

High-temperature phthalonitrile matrix containing silane fragments

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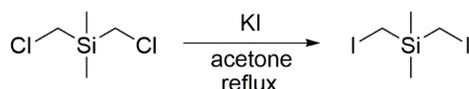
Materials and methods

All the manipulations with oxidation and moisture sensitive compounds were carried out under inert atmosphere using the standard Schlenk technique. *N,N*-dimethylacetamide (DMAA), dichloromethane (DCM) and petroleum ether were purchased from Alfa Aesar Company and were used as received. Acetone was also purchased from Alfa Aesar Company and was further purified by distillation over calcium hydride in an argon atmosphere. Silica gel (0.04–0.065 mm seed), bis(chloromethyl)dimethylsilane, potassium carbonate, resorcinol, 4-nitrophthalonitrile and 1,3-bis(4-aminophenoxy)benzene (APB) were obtained from Sigma-Aldrich and used as received.

Nuclear magnetic resonance (NMR) studies were run on a Bruker Advance 600 at 600 MHz for ^1H , 151 MHz for ^{13}C and 79 MHz for ^{29}Si with dimethyl sulfoxide- d_6 as solvent. Elemental analyses were performed on a Carlo Erba EA1108 CHNS-O elemental analyzer. Differential scanning calorimetry (DSC) was performed on Netzsch DSC 204 Phoenix, at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ and an Ar purge rate of 50 ml min^{-1} and was applied for the determination of glass transition temperature of the monomer. Thermal stability was evaluated by thermogravimetric analysis (TGA) on Netzsch TG 209 P3 Tarsus at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in range 40–1000 $^\circ\text{C}$ and Ar or air purge rate of 50 ml min^{-1} . Dynamic mechanical analysis was performed on DMA Q800. Melt viscosity was measured with MCR 302 rheometer with cone 7 at 40 rpm.

Synthesis of 4-(3-hydroxyphenoxy)benzene-1,2-dicarbonitrile

4-(3-hydroxyphenoxy)benzene-1,2-dicarbonitrile was synthesized in accordance with the published procedures.¹



Synthesis of bis(iodomethyl)dimethylsilane

To a one-necked flask equipped with a reflux condenser bis(chloromethyl)dimethylsilane (20.0 g, 0.127 mol), potassium iodide (42.3 g, 0.254 mol) and dry acetone (200 ml) were added. The mixture was refluxed for 5 hours under an argon atmosphere, allowed to cool to room temperature and filtered. The precipitate was washed with acetone (2x50 ml) and combined filtrate was concentrated on a rotary evaporator under reduced pressure to leave 99 % of the titled product (42.8 g).

^1H NMR (600 MHz, $\text{DMSO-}d_6$), δ (ppm): 0.24 (s, 6 H), 2.19 (s, 4 H).

^{13}C NMR (151 MHz, $\text{DMSO-}d_6$), δ (ppm): -14.14, -3.29.

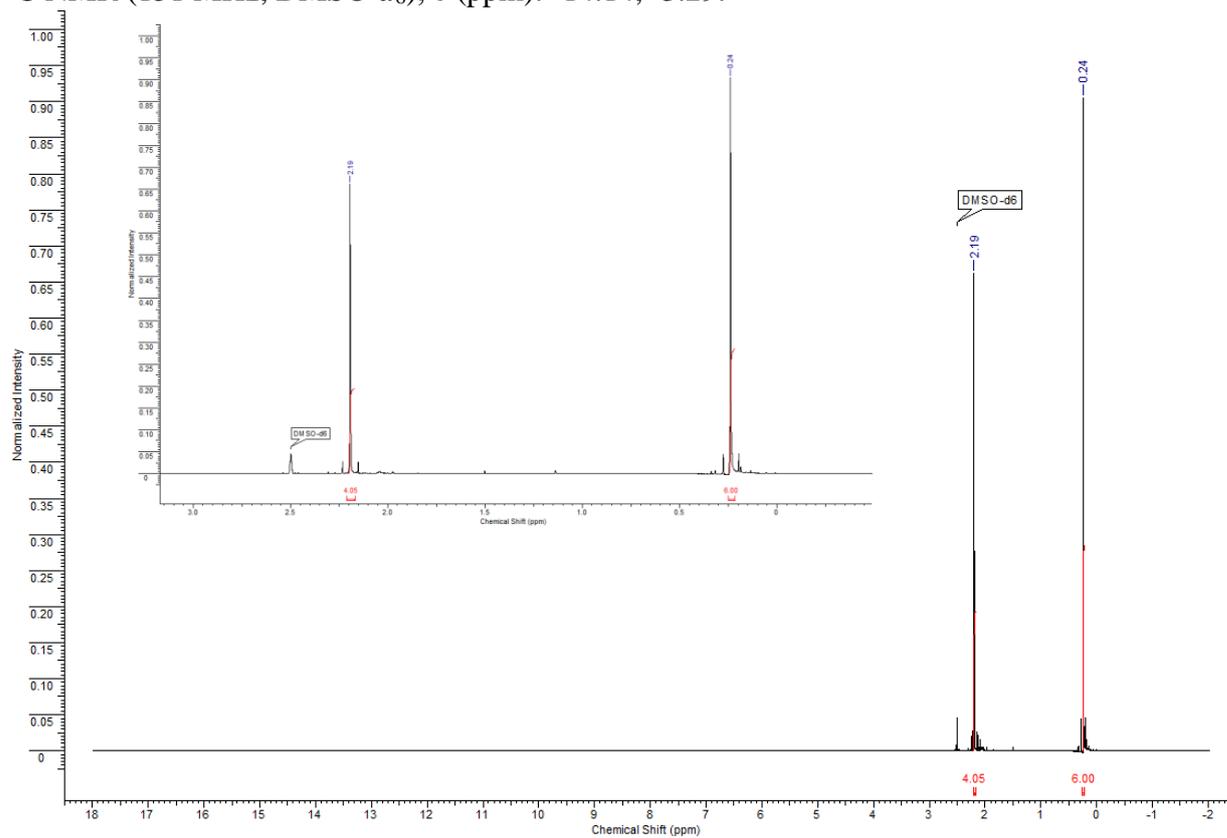


Figure S1 ^1H NMR spectrum of bis(iodomethyl)dimethylsilane

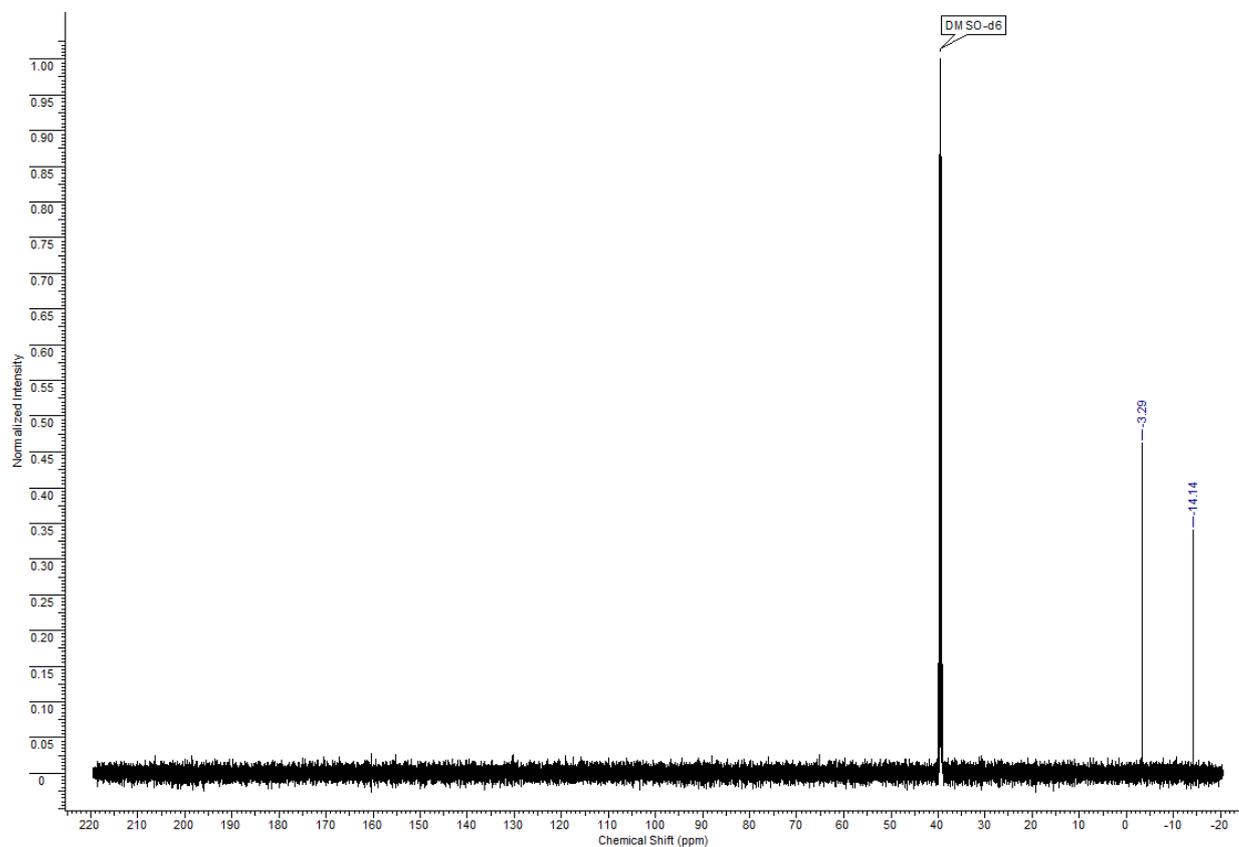
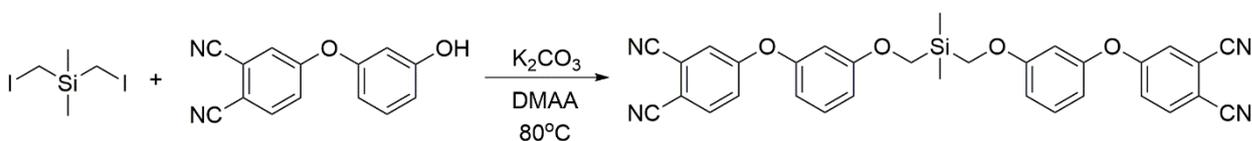


Figure S2 ^{13}C NMR spectrum of bis(iodomethyl)dimethylsilane



Synthesis of 4,4'-((((dimethylsilanediyl)bis(methylene))bis(oxy))bis(3,1-phenylene))-bis(oxy)diphthalonitrile (**3**)

To a three-necked flask (1000 ml) equipped with a reflux condenser 4-(3-hydroxyphenoxy)benzene-1,2-dicarbonitrile (20.9 g, 88.5 mmol), potassium carbonate (14.7 g, 106 mmol) and DMAA (450 ml) were added under an argon atmosphere. The mixture was stirred at room temperature for one hour. Then, bis(iodomethyl)dimethylsilane (15.1 g, 44.4 mmol) were added. The resulting mixture was stirred at 80 °C for 24 hours. The reaction mixture was filtered. The precipitate was washed with DCM (3x50 ml). The filtrate was poured into 1000 ml of water and put into a separatory funnel. The lower layer was separated and washed successively with brine (2x100 ml) and water (3x100 ml). The organic phase was dried over anhydrous sodium sulfate. After filtration, the solvent was evaporated on a rotary evaporator. The residue was purified by column chromatography on silica gel to achieve a purity above 99%. A mixture of DCM:petroleum ether (3:1) was used as an eluent. After evaporating of the solvent, 87 % of the titled product **3** (21.5 g) was achieved as an amorphous colorless substance.

^1H NMR (600 MHz, $\text{DMSO-}d_6$), δ (ppm): 0.22 (s, 6H), 3.80 (s, 4H), 6.71 (dd, $J=8.03$, 1.67 Hz, 2H), 6.81 (t, $J=2.26$ Hz, 2H), 6.91 (dd, $J=8.37$, 1.84 Hz, 2H), 7.27 - 7.43 (m, 4H), 7.73 (d, $J=2.51$ Hz, 1 H), 8.07 (d, $J=8.70$ Hz, 2H).

^{13}C NMR (151 MHz, $\text{DMSO-}d_6$), δ (ppm): -6.18, 58.87, 106.28, 108.08, 112.05, 112.07, 115.35, 115.86, 116.62, 121.95, 122.58, 130.95, 136.22, 154.72, 161.01, 162.59.

^{29}Si NMR (79 MHz, $\text{DMSO-}d_6$), δ (ppm): -1.35.

Anal. Found: C, 68.92; H, 4.36; N, 10.05. $\text{C}_{32}\text{H}_{24}\text{N}_4\text{O}_4\text{Si}$ requires C, 69.05; H, 4.35; N, 10.07%.

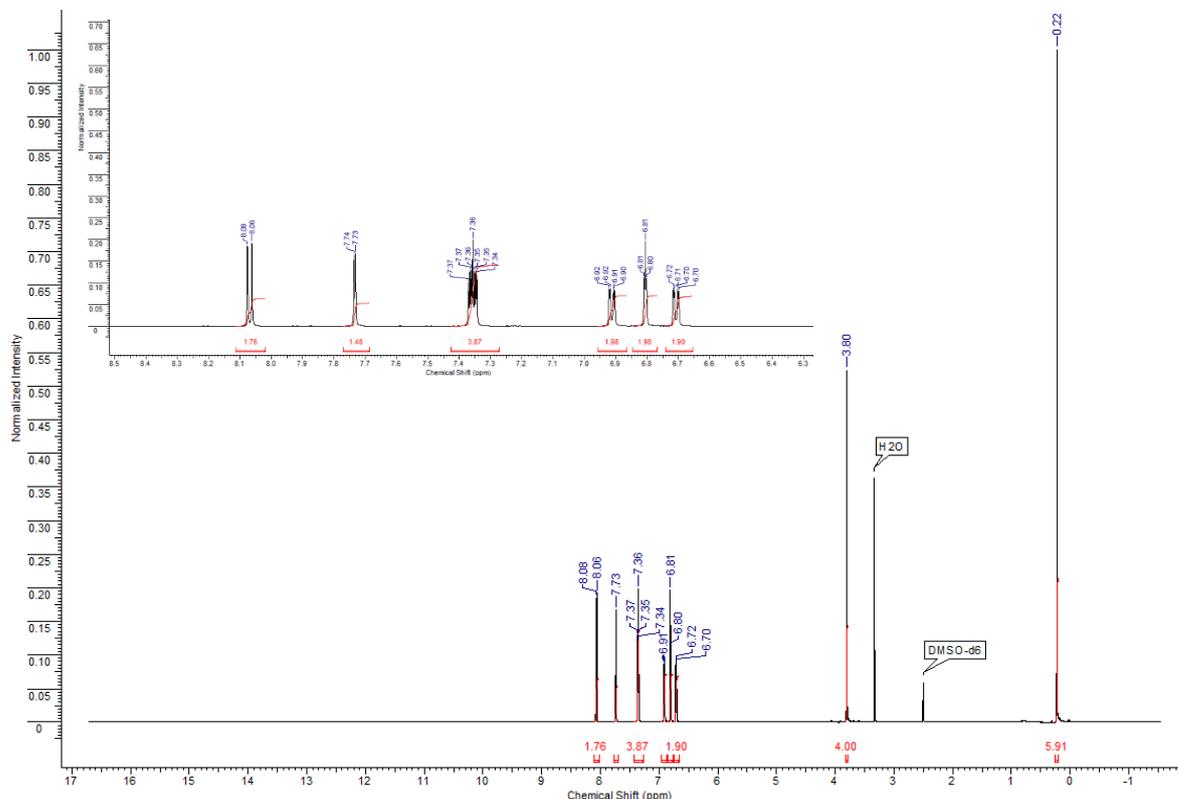


Figure S3 ^1H NMR spectrum of monomer **3**

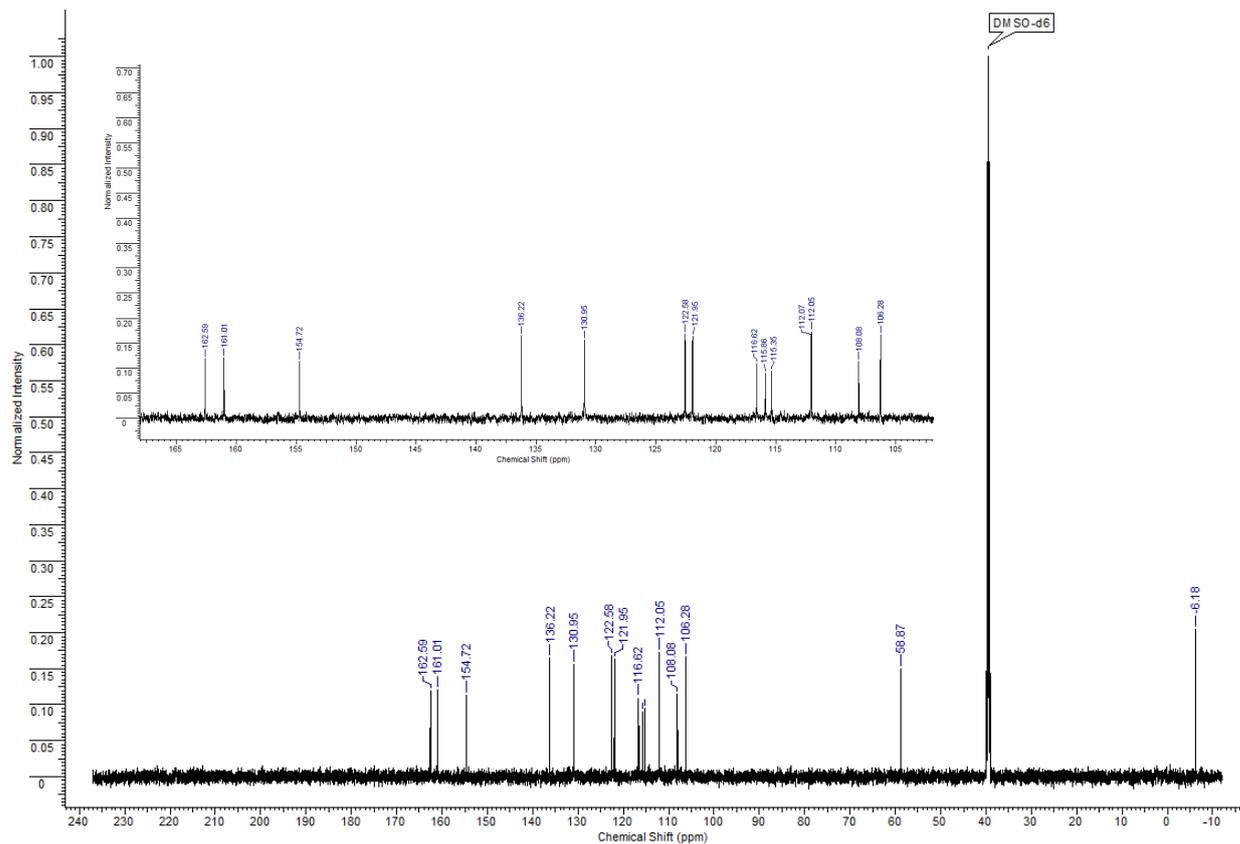


Figure S4 ^{13}C NMR spectrum of monomer 3

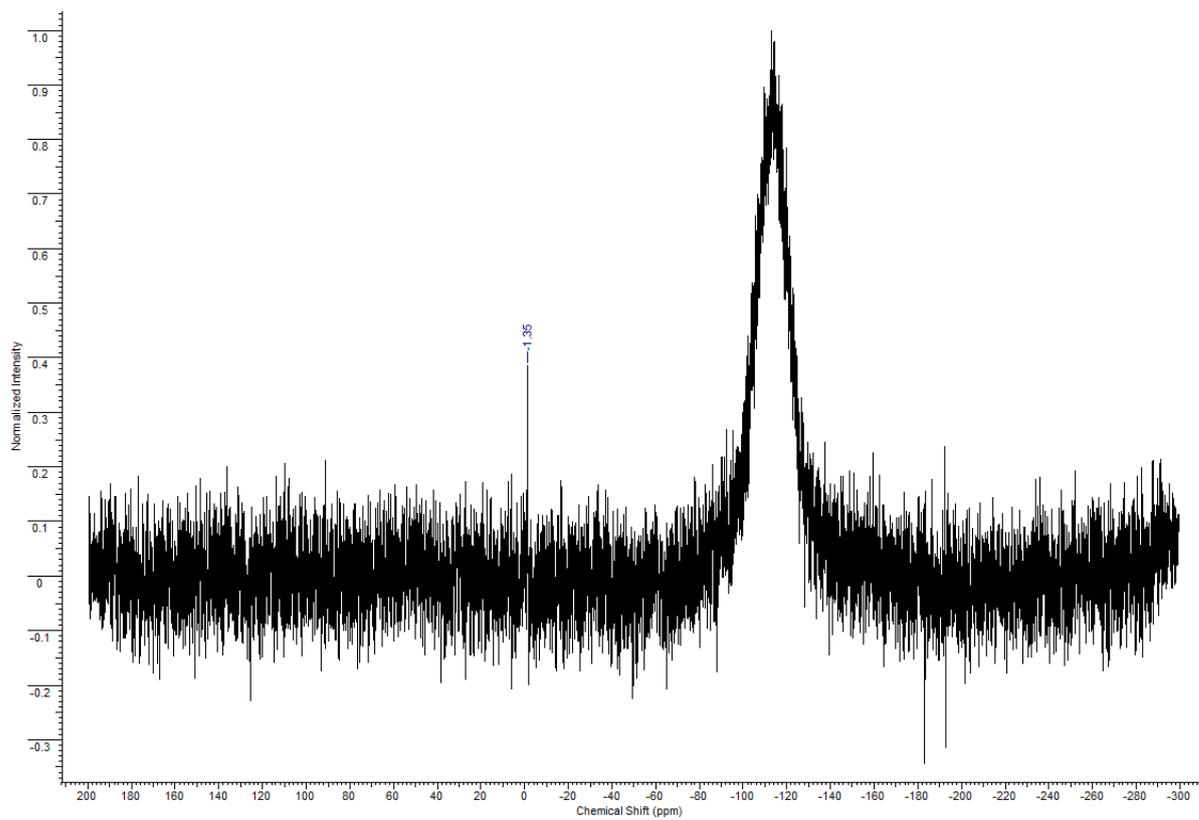


Figure S5 ^{29}Si NMR spectrum of monomer 3.

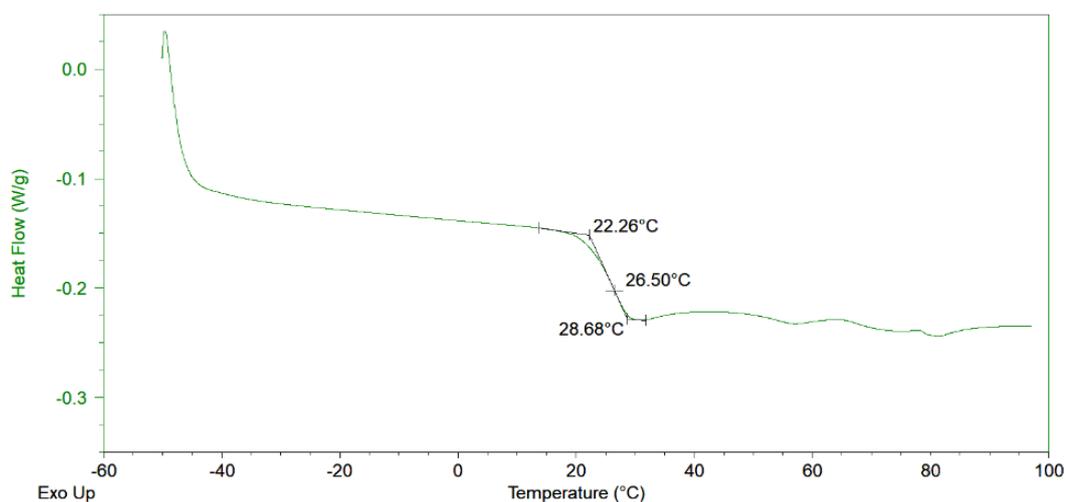


Figure S6 DSC curve of monomer **3**.

Curing program

The monomer **3** (~15 g) and 4 mol. % of **APB** were added into a 100 ml flask. The mixture was melted and degassed by stirring under vacuum at 150 °C until no bubbles on the surface appeared. Next, the mixture was poured into a stainless steel mold, which was placed in an air circulated heated oven and cured in accordance with the following program: heating to 250 °C (2 °C min⁻¹), holding for 8 h, heating to 315 °C (2 °C min⁻¹), holding for 5 h, heating to 375 °C (2 °C min⁻¹), holding for 8 h.

References

- 1 B. A. Bulgakov, A. V. Sulimov, A. V. Babkin, A. V. Kepman, A. P. Malakho and V. V. Avdeev, *J. Appl. Polym. Sci.*, 2017, **134**, 44786.