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Polydimethylsiloxanes with bulk end groups: synthesis and properties

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Solvents were prepared according to earlier described procedures [1]. All solvents were purified before use. Ethanol was distilled from sodium under argon. Toluene was distilled from calcium hydride under argon. Calcium hydride and trichlorosilane were purchased from Acros Organics. The Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt ~2%) was purchased from Aldrich. 9-Allyl-*m*-carborane was synthesized by earlier described method [2]. 1-(Chlorodimethylsilyl)-2-[tris(4-trimethylsilylphenyl)silyl]ethane was synthesized by earlier described method [3]. PDMS was synthesized by earlier described method [4].

NMR spectra were recorded on a Bruker Avance™ 600 spectrometer operating at 600.22, 150.93 and 119.26 MHz for ^{1}H, ^{13}C and ^{29}Si respectively and Bruker Avance-III HD 300 spectrometer operating at 300.1, 75.5, 96.3 and 59.6 MHz for ^{1}H, ^{13}C, ^{11}B and ^{29}Si, respectively. The chemical shifts for ^{1}H and ^{13}C were indirectly referenced TMS *via* the solvent signals. The chemical shifts for ^{29}Si were measured with TMS as an external standard.

IR spectra were obtained using an IR spectrometer with a Fourier transformer Bruker "Tensor 37". The samples were prepared by pressing KBr pellets.

High-resolution mass spectra (HRMS) were measured using a Bruker micrOTOF II instrument with electrospray ionization (ESI).

GPC analysis was performed on the "Shimadzu", the detector - refractometer RID - 20A, the column - PSS SDV analytical 100 000A (Size 300 x 8 mm); eluent - toluene.

A DSC study was carried out on a Mettler-822e differential scanning calorimeter at a heating rate of (10 ^{0}C min^{-1} under an argon atmosphere. Thermogravimetric analysis (TGA) was performed by Derivatograph-C on samples with weight of about 20 mg at a heating rate of 5 ^{0}C

min^{-1} in air. The temperature at which a weight loss of 1% was detected was considered to be the decomposition onset temperature.

The rheological behavior study was carried out on Anton Paar MCR 302 rheometer.

1. Synthesis of 9-[(3-chlrodimethylsilyl)propyl]-m-carborane

9-allyl-*m*-carborane (0.5 g, 2.7 mmol), dimethylchlorosilane (0.6 ml, 0.51 g, 5.4 mmol) and 10 ml of toluene were charged into a flask and 2 μl of the Karsted's catalyst was added under argon and stirring to the reaction mixture. The mixture was stirred for 24 hours. The solvent was removed under vacuum (1 Terr, r.t.) and a residue was heated additionally at 100°C for 30 min. A viscous liquid was obtained. Yield: 0.75 g (~100%)

Calc. (%) for $C_7H_{23}B_{10}ClSi$, MM: 278.91, C, 30.14; H, 8.31; B, 38.76; Cl, 12.71; Si, 10.07. Found: (%) C, 30.04; H, 8.39; B, 38.70; Cl, 12.60 Si, 10.27.

^{1}H NMR (600.22 MHz, $CDCl_3$, ppm) 2.88 (br s, 4H, C_{carb}-H), 2.8-1.7 (18H, B-H), 1.42 (m, 4H, Si-CH_2**$\underline{CH_2}$**CH_2), 0.93 (t, 4H, Si-CH_2CH_2**$\underline{CH_2}$**), 0.61 (t, 4H, Si-**$\underline{CH_2}$**CH_2CH_2), 0.07 (s, 12H, Si-**$\underline{CH_3}$**)

^{13}C NMR (150.93 MHz, $CDCl_3$, ppm) 53.99, 24.09, 21.97, 19.92, 0.58.

^{29}Si NMR (119.26 MHz, $CDCl_3$, ppm) 6.9.

^{11}B NMR (193 MHz, $CDCl_3$, ppm) 1.12, -6.56, -10.09, -13.32, -14.14, -17.75, -20.52.

IR (cm^{-1}): 3068, 2929-2825, 585-452 .

2. Synthesis of 1,3-bis[3-(m-carboran-9-yl)propyl]tetramethyldisiloxane (2)

Water (0.03 ml, 1.5 mmol), pyridine (0.26 ml, 3.1 mmol) and 10 ml of acetone were charged into three-necked flask and the above monochlorosilane derivative (0.85g, 3.1 mmol) was added dropwise under stirring. The mixture was heated to boiling and refluxed for 8 hours. The mixture was cooled to and filtered. The filtrate was washed with water to remove Cl^-, dried over Na_2SO_4 and the solvent evaporated at 1 Torr. The viscous colorless residue was purified by preparative chromatography to give 0.57 g (71%) of viscous liquid.

Calc. (%) for $C_{14}H_{46}B_{20}OSi_2$, MM: 502.91, C, 33.44; H, 9.22; B, 42.99; Si, 11.17. Found: (%) C, 33.34; H, 9.18; B, 42.72; Si, 10.27.

^{1}H NMR (600.22 MHz, $CDCl_3$, ppm) 2.88 (br s, 4H, C_{carb}-H), 2.8-1.7 (18H, B-H), 1.42 (m, 4H, Si-CH_2**$\underline{CH_2}$**CH_2), 0.93 (t, 4H, Si-CH_2CH_2**$\underline{CH_2}$**), 0.61 (t, 4H, Si-**$\underline{CH_2}$**CH_2CH_2), 0.07 (s, 12H, Si-**$\underline{CH_3}$**)

^{13}C NMR (150.93 MHz, $CDCl_3$, ppm) 53.99, 24.09, 21.97, 19.92, 0.58.

^{29}Si NMR (119.26 MHz, $CDCl_3$, ppm) 6.9.

^{11}B NMR (193 MHz, $CDCl_3$, ppm) 1.12, -6.56, -10.09, -13.32, -14.14, -17.75, -20.52.

IR (cm^{-1}): 3067, 2924-2860, 2596, 1119.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{46}B_{20}OSi_2$ [$(M+Na)^+$]: 525.89, found 525.50.

3. ***Polymer 1***

   Octamethylcyclotetrasiloxane (1.8 g, 6.1 mmol), 1,3-bis[3-(*m*-carboran-9-yl)propyl]tetramethyldisiloxane 0.31g (0.61 mmol) and 0.1 ml of CF_3SO_3H were charged into a flask and stirred for 24 h. Potassium carbonate (0.2 g) was added to the reaction mixture. The precipitate was filtered off. Viscous colorless product (1.58 g, 75 %) was obtained after drying in vacuum (1 Torr, 100 °C, 6 h).

4. ***Polymer 3***

   Butyllithium (1.6 M solution in hexane) was added dropwise to the solution of tetramethyldisiloxanediol (0.1 g, 0.6 mmol) in THF (5 ml) at -78ºC under argon. The resulting mixture was stirred for 1 h and then heated to r.t. After that a solution of hexamethylcyclotrisiloxane (2 g, 90 mmol) in benzene (2 ml) was added dropwise and the reaction mass was stirred for more 3 h. A solution of 1-(chlorodimethylsilyl)-2-[tris(4-trimethylsilylphenyl)silyl]ethane (0.73 g, 1.2 mmol) in benzene was added to the reaction mixture, which was stirred additionally for 3 h. A viscous liquid (1.7 g, 85%) was obtained after solvents removing and heating in vacuum (1 Torr, 100 ºC).

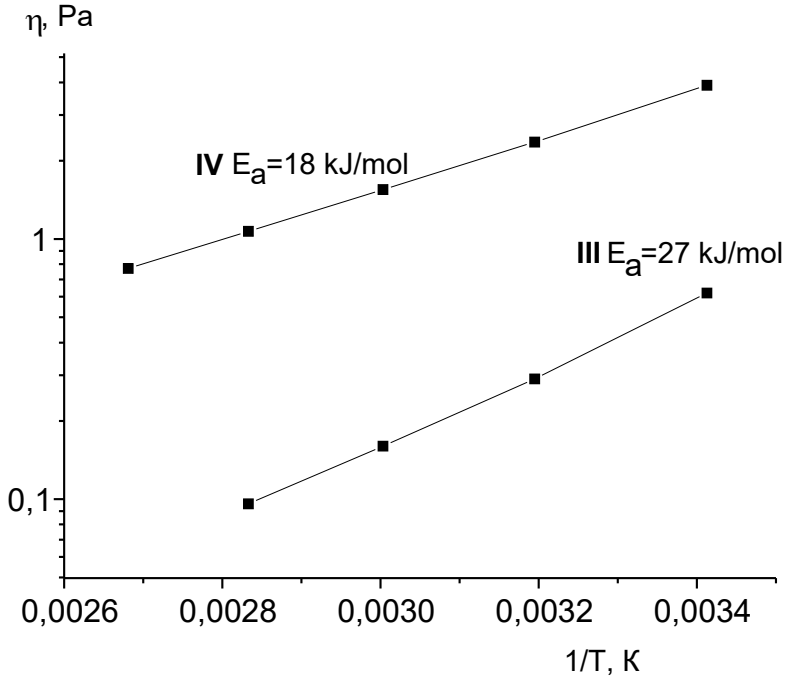
5. ***Polymer 4***

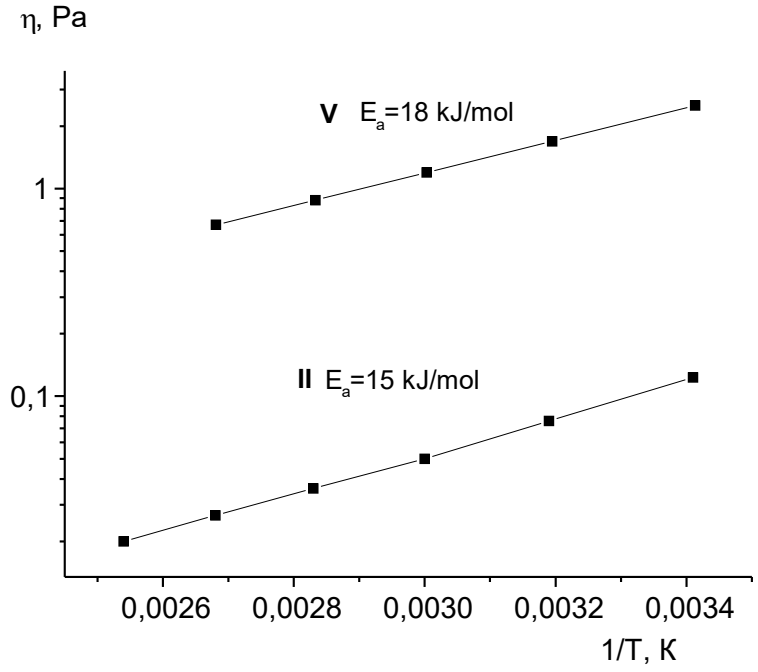
   A solution of PDMS (1 g, 0.03 mmol) and pyridine (0.02 ml, 0.24 mmol) in 5 ml of toluene was added dropwise to a three-neck flask containing a solution of 9-[3-(chlorodimethylsilyl)propyl-*m*-carborane (0.07 g , 0.24 mmol) in toluene (5 ml) The obtained reaction mass was heated to boiling and refluxed for 8 h and cooled to r.t. Filtration through silica gel gave a transparent solution. After removing the solvent and drying in vacuum (1 Torr, 100 ºC) a transparent viscous liquid was obtained (0.85 g, 92%).

6. ***Polymer 5***

   A solution of PDMS (1 g, 0.03 mmol) and pyridine (0.02 ml, 0.24 mmol) in toluene (5 ml) was added dropwise to a three-neck flask containing a solution of 1-(chlorodimethylsilyl)-2-[tris(4-trimethylsilylphenyl)silyl]ethane (0.14 g, 0.24 mmol) in toluene (5 ml). The resulting reaction mixture was refluxed then for 8 h. Further PDMS **5** (0.87 g, 86%) was obtained as above.

Rheological data





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