Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 341–343

Design of star-shaped azido-containing polymer

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Materials

3,3-Bis(azidomethyl)oxetane was synthesized at the Institute of Problems of Chemical Physics of Russian Academy of Sciences according to the standard procedure [M. B. Frankel, and E. R. Wilson J, *Chem. Eng. Data*, 1981, **26**, 219]. The purity of monomer was evaluated by reversed phase chromatography, IR spectroscopy, and elemental analysis. The impurity content in 3,3-bis(azidomethyl)oxetane was <1%.

1,2-Dichloroethane (ZAO Ekos-1) was purified following standard procedures [A. Weissberger, E. Proskauer, J. Riddick, and E. Toops, Organic Solvents. Physical Properties and Methods of Purification (Wiley, New York, 1955).

Boron trifluoride etherate (Acros Organics) was used without further purification.

Synthesis

β-Cyclodextrin partial nitrate (CDPN) was obtained by nitration of β-cyclodextrin (β-CD) according to the previously developed procedure [Y. M. Mikhailov, L. B. Romanova, A. E. Tarasov, M. A. Rakhimova, A. V. Darovskikh, L. S. Barinova, *Russ. J. Appl. Chem.*, 2018, **91**, 1217].

The β-CD (Aldrich) was dried for 10 h at 100°C before nitration. The water content after drying was ~ 1 wt%. Nitration was performed with 90% nitric acid, which was obtained by diluting concentrated nitric acid with water. HNO_3 (8 ml) cooled to 3-5 °C, β-CD (1 g) was slowly added under intensive stirring (molar ratio of the amount of HNO_3 to the amount of β-CD, equal to 10). Then the temperature was gradually increased to room temperature (20 °C), and the reaction mixture was stirred for 1 h. The mixture was poured into ice water, the precipitate was filtered off, washed with water and 1% $NaHCO_3$ solution to pH=6.5-7.

CDPN is a white powdery substance with decomposition temperature ranging 190-193°C.

Sample	Element composition, %				pycnometric density, g cm^{-3}	degree of substitution, %
	C	H	N	O		
CDPN	27.5	3.0	11.9	57.6	1.64	74

The amount of nitrate groups in CDPN was determined by previously developed methods [L. B. Romanova, L. S. Barinova, G. V. Lagodzinskaya, A. I. Kazakov, Y. M. Mikhailov, *Russ. J. Appl. Chem.*, 2014, **87**, 1884, M. D. Rodin, L. B. Romanova, A. V. Darovskih, M. A. Gorbunova and A. E. Tarasov, *J. Appl. Spectrosc.*, 2018, **76**, 639] using high resolution NMR spectroscopy (Figure S1), as well as by FTIR spectroscopy (Figure S2).

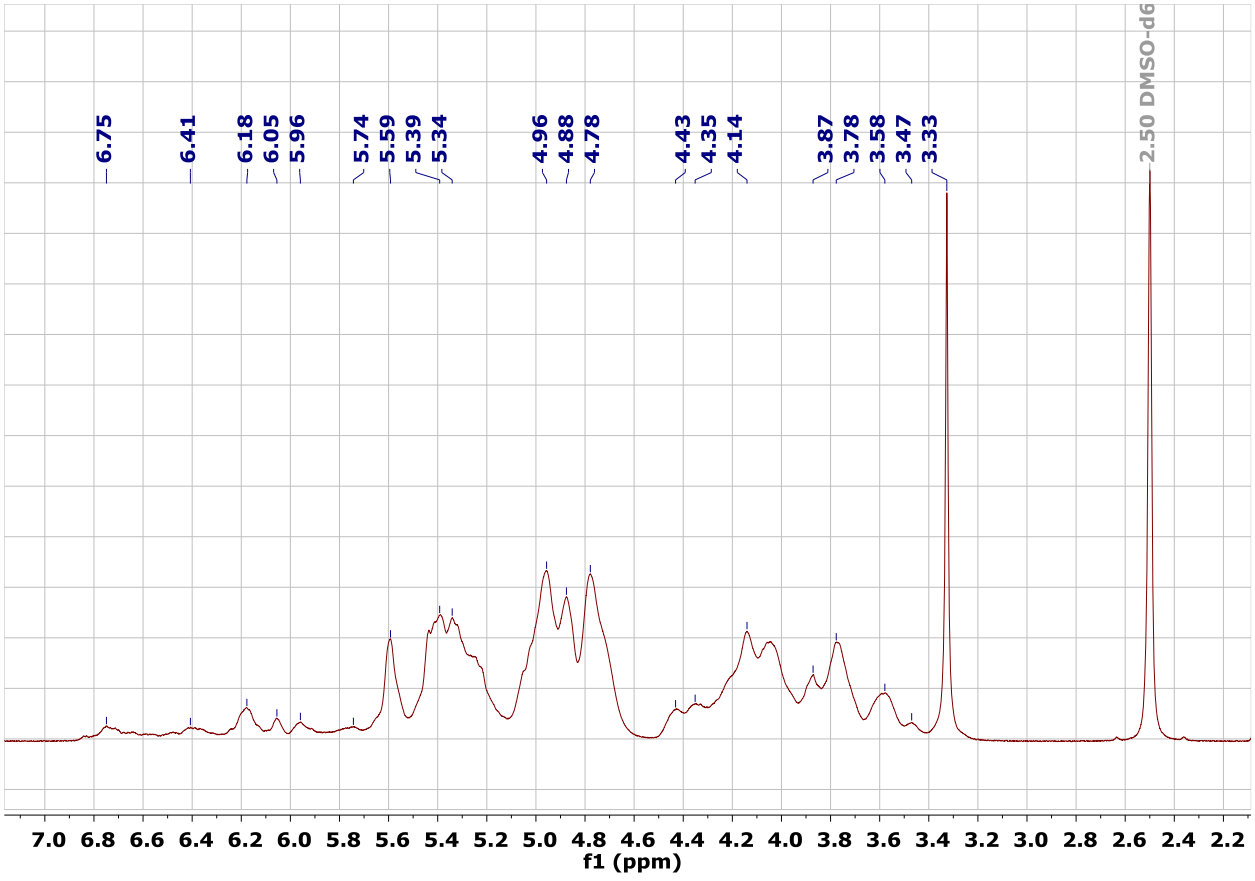

Figure S1 ^{1}H NMR spectrum of CDPN

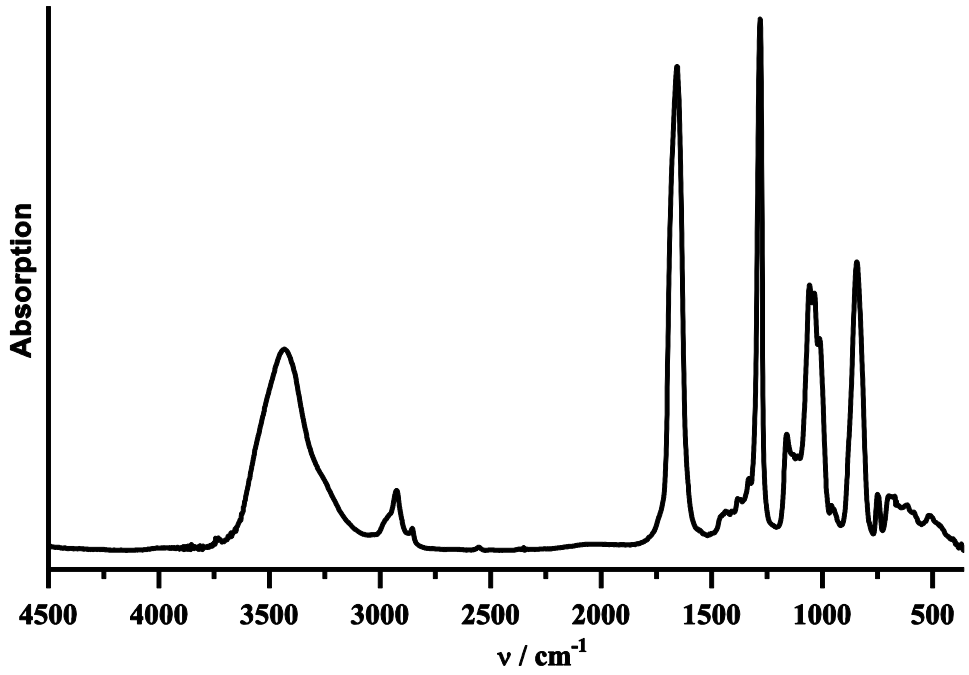

Figure S2 IR spectrum of CDPN

The degree of substitution of hydroxy groups for nitrate ones in CDPN was calculated as the ratio of the number of ONO_2-groups formed in the CDPN to the maximum possible number (21 groups). The calculated degree of substitution is an average statistical value, since the resulting CDPN have molecular structural heterogeneity largely depending on the conditions of the nitration reaction.

Synthesis of star-shaped polymer based on CDPN and BAMO (SSP C-B).

BAMO was polymerized in 1,2-dichloroethane catalyzed by $BF_3 \cdot Et_2O$ in the presence of CDPN in a thermally controlled glass reactor equipped with a stirrer. CDPN (0.73 g), solvent (6 ml) and $BF_3 \cdot Et_2O$ (0.27 ml) were placed into the reactor, the reagents were stirred and kept at 8 °C for 10 min. Then, BAMO (6.00 ml) was dropped using a batcher at a rate of 2 ml h^{-1}. After the monomer being completely loaded into the reaction mixture, it was stirred and kept at 8 °C overnight. The reaction was terminated by adding water, the mixture was washed to remove the catalyst, and then water and the solvent were removed at the rotary evaporator.

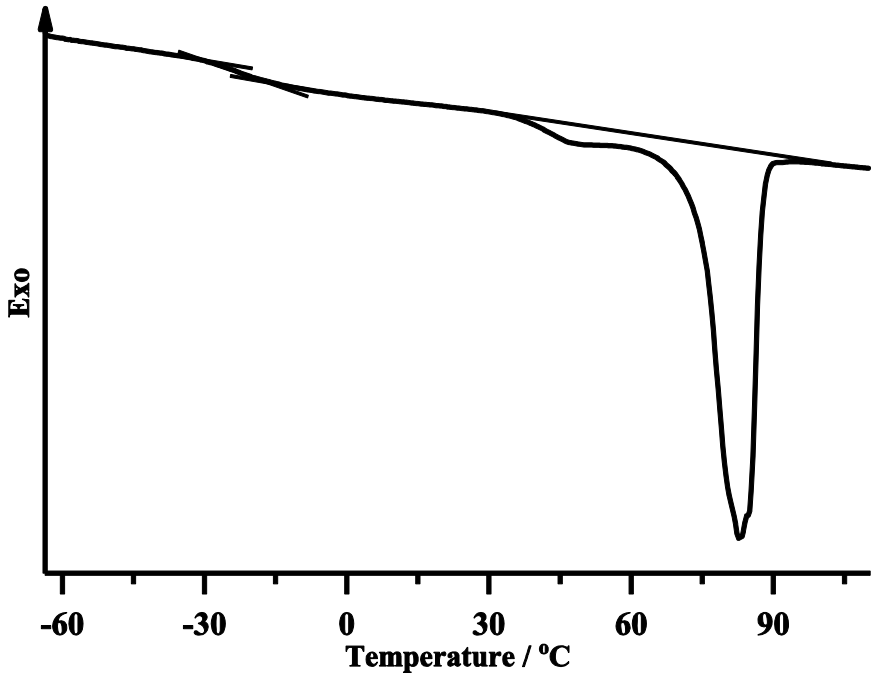

Figure S3 DSC curve of SSP C-B

Instrumentation

The GPC analysis of the samples was performed using a Waters 2414 chromatograph equipped with two PLgel 5-μm MIXED-C styrene gel columns: column length of 300 mm and diameter of 7.6 mm. The volume of the input loop was 20 μl. The detectors were a refractometer, spectrophotometer and a Wyatt DAWN Heleos II light-scattering detector. THF was used as an eluent, the elution rate was 1.0 mL/min, and the column temperature was 35°C. A solution with polymer content of 10–15 g dm^{-3} was prepared for the analysis. The use of the light-scattering detector made it possible to estimate molecular weight distribution parameters without any calibration relative to references.

DSC analysis of the sample was performed on a Mettler Toledo DSC822e thermal analyzer; heating rate was 10 K min^{-1}.

The density of the CDPN samples under study was determined by pycnometry method. Heptane, in which the substance is insoluble, was used as a pycnometric liquid.

NMR spectroscopy of CDPN carried out on a Bruker AVANCE-3 500 with an operating frequency of ^{13}C - 125. 8 MHz, ^{1}H - 500 MHz, internal reference – tetramethylsilane

FTIR spectroscopy of CDPN carried out on a Bruker Alpha spectrophotometer (scan step 2 cm^{-1}, measuring range 4000-360 cm^{-1}, number of scans of sample and background 56) in a NaCl cuvette with a fixed thickness of 0.00506 cm.

The contents of carbon, hydrogen, nitrogen, and oxygen of CDPN were determined by adsorption pyrolytic chromatography on a CHNS/O elemental analyzer Vario MICRO cube Elementar GmbH.