Electronic Supporting Information (ESI)

Reversible crosslinking and fast stress relaxation in dynamic polymer networks via transalkylation using 1,4-diazabicyclo[2.2.2]octane

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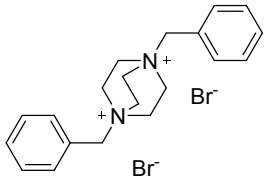
Synthesis of small molecules

Synthesis of 1,4-dibenzyl-1,4-diazabicyclo[2.2.2]octane-1,4-diium dibromide:[1]



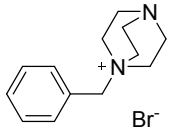
Benzyl bromide (0.48 mL, 2.1 eq.) was dissolved in methanol (20 mL, 0.3 M). Subsequently, DABCO (224 mg, 1.0 eq.) was added to the solution. The reaction mixture was stirred overnight at room temperature. The reaction mixture was then precipitated in diethyl ether. The obtained product was filtered, washed three times with diethyl ether and dried under high vacuum. The final product was obtained as a white solid (yield: 73.8%).

^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 7.61 – 7.47 (m, 10H), 4.85 (s, 4H), 3.89 (s, 12H).

^{13}C NMR (101 MHz, DMSO-d_6): δ [ppm] = 133.5, 131.18, 129.6, 126.9, 66. 8, 50.6

HRMS (MALDI-TOF): calcd for $C_{20}H_{26}N_2^{2+}$: 294.21; found, [M + Br]: 375.18.

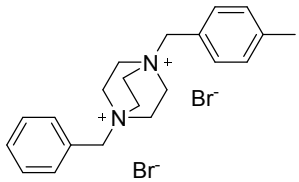
Synthesis of 1-benzyl-1,4-diazabicyclo[2.2.2]octan-1-ium bromide:



DABCO (0.5 g, 1 eq.) was dissolved in methanol (50 mL, 0.09 M) yielding a colorless solution. Benzyl bromide (1 eq.) was added dropwise under vigorous stirring. The reaction mixture was stirred overnight at room temperature. The reaction mixture was concentrated in vacuo and dried under high vacuum. The final product was obtained together with 10 mol% disubstituted DABCO as a byproduct, (yield: 98.8%).

^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 7.53 (s, 5H), 4.55 (s, 2H), 3.32 (t, J = 6.9 Hz, 6H), 3.02 (t, J = 6.9, Hz, 6H). About 10 mol % of bisbenzyl-DABCO was formed as a byproduct.

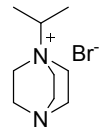
Synthesis of 1-benzyl-4-(4-methylbenzyl)-1,4-diazabicyclo [2.2.2]octane-1,4-diium dibromide:



A solution of 1-benzyl-1,4-diazabicyclo[2.2.2]octan-1-ium bromide in DMSO-d_6 (51 mg in 0.5 mL, 0.36 M), and a solution of 4-methylbenzylbromide (67 mg in 1 mL in DMSO-d_6, 0.36M) are prepared. The solutions are combined in a 1:1 ratio and left to react overnight at room temperature. Product was not isolated, so yield can not be given, but an NMR reference spectrum of the compound was obtained.

^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 7.61 – 7.49 (m, 5H), 7.37 (dd, J = 8.0 Hz and 19.9 Hz, 4H), 4.85 (s, 2H), 4.80 (s, 2H), 3.87 (s, 12H), 2.35 (s, 3H). Some 4-methylbenzylbromide is still present in the product.

Synthesis of 1-isopropyl-1,4-diazabicyclo[2.2.2]octan-1-ium bromide:[2]



DABCO (1 g, 1 eq.) was dissolved in acetone (45 mL, 0.2 M) and 2-bromopropane (1 eq.) was added dropwise under magnetic stirring. The reaction mixture was stirred for 3 nights at room temperature. The formed white precipitate was filtered, washed with ethyl acetate, and dried under high vacuum. The final product was obtained as a white solid (yield: 25,2%).

^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 3.53 – 3.47 (m, 1H), 3.26 (t, J = 7.3 Hz, 6H), 3.02 (t, J = 7.3 Hz, 6H), 1.28 (dt, J = 6.6, 1.8 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6): δ [ppm] = 65.5, 49.1, 45.2, 16.2.

^{1}H NMR kinetic study of DABCO transalkylation with excess DABCO

For the kinetic analysis the signals of the aromatic protons were used as internal standard as this peak is at the same position for substrate and product. Product formation was monitored using the benzylic CH_2 signal (Figure **S1,** peak A).

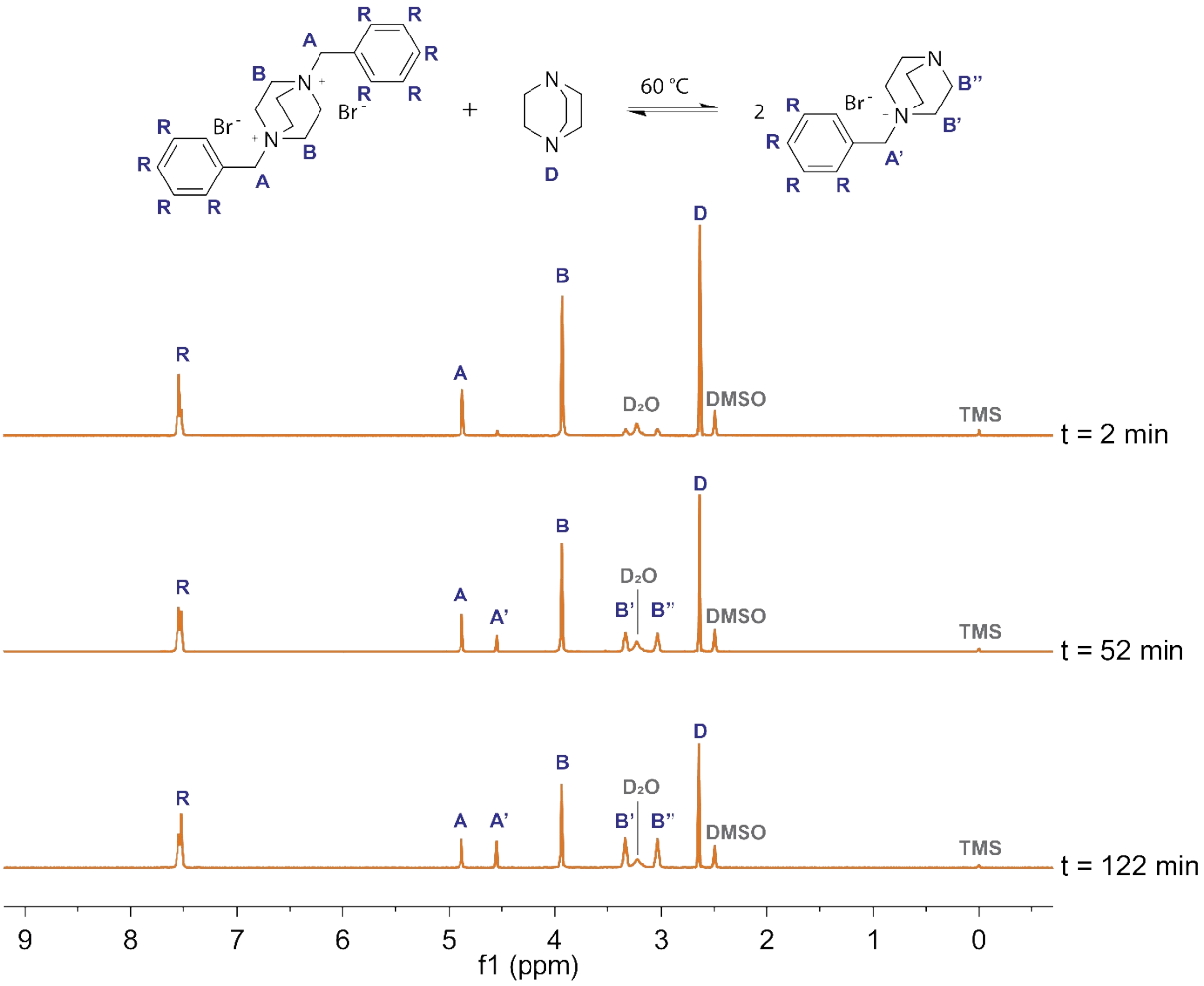


Figure S1 Selected ^{1}H NMR spectra from the kinetic experiment with initial concentrations $[S]_0 = [D]_0 = 40$ mM at 60 °C.

Kinetic analysis

When plotting the concentration monobenzyl-DABCO [P] as a function of reaction time using different initial concentrations, the results are consistent with a reaction rate that is first-order in both reactant concentrations (the initial slopes are proportional to $[S]_0 \times [D]_0$), which leads to the following rate equation for the forward (batch) reaction,

$$-\frac{d[S]}{dt} = -\frac{d[D]}{dt} = \frac{1}{2}\frac{d[P]}{dt} = k[S][D] \qquad (S1)$$

which in turn leads to the integrated rate equation (S2a) in the case of equimolar starting concentrations $[S]_0 = [D]_0$ and (S2b) in the case of $[S]_0 = [D]_0 + e$, where e is an excess amount of DABCO.

$$\frac{1}{[S]} = k \cdot t + \frac{1}{[S]_0} \qquad (S2a)$$

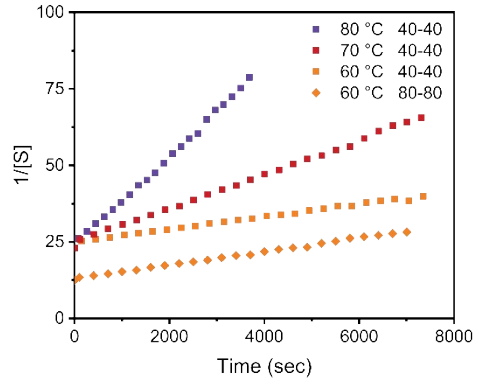
$$\frac{1}{e}\ln\left(\frac{e + [S]}{[S]}\right) = k \cdot t + \text{constant} \qquad (S2b)$$

All kinetic experiments were analyzed using equation 2b (except for those that exactly corresponded to $e = 0$) and the second order rate coefficient k for each experiment is shown in Figure **S2a**. In Figure **S2b**, a representative selection of the analyses is shown, the slopes of these plots correspond to k, and in Figure S2b the corresponding Arrhenius plot of the rate coefficients is shown. Regression of all data of Figure S2a in Figure S2c yields an activation energy $E_a \approx 93$ kJ·mol^{-1} and frequency factor $A \approx 7 \cdot 10^{11}$ L·mol^{-1}.s^{-1}.

(a)

Temperature [°C]	$[S]_0$ [mM]	$[D]_0$ [mM]	k [L mol^{-1} s^{-1}]
40	40	40	2.42×10^{-4}
50	40	40	6.90×10^{-4}
60	40	40	2.11×10^{-3}
60	80	80	2.14×10^{-3}
60	80	40	2.28×10^{-3}
60	40	80	2.21×10^{-3}
60	40	10	1.94×10^{-3}
70	40	40	5.30×10^{-3}
80	40	40	1.33×10^{-2}

(b)



(c)

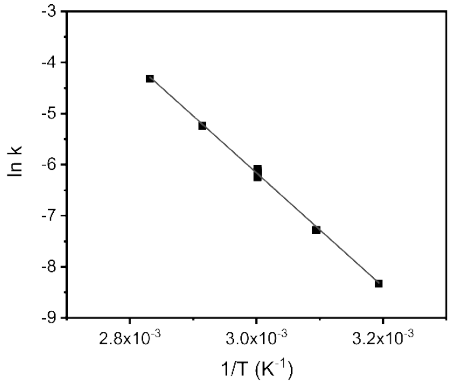


Figure S2 (a) The absolute value of the second order rate coefficient *k* for each experiment at the start of the reaction (b) Representative second-order kinetic plots for a range of temperatures and starting concentrations. (c) Arrhenius plot of the kinetic study with free DABCO used to determine the activation energy.

^{1}H NMR kinetic study of monosubstituted DABCO transalkylation

The exchange reaction of a monosubstituted DABCO with bisbenzyl-DABCO (Figure **S3**) was monitored *in situ* with ^{1}H NMR. Equimolar initial concentrations of 40 mM and a temperature of 70 °C were used. For the kinetic analysis the signals of the aromatic protons were used as internal standard as this peak is at the same position for substrate and product. Product formation was monitored using the signals of peak A and D (Figure S3). A comparison between the unsubstituted and substituted DABCO is made and the data shows that the initial rate of bisbenzyl-DABCO disappearance is a factor of 5 - 10 slower with monosubstituted DABCO than with DABCO itself. Taking into account the presence of a single amino group in benzyl DABCO instead of two, the amino group in benzyl DABCO is a factor of 3 - 5 less reactive than those in DABCO.

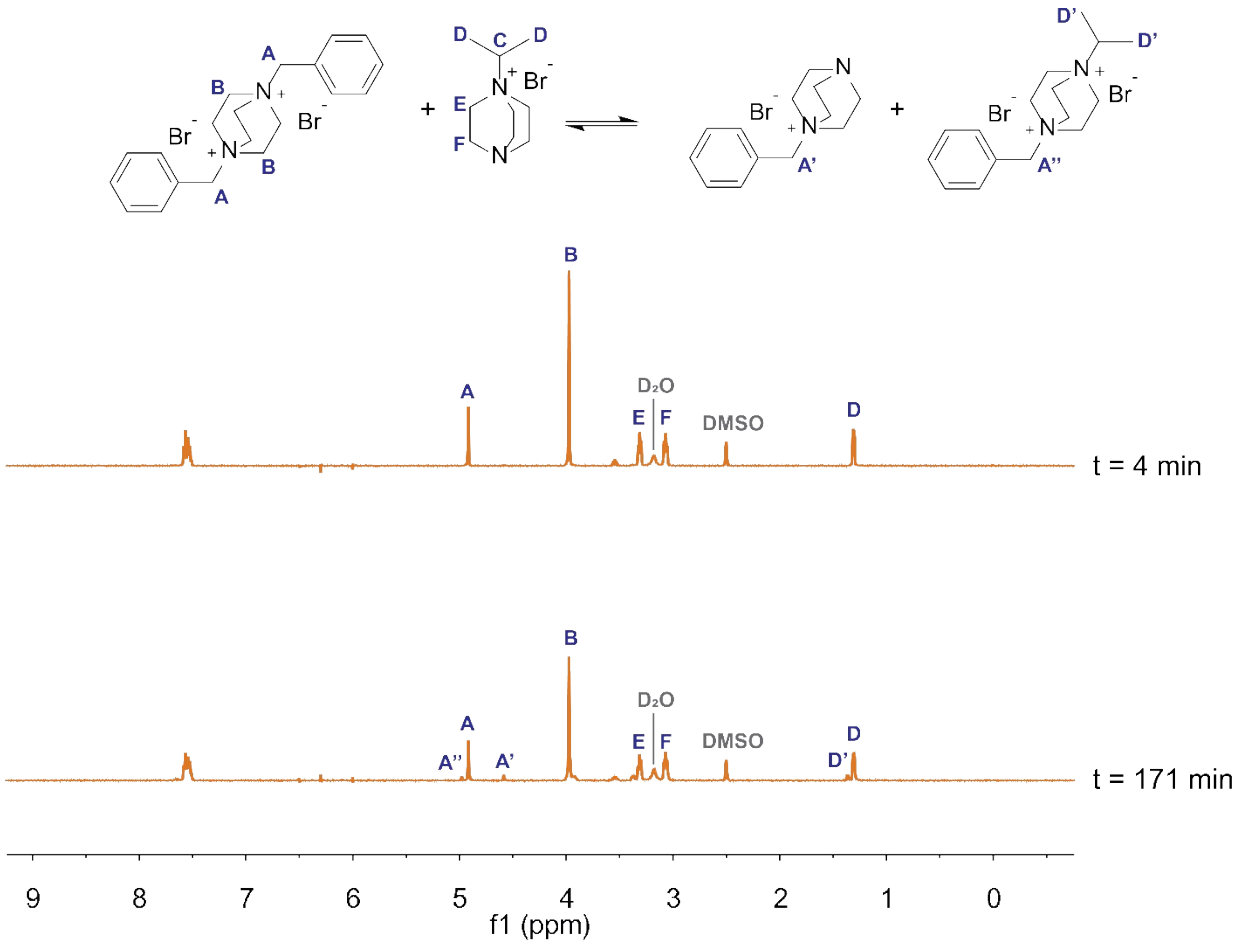


Figure S3 Selected ^{1}H NMR spectra from the kinetic experiment with monosubstituted DABCO, initial concentrations $[S]_0 = [D]_0 = 40$ mM at 70 °C.

^{1}H NMR kinetic study of DABCO transalkylation with excess benzyl bromide

A kinetic experiment with excess alkylating agent, 4-methylbenzyl bromide, was performed, Figure **S4**. In order to minimize competing hydrolysis to benzyl alcohol, the reaction was performed in the presence of molecular sieves making it difficult to do NMR measurements *in situ*.

A solution of 80 mM 4-methylbenzyl bromide and a solution of bisbenzyl-DABCO in dry DMSO were mixed in a 1:1 ratio yielding a mixture with a concentration of 40 mM for both reactants. Molecular sieves were added and the mixture was left overnight to dry. The mixture was reacted for 2 hours at 70 °C after which the reaction was quench cooled an immediately measured in ^{1}H NMR. Product formation was monitored using the signals of peak A, B and C (Figure S4). The reaction mixture contained 5 mM of the reaction product and 3 mM of hydrolysis product. In the kinetic experiment of bisbenzyl-DABCO with free DABCO 60 mM of product was formed after 2 hours using the same initial concentrations of substrates and the same temperature. As one DABCO molecule contains two amine groups the concentration of product is 30 mM per reactive group. This product formation in the reaction with free benzyl bromide is significantly slower than that for the reaction with free amine, but exchange still occurs.

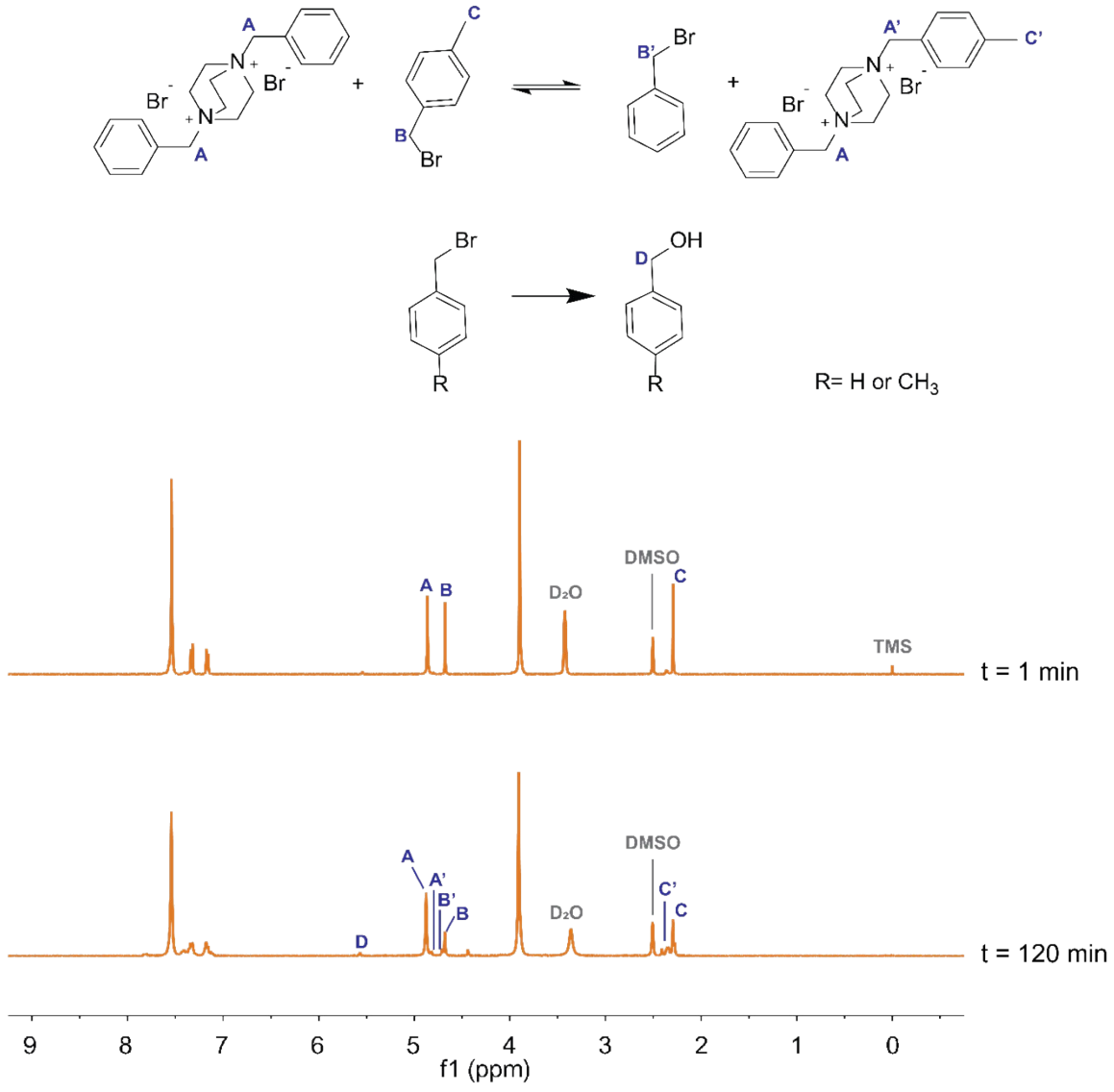
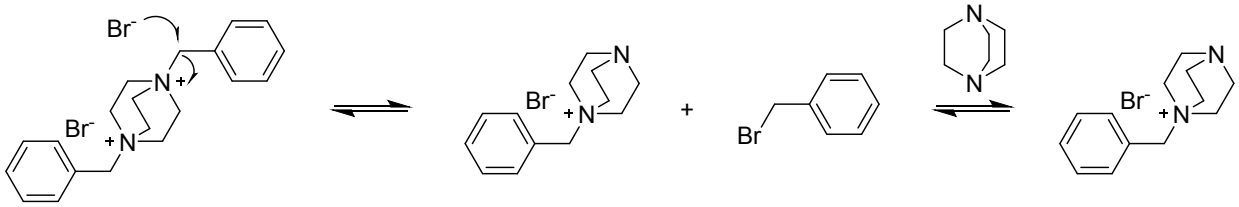


Figure S4 ^{1}H NMR spectra from a reaction of bisbenzyl-DABCO with 4-methylbenzyl bromide, initial concentrations $[S]_0 = [B]_0 =$ 40 mM at 70 °C.

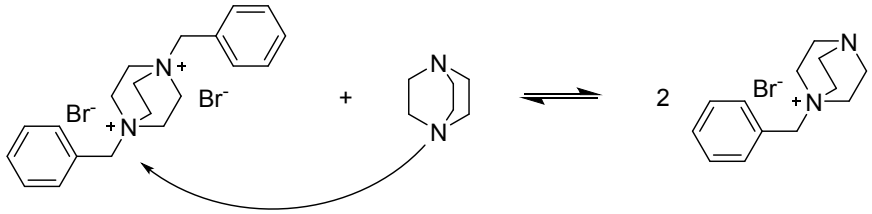
Transalkylation reaction mechanisms

A recent article from the group of Lehn investigates the use of nucleophilic substitution reactions with amines in dynamic covalent networks, and describes two possible pathways for S_N2 exchange.[3] The pathways are illustrated for quaternized DABCO derivatives in Scheme **S1**. The indirect pathway is a dissociative mechanism in which the bisbenzyl-DABCO dissociates by nucleophilic attack of a bromide anion. The resulting products are a monobenzyl-DABCO and a benzylbromide. The benzylbromide can react with another tertiary amino group of monobenzyl-DABCO to form a new crosslink. This reaction occurs without the presence of DABCO. The direct pathway is associative, and requires the presence of a free amine. The DABCO will react directly with the bisbenzyl-DABCO substrate, resulting in the formation of two monobenzyl-DABCO products.

(a)



(b)



Scheme S1 S_N2 exchange pathways proposed by Lehn et al. illustrated for DABCO. (a) Indirect pathway, initiated by nucleophilic attack of the bromide anion on the benzylic carbon of the quaternary ammonium salt. (b) Direct pathway with nucleophilic attack of the amine on the benzylic carbon of the quaternary ammonium salt.[3]

^{1}H NMR of linear polymer

The bromobenzyl-functional monomer (BrEMA) was copolymerized with *n*-butyl methacrylate (BMA) in a free radical polymerization at 50 °C, using AIBN as an initiator and decanethiol (DT) as a chain transfer agent to yield a linear polymer with benzyl bromine side groups (SEC: M_n = 33·10^3 g/mol and $Đ \approx 1.7$). The ^{1}H NMR spectrum of this polymer is shown in Figure **S5**. and 7.60 ppm were averaged to determine the BrEMA fraction. The integration signals of peak F, G and H at δ= 3.96, 1.61 and 1.42 ppm were used to calculate the BMA fraction.

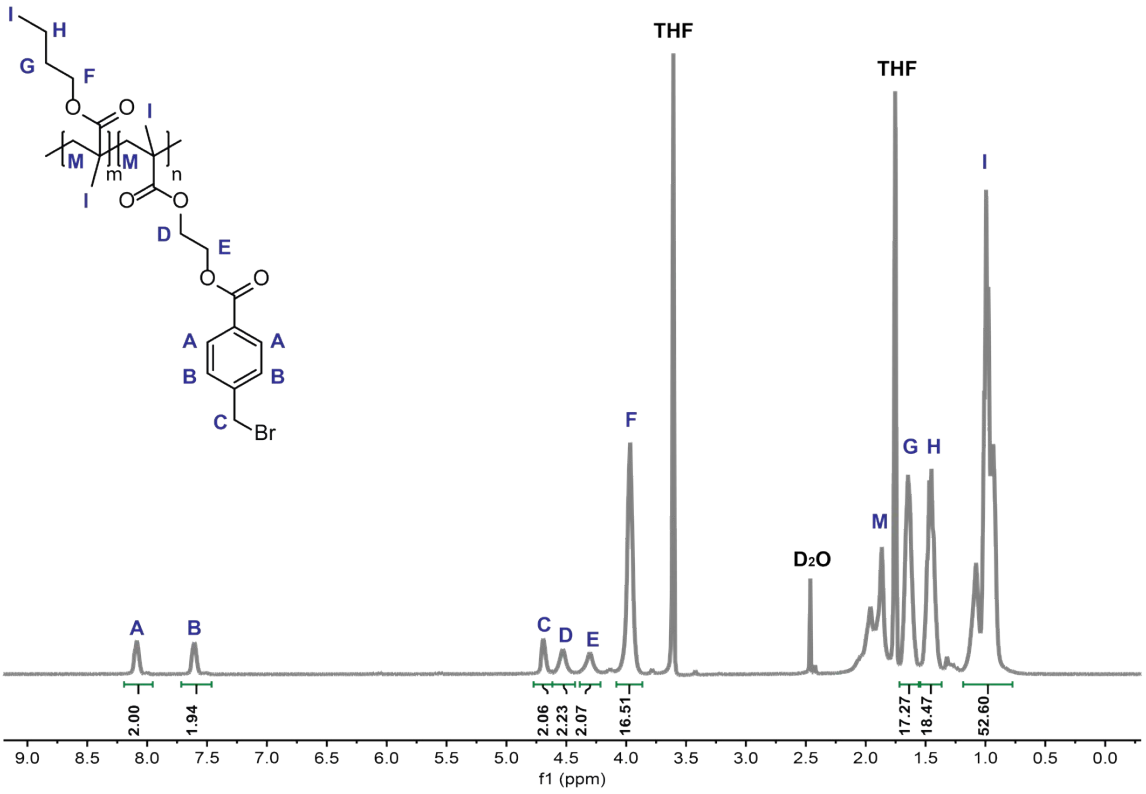


Figure S5 ^{1}H NMR spectrum from the linear poly(BMA-*co*-BrEMA) polymer.

Crosslinking in THF

Since the polymer does not readily dissolve in DMSO but dissolves well in THF, the efficiency of the crosslinking reaction in THF was tested. Two identical solutions of benzyl bromide (51 mg, 0.3 mmol) and DABCO (17 mg, 0.15 mmol) in 5 mL THF were prepared. A precipitate was formed instantaneously after combining the reactants. The solutions were kept at room temperature and at 60 °C, respectively. After 1h the precipitate was filtered and both the filtrate and the residue were analyzed by ^{1}H NMR, Figure **S6**. When reacted at room temperature, the solid product was mono-reacted DABCO. When reacted at 60 °C both mono- and di-reacted solid product was obtained.

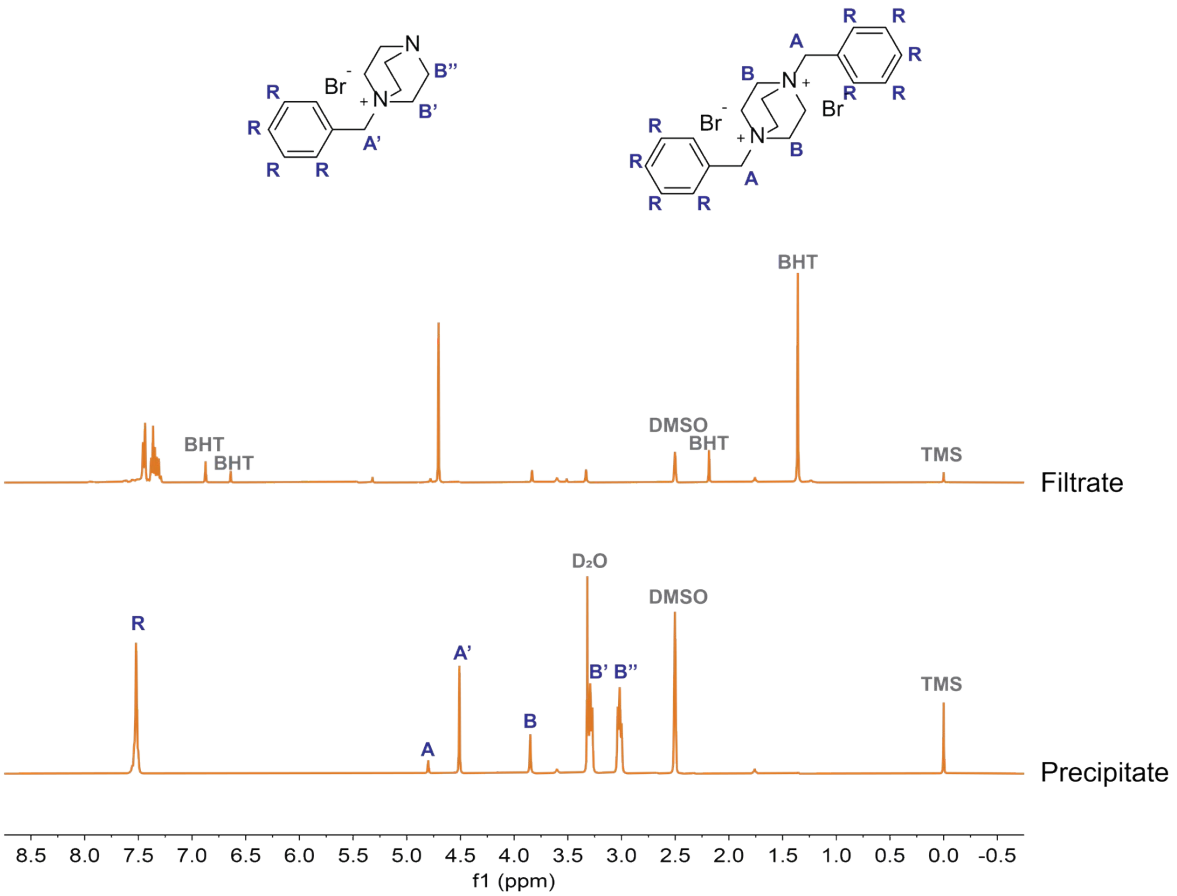
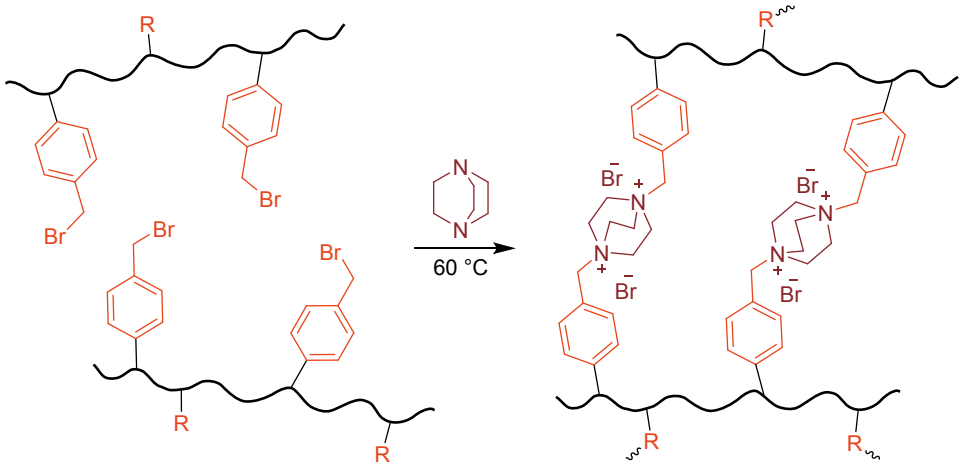


Figure S6 ^{1}H NMR spectra of the filtrate and precipitate of the product of the reaction of benzyl bromide and DABCO in THF at 60°C.

Both filtrates contained unreacted benzyl bromide and no product. This shows that the crosslinking reaction of benzyl bromide and DABCO occurs in THF at elevated temperatures and linear chains can crosslinked (scheme **S2**).



Scheme S2 Crosslinking of linear chains with benzyl bromide side groups by DABCO.

Thermal characterization of crosslinked networks

The T_g of the crosslinked copolymers was 32 °C and 33 °C for the systems with [DABCO]/[Br] = 0.6 and [DABCO]/[Br] = 0.4 respectively as determined by DSC (Figure **S7a** and **S7c**). Both systems showed excellent thermal stability in TGA up to 180 °C and fast thermal degradation above 220 °C (Figure **S7a** and **S7c**).

The dotted lines in Figure **S7** show repeat experiments after compression molding of crosslinked polymer and demonstrate that there are no significant changes in thermal properties or thermal stability of the material

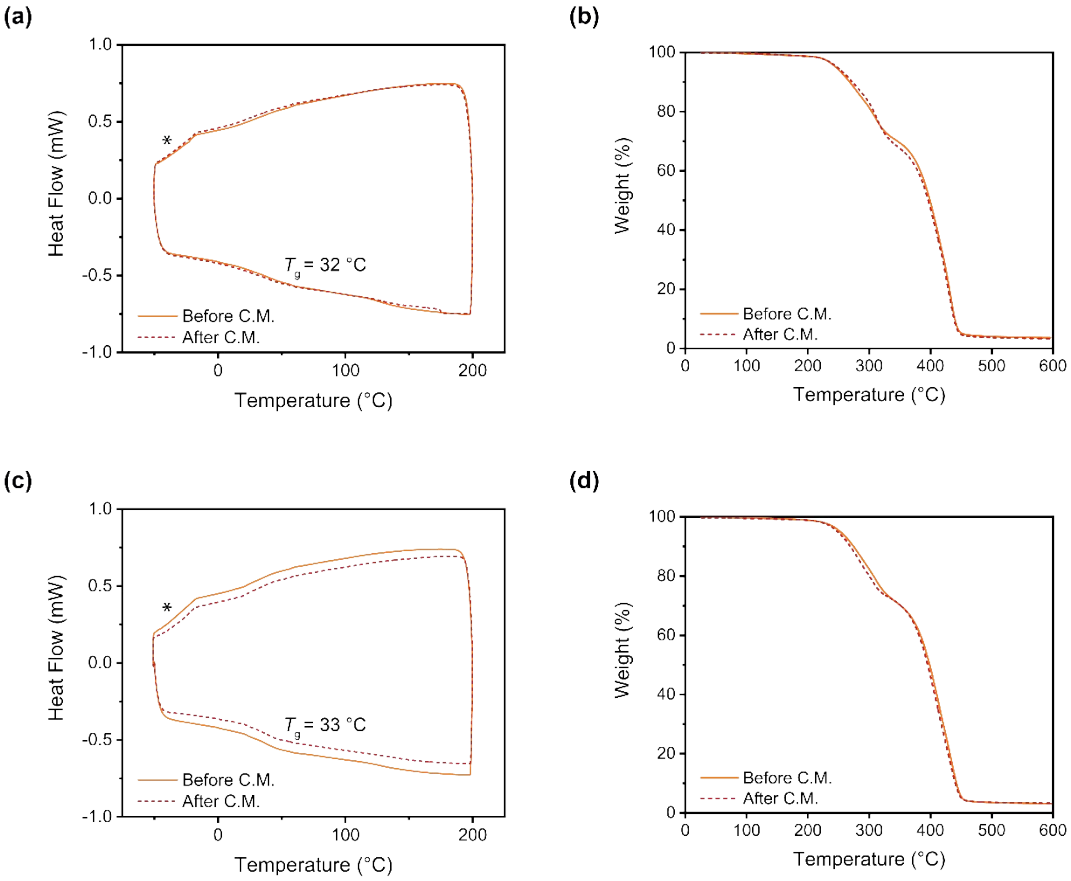


Figure S7 Thermal properties of crosslinked material before and after compression molding (C.M.). (a,c) The T_g by DSC measured from -50 °C to 200 °C with a rate of 20 °C/min. (b,d) The thermal stability via TGA measured under N_2 with a heating rate of 10 °C/min. On top [DABCO]/[Br] = 0.6, bottom graphs [DABCO]/[Br] = 0.4 eq. * is an artifact related to the cooling rate programmed for the experiment.

Stress relaxation experiments

The raw relaxation moduli are shown in Figure **S8**. The signal is unstable below 0.02 s.

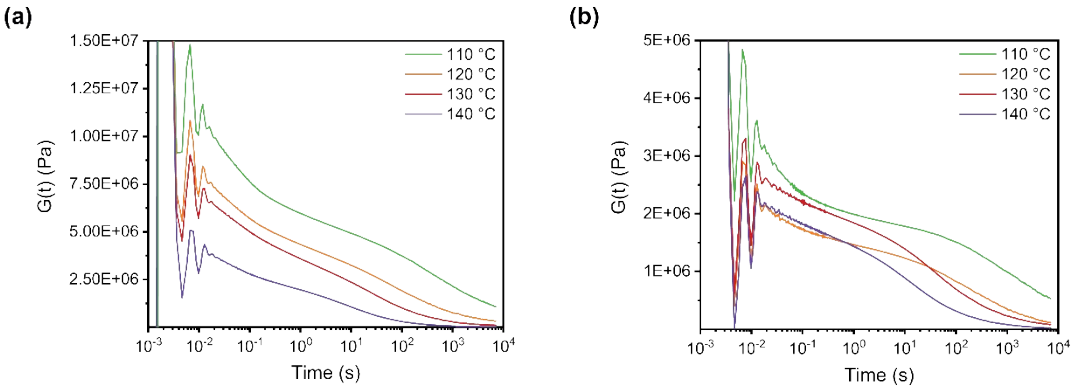


Figure S8 Raw stress relaxation data at various temperatures after a 1% step strain is applied at t = 0.001 s (a) System with 0.6 eq. of DABCO (excess amine). (b) System with 0.4 eq. of DABCO (excess benzyl bromide).

Relaxation time τ was obtained by fitting the data to a stretched exponential function (equation S3)

$$G(t) = G_0\, e^{-\left(\frac{t}{\tau}\right)^{\beta}} \qquad \text{(S3)}$$

with G_0. τ, and β as fitting parameters and exclusion of data for the first 0.02, 0.1, or 1 s. The fitted parameters are shown in Table S1. From the relatively poor fits at short times in Figs S8a-d, it is evident that below 1s, relaxation behavior is not properly represented by a stretched exponential, and additional relaxation mechanisms play a role. In order to analyze the slower relaxation process that is described by a stretched exponential, further analysis was performed with exclusion of data before *t* = 1s (Figure **S9e-f**).

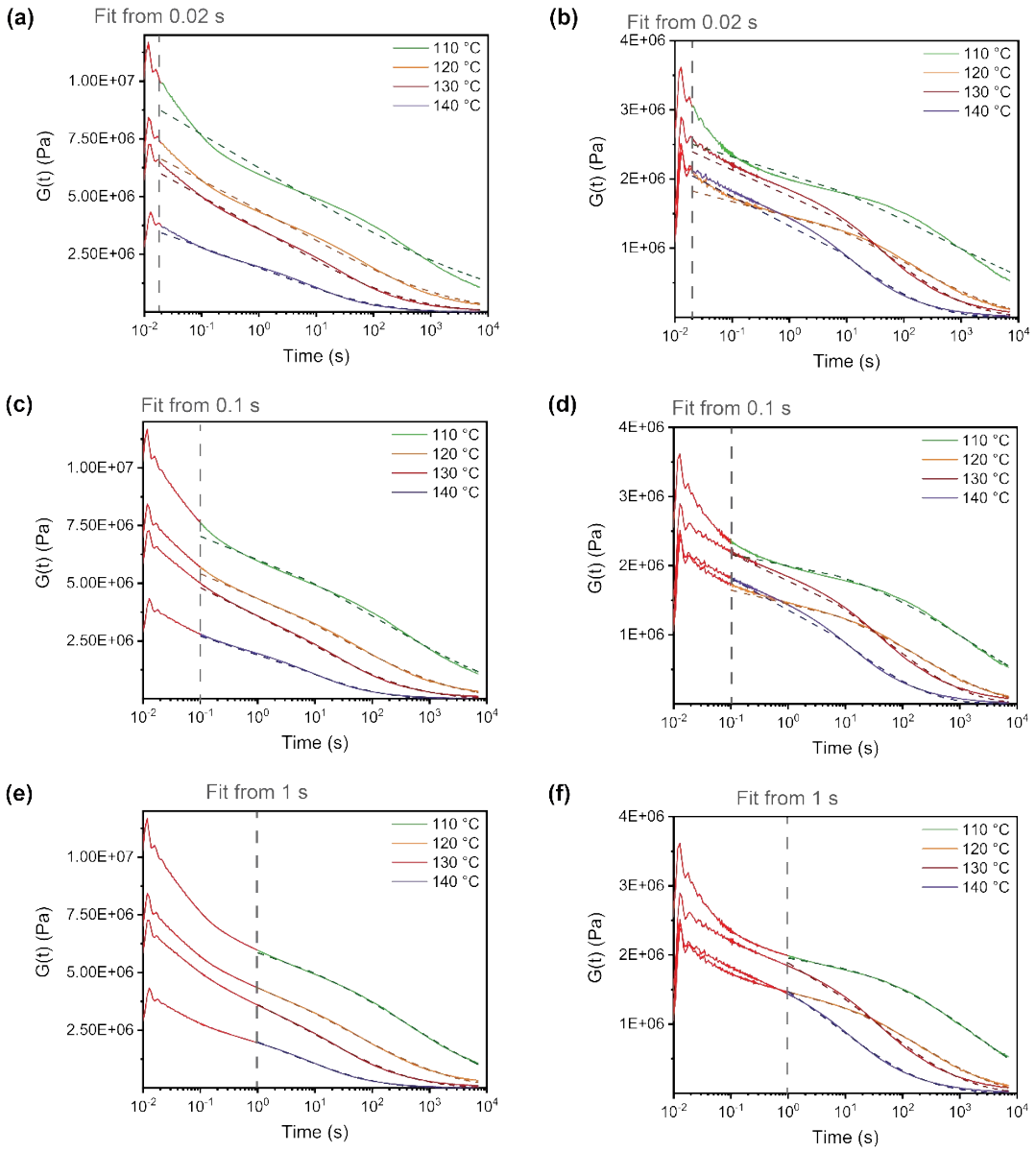


Figure S9. Stress relaxation data at various temperatures at 1% initial strain, and their fits (dotted lines) using a stretched exponential function. Data of the initial 0.02s, 0.1s, or 1s were excluded from the analysis. (a, c, e) System with 0.6 eq. of DABCO. (b, d, f) System with 0.4 eq. of DABCO.

Table S1. Best-fit parameter values.

Fitted from [s]	Temperature [°C]	0.6 eq. DABCO $G_{0\,fit}$ [Pa]	0.6 eq. DABCO τ_{fit} [s]	0.6 eq. DABCO β	0.4 eq. DABCO $G_{0\,fit}$ [Pa]	0.4 eq. DABCO τ_{fit} [s]	0.4 eq. DABCO β
0.02	110	1.7×10^7	0.8	0.10	3.1×10^6	482	0.16
	120	1.1×10^7	2.5	0.15	2.0×10^6	132	0.26
	130	9.8×10^6	1.1	0.18	2.7×10^6	35	0.27
	140	5.1×10^6	1.1	0.22	2.4×10^6	9	0.29
0.1	110	9.1×10^6	145	0.19	2.3×10^6	1789	0.27
	120	7.5×10^6	21	0.21	1.8×10^6	215	0.31
	130	7.2×10^6	5	0.23	2.6×10^6	47	0.30
	140	3.8×10^6	4	0.29	2.3×10^6	11	0.31
1	110	7.2×10^6	484	0.25	2.1×10^6	2432	0.34
	120	6.6×10^6	42	0.24	1.7×10^6	264	0.33
	130	6.4×10^6	9	0.25	2.7×10^6	37	0.28
	140	4.1×10^6	3	0.28	2.8×10^6	6	0.26

Activation energies from stress relaxation experiments

The best-fit values τ_{fit} obtained with exclusion of the initial 1s of data were used to calculate an activation energy for the relaxation process (Figure **S10**). The activation energies were shown to be affected little by fixing beta for all temperatures to an intermediate value (β = 0.25 for 0.6eq DABCO; 0.3 for 0.4 eq DABCO).

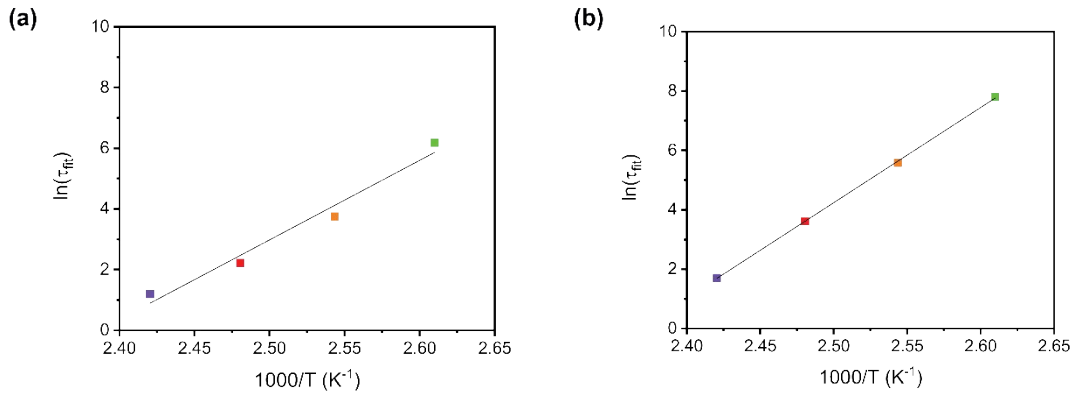


Figure S10. Arrhenius relationships from which the activation energies were calculated. (a) System with 0.6 eq. of DABCO. (b) System with 0.4 eq. of DABCO.

Table S2. Activation energies calculated form best-fit values of the relaxation time τ_{fit}.

System	β	E_a (kJ·mol^{-1}]
0.6 eq. DABCO	best fit values fixed at 0.25	216
0.4 eq. DABCO	best fit values fixed at 0.3	266

Table S3 Comparison of the Arrhenius parameters E_a and A of transalkylation reactions of small molecules

System	E_a [kJ·mol^{-1}]	A [L·mol^{-1}s^{-1}]	Ref.
Anilines:			[4]
➢ Association step	58		
➢ Dissociation step	61		
DABCO	93	$7 \cdot 10^{11}$	This work
thioethers	108 ± 4	$2 \cdot 10^{11}$	[5]

Table S4 Comparison of mechanical relaxation times and activation energies of selected transalkylation networks

Network	E_a [kJ/mol]	τ_{T^*} [s]	$\tau_{0^{**}}$ [s]	$\tau_{140^{**}}$ [s]	Ref.
Pyridinium (VSB-35)	45	$2.5 \cdot 10^3$ at 170 °C	$1.2 \cdot 10^{-2}$	$6.1 \cdot 10^3$	[6]
Anilinium Salts:					[4]
➢ PMSEA - 5% VBABr	57	$5.0 \cdot 10^3$ at 100 °C	$5.2 \cdot 10^{-5}$	$8.4 \cdot 10^2$	
➢ PMSEA - 3% VBABr	60	$7.0 \cdot 10^3$ at 100 °C	$2.8 \cdot 10^{-5}$	$1.1 \cdot 10^3$	
➢ PHEA - 5% VBABr	74	$25 \cdot 10^3$ at 100 °C	$1.1 \cdot 10^{-6}$	$2.5 \cdot 10^3$	
➢ PHEA - 3% VBABr	71	$30 \cdot 10^3$ at 100 °C	$3.5 \cdot 10^{-6}$	$3.3 \cdot 10^3$	
Pyridinium (VB)	88	$3.0 \cdot 10^3$ at 170 °C	$1.3 \cdot 10^{-7}$	$17 \cdot 10^3$	[6]
Poly(thioethers) 5% alkylating agent	113	$8.0 \cdot 10^2$ at 150 °C	$9.0 \cdot 10^{-12}$	$1.7 \cdot 10^3$	[5]
1,2,3-Triazolium	140	$1.8 \cdot 10^3$ at 130 °C	$1.3 \cdot 10^{-15}$	$6.6 \cdot 10^2$	[7]
DABCO					
➢ 0.6 eq - excess amine	~216	-	$4.6 \cdot 10^{-17}$	3.3	This
➢ 0.4 eq - excess benzyl bromide	~266	-	$3.3 \cdot 10^{-23}$	5.5	work

* Characteristic relaxation times, τ, ($G(t)/G_0$) = 1/e) were estimated from stress relaxation plots.

** Calculated using: $$\tau_T = \tau_0 \exp\left(\frac{E_a}{RT}\right)$$

References

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