW PMEs that would allow us to probe the kinetics of their transesterification reactions.

In general, PMEs can be readily and selectively prepared by the reaction of a phthalic anhydride with one equivalent of an alcohol. Even when an excess of the alcohol is used, only the PME is formed, as the second esterification step of the released carboxylic acid is very slow in the absence of a catalyst. Synthesis of the phthalate diesters typically requires prolonged heating in an excess of alcohol in the presence of a strong acid (Fischer esterification) or heating above 200°C in the absence of catalyst. For the synthesis of our model compounds (Scheme 2), phthalic anhydride was reacted with 1-decanol or with 2-phenylethanol to obtain the 'neighboring group' model compounds phthalate monodecylester **1a** and phthalate mono-2-phenylethylester **1b**. Next to this, two reference esters (i.e. **2a** and **2b**), lacking a pendant carboxyl group, were synthesized starting from benzoyl chloride.



Scheme 2: Synthetic procedure of mono-1-decyl phthalate (1a), mono-2-phenylethyl phthalate 1b, 1-decyl benzoate (2a) and 2-phenylethyl benzoate (2b).

With the model compounds 1a and 1b in hand, the transesterification kinetics of PMEs were investigated. Decyl ester 1a was reacted with 5 equiv. of 2-phenylethanol at different temperatures (X = COOH, Figure 2a). Under these conditions, a clear exchange could be observed at temperatures of 100°C and above. Monitoring of the progression of this exchange was possible by <sup>1</sup>H-NMR for a range of temperatures (i.e. from 120°C to 160°C) by measuring the conversion of the decyl ester into phenylethyl ester. As depicted in Figure 2b, an equilibrium is reached at longer reaction times, and a strong temperature dependence is observed. By fitting the experimental data of the mono-phthalate transesterification with a theoretical equation (see Equation S1),<sup>58</sup> the rate constants k were obtained for every temperature and plotted in an Arrhenius plot, resulting in an observed activation energy of  $96 \pm 5$  kJ/mol (see Figure 2c and SI-file). When the reference compound 1-decyl benzoate **2a** (X = H) was treated under the conditions, no trace of a transesterified product could be detected after heating to 140°C (Figure 2d), which shows that the free carboxylic acid is vital for a swift exchange. Finally, in order to focus on the role of proximity of the neighboring carboxylic group, the same reference experiment was repeated in the presence of one equivalent of benzoic acid. At 140°C, this resulted in a detectable exchange reaction (blue triangles, Figure 2d), but with a forward reaction rate constant  $k_{BA}$  that is around 20 times smaller than for the neighboring group reaction  $k_{NGP}$  (0.00190 vs 0.0388s<sup>-1</sup> respectively). Thus, despite the very high concentration of benzoic acid in these reference experiments, still an acceleration can be observed. These experiments thus demonstrate the clear NGP effect in PMEs, compared to normal benzoyl esters.



Figure 2: a) Model reaction used for the kinetic study (X = COOH or H) b) Exchange kinetics between **1a** and 2-phenylethanol from 110 to 160 °C. c) Arrhenius plot of **1a** and 2-phenylethanol exchange kinetics. d) Comparison of the exchange reaction with 2-phenylethanol at 140 °C of **1a** (with a neighboring effect) and **2a** (reference whit and without external catalyst) e) Kinetic study at 160 °C with stoichiometric ratio of **1a** and 2-phenylethanol (black square), 2 eq. of 2-phenylethanol (blue triangle) and 2 eq. of **1a** (red circle).

Since the nature of the exchange mechanism can significantly influence the viscoelastic behavior of the materials at elevated temperatures, we further explored some model reactions to probe the reaction mechanism of PME transesterification. A dissociative pathway involves cyclative cleavage of the ester bond, with the formation of an intermediate anhydride and the release of an alcohol, followed by the reverse reaction with another alcohol. In an associative mechanism on the other hand, a new ester bond is directly formed by intermolecular addition of an alcohol to form a tetrahedral intermediate, followed by expulsion of the other alcohol moiety (See Figure 3a). For hydrolysis of PMEs, the prevailing mechanism is pH and solvent dependent, but is usually confirmed as a dissociative pathway via an intermediate phthalic anhydride, and with the pendant carboxylic acid as a 'general nucleophilic catalyst'.<sup>54</sup> In our case, such a dissociative pathway was also confirmed via investigating the influence of the concentration of the alcohol in a dilute solution. In DMSO-d6, a reference exchange reaction was kinetically monitored starting from a 1:1 mixture of PME (**1a**) and alcohol, both at a 0.1 M concentration. Only changing the concentration of the PME, not of the alcohol, had a significant effect on the reaction rate (Figure 2e). This result can only be explained via a 'monomolecular' rate

determining step, such as the cyclative formation of the phthalic anhydride, and cannot be reconciled with an associative addition of the alcohol to the PME. We further conducted some cross-over experiments between different PMEs in the absence of alcohol to confirm the dissociative pathway. Here, **1a** and tetrafluorophthalic anhydride were mixed in a 1:5 ratio and heated in bulk for two hours at 160°C in the absence of any alcohol (See Figure 3b). As can be seen from the NMR spectra, the reaction is nearly quantitative because the aromatic signals of **1a** (between 7.5 and 8 ppm) almost completely disappeared. Furthermore, new signals appeared between 8 and 8.5 ppm, which can be assigned to phthalic anhydride, clearly proving the dissociative mechanism.



Figure 3: a) The two possible mechanisms (dissociative or associative) that could in principle be followed for the PME transesterification. b) Exchange experiment without free alcohol. Tetrafluorophthalic anhydride is heated at 160°C for 2h together with mono-decyl phthalate. The disappearance of **1a** signals is a clear proof of a dissociative mechanism.

**Material Synthesis.** Motivated by the rapid transesterification kinetics observed in the model study, the next step consisted of the implementation of reversible PME cross-links within polymer networks, which could constitute internally catalyzed CANs. The general strategy for the material synthesis is straightforward and is outlined in Figure 4. The trifunctional alcohol trimethylolpropane (TMP, 3) was selected as cross-linker and combined with a diol as a chain extender, together with one of the bis-phthalic anhydrides (**6a**, **6b**, **6c** or **7**). Most commercially available bisanhydrides, such as **7**, are highly rigid polyaromatic monomers. To expand our study towards a wider range of material properties, aliphatic bisanhydride monomers of different chain lengths were synthesized from the reaction of commercial trimellitic anhydride chloride (**5**) with the diols 2,4-diethyl-1,5-pentanediol (DEPD),

polytetrahydrofuran diol (PTHF) or Pripol 2033 to obtain compounds **6a**, **6b** and **6c** respectively. This one-step process is high yielding and has been performed on a 50 gram scale. In order to obtain a rigid (high T<sub>g</sub>) reference material, the highly constrained commercially pyromellitic dianhydride (PMDA, **7**) was used as a chain mobility-limiting bisphthalic anhydride-type monomer.

Below, we refer to the synthesized materials in terms of the bisanhydride monomer that was used (ranging from very flexible to very rigid), so we were able to prepare DEPD-networks, PTHF-networks, Pripol-networks and PMDA-networks from bisanhydride monomers **6a**, **6b**, **6c** and **7**, respectively. For these initial reference materials, a fixed molar ratio of 0.4:0.4:1.0 triol:diol:bisanhydride was used for the synthesis, which theoretically gives molar equivalence of the anhydride and hydroxyl functionalities. This would thus result in a very densely cross-linked network of PMEs, if a complete conversion of the anhydrides is achieved. Such fully cured networks would also contain very few remaining hydroxyl functions, present only as network defects or incompletely reacted chain ends. Following the mixing of the polyol mixture and the bisanhydride, which is feasible without any solvent (except for PMDA-network), a curing step at 100 °C for 16 hours was performed. The reaction between the anhydride and alcohol functions during this curing has been readily monitored by FTIR, as shown for the DEPD-network in Figure S5 (see SI). The characteristic signals of the phthalic anhydride function gradually disappeared upon prolonged heating, indicative of a full conversion.<sup>59</sup>

Taking into account the dissociative transesterification mechanism established on low MW model compounds, we reasoned that heating to higher temperature would shift the equilibrium to the endothermic, entropically favored side for the anhydride ring opening reaction. Indeed, heating the fully cured sample at 180°C for 30 minutes revealed the reversible reappearance of the characteristic absorption bands of the phthalic anhydride moiety. FTIR analysis shows that the anhydride stretches appeared again after the heating step as a result of a small shift in the bond equilibrium towards the dissociative side. Furthermore, when the material was subsequently annealed at 100°C for 30 minutes, these signals completely disappeared again. This experiment confirmed the dynamic nature of the mono-phthalate moiety and the dissociative pathway for the mechanism. Moreover, it also showed that the phthalate ester structure is dominant at lower temperatures, while the equilibrium shifts more and more to the dissociated state upon heating.

Although poly-PME materials have not been reported in the literature so far, it is interesting that several industrial patents report formulations of phthalic anhydrides with alcohols to prepare polyester networks, so-called alkyd resins, applied in coating formulations.<sup>60-64</sup> However, to the best of our knowledge, this chemistry is always driven to full curing by making use of a thermal vacuum curing step, also using a 2:1 molar ratio of hydroxyl and anhydride functions, via a dehydrative (slow) ester condensation at very high temperature (>200°C). Furthermore, such resins have also not been described or studied in the context of dynamic and recyclable materials.

Thus, our formulation with 1:1 equivalence of hydroxyls and anhydrides, selectively leading to PME formation, is quite distinct from these classical formulations, and leads to large differences in properties. The fact that the chemistry and building blocks developed herein are already applied industrially in thermosets, is actually quite appealing as it has the potential to be used as a 'drop-in' technology for industrial implementations. Indeed, the commercial availability of cheap and diverse polyol monomers is very high because of their common use in several step-growth polymers. On the other hand, while bifunctional phthalic anhydrides are also commercially available, the diversity is more limited. Aromatic and rigid anhydrides are commonly used as bulk chemicals in the synthesis of polyimides or polyesters, but flexible counterparts are much less available. Nevertheless, we demonstrated the straightforward synthesis of several aliphatic bisanhydrides (i.e. **6a**, **6b** and **6c**) starting from flexible diols in a one-step strategy (*vide supra*).



Figure 4: General strategy for the material synthesis. Dianhydride monomers were synthesised from a diol and trimellitic anhydride chloride (5) or commercially available (7). A di- and triol were mixed with the bifunctional anhydride and cured at 100°C to obtain the mono-phthalate containing network.

**Material Characterization.** The material properties of the different sets of materials were analyzed as a function of the bisanhydride structure and are summarized in Table 1 (see also Figure S1-S4). As a result of the used molar ratio of 0.4:0.4:1.0 (triol:diol:bisanhydride) in the formulations, and because of the relatively high molecular weight of the bisanhydride, the anhydrides monomer represented the highest weight fraction of the networks and will have the most significant impact on the material properties, explaining the observed wide range of properties. For each formulation, DEPD and TMP were used as polyols (Figure 4), in order to be able to compare the influence of the anhydride on the material properties. All materials showed a good swelling in tetrahydrofuran (THF) at room temperature, which made THF the solvent of choice for soluble fraction measurements, using a Soxhlet extraction setup. While three materials show a soluble fraction below 10%, the PTHF-network (33%) had higher measured soluble fractions. Because of the polymeric structure and thus inherent dispersity of the reagents that build up this material, further optimization of the reaction conditions should be performed. However, the PTHF-material was only prepared to show the versatility in terms of glass transition and mechanical properties.

As the characterization and processing of CANs require numerous heating steps at high temperatures (*vide infra*), the thermal stability of the materials was measured with TGA. For all four networks, a similar  $T_{deg,5\%}$  around 270°C was obtained (N<sub>2</sub> atmosphere). However, a markedly lower degradation temperature of 218°C was obtained for the PMDA-network. The nature of the bisanhydride monomer had a large influence on the glass transition temperature ( $T_g$ ) of the networks, measured via DSC analysis. Higher Tg-values were obtained for the low MW and more rigid DEPD-dianhydride (72°C) or PMDA (93°C), while elastomeric materials with low  $T_g$ 's were obtained when starting from the flexible PTHF-and Pripol-dianhydride (with a  $T_g$  of -30 and 4 °C respectively). The differences related to the choice of the bisanhydride monomer also manifested themselves in the tensile properties. The

elastomeric materials Pripol- and PTHF-network proved to be (very) elastic with a strain at break between 500 up to almost 900%, respectively. As expected, this high elasticity is accompanied by a low Young's modulus and maximum stress at break. On the other hand, DEPD- and PMDA-network were both characterized by a high E-modulus and stress at break, also resulting in a higher brittleness. Because of its good thermal and mechanical properties, DEPD-network was chosen for a more in-depth characterization in terms of recycling and rheological analysis.

Material properties	DEPD ( <b>6a</b> )	PTHF ( <b>6b</b> )	Pripol ( <b>6c</b> )	PMDA ( <b>7</b> )
Swelling degree (25°C, %, THF)	176	648	416	80
Measured soluble fraction (%, THF, Soxhlet)	8.7 ± 1.6	33.0 ± 1.5	$6.4 \pm 0.1$	8.3 ± 0.6
T <sub>deg,5%</sub> (N <sub>2</sub> , °C)	270	271	287	218
T <sub>g</sub> (°C) (DSC)	72	-30	4	93
E-modulus (MPa)	1430 ± 86	0.46 ± 0.02	2.70 ± 0.06	1970 ± 69
Strain at break (%)	5.0 ± 0.6	889 ± 39	503 ± 29	2.6 ± 0.2
Stress at break (MPa)	52.1 ± 3.4	1.57 ± 0.26	4.38 ± 0.52	48.6 ± 2.4

 Table 1: Swelling, mechanical and thermal properties of the anhydride-derived CANs.

*Thermal recycling.* An important feature of CANs is their recyclability, both chemically and thermally. In this context, the thermal reprocessing and recyclability of the DEPD-network was first tested. For this purpose, a crosslinked sample was ground to granules of around 1 mm and subsequently pressed for 60 minutes at 150°C with 4 metric tons of pressure. A perfectly homogeneous and transparent material was obtained, which strongly supports the dynamic character of the polyester networks (see Figure 5a and Figure S6). This recycling step was repeated three times for the DEPD-network and some of its properties were measured again after each cycle to characterize possible material degradation. Thus, materials obtained after each cycle (networks P1, P2 and P3) were analyzed. Regarding the chemical integrity of the network, no significant differences could be noticed via ATR-IR between the recycled and initial samples (see Figure 5b). Hence, we can exclude significant side reactions that could deteriorate and change the chemical nature of the material. The overall network integrity was also confirmed by the similarity of the T<sub>g</sub>-value after every recycling step (Figure 5c).

Finally, tensile strength measurements were performed on the recycled networks P1 – P3. The original material could not be tested because no defect-free samples were obtained as the result of trapped air bubbles, which appeared during the mixing process. However, degassing steps during heating could easily solve this issue in industrial applications. As shown in the tensile graphs (Figure 5d), P2 showed a lower stress and strain at break than P1, while its Young's modulus slightly increased. In the next recycling step, a steady state was obtained since P3 didn't show a significant difference compared to P2. The lower strain at break for P2 and P3 could be ascribed to a higher heterogeneity caused by the subsequent grinding and pressing, making the material slightly more brittle.



Figure 5: DEPD-network could be recycled multiple times without significant change or loss in properties.

*Rheological analysis.* Next to recycling experiments, the dynamic nature of the PME networks was characterized extensively with rheology. In a first stage, stress relaxation experiments were performed on the P1 DEPD-network. As shown in Figure 6a, the network readily relaxed stress, following an exponential Maxwell decay (See also Figure S8). The noisy data at the beginning of each experiment were replaced by a theoretical exponential fit (see SI for full details). The relaxation times ranged from more than 7h at 100°C to around 1 minute (63s) at 180°C. When the results were plotted in an Arrhenius plot, a linear correlation was obtained and an activation energy of 120 kJ/mole was calculated from the slope (See Equation S7 to S9 for the calculations). Despite the dissociative nature of the phthalate ester exchange, a linear evolution of the viscosity as a function of temperature was observed in the viscosity plot, indicating that the degree of depolymerization (net loss of network integrity) is negligible within the investigated temperature window. Although the equilibrium should shift relatively to the endothermic side, the extent of decrosslinking does not affect the rheological behavior, although a slight off-linearity and acceleration can be seen at the highest temperature data point. This could also be related to some de-crosslinking, which prompted us to further investigate this possibility.



*Figure 6: a) Stress relaxation from 100 °C to 180 °C with 20 °C interval of DEPD material b) Arrhenius plot of DEPD (0.4:0.4:1.0) with a linear correlation. Arrhenius plots of DEPD with changing amount of alcohol (c) or anhydride monomers (d).* 

In addition to the standard formulations used so far for our PME networks (i.e. 0.4:0.4:1.00 triol:diol:bisanhydride), different ratios of monomers were investigated to compare the influence of free hydroxyls or unreacted anhydride on the relaxation kinetics. For this, we first kept the amount of diol and triol monomers constant for each formulation and varied the relative amount of the bisanhydride from 0.9 to 1.1 equivalents. We also prepared two stoichiometric formulations with a different ratio of the triol cross-linker: a very weakly crosslinked network with only 22% triol (0.2:0.7 triol:diol, having a theoretical gel-point at 88% conversion), and a very densely crosslinked one with 86% triol (0.6:0.1 triol:diol), in comparison to all the other networks that have 50% triol (0.4:0.4).

The combined Arrhenius plots for all different formulations showed very similar kinetics and activation energies (See Table S1 and S2), except for two (Figure 6, c and d). The weakly crosslinked material (22% triol) showed significantly lower relaxation times, as can be expected. Conversely, the more strongly crosslinked PME network (86% triol) did not show slower exchange kinetics. The network with a large excess (10%) of hydroxyls (0.4:0.4:0.9 ratio), showed a clear deflection in the Arrhenius plot, with similar kinetic at lower temperatures but slower rheology at higher temperatures. This translates into a lower measured activation energy compared to other formulations materials (97 vs 120 kJ/mol respectively). This effect could also be explained by the formation of additional and irreversible phthalate diester bonds, by the reaction of the small excess of hydroxyls groups and free carboxylic acids of the mono-phthalate moieties, which is known to occur around 200°C from the literature on alkyd resins.<sup>60-64</sup> The small amount of irreversible cross-links does not affect the dynamic behavior. On the other hand, if even larger excesses of hydroxyl groups would be employed in the formulations, an irreversibly cross-linked alkyd resin would result.

The same rheological behavior was observed for the elastomeric Pripol-network (TMP:Pripol:Pripoldianhydride 0.4:0.4:1.0, see Figure S9). Furthermore, temperature and frequency sweep experiments didn't show a significant drop in viscosity because of a loss in cross-link density, confirming the Arrhenius-like behavior (Figure S10). The small deflection from the linearity at the highest temperature (180°C) could be ascribed to the dehydration of two free carboxylic acids to give a linear anhydride, which is a known condensation reaction for carboxylic acid containing polymers, like poly(acrylic acid).<sup>65,66</sup> Such dehydrative cross-links are formed irreversibly by the removal of water, but would be reversible as long as free carboxylic acids remain in the network, that can exchange via trans-reactions (addition elimination to activated anhydride cross-links).<sup>9</sup> The formation of anhydrides between carboxylic acids is slow because of the poor nucleophilicity of carboxylic acids. Thus, it will only present itself during long thermal treatments, such as the rheology measurements with slow temperature sweeps (1.5 °C/min). Flexible anhydride monomers as used in the pripol PME networks are indeed expected to have better opportunities to form chain-to-chain additional crosslinks in this manner.

From the above experiments, it can be concluded that a (small) excess of one of the reactive groups (i.e. hydroxyl or anhydride) is not necessary and does not have a significant impact on the dynamic properties, as expected for the monomolecular dissociative exchange mechanism of the PME transesterification. The dissociation of the PME crosslink is a chemical equilibrium, which can shift to the dissociated state with increasing temperature. Hence, each material should at least in theory have a temperature where a gel-to-sol transition can be reached, resulting in a sudden and pronounced drop in viscosity because of viscous flow. For all materials in this experiment, however, it was not possible to observe such a transition in the investigated temperature range (100-180°C). This can be rationalized by the high forward (exothermic) reactivity of the released anhydride in the investigated conditions. As a result, only a small net amount of reformed anhydride will be able to accumulate, even at elevated temperatures. From a theoretical point of view, the Boltzmann distribution between open and closed states is sufficient to allow fast exchange but is insignificant in terms of network constitution and net crosslinking density. At higher temperature, or under conditions that influence the equilibration of open and closed forms, a different situation may thus arise.

As mentioned earlier, the synthesized materials show a high resemblance in terms of molecular structure with well-known alkyd resins. To prove the static behavior of such alkyd resins, a reference Pripol-network was made with a molar ratio of 2:1 OH:anhydride, enabling further esterification of the free carboxylic acid in the PME. The curing step at 100°C (16h) was subsequently followed by a second curing at 180°C under vacuum, which was the limit of the used equipment. As shown in Figure S11, this alkyd reference could not relax stress or be recycled.

*Solubility and hydrolytic stability.* One way to establish decrosslinking at higher temperatures, would be rheology measurements above 180°C, which is the limit of our experimental setup. Furthermore, it was shown that extra cross-linking side reactions can occur above 180°C. Thus, other experiments were performed, in which a solvent was used to impose the possible gel-to-sol transition and thus dissolve the PME networks. For sure, also vitrimers, or associative CANs in general, can be dissolved, but only with a reactive solvent that depolymerizes the dynamic crosslinks.<sup>6,67</sup> Although no gel-sol transition, or sudden drop in viscosity, can be observed in rheology measurements for our standard PME formulations (see Figure 6 and S5), heating them to high temperatures in a high boiling solvent may shift the dynamic equilibrium towards the depolymerized, dissolved state. The solubility of 0.4:0.4:1.0 DEPD-and Pripol-PME networks in non-hydroxylic, inert solvents was thus explored by immersing a sample of the material in a vial filled with xylene. The vials were subsequently heated at 140°C for 16 hours and the samples were qualitatively compared. As shown in Figure S12, DEPD-network remained insoluble in xylene at 140°C (even after 72h). However, the DEPD-network only shows a swelling

 degree of 1% in xylene at room temperature, which can explain its stability in this particular solvent. Indeed, when diglyme was used, the swelling degree increased above 300% at room temperature and the material dissolved at 140°C without the need to add a reactive alcohol. The more hydrophobic Pripol-network on the other hand, had a high swelling degree in xylene (154%) and dissolved completely in this solvent. The dissolution of both DEPD- and Pripol-network is in line with the dissociative nature of the dynamic cross-links. We speculate that previous chemistries that have been referred to as 'vitrimers',<sup>23,24</sup> will also show this limited resistance to hot, inert solvents that can swell the network at room temperature. However, it might be difficult to find a good or suitable solvent for some networks. Thus, a simple experimental protocol can be put forward that is able to make the distinction between 'true' associative vitrimers, and CANs that merely mimic their behavior because of very fast network exchanges with no net depolymerizations in condensed phases. From the point of view of processing applications, this distinction may have little importance, as in many contexts the properties of both material classes will be indistinguishable. Still, it is an easy test to perform that can and in fact should be performed for any new dynamic chemistry introduced into crosslinked materials.

The limited resistance to (hot) solvents of dissociative CANs can be considered as a drawback compared to vitrimers that can retain their structural integrity under a wider range of conditions. However, this 'reactive dissolution' could also have some benefits. Interestingly, when the dissolved Pripol-network was left in xylene at room temperature for one month, the dissolved network fragments precipitated again on the bottom of the vial. After removal of the solvent and a heating step at 100°C, a network was formed again. To check the generality of such a solvent-based recycling approach, a freshly made Pripol-network xylene 'solution' - in fact a prepolymer mix that is reversibly generated - was concentrated by heating to 100°C for 4h under a flow of N<sub>2</sub>, and the material was recovered. TGA, DSC, infrared spectroscopy and tensile tests showed that the thermal, chemical and mechanical properties of the material did not change after multiple dissolving and heating steps (Figure S13).

As described in the introduction, PMEs are known to be prone to hydrolysis,<sup>54</sup> which may be a serious limitation of the application potential of PME materials. To investigate the extent of this potential issue of PME networks, a DEPD-sample was immersed in water and left at room temperature for two weeks or at 80°C for 24 hours. At room temperature, the network had a swelling degree of 4.2% and soluble fraction of only 1.6%. The swelling at 80°C increased to 13.9%, but the sol fraction remained about the same. The fact that the soluble fraction did not increase at higher temperatures can exclude hydrolysis. Furthermore, the mechanical properties were measured after the hydrolysis test. As depicted in Figure S15 (b), the Young's modulus did not change. However, an increase in elongation is observed, which could be the result of the drying step (100°C) in vacuum prior to the analysis.

As PME materials are polycarboxylic acids, they might be hygroscopic and show water uptake over time, which can lead to hydrolysis in subsequent thermal treatments (> 80°C). Hydrolysis issues could be expected at these higher processing temperatures if water is present in the material. In this context, the hygroscopic nature of the DEPD-network was investigated. A TGA thermogram from a freshly made (and thus dry) sample was compared with one that had been standing in open air for two weeks. As depicted in Figure S14, absolutely no difference could be observed from the thermograms. In general, no issues with hydrolysis were observed for DEPD-, Pripol- or PMDA-networks during all processing and characterization steps. Only the more hydrophilic polyether PTHF-network seemed to be prone to hydrolysis when heating, as was observed during a recycling experiment at 150°C. However, this problem was circumvented when the network was dried before processing. Hydrophilic backbones should thus be avoided in PME materials if applications require hydrolytic stability.

#### Conclusion

In this work, we have developed phthalate monoester (PME) transesterification as a new dynamic chemistry for CANs. It was shown with model compounds and on material level that this type of esters can undergo fast bond exchanges with free hydroxyl moieties. Because the reaction is 'catalyzed' by the pendant carboxylic phthalate acid, as an example of the neighboring group participation effect, the need of a highly active external catalyst was avoided. As a design principle for CANs, this approach is quite attractive because exchange reactions that are catalyzed in this way can show relatively high enthalpic activation barriers, which translates into much more pronounced temperature response of the dynamic bond exchange and the corresponding rheological behavior. This is exemplified by our PME networks that span a wide range of properties and all have a strong temperature dependence of their viscosity with a high activation energy of ~120 kJ/mol.

Intrigued by the combination of a dissociative bond exchange mechanism and the dynamic properties usually observed in associative CANs, a lot of focus was put on the rheological behavior of these dynamic materials. In all the materials, only a gradual Arrhenius-type rheological behavior was observed, despite the dissociative mechanism which could lead to depolymerization and a gel-to-sol transition. Depending on the nature of the solvent (swelling or non-swelling), PME networks are either completely insoluble or completely soluble at high temperatures. Hence, we put forward a simple and essential test that can be performed on any CAN to establish its dissociative or its associative (vitrimer) nature.

This study was performed primarily as a fundamental inquiry into the relation between dynamic material properties and the mechanism of novel network exchange reactions, inspired by the classical concept of NGP. However, we also believe that the PME chemistry platform for CANs introduced herein is in fact a powerful, and partly overlooked polymer system with promising applications in dynamic polymer systems, including applications more typically envisaged for vitrimers. Indeed, cheap and easily accessible phthalic anhydride and polyol monomers can be used, and the material design is straightforward. This chemistry, albeit at different stoichiometries, is already used widely in industrial applications, such as for alkyd resins, making the PME platform a drop-in technology that does not require custom made monomers. Finally, a broad range of material properties could be easily obtained by changing the nature of the monomers in the network formulation, and the dynamic properties can be related to the straightforward exchange chemistry. Further implementation of this platform into common network formulations is part of ongoing research.

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#### Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### **Supporting Information**

Synthetic procedures, NMR Spectroscopy, material synthesis and characterization, FTIR, thermal analysis (DSC, TGA), stress relaxations, solubility, and hydrolytic stability.

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