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Design of star-shaped azido-containing polymer

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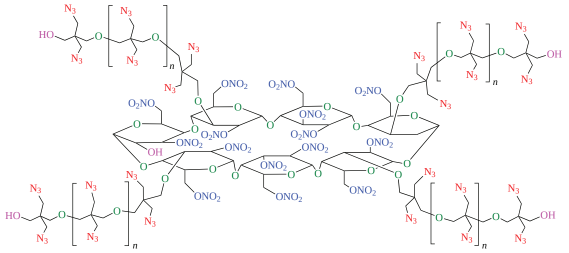
An efficient synthesis of the new star-shaped polymer with azido-containing oligomer rays is based on construsion of these rays on the β-cyclodextrin nitrate core employing 3,3-bis(azidomethyl)oxetane as the key reactant. The formation of star-shaped structure was proved. Thermal and optical properties of the synthesized polymers were assessed.



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Design and investigation of new energetic substances, especially polymeric ones, are currently of high importance. Polymers comprising energetic groups such as nitro, nitrate, azido and others, commonly used as binders in fuels and explosives are known as energetic polymers.[1] Polymers containing azido groups are considered as promising energetic materials.[2–5] For instance, polymers derived from 3,3-bis(azidomethyl)oxetane (BAMO) are of great interest due to high nitrogen content (about 50 wt%). However, this compound possesses symmetric structure and demonstrates partial crystallinity; hence, its applications is somewhat limited. Some of technological operations with crystalline and semicrystalline polymers can be performed only at temperatures higher than their melting points, which is not suitable for energy-intensive compounds. The synthesis of linear BAMO copolymers seems to be an efficient solution to this problem,[6,7] although it can lead to some decrease in energy characteristics of the obtained substances.

An alternative approach could be the design of star-shaped polymers comprising BAMO and β-cyclodextrin partial nitrate (CDPN) when some of hydroxy groups are replaced by nitrate substituents.[8] Star-shaped polymers are the class of branched polymers with several (at least three) linear chains connected to a central core. The core, or center, of the polymer can be an atom, molecule or macromolecule, while chains, or ‘rays’, consist of organic chains of variable length.[9] Branched globular star-shaped polymers have lower solution or melt viscosity, no or lower chain entanglement, and better solubility, comparable with those of dendrimers.[10] Star-shaped energetic polymers can be potentially used as technological materials with improved mechanical properties, retaining their energetic characteristics or surpassing those of their linear counterparts. In this regard, the synthesis of new energetic star-shaped polymer based on CDPN and BAMO (SSP C–B) is an important task.

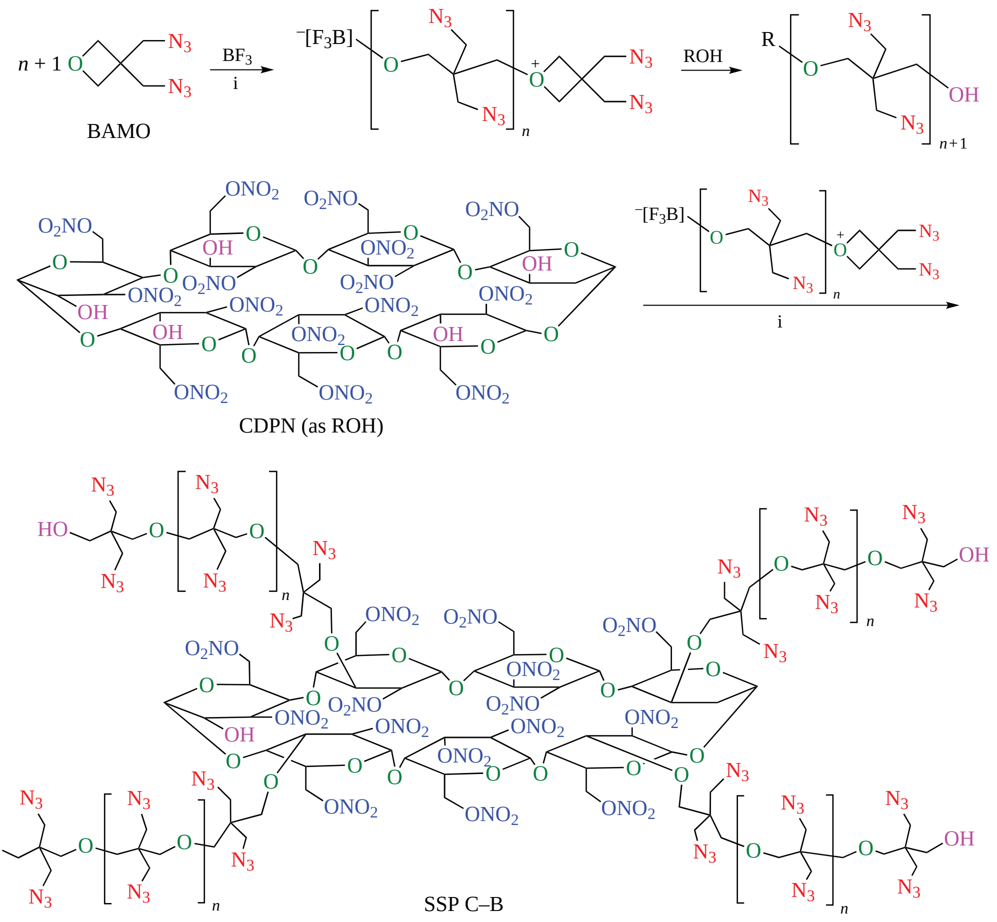
The ‘from-core’ approach was used when synthesizing SSP C–B. The implementation of this approach was carried out by cationic ring-opening polymerization of BAMO in the presence of hydroxy-containing CDPN, catalyzed by boron trifluoride etherate (Scheme 1). This approach was previously established when studying similar cationic polymerization of 3-azidomethyl-3-methyloxetane in the presence of ethylene glycol.[11] It was shown that the polymerization of BAMO proceeds with the same mechanism.[12]

Here, CDPN with the substitution degree of hydroxy groups to nitrate groups of 74% acts as a chain transfer agent. It contains *ca*. 5.5 hydroxy groups per molecule which can be the centers for formation of BAMO oligomer rays. We note that CDPN is insoluble in commonly used for cationic polymerization 1,2-dichloroethane, whereas the solubility of product with BAMO oligomer chains becomes much higher.

Polymer formation was confirmed by liquid chromatography analysis of the products. Based on comparison between the chromatograms of CDPN and the polymerization products of BAMO catalyzed by BTE in the presence of CDPN, the formation of a significant amount of the polymer fraction (the peak at a retention volume V_r of ~14 ml) and oligomeric products (peaks at V_r ~ 16 ml and 16.5 ml, fractions 1 and 2, respectively) was found [Figure 1(*a*)]. Noteworthy that fraction 1 can contain non-incorporated into the polymer chain CDPN units as well as cyclic tetramer of BAMO whose formation is typical under the specific conditions. The fraction 2 can consist of cyclic trimer of BAMO whose formation also cannot be discarded.

The products obtained were identified by UV spectroscopy. The spectra of fractions 1, 2 and of the polymer fraction were compared to those of CDPN and of separately synthesized BAMO oligomer [Figure 1(*b*)]. The UV spectrum of the polymer fraction compound differs from the spectra of CDPN and polymer of BAMO. Fractions 1 and 2 are characterized by both wavelength and width of the absorption band close to that of the BAMO polymer. The results obtained allow us to conclude that oligomeric fractions 1 and 2 can be attributed to the cyclization products of BAMO, *i.e.*, cyclic tetramer and trimer, while CDPN is a part of the polymer fraction.

The evidence of the star-shaped structure of the synthesized polymer comes from comparison of its radius of gyration with



Scheme 1 *Reagents and conditions*: i, $BF_3{\cdot}Et_2O$, 1,2-dichloroethane, 10 °C.

that of a linear polymer of BAMO possessing similar molecular weight (Figure 2), which was synthesized according to the standard procedure.[12]

The star-shaped polymer possesses more compact structure than a linear polymer of the same composition at comparable molecular weights. The structure of star-shaped polymer can be quantitatively characterized by the ‘g-factor’, and it is known that it equals the ratio of gyration radii of the star-shaped and linear polymers.[13,14] However, for star-shaped polymers with polydisperse rays the value of the g-factor can be determined from the equation $g = 3f/(f+1)^2$ (1), where f is the core functionality.[5,6] In our case, the g-factor, determined for copolymer based on CDPN and BAMO, using the dependences shown in Figure 2, equals 0.4. Substituting this g value into the equation (1), we found that the core (CDPN) functionality of the synthesized copolymer is of 5.3. This functionality value coincides with the content of hydroxy groups in CDPN (~5.5). Therefore, we assume that each hydroxy group in CDPN molecule formed the rays in the reaction with BAMO oligomer.

The results obtained indicate that the high molecular weight fraction of the sample is a star-shaped polymer, where BAMO oligomer rays are attached to the CDPN core due to the chain transfer according to the scheme presented above.

Thermal properties of the SSP C–B were investigated. DSC analysis indicates (Figure S2) the glass transition temperature of –21 °C, melting point temperature of 82 °C, and melting enthalpy of 44 J g^{-1}. The glass transition temperature can be attributed to the devitrification of BAMO oligomeric blocks, since a BAMO homopolymer with similar molecular weight[15] has glass transition temperature of –25 °C and crystalline melting temperature of 79°C, which are close to those for the obtained SSP C–B. The degree of crystallinity of the star-shaped polymer determined by DSC (33%) was found to be lower than that of the BAMO homopolymer (40%). The fact that glass transition temperatures of the star-shaped polymer and the related

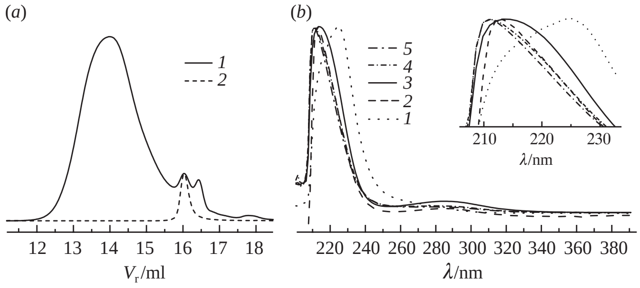


Figure 1 (*a*) Exclusion chromatograms for polymers based on (*1*) CDPN and BAMO, (*2*) CDPN. (*b*) UV spectra of (*1*) CDPN, (*2*) oligomer BAMO, products of reaction between CDPN and BAMO: (*3*) polymer fraction, (*4*) fraction 1, (*5*) fraction 2.

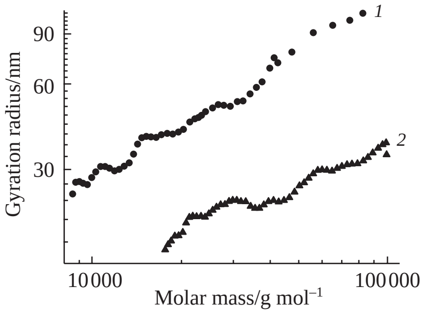


Figure 2 The dependence of the gyration radius value on the molecular weight of (*1*) BAMO polymer and (*2*) SSP C–B.

copolymer exhibited minor difference also confirms the formation of the CDPN–BAMO copolymer.

In conclusion, BAMO cationic polymerization catalyzed by boron trifluoride etherate in the presence of a hydroxy-containing β-cyclodextrin partial nitrate results in a star-shaped polymer formation. The product contains both polyether and cyclodextrin units. The obtained star-shaped copolymer possesses lower degree of crystallinity compared to the BAMO homopolymer. This favorable property of star-shaped copolymer makes it promising compared to linear copolymers comprising 60% of BAMO. Decrease in crystallinity of star-shaped polymer based on CDPN and BAMO occurs when containing the BAMO of 88% that indicates comparable energetic characteristics of both polymers.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.016.

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