Supporting Information
Double neighbouring group participation for ultrafast exchange in phthalate monoester networks

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1 Materials

Benzoyl chloride (99%), dimethylethanolamine (>95%), N-methyl diethanolamine (>95%), phthalic anhydride (99%), tributylamine (98.5%) trimellitic anhydride chloride (98%) and 1,1,1-tris(hydroxymethyl)propane (trimethylolpropane, 98%) were purchased from Sigma Aldrich. 1,6-Hexanediol and 2-methoxyethanol (>99%) were purchased from TCI Europe. Sodium hydrogen carbonate (99%) was purchased from Carl Roth. 2-phenylethanol (Fluka, >99%), pyridine (anhydrous, Acros Organics, 99.5%) and previously mentioned chemicals were all used as received. Solvents were HPLC grade and purchased from Acros Organics, except for toluene (VWR Chemicals). CDCl₃ (99.5%) and DMSO-d₆ (99.5%) were obtained from Euriso-top.

Pripol 2033 (98%) was kindly provided by Croda.

2 Instrumentation

Differential scanning calorimetry (DSC) analyses were performed with a Mettler-Toledo 1/700 under nitrogen atmosphere. The samples were analysed in aluminium sample pans which contained 5–15 mg of the sample. Tgs’s were determined from the onsets in the second heating using the STARre software of Mettler-Toledo. Measurements were performed with a rate of 10 Kmin⁻¹. Extrusion of N100 was performed with a double-screw mini extruder Haake Minilab at 150 °C, with a rotation speed of 5 rpm. Fourier-transform infrared spectroscopy (FTIR) were recorded with a Perkin Elmer FTIR SPECTRUM 1000 spectrometer, equipped with a PIKE Miracle attenuated total reflectance (ATR) unit. All spectra were recorded with a resolution of 4 cm⁻¹ and 8 scans were made for each measurement. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 (300MHz) or a Bruker Avance 400 (400MHz) FT-NMR spectrometer in the indicated solvent at room temperature. Chemical shifts are presented in parts per million (δ) with the residual solvent peak as an internal standard.¹ The resonance multiplicities are described as (br. (broad)) s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintuplet), sext (sextuplet) or m (multiplet). The obtained spectra were analysed with the ACD/NMR Processor Academic Edition of ACD/Labs. Rheology experiments were conducted on an Anton-Paar Physica MCR 302 in shear geometry with a plate diameter of 8mm. The measurements were performed once, and were sometimes repeated a second time in case of irregular results. An initial compression force of 2N was applied, after which the measurements were performed with a fixed gap and a deformation of 5%, which was within the linear viscoelastic region. The samples had thickness of around 2mm and were cut with a hollow puncher of Boehm with a diameter of 8mm. Network formulations were mixed with a DAC 150.1 FVZ Speedmixer™. Mixing was performed twice at 3500 rpm for 60 s. Tensile testing was performed on a Tinius-Olsen H10KT tensile tester, equipped with a 5000N load cell, using a flat dog bone-type specimen with an effective gage length of 12 mm, a width of 2 mm, and a thickness of varying between 1.5 and 2 mm. The samples were cut out using a Ray-Ran dog bone cutter. The tensile test was run at a speed of 10 mmm⁻¹. Thermogravimetric analyses (TGA) was performed on a Mettler-Toledo TGA/SDTA 851e under N₂-atmosphere with a heating rate of 10 °C/min from 25 °C to 800 °C, or isothermally at 150 °C/min for 90 min. The thermograms were analysed with the STARre software from Mettler-Toledo.
3 Synthesis procedures

3.1 Synthesis of mono-ethyl phthalate

2 g of phthalic anhydride (13.50 mmol, 1 eq) was dissolved in 20mL dry ethanol (342.97 mmol, 25.4 eq) and heated for 16 h at 80 °C. Afterwards, the excess ethanol was removed in vacuo and after standing for a while, two phases could be observed - one oily phase and a white crystalline phase. Chloroform was added to selectively dissolve the oily phase. The insoluble white crystals (= phthalic acid) were removed via filtration. The solvent was removed under reduced pressure to obtain the product as a colourless oil (2.15 g, 11.07 mmol, 82 %).

**Formula:** $\text{C}_{10}\text{H}_{10}\text{O}_4$. **MW:** 194.06 g/mol. **LC-MS (m/z):** 195.1 [M+H]$.^+$ **$^1$H-NMR (300 MHz, CDCl$_3$):** $\delta$ (ppm) = 1.39 (t, 3H, CH$_3$, J = 7.1 Hz), 4.41 (q, 2H, CH$_2$, J = 7.2 Hz), 7.53-7.68 (2H, 2xAr-H), 7.73 (m, 1H, Ar-H), 7.93 (m, 1H, Ar-H), 11.28 (br. s, 1H, COOH).

**13C-NMR (100 MHz, CDCl$_3$):** $\delta$ (ppm) = 13.79 (CH$_3$), 61.89 (CH$_2$), 128.64 (CH), 129.66 (CH), 129.91 (C), 130.69 (CH), 132.09 (CH), 133.43 (C), 168.11 (C), 172.48 (C).

3.2 Synthesis of mono-2-methoxyethyl phthalate

10 g of phthalic anhydride (67.52 mmol, 1 eq) was suspended in 30mL toluene and 6.2 g of 2-methoxyethanol (81.48 mmol, 1.2 eq) was added to this suspension. The mixture was stirred under a nitrogen atmosphere for 16 h at 100 °C. The white precipitate that was formed was isolated by filtration and dried under vacuum at 40°C. Chloroform was added to dissolve the desired product and the insoluble white crystals (= phthalic acid) were removed via filtration. The solvent was removed under reduced pressure to obtain the product as a colourless oil (11.603 g, 51.75 mmol, 77%).

**Formula:** $\text{C}_{11}\text{H}_{12}\text{O}_5$. **MW:** 224.21 g/mol. **ESI-MS (m/z):** 225.1 [M+H]$^+$ **$^1$H-NMR (300 MHz, CDCl$_3$):** $\delta$ (ppm) = 3.39 (s, 3H, CH$_3$), 3.71 (m, 2H, CH$_2$-O-CH$_3$), 4.48 (m, 2H, CH$_2$-O-CO), 7.49-7.61 (m, 2H, 2xAr-H), 7.69 (m, 1H, Ar-H), 7.87 (m, 1H, Ar-H). **$^{13}$C-NMR (100 MHz, CDCl$_3$):** $\delta$ (ppm) = 58.78 (CH$_3$), 64.58 (CH$_2$), 70.03 (CH$_2$), 128.65 (CH), 129.64 (CH), 130.01 (C), 130.73 (CH), 132.01 (CH), 133.11 (C), 168.07 (C), 171.54 (C).

3.3 Synthesis of mono-2-(dimethylamino)ethyl phthalate

10 g of phthalic anhydride (67.52 mmol, 1 eq) was suspended in 30mL toluene and 6.2 g of 2-methoxyethanol (81.48 mmol, 1.2 eq) was added to this suspension. The mixture was stirred under a nitrogen atmosphere for 16 h at 100 °C. The white precipitate that was formed was isolated by filtration and dried under vacuum at 40°C. Chloroform was added to dissolve the desired product and the insoluble white crystals (= phthalic acid) were removed via filtration. The solvent was removed under reduced pressure to obtain the product as a colourless oil (11.603 g, 51.75 mmol, 77%).
10 g of phthalic anhydride (67.52 mmol, 1 eq) was suspended in 30 mL toluene and 2-(dimethylamino)ethanol (8.15 mL, 81.48 mmol, 1.2 eq) was added to the suspension. The mixture was stirred for 16 h at 100 °C under nitrogen atmosphere and the white precipitate formed was isolated by filtration followed by drying under vacuum at 40 °C. The product was purified by recrystallisation in DMF to obtain the desired product as a white powder (13.24 g, 55.81 mmol, 83%).

**Formula:** C_{12}H_{15}NO_4. **MW:** 237.26 g/mol. **ESI-MS (m/z):** 238.2 [M+H]+. **1H-NMR (300 MHz, DMSO-d_6):** δ (ppm) = 2.68 (s, 6H, 2xCH_3), 3.17-3.22 (m, 2H, CH_2-N), 4.46-4.52 (m, 2H, CH2-O), 7.40-7.52 (3H, 3xAr-H), 7.58 (m, 1H, Ar-H). **13C-NMR (100 MHz, DMSO-d_6):** δ (ppm) = 42.64 (2xCH_3), 55.62 (CH_2), 58.90 (CH_2), 127.41 (CH), 128.03 (CH), 128.73 (CH), 130.67 (CH), 131.45 (C), 139.43 (C), 168.85 (C), 170.35 (C).

### 3.4 Synthesis of 2-(dimethylamino)ethyl benzoate

Benzoyl chloride (1.55 mL, 13.34 mmol, 1 eq) was dissolved in 75 mL of diethyl ether under inert atmosphere and cooled at 0 °C. 2-(dimethylamino)ethanol (2 mL, 19.98 mmol, 1.5 eq) was added dropwise. Another 50 mL of diethyl ether was added and the mixture was stirred at room temperature for 6 h. The formed white precipitate was isolated by filtration and dissolved in a saturated solution of NaHCO_3 after which the product was extracted with diethyl ether (3x25 mL). The combined organic phases were dried *in vacuo* to obtain the product, which was used without further purification (0.86 g, 4.45 mmol, 33%).

**Formula:** C_{11}H_{15}NO_2. **MW:** 193.25 g/mol. **ESI-MS (m/z):** 252.0 [M+H+NaCl]+. **1H-NMR (300 MHz, DMSO-d_6):** δ (ppm) = 2.73 (s, 6H, 2xCH_3), 4.45 (t, 2H, CH-N, J = 5.8 Hz), 4.49 (t, 2H, CH2-O, J = 5.8 Hz), 7.44 (m, 1H, Ar-H), 7.56 (3H, 3xAr-H), 8.06 (m, 1H, Ar-H). **13C-NMR (100 MHz, DMSO-d_6):** δ (ppm) = 45.76 (2xCH_3), 57.74 (CH_2), 62.96 (CH_2), 128.21 (2xCH), 129.53 (2xCH), 130.12 (C), 132.81 (CH), 166.45 (C).

### 3.5 Synthesis of the phthalic anhydride of Pripol 2033 (Pripol-dianhydride)
Pripol-dianhydride was synthesised according to a previously described procedure.² In a two-neck round bottom flask, 39.214 g of trimellitic anhydride chloride (186.2 mmol, 1 eq) was dissolved in 300 mL of a mixture of toluene containing a small amount of MgSO₄. The mixture was cooled to 0 °C and placed under nitrogen. 50 g of Pripol 2033 (96.1 mmol, 0.5 eq) was dissolved in 100 mL of toluene together with 15.0 mL dry pyridine (186.2 mmol, 1 eq). This alcohol solution was added dropwise to the cooled acid chloride. The mixture was slowly heated to room temperature and stirred for another 16 hours. The mixture was filtered to remove the formed pyridine salts and concentrated in vacuo to obtain the product as a yellowish viscous oil. The anhydride was used without further purification (79.11 g, 89.4 mmol, 96%).

**Formula:** C₅₄H₇₆O₁₀. **MW:** 885.19. **¹H-NMR (300 MHz, CDCl₃):** δ (ppm) = 0.74-0.97 (6H, 2xC₃H₃), 0.98-1.93 (58H, 29xC₂H₅), 4.41 (t, 4H, 2xCH₂-O, J = 6.7 Hz), 8.11 (m, 2H, 2xAr-H), 8.57 (m, 2H, 2xAr-H), 8.64 (s, 2H, 2xAr-H). **¹³C-NMR (100 MHz, CDCl₃):** δ (ppm) = 14.06 (2xC₃H₃), 22.29-37.80 (32xC₂H₅), 66.61 (2xC₂H₅), 125.75 (2xC₆H₅), 126.65 (2xC₆H₅), 131.55 (2xC), 134.18 (2xC), 137.01 (2xC), 137.92 (2xC), 161.76 (2xC), 161.82 (2xC), 163.87 (2xC).

### 3.6 General network synthesis

An amount (see table below) of trimethylolpropane (TMP) was put in a plastic cup (Speedmixer cup) together with a mixture of 1,6-hexanediol (HD) and N-methyl diethanolamine (MDEA). The cup was subsequently heated in an oven at 80 °C for 5 min to melt the alcohol mixture. Pripol-dianhydride was added and the monomers were mixed using a Speedmixer (3500 rpm, 60 s). The heating and mixing step was repeated once to obtain a homogeneous mixture. The cup was put in an oven at 100 °C for 2 h, followed by a curing under vacuum at 100 °C for 16 h to remove last traces of toluene (from dianhydride) and suppress amine oxidation. The obtained (foamed) network was cut in small pieces and pressed in a hot press for 20 min (or 60 min for N-0) at 150 °C (2 t) to obtain a homogeneous and transparent network.

<table>
<thead>
<tr>
<th>Network</th>
<th>Pripol dianhydride (mmol)</th>
<th>HD (mmol)</th>
<th>MDEA (mmol)</th>
<th>TMP (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-0</td>
<td>6.20</td>
<td>2.48</td>
<td>-</td>
<td>2.48</td>
</tr>
<tr>
<td>N-20</td>
<td>6.20</td>
<td>1.98</td>
<td>0.50</td>
<td>2.48</td>
</tr>
<tr>
<td>N-40</td>
<td>6.20</td>
<td>1.49</td>
<td>0.99</td>
<td>2.48</td>
</tr>
<tr>
<td>N-60</td>
<td>6.20</td>
<td>0.99</td>
<td>1.49</td>
<td>2.48</td>
</tr>
<tr>
<td>N-80</td>
<td>6.20</td>
<td>0.50</td>
<td>1.98</td>
<td>2.48</td>
</tr>
<tr>
<td>N-100</td>
<td>6.20</td>
<td>-</td>
<td>2.48</td>
<td>2.48</td>
</tr>
</tbody>
</table>
4 Methods

4.1 Model exchange experiments

5 equivalents of PME (1.26 mmol) were mixed with 30.9 mg of 2-phenylethanol (0.25 mmol, 1 eq). For the reactions with the β-amino PME (6), 0.3 mL of deuterated DMSO was also added to dissolve the solid ester. The mixture was put in a pressure tube and heated in an oil bath at elevated temperatures (100 or 140 °C). After 0, 2.5, 5, 7.5, 10, 15, 20, 30 and 60 minutes, the pressure tube was cooled down in a water bath and a small amount of the reaction mixtures was dissolved in 0.6 mL of d-DMSO and analysed by 1H-NMR in order to monitor the reaction conversion.

4.2 Swelling degree and soluble fraction measurements

The swelling degree was measured by immersing a material sample (with a dry mass $m_{\text{dry}}$) in THF for 24h. After swelling, the sample was weighed again to obtain the swollen mass ($m_{\text{wet}}$). This was performed on one sample of each network. The swelling degree was finally calculated using following formula:

\[ \text{Swelling degree} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\% \]  

(Equation S1)

Soluble fractions were measured by immersing the networks in THF at room temperature for 24h. During this period, the THF was refreshed multiple times. The extracted gel fraction was dried in a vacuum oven at 120 °C for 6 h. Finally, the soluble fraction was calculated using the following equation ($m_0 = \text{starting mass}, m_g = \text{mass of dried gel fraction after extraction}$):

\[ \text{Soluble fraction} = \frac{m_0 - m_g}{m_0} \times 100\% \]  

(Equation S2)

4.3 Frequency sweep measurements

Frequency sweep experiments were performed at different temperatures, with a logarithmically changing frequency from 100 rad/s (or 628 for N-20) to 0.01 rad/s. A strain of 5 % and (initial) normal force of 2 N was applied. Relaxation times were calculated using the following equation ($\omega$ is the angular frequency at the cross-over of $G'$ and $G''$):

\[ \tau = \frac{1}{\omega} \]  

(Equation S3)
5 Figures

![Isothermal TGA of N-100 at 150 °C for 120 minutes.](image)

**Figure S1**: Isothermal TGA of N-100 at 150 °C for 120 minutes.

![DSC thermograms of the second heating step from -50°C to 100°C.](image)

**Figure S2**: DSC thermograms of the second heating step from -50°C to 100°C.

![Average stress-strain curves of the different networks, showing no change in the stress at break.](image)

**Figure S3**: Average stress-strain curves of the different networks, showing no change in the stress at break.
Figure S4: Stress relaxation curves for N-0 (a), N-20 (b), N-40 (c), N-60 (d), N-80 (e) and N-100 (f) and theoretical Maxwell relaxation for the network at 160°C with the same relaxation time (grey dotted line).
Figure S5: Stress relaxation curves for N-0 (a), using a mono-exponential fit and N-20 (b), N-40 (c), N-60 (d), N-80 (e) and N-100 (f) using a double exponential fit.
Figure S6: (a) Stress relaxation curves for N-100, from 120 to 160 °C. (b) Frequency sweep measurements of N-100, from 110 to 150 °C. (c) Table comparing the relaxation times, determined via the two different measurements. (d) Arrhenius plot of N-100, obtained from stress-relaxation and frequency sweep experiments, from which the same activation energy was calculated.

Figure S7: Comparison of stress-relaxation (a) and frequency sweep (b) behaviour at 160 °C between an internal tertiary amine (N-100) and an external amine (N-0 + tributyl amine), showing five times faster relaxation rate for the internal catalysed network.
Figure S8: FTIR-spectra of N-100 before and after MFI and extrusion. The spectrum of the uncured network showed distinctive anhydride signals (shaded band), which were not observed in the other spectra.

Figure S9: Creep experiment for N-0 and N-100 at 50 °C. During the period between 300 and 1500 s, a constant shear stress of 2000Pa was applied to the sample.
Figure S10: Swelling degree (%) of the networks in THF and water after immersing at room temperature for 24 h.

Figure S11: TGA of N-100 immediately after curing and after one month in open air.

6 Bibliography