

Supplementary Information

Soft to hard transformation of the mechanical properties of dynamic polymers through component incorporation

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1. General aspects

All reagents and solvents were purchased at the highest commercial quality and were used without further purification unless otherwise noted. ¹H NMR spectra were recorded on Bruker Avance 400 spectrometers. The spectra were internally referenced to the residual proton solvent signal. Microanalyses were performed by the Service de Microanalyse, Institut de Chimie, Université Louis Pasteur.

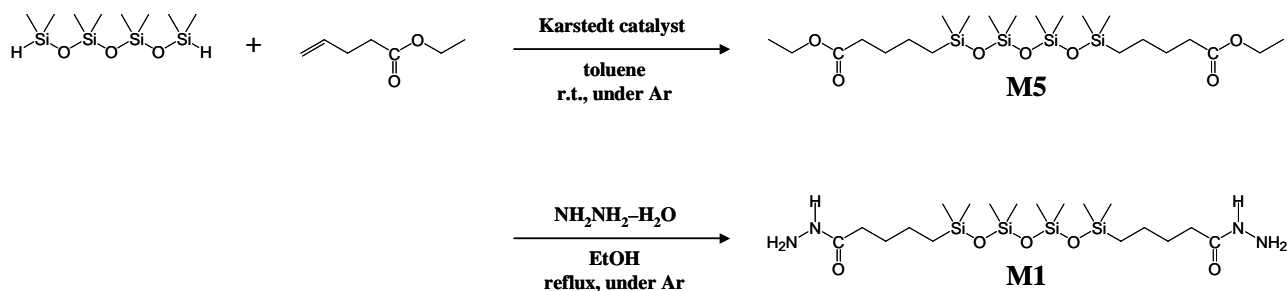
2. Synthesis of monomers

1,7-bis(4-ethoxycarbonylbutyl)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (M5)

To a solution of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (5.00 g, 17.69 mmol) and Karstedt catalyst¹ (100ppm/Si-Hmol) in toluene (80 mL) was slowly added ethyl pent-4-enoate (5.35 g, 41.74 mmol) using a pressure-equalizing additional funnel at room temperature under Ar atmosphere, then the mixture was stirred for one night. The reaction was monitored by ¹H NMR analysis. After the reaction was complete, toluene and excess amount of ethyl pent-4-enoate was roughly removed by evaporation, and the residue was passed through a short silica gel column (eluent: ethyl acetate) to separate the Karstedt catalyst. The volatiles were then removed in vacuo to give the roughly purified compound **M5** (9.00g, 16.70 mmol) in 94% yield as a transparent and colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 4.12 (q, ³J = 7.0Hz, 4H), 2.29 (t, ³J = 7.3Hz, 4H), 1.65 (qui, ³J = 7.6Hz, 4H), 1.35 (tt, ³J = 7.6Hz, ³J' = 8.2Hz, 4H), 1.25 (t, ³J = 7.0Hz, 6H), 0.54 (t, ³J = 8.2Hz, 4H), 0.06 (s, 12H), 0.01ppm (s, 12H).

1,7-bis(5-hydrazino-5-oxopentyl)-1,1,3,3,5,5,7,7-octamethyltetrasiloxane (M1)

To a solution of **M5** (9.00 g, 16.70 mmol) in EtOH (100 mL) was added dropwise hydrazine monohydrate (8.36 g, 166.99 mmol), followed by refluxing for 2 days under Ar atmosphere. The volatiles were removed in vacuo and the residue was purified by column chromatography on silica gel (eluent: EtOH/dichloromethane, 1:4) to give the desired compound **M1** in 59% yield as a transparent and colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.15 (br, 2H), 3.92 (br, 4H), 2.16 (t, ³J = 7.8Hz, 4H), 1.66 (qui, ³J = 7.4Hz, 4H), 1.35 (tt, ³J = 7.4Hz, ³J' = 8.2Hz, 4H), 0.54 (t, ³J = 8.2Hz, 4H), 0.06 (s, 12H), 0.02ppm (s, 12H); elemental analysis calcd (%) for C₁₈H₄₆ N₄O₅Si₄: C 42.31, H 9.07, N 10.97; found: C 41.71, H 9.33, N 10.64.

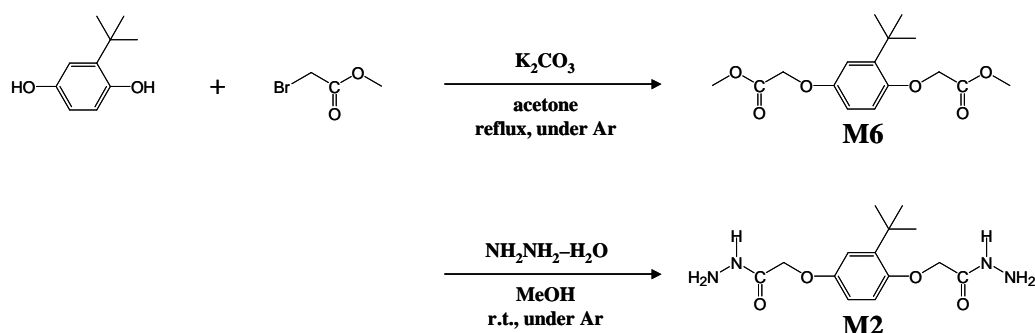


***tert*-butyl-2,5-bis(methoxycarbonylmethoxy)benzene (M6)**

tert-butylhydroquinone (19.93 g, 120 mmol) and methyl bromoacetate (26 mL, 275 mmol) were added to a suspension of K_2CO_3 (44.3 g, 321 mmol) in acetone (150 mL) and the stirred mixture was heated to reflux for 12 h under Ar atmosphere. The mixture was taken up in H_2O (200 mL) / CHCl_3 (300 mL). The organic layer was washed with H_2O (200 mL) 4 times, dried over Na_2SO_4 and the solvents were evaporated to dryness. The crude product was roughly purified by column chromatography on silica gel (eluent: CH_2Cl_2) affording roughly purified **M6** (26.1 g, 84 mmol) in 70% yield as a light orange oil. ^1H NMR (400 MHz, CDCl_3): δ = 6.97 (d, 3J = 2.4 Hz, 1H), 6.59–6.65 (m, 2H), 4.60 (s, 2H), 4.58 (s, 2H), 3.81 (s, 6H), 1.39 ppm (s, 9H).

***tert*-butyl-2,5-bis(2-hydrazino-2-oxoethoxy)benzene (M2)**

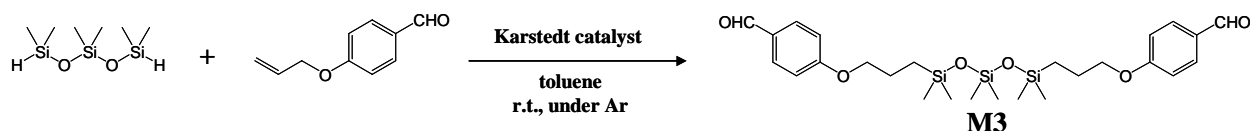
M6 (11.05 g, 35.6 mmol) in MeOH (40 mL) was added dropwise into a stirred mixture of hydrazine monohydrate (57.4 g, 1.15 mol) in MeOH (100 mL) at room temperature. The mixture was stirred for 1 h under Ar atmosphere, then the MeOH was removed in vacuo giving a two phases solution. The upper phase of the solution was roughly purified by column chromatography on silica gel (eluent: $\text{CHCl}_3/\text{MeOH}$, 10:1) to give crude **M2** as a viscous oil. The crude **M2** was recrystallized from mixture of CHCl_3 and *n*-hexane, followed by purification of column chromatography on silica gel (eluent: $\text{CHCl}_3/\text{MeOH}$, 10:1) affording the desired compound **M2** (7.08 g, 22.8 mmol) in 64 % yield. ^1H NMR (400 MHz, CDCl_3): δ = 7.98 (br, 1H), 7.74 (br, 1H), 6.89 (d, 3J = 2.9 Hz, 1H), 6.70 (d, 3J = 8.8 Hz, 1H), 6.69 (dd, 3J = 8.8 Hz, 3J = 2.9 Hz, 1H), 4.52 (s, 2H), 4.47 (s, 2H), 3.96 (br, 4H), 1.35 ppm (s, 9H); elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{46}\text{N}_8\text{O}_9$: C 52.65, H 7.26, N 17.54; found: C 52.38, H 7.05, N 17.81.



1,5-bis(3-(4-formylphenoxy)propyl)-1,1,3,3,5,5-hexamethyltrisiloxane (M3)

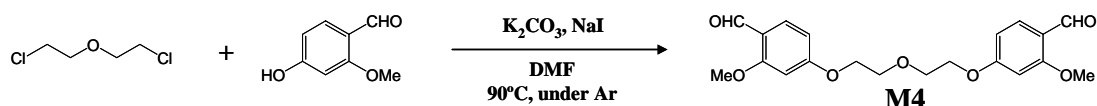
To a solution of 1,1,3,3,5,5-hexamethyltrisiloxane (4.26 g, 20.43 mmol) and Karstedt catalyst¹ (100ppm/Si-Hmol) in toluene (80 mL) was slowly added 4-allyloxybenzaldehyde (9.00 g, 51.08 mmol) using a pressure-equalizing additional funnel over 30 min at room temperature under Ar atmosphere, then the mixture was stirred for one night.

The reaction was monitored by ^1H NMR analysis. After the reaction was complete, toluene was evaporated and the residue was subjected to column chromatography on silica gel (eluent: cyclohexane/dichloromethane, 1:3) to give desired compound **M3** (4.51 g, 8.46 mmol) in 41% yield as a pale yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 9.87 (s, 2H), 7.82 (d, 3J = 8.8 Hz, 4H), 6.98 (d, 3J = 8.8 Hz, 4H), 3.99 (t, 3J = 6.7 Hz, 4H), 1.89-1.81 (tt, 3J = 6.8 Hz, $^3J'$ = 8.8 Hz, 4H), 0.69 (t, 3J = 8.8 Hz, 2J = 3.2 Hz, 4H), 0.12 (s, 12H), 0.05 ppm (s, 6H); elemental analysis calcd (%) for $\text{C}_{26}\text{H}_{40}\text{O}_6\text{Si}_3$: C 58.61, H 7.57; found: C 58.46, H 7.93.



bis(2-(4-formyl-3-methoxyphenoxy)ethyl)ether (**M4**)

4-hydroxy-2-methoxybenzaldehyde (2.33 g, 15.3 mmol) and 2-chloroethoxyether (1.05 g, 7.3 mmol) were added to a suspension of K_2CO_3 (5.19 g, 37.6 mmol) and NaI (3.07 g, 20.5 mmol) in DMF (20 mL) and the stirred mixture was heated to 90 °C for 17 h under argon atmosphere. The mixture was taken up in H_2O (500 mL) and extracted with CHCl_3 (100 mL) 5 times. The combined organic layer (about 500 mL) was washed with H_2O (100 mL) twice, dried over Na_2SO_4 and the solvents were evaporated to dryness to give a slightly orange powder (2.52 g). The powder was recrystallized from mixture of CHCl_3 and acetone to give the desired compound **M4** (1.91 g, 5.1 mmol) in 70 % yield as a white powder. ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): δ = 10.16 (s, 2H), 7.66 (d, 3J = 8.8 Hz, 2H), 6.69 (d, 3J = 2.4 Hz, 2H), 6.67 (dd, J = 8.8 Hz, J' = 2.4 Hz, 2H), 4.27 (t, 3J = 4.4 Hz, 4H), 3.88 (s, 6H), 3.86 (t, 3J = 4.4 Hz, 4H); elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{22}\text{O}_7$: C 64.16, H 5.92; found: C 63.97, H 5.76.



3. References

- 1) The catalyst referred to as Karstedt catalyst is bis(divinyltetramethyldisiloxane) platinum(0) in xylene purchased from Gelest inc. (a) Karstedt, B. D., US. Patent 3,775,452,1973. (b) Ashby, B. A.; Modic, F. J. US. Patent 4,288,345, 1981. (c) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F., *Organometallics* 1987, 6, 191.