Synthesis and copolymerization of azidomethyl-substituted oxetanes: the morphology of statistical block copolymers

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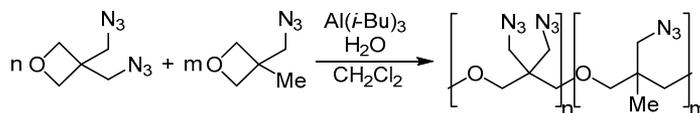
3,3-Bis(azidomethyl)oxetane and 3-azidomethyl-3-methyloxetane were obtained by bromination of pentaerythritol and metriol with a mixture of hydrobromic, acetic, and sulfuric acids, followed by cyclization in the presence of a phase-transfer catalyst TBAB, with the formation of oxetane ring and replacement of bromide substituents with azide ions. The copolymerization reaction of 3,3-bis-(azidomethyl)oxetane and 3-azidomethyl-3-methyloxetane was performed in the presence of a catalytic system prepared from triisobutylaluminum and water. The methods of small-angle and wide-angle X-ray diffraction analysis were used to determine the amorphous-crystalline and domain structures of the synthesized copolymers. We also present data about conformational and relaxation transitions in these statistical copolymers.

Keywords: 3-azidomethyl-3-methyloxetane, 3,3-bis(azidomethyl)oxetane, trialkylaluminum, amorphous-crystalline structure, domain structure, cationic ring-opening polymerization.

A promising direction in the chemistry of energetic polymers is the application of azidomethyl derivatives of oxetane for the synthesis of copolymers. The most studied examples among such materials are the copolymers of 3,3-bis(azidomethyl)oxetane (BAMO) and 3-azidomethyl-3-methyloxetane (AMMO), which are characterized by a useful combination of good thermochemical, thermo-mechanical, and yield strength properties.[1–9] The presence of ether linkers in the polymer chain allows for significant flexibility of these macromolecules, while the polarity of oxygen atoms in the ether groups enables strong intra- and intermolecular interactions.

The synthesis of polymers from four-membered cyclic ethers was first described by Farthing in 1955.[10] Subsequently, the mechanism for polymerization of 3,3-bis-(chloromethyl)oxetane in the presence of gaseous boron trifluoride as a catalyst was studied by Rose.[11] The main trends in oxetane polymerization in the presence of boron trifluoride and its etherates have been presented in the proceedings of symposia[12,13] and a series of monographs,[14–18] where it was shown that performing the process at low

temperatures promoted the formation of high molecular mass products.[15] It was proved that the polymerization of oxetanes proceeded according to a cationic mechanism.[19–42]
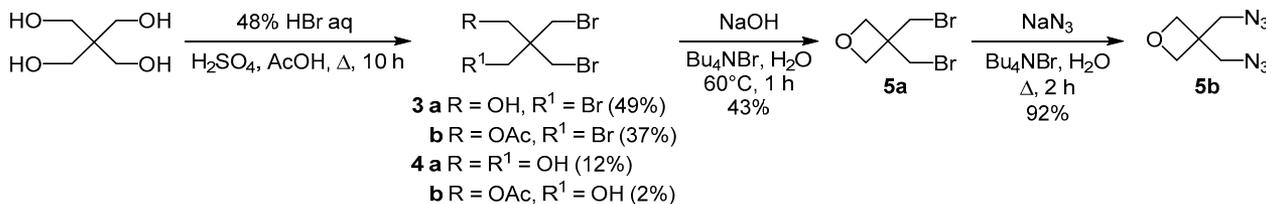
As reported earlier,[9] the preparation of polymeric oxetanes with azidomethyl groups can be accomplished by nucleophilic substitution of chlorine atoms in the appropriate chlorinated derivatives with azide groups, cationic copolymerization of azidomethyl-substituted monomers, as well as by synthesizing urethane block copolymers on the basis of oligomers of azidomethyl-substituted oxetanes. The first approach is more preferable, since it tends to produce polymers with better purity. At the same time, a disadvantage encountered with most of the catalysts used ($AlCl_3$, BF_3, $SnCl_3$, $TiCl_4$) is the low molecular mass of the obtained polymers.[3]

Polymerization of oxetanes, catalyzed by alkyl derivatives of aluminum, was studied by Kambara and Hatano.[22] Methods have been described for improving the effectiveness of catalytic systems on the basis of AlR_3 compounds.[23–25] The details of cationic polymerization of oxetanes in the presence of such catalysts have been

Scheme 1

1 a R = OH (46%)
  b R = OAc (46.8%)

Scheme 2
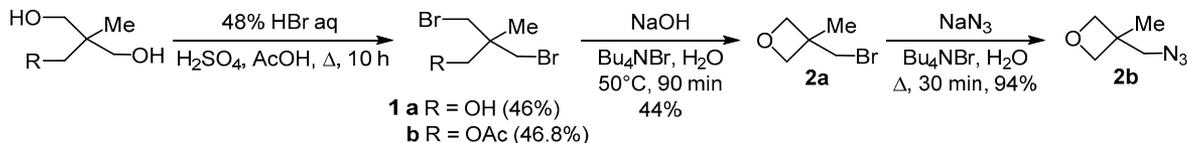
3 a R = OH, R^1 = Br (49%)
  b R = OAc, R^1 = Br (37%)
4 a R = R^1 = OH (12%)
  b R = OAc, R^1 = OH (2%)

described.[26–32] An important advantage of this catalytic system is the ability to promote the formation of high molecular mass polymers and copolymers. However, the polymerization of oxetanes bearing azidomethyl groups can be complicated by side reactions between the highly active trialkylaluminum reagents and the azide groups.

The goal of this study was to develop an effective method for the synthesis of BAMO and AMMO, as well as to study their copolymerization reactions in the presence of a catalytic system derived from triisobutylaluminum (TIBA). It is known from the literature[43] that AMMO (**2b**) can be synthesized from 3-bromomethyl-3-methyloxetane (**2a**), obtained in turn by bromination of metriol with sodium bromide in a mixture of acetic and sulfuric acids, followed by cyclization of the metriol bromo derivative formed at the first stage with alkali in the presence of a phase-transfer catalyst. The catalyst selected for this study was tetrabutylammonium bromide (TBAB). We have shown that sodium bromide can be replaced with hydrobromic acid (Scheme 1), resulting in 12-fold shortening of bromination time, as well as reduced consumption of acetic acid. We have also found that the cyclization step can be performed in aqueous medium in the absence of any organic solvent. This approach allowed to increase the reaction temperature and to reduce the reaction duration several-fold. Performing the azidation of oxetane in aqueous medium under the conditions of phase-transfer catalysis (in the presence of TBAB) enabled a 20-fold shortening of reaction time compared to the published procedure.[44] The overall route for the synthesis of AMMO (**2b**) is presented in Scheme 1.

It should be noted that a mixture of 3-bromo-2-(bromo-methyl)-2-methylpropan-1-ol (**1a**) (49.0 mol %, 46.0 mass %) and 3-bromo-2-(bromomethyl)-2-methylpropyl acetate (**1b**) (42.6 mol %, 46.8 mass %) was formed during the first stage of this reaction. Both of these products were converted to oxetane **2a** (Scheme 3) upon treatment with alkali, therefore their separation was not required. The overall yield was 77% (92% according to a patent[43]).

Bromination of pentaerythritol was performed under analogous conditions by increasing the amount of brominating agent in proportion to the number of hydroxy groups. The overall scheme for the preparation of 3,3-bis-

(azidomethyl)oxetane (BAMO) (**5b**) is presented in Scheme 2. The reaction duration was decreased 2.5 times compared to the literature data,[45,46] while the yield was comparable.

We performed the cyclization of a mixture containing pentaerythritol bromo derivatives **3** and **4** in aqueous alkali medium at 60°C, while employing phase-transfer catalysis with TBAB. This approach allowed us to reduce the reaction duration 36-fold, but the obtained yield was 1.5 times lower compared to the yield claimed in the published procedure.[44] The azidation of 3,3-bis(bromomethyl)oxetane (**5a**) was performed by refluxing with aqueous sodium azide solution with TBAB used as phase-transfer catalyst in the absence of any organic solvent, which allowed to reduce the reaction duration 12-fold, while obtaining the same yield as claimed in a patent.[44]
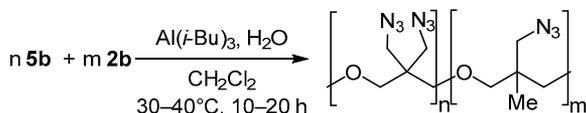
The bromination stage resulted in a mixture of 3-bromo-2,2-bis-(bromomethyl)propan-1-ol (**3a**) (50.3 mol %, 48.9 mass %), 3-bromo-2,2-bis(bromomethyl)propyl acetate (**3b**) (33.7 mol %, 37.0 mass %), 3-bromo-2-(bromomethyl)-2-(hydroxy-methyl)propyl acetate (**4a**) (13.0 mol %, 11.8 mass %), and 2,2-bis(bromomethyl)-1,3-propanediol (**4b**) (3.0 mol %, 2.3 mass %). All of these intermediate products were suitable for the subsequent cyclization, leading to oxetane **5a**. The overall yield of compound **5b** calculated from pentaerythritol was 27.6%.

The copolymerization of monomers BAMO (**5b**) and AMMO (**2b**) was performed in CH_2Cl_2 medium (Scheme 3). The amounts of monomers used are shown in Table 1. The catalyst was prepared from triisobutylaluminum and water.

It was established that the maximum activity of such catalytic systems was observed when the molar ratio of trialkylaluminum and water was in the range of 1.0:(0.8–0.9).[9] The concentration of TIBA added to the reaction mixture was 0.2 mol/l, while the concentration of water was 0.18 mol/l. The actual catalytic species that promoted the polymerization of four-membered cyclic ethers with azidomethyl substituents in the presence of trialkyl-aluminum compounds and water were formed by interaction of alkylaluminum derivatives with water and represented mixtures of alumoxanes (Fig. 1).

Thus, the trialkylaluminum reagent was converted in the presence of water into a modified Lewis acid, and only part

Scheme 3

n **5b** + m **2b** $\xrightarrow[\substack{\text{CH}_2\text{Cl}_2 \\ 30-40°C, 10-20 \text{ h}}]{\text{Al}(i\text{-Bu})_3, \text{H}_2\text{O}}$ [structure]

Table 1. The conditions for the synthesis of AMMO–BAMO copolymers

Copolymer	Ratio of monomers				Water, g	CH$_2$Cl$_2$, ml (g)
	AMMO (**2b**)		BAMO (**5b**)			
	mass %	mol %	mass %	mol %		
SAMB-7.75	7.75	10	92.25	90	0.14	6.8 (0.20)
SAMB-15.9	15.9	20	84.1	80	0.14	6.8 (0.20)
SAMB-20	20.0	24.84	80.0	75.16	0.18	8.25 (0.16)
SAMB-25	25.0	30.54	75.0	69.41	0.28	10.0 (0.13)
SAMB-30	30.0	36.17	70.0	63.83	0.19	10.0 (0.13)
SAMB-40	40.0	46.85	60.0	53.15	0.19	10.0 (0.13)

$-[\text{Al}-\text{O}-[\text{OAlR}_2]_n$ R = alkyl radical
                                              n = 0, 1, 2, 3, ...
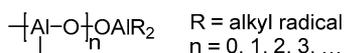
Figure 1. The structure of catalytic species obtained from TIBA and water.

of the added water acted as a cocatalyst, participating in the transformation of modified Lewis acid into a Brønsted acid. Taking into account the fact that performing the reaction in solvents with high boiling points resulted in uncontrolled increase of the temperature in the reaction zone,[27–30] it was preferable to use CH$_2$Cl$_2$ where the reaction smoothly proceeded in the temperature range of 20–40°C. This approach allowed to achieve high degrees of conversion, while simplifying the temperature control without the need for low temperature coolants and decreasing the risks due to overheating during copolymerization of heterocyclic monomers BAMO (**5b**) and AMMO (**2b**) at the stages of initiation and polymer chain growth. Thus, in the case of temperature increase to the boiling point of CH$_2$Cl$_2$, the reaction heat can be removed through refluxing of CH$_2$Cl$_2$.

As indicated by the intrinsic viscosity (1.50–0.37 dl/g at 20°C in cyclohexanone), the catalytic system based on TIBA–water allowed to obtain AMMO–BAMO copolymers (containing 60–90 mass % of BAMO) with high molecular mass in good yields – 13.2–18.7 g (82.1–93.5%). Due to these properties, the obtained copolymers had a good solubility only in cyclohexanone at 105–110°C.[9] According to the results of DCS analysis, these were thermoelastoplastic polymers that could be processed into composites in molten state, as the softening temperature was relatively low (54.1–78.9°C).

The molecular structure of AMMO–BAMO copolymers was studied by using the method of FT-IR spectroscopy. The obtained IR spectra of copolymers over the wavenumber range of 4000–400 cm^{-1} are shown in Figure 2.
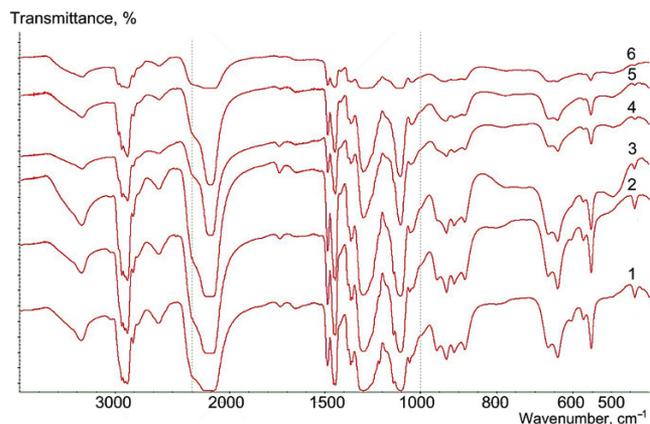
Figure 2. FT-IR spectra of AMMO–BAMO copolymers: 1 – SAMB-7.75, 2 – SAMB-15.9, 3 – SAMB-20, 4 – SAMB-25, 5 – SAMB-30, 6 – SAMB-40.

Oxetanes are characterized by strong absorption bands in the range of 930–990 cm^{-1}, which are observed in the IR spectra of the starting monomers. The indicated absorption bands practically disappeared in copolymers, which was caused by the opening of trimethylene oxide rings, and new absorption bands appeared at 1150–1060 cm^{-1}, associated with symmetrical vibrations of the C–O–C ether bond.[47–49] The stretching vibrations of azide group were observed at 2100 (ν_{as}) and 1290 cm^{-1} (ν_s), while the nonplanar vibrations of N$_3$ group could be identified over the wavenumber range of 520–580 cm^{-1}. The bands at 2900 cm^{-1} were assigned to stretching vibrations of CH$_2$ groups. The deformation vibrations of CH$_2$ groups were manifested as a doublet in the range of 1460–1500 cm^{-1}.[48,49]

Experimental studies confirmed the possibility of using catalytic systems based on trialkylaluminum reagents for the polymerization of azidomethyl-substituted oxetanes, while the unchanged absorption bands in the FT-IR spectra pointed to the absence of reactions between the azide groups of monomers and the trialkylaluminum reagents, since the actual catalytic species were mixtures of alumoxanes. The amorphous-crystalline structure is known to be associated with a range of mechanical and physical properties of copolymers, while also affecting the selection of optimal technological conditions for the processing of polymers.[50] For this reason, we performed an X-ray diffraction analysis to identify the structures of the obtained copolymers. The X-ray diffraction data for samples of *poly*-BAMO and statistical copolymers containing various amounts of AMMO (**2b**) units in the copolymer chain are presented in Figure 3.

An important structural characteristic of polymers is the degree of crystallinity according to X-ray diffraction analysis, which indicates the fraction of molecular units in the polymer sample that are packed in a regular three-dimensional lattice. The criterion that is associated with changing from a disordered structure to regular packing of molecules is the emergence of crystal reflexes corresponding to reflections of X-rays from various planes of a three-dimensional lattice.[50] Thus, as can be observed from X-ray diffraction data, the AMMO–BAMO copolymers
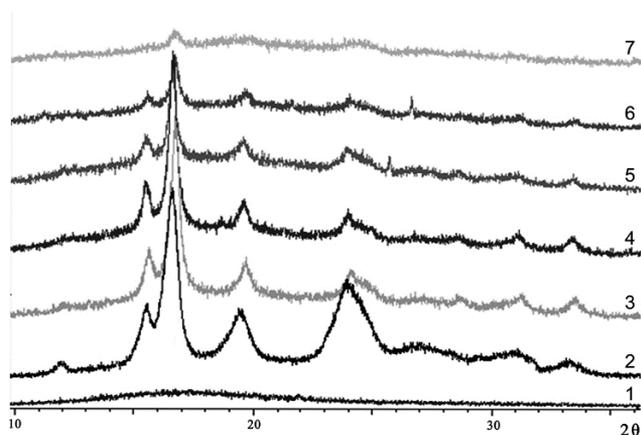
Figure 3. X-ray diffraction data for statistical AMMO–BAMO copolymers: 1 – *poly*-AMMO, 2 – *poly*-BAMO, 3 – SAMB-15.9, 4 – SAMB-20, 5 – SAMB-25, 6 – SAMB-30, 7 – SAMB-40.

Figure 4. The small-angle X-ray diffraction data for polymer samples: 1 – SAMB-15.9, 2 – SAMB-25, 3 – SAMB-40, 4 – *poly*-BAMO.
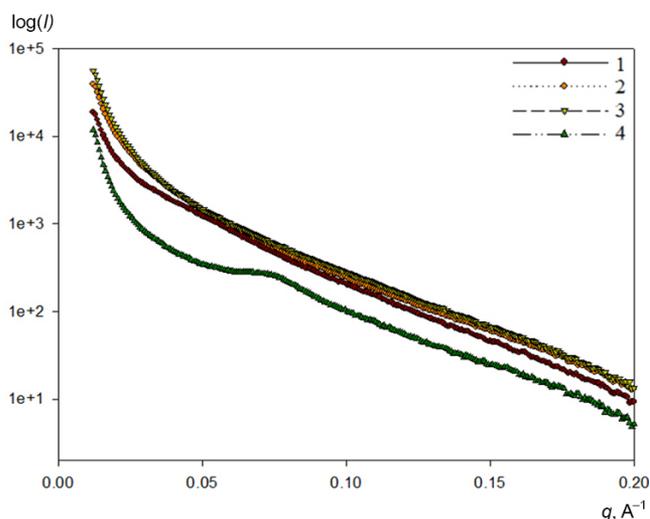
had an amorphous-crystalline structure, in contrast to *poly*-AMMO, which lacked any X-ray diffraction reflexes associated with crystalline structure. This indicated that the formation of an ordered copolymer structure was enabled by the introduction of BAMO (**5b**) units during the synthesis of copolymer. The identified trends in the change of crystallinity depending on the amounts of BAMO (**5b**) and AMMO (**2b**) units in copolymer are presented in Table 2, and show a gradual decrease in the degree of crystallinity of copolymer that correlated with increasing fraction of AMMO (**2b**) units. This observation confirmed the available literature data about the influence of amorphous blocks on the crystalline structure of AMMO–BAMO copolymers.[51]

The study of deformation yield strength properties of copolymers depending on the content of crystalline phase showed that the saturation of copolymer with AMMO (**2b**) units caused more deformation and lower yield strength, which is characteristic for polymers of this type and is in agreement with the results of earlier studies.[9]

Along with the amorphous-crystalline structure of copolymers, the domain structure of AMMO–BAMO copolymers is also an important factor that affects the deformation yield strength properties. The domain structure was studied by using the method of small-angle X-ray diffraction analysis. Figure 4 shows the small-angle X-ray diffractograms for samples of SAMB-15.9, SAMB-25, SAMB-40, and *poly*-BAMO polymers, which were obtained
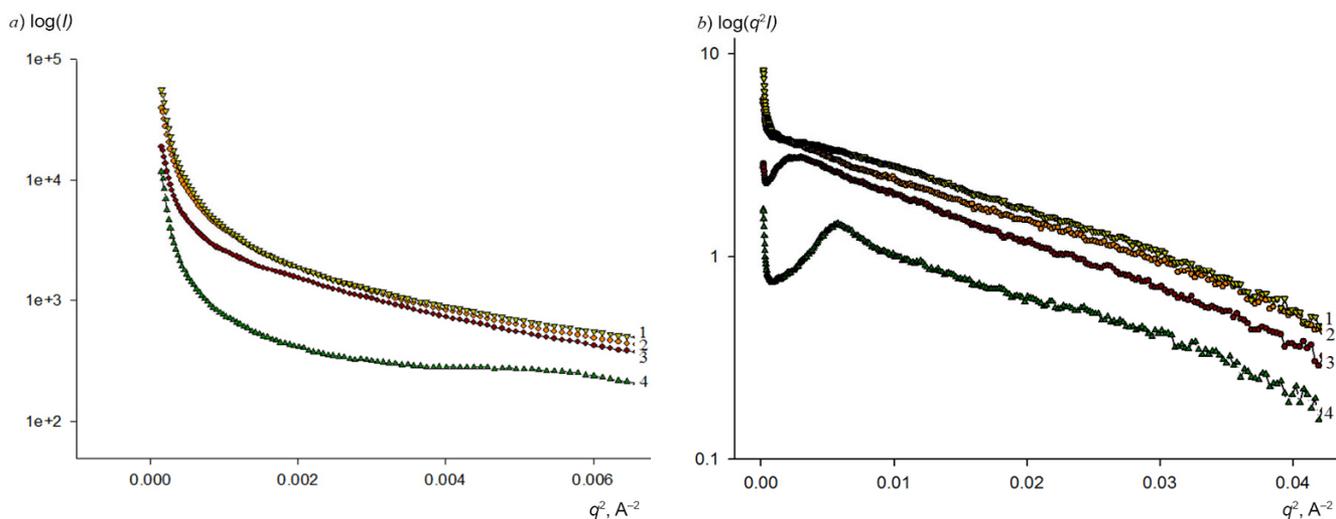
by integration of two-dimensional diffractograms after subtraction of background scattering on logarithmic scale.

The presence of sufficiently strong scattering pointed to the heterogeneous nature of *poly*-BAMO, SAMB-15.9, SAMB-25, and SAMB-40 samples. In other words, there were variations in electron density due to particles with sizes in the detection range of small-angle X-ray scattering technique (1–100 nm).

In order to determine the shape of scattering particles and their inertial radius, we analyzed various functions that allowed us to identify the linear regions near the start of the graphs. The most suitable model of the domains corresponded to monodisperse platelets, the largest radius of which was determined by plotting the dependence of logarithmic intensity $\log(I)$ on wave vector squared q^2 (Guinier plot, Fig. 5*a*), while the thickness of platelets was determined by plotting the dependence of $\log(q^2 I)$ (Fig. 5*b*) on wave vector squared q^2. The correlation analysis of linear regions by method of least squares allowed to determine the effective inertial radii for particles in the samples and the thickness of platelet-shaped particles, with the results presented in Table 3.

In the case of *poly*-BAMO, the intensity of small-angle X-ray scattering was primarily determined by the electron density differences between the amorphous and crystalline phases of BAMO (**5b**), even though these differences are known to be rather small[50]. Thus, the observed small-angle scattering in sample of *poly*-BAMO must be explained by scattering on crystal domains, while the presence of an inflection point on the diffraction plot points to some correlated arrangement of these domains (Fig. 4).

At the same time, it must be assumed that the shape and size distribution of the crystalline domains are far from ideal and must have a sufficiently polydisperse nature, as indicated by the broadened profile of diffraction peak on the background of relatively strong diffuse scattering. It is assumed that the formation of crystalline domains occurs by parallel packing of copolymer units, even though their

Table 2. The calculated structural characteristics of AMMO–BAMO copolymers

Copolymer	Degree of crystallinity, %	Crystallite size, Å	
		minimum	maximum
SAMB-15.9	40.5	90.1	187.2
SAMB-20	31.6	138.6	326.9
SAMB-25	24.7	51.1	163.1
SAMB-30	19.1	105.2	294.9
SAMB-40	11.6	105.2	261.5
poly-BAMO	48.9	108.3	271.8

Figure 5. The graphs of *a*) log(*I*) as a function of q^2; *b*) log($q^2 I$) as a function of q^2 for statistical copolymers: 1 – SAMB-15.9, 2 – SAMB-25, 3 – SAMB-40, 4 – *poly*-BAMO.

Table 3. The geometry parameters for the domain structure of the studied polymers

Copolymer	Thickness, Å	R_g, Å	R_{sphere}, Å
SAMB-40	24.56	142.20	183.6
SAMB-25	23.71	133.20	171.9
SAMB-15.9	25.36	128.27	165.6
poly-BAMO	23.30	153.01	197.5

regular arrangement and crystallization along the entire polymer chain would be quite difficult, leading instead to the formation of anisotropic density fluctuations and a lamellar structure. The further crystallization of domains and their growth occurred in directions that were perpendicular to the main polymer chain. As shown by calculations, at the lamellar thickness of 23 Å the structure may include on average 6 monomeric units. Taking into account that no more than 60% of molecules crystallized in a pure *poly*-BAMO material, the amorphous component in this heterogeneous system was interpreted as representing irregular matrix.

The introduction of AMMO (**2b**) units in the polymeric system substantially altered the morphology of copolymer. First of all, this was true with regard to the electron density differences between the two components forming the microphasic system. Obviously, the primary scattering inhomogeneities were crystallites of BAMO (**5b**), as evidenced by the presence of the crystalline component of BAMO (**5b**) in the diffractograms of all copolymers (Fig. 2). For this reason, when evaluating the inertial radius of microphase particles, they would be more appropriately described by flattened anisotropic forms with similar characteristics (thickness), since the mechanism of formation and crystallization of these domains remains unchanged. The only substantial difference in the given case is the presence of flexible non-crystallizing block spacers between the blocks of BAMO (**5b**). On one hand,

this allows one polymer chain to participate several times in the formation of one crystallite and, on the other hand, presents no steric obstacles to the emergence of a large number of crystallization and domain formation sites in the polymer. It is probable that these factors can be the reason for the reduction in cross section of lamellar structures, while their thickness remains practically unchanged. At the same time, the presence of flexible chains (and additional uncrystallized fragments of BAMO (**5b**)) allows for a greater freedom of crystalline domains, manifested in the lack of order in the positioning of domains.

The increased content of BAMO (**5b**) in the series of studied polymers was associated with the presence of a large number of crystalline domains of somewhat smaller sizes, which apparently facilitated the formation of disperse structure. However, taking into account the observed decrease of the degree of crystallinity in the polymer of given series, it is not possible to exclude the possible presence of domains formed not by crystalline, but rather by disordered molecular fragments of BAMO (**5b**), or possibly mixed type domains.

It is known that the constant background large-angle component of small-angle X-ray scattering in the region of the smallest angles is related to the isothermal compressibility of the sample and the fluctuations of the electron density in it.[51] Comparing the level of this background for the studied samples (Fig. 6) showed its increase in the case of the first two samples relative to *poly*-BAMO, and stabilization in the further samples. This observation indicates that the decreased content of BAMO (**5b**) also led to a lower degree of its crystallization and to "dissolution" of a large number of amorphous BAMO (**5b**) units in the amorphous matrix, likely resulting in stronger inhomogeneities of the electron density in these materials.

Thus, the studies of supramolecular structure in statistical AMMO–BAMO copolymers allowed to establish the mechanism for the origin of domains, which involved parallel packing of copolymer chains, resulting in
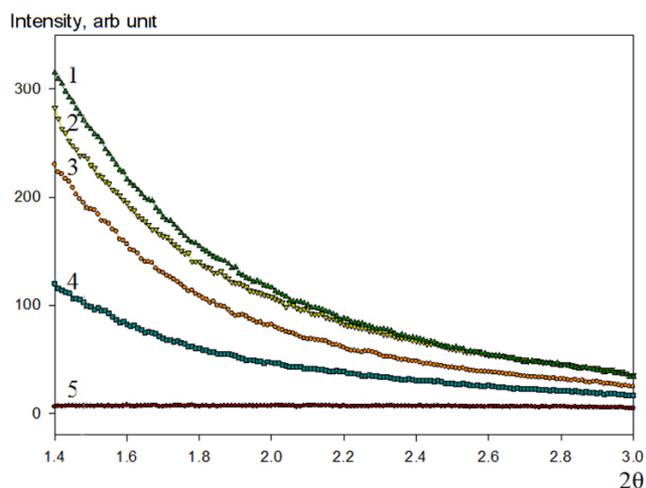
Figure 6. The baseline plot of small-angle X-ray scattering by statistical copolymers and *poly*-BAMO: 1 – SAMB-40, 2 – SAMB-25, 3 – SAMB-15.9, 4 – *poly*-BAMO, 5 – background.

Figure 7. DSC thermograms of AMMO–BAMO copolymers: 1 – SAMB-7.75, 2 – SAMB-15.9, 3 – SAMB-20, 4 – SAMB-30, 5 – SAMB-40.

anisotropic flattened disk-shaped domains and the formation of lamellar structures.

In order to study the phase transitions, as well as structural characteristics, DSC thermograms were obtained for samples of copolymers (Figs. 7, 8).

The double or triple endothermic effects in the ranges of 38–40 and 78–82°C for these copolymers could be explained by the presence of crystalline structures consisting of sequences of BAMO (**5b**) units in specific *trans* and *gauche* conformations, which is known to be characteristic for poly[3,3-bis(azidomethyl)oxetane].[7] The endothermic effect in the region of 38–40°C disappeared after repeated heating, but an exothermic effect emerged in the same region, probably corresponding to recrystallization of the less stable *gauche* conformation to the more stable *trans* conformation, observed as a single peak on repeated thermograms (Fig. 7). The presence of two and three melting peaks on the thermograms (Fig. 6) can be associated with the reorganization of metastable crystals, as well as by the presence of crystals at several preferred sizes. As previously shown by using the method of X-ray diffraction analysis, samples of SAMB copolymers showed broad distributions of minimum and maximum crystallite sizes (Table 2), which also explains the presence of several melting peaks on the thermograms.

The melting and recrystallization of smaller crystallites occurred at lower temperatures, while larger crystallites melted at higher temperatures. In addition, some structural reorganization of non-equilibrium crystals involving thickening of the thinnest lamelles occurred in solid phase prior to melting, and accelerated as the melting point was approached.

Thus, effective methods have been developed for the synthesis of useful monomers – 3-azidomethyl-3-methyl-oxetane and 3,3-bis(azidomethyl)oxetane. It was shown that copolymerization of 3-azidomethyl-3-methyloxetane and 3,3-bis(azidomethyl)oxetane in the presence of a catalytic system prepared from triisobutylaluminum and water resulted in the formation of block copolymers with
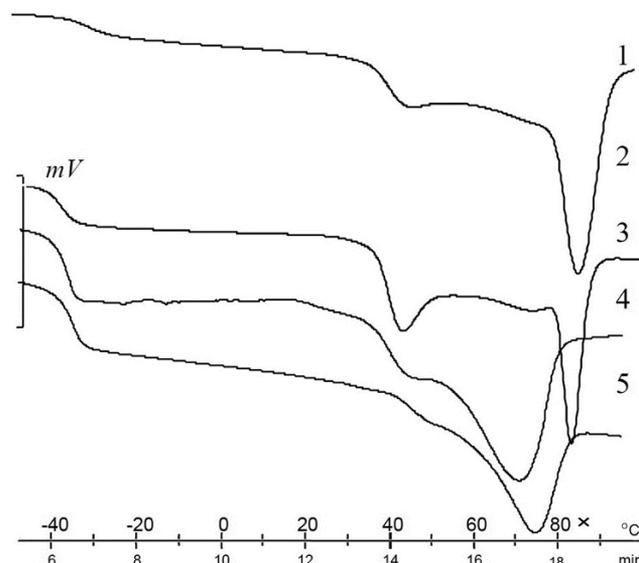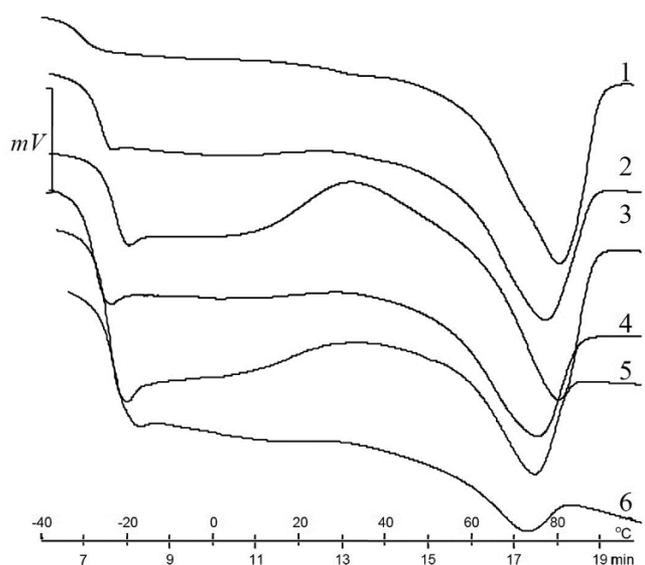
Figure 8. Repeated DSC thermograms for AMMO–BAMO copolymers after cooling: 1 – SAMB-7.75, 2 – SAMB-15.9, 3 – SAMB-20, 4 – SAMB-25, 5 – SAMB-30, 6 – SAMB-40.

Table 4. Thermochemical characteristics of AMMO–BAMO copolymers*

Copolymer	$T_{glass\ tr.}$,°C	Mp,°C	$T_{vigor.\ decomp.}$,°C
SAMB-7.75	–33.8	78.8	188
SAMB-15.9	–37.4	72.9	184
SAMB-20	–38.0	77.9	200
SAMB-25	–38.8	67.1	189
SAMB-30	–39.8	50.0	187
SAMB-40	–39.4	54.1	190

$T_{glass\ tr.}$ – glass transition temperature, Mp – melting point,
$T_{vigor.\ decomp.}$ – temperature of the start of vigorous decomposition

amorphous-crystalline structure. No reactions occurred between the azide groups of monomers and trialkyl-aluminum reagents, because the actual catalytic species were mixtures of alumoxanes. Decreasing the amount of 3,3-bis(azidomethyl)oxetane in copolymers resulted both in a lower degree of crystallization and "dissolving" of larger number of amorphous 3,3-bis(azidomethyl)oxetane units in the amorphous matrix, which led to increased inhomogeneity of electron density. Taking into account the observed trends in molecular and domain structure of copolymers, it becomes possible to adjust the set of their physicochemical properties, while taking into account the structural features of copolymers caused by the introduction of asymmetric 3-azidomethyl-3-methyl-oxetane units, which affect the regularity of structure and change the packing density of macromolecules.

Experimental

The structure of AMMO–BAMO copolymers was confirmed by using a Nicolet iS10 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance 300 instrument at 300 and 100 MHz, respectively, using solvent signals as internal standard (δ 2.51 ppm for ^{1}H nuclei in DMSO-d_6 and 77.106 ppm for ^{13}C nuclei in CDCl$_3$).

The solvents were purified and dried prior to use according to standard procedures. Elemental analysis was performed on a Vario EL III CHN-analyzer. Powder X-ray diffractograms for statistical AMMO–BAMO copolymers were recorded on a Bruker D8 Advance automatic X-ray diffractometer equipped with a Vario accessory and a Vantec linear CCD detector, using CuKα radiation that was monochromatized by a curved Johansson monochromator. The small-angle X-ray diffraction studies of samples were performed on a Bruker NanoStar small-angle diffracto-meter, equipped with a HIStar two-dimensional CCD detector, using CuKα radiation that was monochromatized by a curved Johansson monochromator. The X-ray tube was operated at 40 kV voltage, 35 mA current, diffracto-grams were recorded over 5000 s. The phase transitions of copolymers were analyzed by using a MettlerToledo DSC 823e instrument with a heating rate of 10°C/min over the range of 70–250°C. The copolymers were subjected to the preliminary analysis over the temperature range from –70 to 100°C, which was repeated after 24 h. The intrinsic viscosity was determined according to a standard procedure[52] at 20°C for solutions of copolymers in cyclohexanone.

The calculation of enthalpy values was performed according to a published procedure.[53]

Commercial reagents were used: 1,1,1-tris(hydroxy-methyl)ethane (metriol) (97%), pentaerythritol (98%), TBAB (99%), hydrobromic acid (48%) (Acros Organics); 96% sulfuric acid (Sigma-Tek, Russia); chemically pure glacial acetic acid (Komponent-Reaktiv, Russia); chemically pure sodium hydroxide (95%) (Khimmed, Russia), sodium azide (99%) (Merck KGaA). The obtained monomers BAMO (**5b**) and AMMO (**2b**) were distilled under vacuum (0.1 mmHg) prior to use. Triisobutyl-aluminum was used for the preparation of catalyst as a 20%

solution in *n*-hexane with 94–96% assay (PJSC Kazanorgsintez, Russia).

Synthesis of 3-azidomethyl-3-methyloxetane (2b). A 2-l Erlenmeyer flask was charged with metriol (300 g, 2.5 mol), 48% hydrobromic acid (1030 ml, 1524.4 g, 9 mol), and glacial acetic acid (140 ml, 147.1 g, 2.45 mol). The stirred mixture was carefully treated by addition of sulfuric acid (380 ml, 696.9 g, 3.9 mol) and refluxed for 4 h. After that, the reaction mixture was cooled to ~15°C and the lower (organic) layer was separated in a separatory funnel, and the upper (aqueous) layer was extracted with chloroform (200 ml and 3×100 ml). The extracts were combined with the organic layer, the obtained solution was washed with water (3×75 ml), then with aqueous 15% Na$_2$CO$_3$ solution (50 ml), and again with water (2×75 ml). The chloroform solution was then evaporated, giving a mixture of products **1a** and **1b** (550.4 g) in the ratio of 46.0 and 46.8% as a brown liquid with low viscosity.

3-Bromo-2-(bromomethyl)-2-methylpropan-1-ol (1a). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.01 (3H, s, CH$_3$); 3.33 (2H, d, *J* = 5.3, CH$_2$OH); 3.48 (4H, s, CH$_2$Br); 4.97 (1H, t, *J* = 5.3, OH).

3-Bromo-2-(bromomethyl)-2-methylpropyl acetate (1b). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.09 (3H, s, CH$_3$); 2.04 (3H, s, OC(O)CH$_3$); 3.55 (4H, s, CH$_2$Br); 3.99 (2H, s, CH$_2$OC(O)CH$_3$). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 170.60; 67.20; 66.25; 40.59; 39.13; 38.32; 20.82; 20.23; 19.87 (for mixture **1a** and **1b**).

A three-neck one liter flask equipped with an overhead stirrer was charged with a mixture of compounds **1a** and **1b** (524.2 g, 2 mol) and TBAB (8.4 g, 26 mmol). The reaction mixture was vigorously stirred and treated by the addition of a solution prepared from NaOH (109.5 g, 2.6 mol) and water (190 ml). The reaction mixture was then thermostated at 50°C while vigorously stirring for 1.5 h. After that, the reaction flask was connected through an intermediate vessel to steam generator and compound **2a** was steam-distilled from the reaction mixture. The organic phase (bottom layer) was obtained with a yield of 174.0 g and contained 84.0% of 3-bromomethyl-3-methyloxetane (**2a**) according to ^{1}H NMR spectrum. Distillation allowed to separate the main fraction (144.7 g) as a colorless liquid with bp 47.5–48°C / 6 Torr (62–64°C / 10 Torr[54]), the content of compound **2a** was 137.47 g (95%), the yield of cyclization step was 43.8%.

3-Bromomethyl-3-methyloxetane (2a). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.34 (3H, s, CH$_3$); 3.78 (2H, s, CH$_2$Br); 4.24 (2H, d, *J* = 5.9, CH$_2$O) and 4.33 (2H, d, *J* = 5.9, CH$_2$O). ^{13}C NMR spectrum (75.47 MHz, CDCl$_3$), δ, ppm: 80.68; 41.31; 40.60; 22.44.

A 500-ml Erlenmeyer flask was charged with NaN$_3$ (91 g, 1.4 mol), TBAB (4.5 g, 14 mmol), and water (200 ml). The mixture was vigorously stirred on a magnetic stirrer (1000 rpm) and treated by the addition of compound **2a** (173.3 g, 1.0 mol). While continuing vigorous stirring, the obtained biphasic reaction mixture was refluxed for 30 min. The reaction flask was then cooled to room temperature on a water bath and, without interrupting the vigorous stirring, treated with solid NaOH (1.5 g, 35.5 mmol), followed by

stirring for another 30 min. The mixture was then extracted with benzene (3×100 ml). The extracts were combined and washed with water (4×40 ml). The benzene solution was dried over anhydrous $MgSO_4$. The solvent was evaporated, the mass of residue was 118.82 g, content of AMMO (**2b**) more than 98%, the yield of azidation stage was 118.82 g (93.6%). The overall yield of AMMO (**2b**) calculated for all stages starting from metriol was 97.8 g (30.8%).

3-Azidomethyl-3-methyloxetane (2b). Colorless liquid. Bp 53°C / 5.5 Torr (64–65°C / 10 Torr[55]). IR spectrum (thin film), ν, cm^{-1}: 2098 (–N_3), 997 (C–O–C in cyclic ethers). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.24 (3H, s, CH_3); 3.59 (2H, s, CH_2N_3); 4.21 (2H, d, *J* = 5.8) and 4.33 (2H, d, *J* = 5.8, CH_2O). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 21.6 (s, CH_3); 40.1 (s, $CH_3CCH_2N_3$); 58.4 (s, CH_2N_3); 79.9 (s, CH_2O). Found, %: C 47.25; H 7.15; N 33.09. $C_5H_9N_3O$. Calculated, %: C 47.23; H 7.14; N 33.05.

Synthesis of 3,3-bis(azidomethyl)oxetane (5b). Method I. A 2-l Erlenmeyer flask was charged with pentaerythritol (136 g, 1 mol), 48% hydrobromic acid (680 ml, 1006.4 g, 6 mol), acetic acid (100 ml, 105.1 g, 1.75 mol), and then sulfuric acid (250 ml, 458.5 g, 4.5 mol) was carefully added while stirring the reaction mixture. The obtained solution was refluxed for 10 h. After that, the reaction mixture was cooled to 15°C. The bottom (organic) layer was separated by using a separatory funnel, and the top (aqueous) layer was extracted with chloroform (3×200 ml). The extracts were combined with the organic phase, the obtained solution was washed with water (3×75 ml). The organic phase was dried over anhydrous K_2CO_3 (20 g) for several hours. Then the chloroform solution was evaporated, providing a brown liquid (275.4 g) with the following composition (according to ^{1}H NMR spectrum): 3-bromo-2,2-bis(bromomethyl)propan-1-ol (**3a**), 3-bromo-2,2-bis(bromomethyl)propyl acetate (**3b**), 2,2-bis(bromomethyl)-1,3-propanediol (**4a**), 3-bromo-2-(bromomethyl)-2-(hydroxymethyl)propyl acetate (**4b**).

3-Bromo-2,2-bis(bromomethyl)propan-1-ol (3a). Yield 134.7 g (48.9%). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.41 (2H, d, *J* = 5.0, C$\underline{H}_2$OH); 3.49 (6H, s, CH_2Br); 5.26 (1H, t, *J* = 5.0, OH).

3-Bromo-2,2-bis(bromomethyl)propyl acetate (3b). Yield 101.9 g (37.0%). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.06 (3H, s, OC(O)CH_3); 3.57 (6H, s, CH_2Br); 4.06 (2H, s, C$\underline{H}_2$OC(O)CH_3).

2,2-Bis(bromomethyl)-1,3-propanediol (4a). Yield 6.3 g (2.3%). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.41 (4H, d, *J* = 5.0, C$\underline{H}_2$OH); 3.44 (4H, s, CH_2Br); 4.84 (1H, t, *J* = 5.0, OH).

3-Bromo-2-(bromomethyl)-2-(hydroxymethyl)propyl acetate (4b). Yield 32.5 g (11.8%). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.03 (3H, s, OC(O)CH_3); 3.40 (2H, d, *J* = 4.1, C$\underline{H}_2$OH); 3.50 (4H, s, CH_2Br); 3.98 (2H, s, C$\underline{H}_2$OC(O)CH_3); 5.10 (1H, t, *J* = 4.6, OH). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 171.22; 170.15; 63.95; 63.78; 63.32; 62.33; 61.82; 44.50; 44.23; 42.67; 42.31; 34.83; 34.51; 34.09; 33.53; 20.78 (for mixture **3a,b** and **4a,b**).

The yield calculated for the target compounds **3a** and **3b** was 236.6 g (69.2%).

Method II. A 500-ml three-neck flask was equipped with an overhead stirrer and charged with the intermediate products **3a,b** and **4a,b** (275.4 g, 0.82 mol) from the bromination of pentaerythritol in the previous stage, and then TBAB (4.6 g, 14 mmol) was added. The mixture was vigorously stirred and treated with a solution of NaOH (61 g, 1.45 mol) in water (90 ml). The reaction mixture was further maintained at 60°C with vigorous stirring for 1 h. After that, the reaction mixture was cooled, and the bottom (organic) layer was separated. The top layer was extracted with chloroform (3×40 ml). The extracts were combined with the organic phase and the obtained solution was washed with water (4×15 ml). The solvent was removed on a rotary evaporator, leaving a residue with mass of 177.1 g. The residue was separated by fractional distillation, giving the main fraction with mass of 91.1 g. Bp 50–51°C / 0.4 Torr (68–69°C / 0.65 Torr[56]), the content of 3,3-bis(bromomethyl)oxetane (**5a**) was 86.5 g (95%), the yield achieved in the cyclization stage was 86.5 g (43.3%). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.93 (4H, s, CH_2Br); 4.34 (4H, s, CH_2O).

Method III. A 500-ml Erlenmeyer flask was charged with a solution of NaN_3 (65 g, 1 mol) and TBAB (3.22 g, 10 mmol) in water (120 ml). The solution was vigorously stirred on a magnetic stirrer (1000 rpm), and compound **5a** (91.1 g, 0.355 mol) was added. While continuing the vigorous stirring, the obtained biphasic reaction mixture was refluxed for 2 h. The reaction flask was then cooled to room temperature and the reaction mixture was extracted with benzene (3×100 ml). The extracts were combined and the obtained solution was washed with water (4×40 ml). The benzene solution was dried over anhydrous $MgSO_4$. The solvent was then evaporated, the mass of residue was 54.88 g, content of 3,3-bis(azidomethyl)oxetane (**5b**) was higher than 98%, the yield of azidation stage was 92.1%.

The overall yield of BAMO (**5b**) for all stages starting from pentaerythritol was 46.4 g (27.6%). The product was a light-yellow liquid. Bp 80–84°C / 0.4 Torr (79–81°C / 0.4 Torr[57]). IR spectrum (thin film), ν, cm^{-1}: 2100 (–N_3), 997 (C–O–C in cyclic ethers). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.72 (4H, s, CH_2N_3); 4.32 (4H, s, CH_2O). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 43.42 (s, $N_3CH_2\underline{C}CH_2N_3$); 54.15 (s, CH_2N_3); 76.41 (s, CH_2O). Found, %: C 35.73; H 4.82; N 50.04. $C_5H_8N_6O$. Calculated, %: C 35.71; H 4.80; N 49.98.

Synthesis of 3,3-bis(azidomethyl)oxetane and 3-azidomethyl-3-methyloxetane copolymers (SAMB) (General method). The synthesis was performed according to a modified version of published procedure.[9] A mixture of monomers (AMMO (**2b**) 7.75–40.00 mass % and BAMO (**5b**) 92.25–60.00 mass %) was charged into a four-neck flask. A catalytic system prepared from triisobutyl-aluminum and water (the molar ratio of triisobutyl-aluminum and water was 1.0:0.8) was gradually added under argon stream into the four-neck flask containing continuously stirred mixture of monomers in CH_2Cl_2 (6.8–10.0 ml), while maintaining the temperature at or below 40°C by external cooling of the flask. Polymerization was

performed for 10–20 h at 30–40°C. After the completion of reaction, the polymer was separated by precipitation with 2-PrOH, removed from the reactor, washed with 5% HCl solution and then multiple times with water until neutral pH was achieved. The obtained copolymer was dried to constant mass at 50–60°C.

Copolymer of 3,3-bis(azidomethyl)oxetane and 3-azido-methyl-3-methyloxetane SAMB-7.75. The synthesis was performed according to a modified version of published procedure.[9] A mixture of monomer AMMO (**2b**) (1.27 g, 0.01 mol) and monomer BAMO (**5b**) (15.10 g, 0.089 mol) was charged into a four-neck flask. The catalytic system was prepared in a Schlenk vessel over 30 min by slow addition of water (0.14 g, 0.08 mol) to TIBA (1.98 g, 0.01 mol) with continuous stirring under argon stream. The catalytic system was gradually added under argon stream to a continuously stirred mixture of monomers in CH_2Cl_2 (6.8 ml), while maintaining the temperature at or below 40°C by external cooling of the flask. The further isolation of product was performed according to the general method.

The copolymer was obtained in the form of a light-yellow gum with softening temperature of 78.8°C. $\Delta H_f°$ 2141.5 kJ/kg. The intrinsic viscosity was 1.41 dl/g. Yield 13.45 g (82.1%). IR spectrum (thin film), ν, cm^{-1}: 2094 (–N$_3$), 1101 (C–O–C). Found, %: C 36.52; H 4.87; N 50.11. $C_{10}H_{8.1}N_{5.7}O$ (unit). Calculated, %: C 36.61; H 4.98; N 48.67.

Copolymer of 3,3-bis(azidomethyl)oxetane and 3-azido-methyl-3-methyloxetane SAMB-15.9. The synthesis was performed according to a modified version of published procedure.[9] A mixture of monomer AMMO (**2b**) (2.54 g, 0.02 mol) and monomer BAMO (**5b**) (13.45 g, 0.08 mol) was charged into a four-neck flask. The catalytic system was prepared in a Schlenk vessel over 30 min by slow addition of water (0.14 g, 0.08 mol) to TIBA (1.98 g, 0.01 mol) with stirring under argon stream. The catalytic system was gradually added under argon stream to a continuously stirred mixture of monomers in CH_2Cl_2 (6.8 ml), while maintaining the temperature at or below 40°C by external cooling of the flask. The polymerization was continued for 10–20 h at 30–40°C. The further isolation of product was performed according to the general method.

The copolymer was obtained in the form of a light-yellow gum with softening temperature of 72.9°C. $\Delta H_f°$ 1990.9 kJ/kg. The intrinsic viscosity was 1.00 dl/g. Yield 13.25 g (82.9%). IR spectrum (thin film), ν, cm^{-1}: 2098 (–N$_3$), 1102 (C–O–C). Found, %: C 37.41; H 5.10; N 45.78. $C_{10}H_{8.2}N_{5.4}O$ (unit). Calculated, %: C 37.54; H 5.17; N 47.29.

Copolymer of 3,3-bis(azidomethyl)oxetane and 3-azido-methyl-3-methyloxetane SAMB-20. The synthesis was performed according to a modified version of published procedure.[9] A mixture of monomer AMMO (**2b**) (4.00 g, 0.032 mol) and monomer BAMO (**5b**) (16.00 g, 0.095 mol) was charged into a four-neck flask. The catalytic system was prepared in a Schlenk vessel over 30 min by slow addition of water (0.18 g, 0.010 mol) to TIBA (2.52 g, 0.013 mol) with continuous stirring under argon stream. The catalytic system was gradually added under argon stream to a continuously stirred mixture of monomers in CH_2Cl_2 (8.25 ml), while maintaining the temperature at or

below 40°C by external cooling of the flask. The polymerization reaction was continued for 10–20 h at 30–40°C. The further isolation of product was performed according to the general method.

The copolymer was obtained in the form of a light-yellow gum with softening temperature of 77.9°C. $\Delta H_f°$ 1988.7 kJ/kg. The intrinsic viscosity was 0.79 dl/g. Yield 18.7 g (93.5%). IR spectrum (thin film), ν, cm^{-1}: 2122 (–N$_3$), 1102 (C–O–C). Found, %: C 37.90; H 5.05; N 45.37. $C_{10}H_{8.24}N_{5.25}O$ (unit). Calculated, %: C 38.02; H 5.26; N 46.59.

Copolymer of 3,3-bis(azidomethyl)oxetane and 3-azido-methyl-3-methyloxetane SAMB-25. The synthesis was performed according to a modified version of published procedure.[9] A mixture of monomer AMMO (**2b**) (7.50 g, 0.059 mol) and monomer BAMO (**5b**) (22.50 g, 0.134 mol) was charged into a four-neck flask. The catalytic system was prepared in a Schlenk vessel over 30 min by slow addition of water (0.28 g, 0.015 mol) to TIBA (3.82 g, 0.019 mol) with continuous stirring under argon stream. The catalytic system was gradually added under argon stream to a continuously stirred mixture of monomers in CH_2Cl_2 (10.0 ml), while maintaining the temperature at or below 40°C by external cooling of the flask. The polymerization reaction was continued for 10–20 h at 30–40°C. The further isolation of the product was performed according to the general method.

The copolymer was obtained in the form of a light-yellow gum with softening temperature of 67.1°C. $\Delta H_f°$ 1987.2 kJ/kg. The characteristic viscosity was 0.64 dl/g. Yield 26.6 g (88.7%). IR spectrum (thin film), ν, cm^{-1}: 2103 (–N$_3$), 1102 (C–O–C). Found, %: C 38.40; H 5.35; N 43.89. $C_{10}H_{8.31}N_{5.08}O$ (unit). Calculated, %: C 38.60; H 5.38; N 45.76.

Copolymer of 3,3-bis(azidomethyl)oxetane and 3-azido-methyl-3-methyloxetane SAMB-30. The synthesis was performed according to a modified version of published procedure.[9] A mixture of monomer AMMO (**2b**) (6.00 g, 0.047 mol) and monomer BAMO (**5b**) (14.00 g, 0.083 mol) was charged into a four-neck flask. The catalytic system was prepared in a Schlenk vessel over 30 min by slow addition of water (0.19 g, 0.011 mol) to TIBA (2.66 g, 0.013 mol) with continuous stirring under argon stream. The catalytic system was gradually added under argon stream to a continuously stirred mixture of monomers in CH_2Cl_2 (10.0 ml), while maintaining the temperature at or below 40°C by external cooling of the flask. The polymerization reaction was continued for 10–20 h at 30–40°C. The further isolation of the product was performed according to the general method.

The copolymer was obtained in the form of a light-yellow, thick resin with softening temperature of 50°C. $\Delta H_f°$ 1953.3 kJ/kg. The characteristic viscosity was 0.50 dl/g. Yield 18 g (90%). IR spectrum (thin film), ν, cm^{-1}: 2103 (–N$_3$), 1104 (C–O–C). Found, %: C 39.26; H 5.40; N 41.21. $C_{10}H_{8.36}N_{4.91}O$ (unit). Calculated, %: C 39.17; H 5.50; N 44.90.

Copolymer of 3,3-bis(azidomethyl)oxetane and 3-azido-methyl-3-methyloxetane SAMB-40. The synthesis was performed according to a modified version of published procedure.[9] A mixture of monomer AMMO (**2b**) (8.00 g,

0.063 mol) and monomer BAMO (**5b**) (12.00 g, 0.071 mol) was charged into a four-neck flask. The catalytic system was prepared in a Schlenk vessel over 30 min by slow addition of water (0.19 g, 0.011 mol) to TIBA (2.66 g, 0.013 mol) with continuous stirring under argon stream. The catalytic system was gradually added under argon stream to a continuously stirred mixture of monomers in CH_2Cl_2 (10.0 ml), while maintaining the temperature at or below 40°C by external cooling of the flask. The polymerization reaction was continued for 10–20 h at 30–40°C. The further isolation of the product was performed according to the general method.

The copolymer was obtained in the form of a light-yellow, thick resin with softening temperature of 54.1°C. $\Delta H_f°$ 1775.0 kJ/kg. The characteristic viscosity was 0.50 dl/g. Yield 18.2 g (91%). IR spectrum (thin film), v, cm^{-1}: 2107 (–N_3), 1101 (C–O–C). Found, %: C 39.72; H 5.47; N 41.87. $C_{10}H_{8.47}N_{4.6}O$ (unit). Calculated, %: C 40.32; H 5.73; N 43.21.

References

1. Kawasaki, H.; Anan, T.; Kimura, E.; Oyumi, Y. *Propellants, Explos., Pyrotech.* **1997**, *22*, 87.
2. Petrov, V. A.; Kuznetsova, N. V.; Muhametshin, T. I.; Gubaydullin, A. T. *Propellants, Explos., Pyrotech.* **2014**, *39*, 545.
3. Provatas, A. *Energetic Polymers and Plasticizers for Explosive Formulations*: *a Review of Recent Aadvances DSTO-TR-0966*; DSTO Aeronautical and Maritime Research Laboratory, Commonwealth of Australia, 2000, p. 38.
4. Petrov, V. A.; Kuznetsova, N. V.; Pleshakov, D. V. *Herald of KGTU* **2011**, *15*, 332.
5. Petrov, V. A.; Kuznetsova, N. V.; Averianova, N. V.; Gubaidullin, A. T.; Mukhametshin, T. I. *J. Struct. Chem.* **2015**, *56*, 324. [*Zh. Strukt. Khim.* **2015**, *56*, 339.]
6. Petrov, V. A.; Averianova, N. V.; Kuznetsova, N. V.; Kostochko, A. V. *Herald of KGTU* **2012**, *15*, 10.
7. Petrov, V. A.; Mingazova, V. K. *Vestn. KGTU* **2013**, *16*, 87.
8. Mikhailov, Yu. M.; Badamshina, E. R. *Energetic Polymers: Synthesis, Structure, Properties* [in Russian]; GosNIP "Raschet", Moscow, 2008, p. 66.
9. Garaev, I. Kh.; Kostochko, A. V.; Petrov, A. I.; Ibragimov, E. N.; Golubev, A. E. *Russ J. Gen. Chem.* **2016**, *86*, 1459. [*Ros. Khim. Zh.* **2014**, *58*, 21.]
10. Farthing, A. C. *J. Chem. Soc.* **1955**, 3648.
11. Rose, J. B. *J. Chem. Soc.* **1956**, 542.
12. Furukawa, J. *J. Macromol. Sci., Chem.* **1972**, *A6*, 993.
13. Dreyfuss, M. P. *J. Macromol. Sci., Chem.* **1973**, *A7*, 1361.
14. Plesh, P. *Cationic Polymerization* [Russian translation]; Mir: Moscow, 1966, p. 367.
15. Furukawa, J.; Saegusa, T. *Polymerization of Aldehydes and Oxides*; Wiley-Interscience: New York, 1963, p. 125.
16. Bresler, S. E.; Erusalimskii, B. L. *Physics and Chemistry of Macromolecules* [in Russian]; Nauka: Moscow, 1965, p. 387.
17. Erusalimskii, B. L. *Ionic Polymerization of Polar Monomers* [in Russian]; Nauka: Leningrad, 1970, p. 130.
18. Rozenberg, B. A.; Irzhak, V. I.; Enikolopyan, N. S. *Interchain Exchange in Polymers* [in Russian]; Khimiya: Moscow, 1975, p. 122.
19. Dreyfuss, M. P. *J. Macromol. Sci., Chem.* **1975**, *A9*, 729.
20. Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Cationic Ring-Opening Polymerization*; *Adv. Polym. Sci.*; Springer Verlag: Berlin, 1985, Vol. 68/69, p. 317.
21. Matyjaszewski, K.; Müller, A. H. E. *Controlled and Living Polymerizations: From Mechanisms to Applications*; Willey-VCH: Weinheim, 2009, p. 241.
22. Hatano, M.; Kambara, S. *J. Polym. Sci.* **1959**, *35*, 275.
23. Saegusa, T.; Imai, H.; Hirai, S.; Furukawa, J. *Makromol. Chem.* **1962**, *53*, 203.
24. Kropachev, V. A.; Dolgoplosk, B. A.; Geller, N. M.; Rozinoer, A. M. *Vysokomol. Soedin.* **1959**, 1, 1844.
25. Kropachev, V. A.; Alferova, L. V.; Dolgoplosk, B. A. *Vysokomol. Soedin.* **1963**, 5, 994.
26. Penczek, S. *J. Polym. Sci.*, *Part A: Polym. Chem.* **2000**, *38*, 1919.
27. Penczek, S.; Kubisa, P. In *Cationic Ring-opening Polymerization: Ethers in Comprehensive Polymer Science*; Alen, G., Ed.; Pergamon Press: Oxford, 1989, Vol. 3, p. 751.
28. Penczek, S.; Kubisa, P. *Makromol. Chem.* **1969**, *130*, 186.
29. Colclough, R. O.; Wilkinson, K. *J. Polym. Sci.*, *Part C: Polym. Symp.* **1963**, *4*, 311.
30. Kubisa, P.; Brzezinski, J.; Penczek, S. *Makromol. Chem.* **1967**, *100*, 286.
31. Hudy, J. A. US patent 2895924A.
32. Goddu, R. F. US patent 2895922A.
33. Ravve, A. *Principles of Polymer Chemistry*; Springer: New York, 1995, p. 177.
34. Inoue, S.; Aida, T. In *Ring Opening Polymerization,* Ivin, K. J.; Saegusa, T., Eds.; Elsevier: New York, 1984, Vol. 1, p. 185.
35. Dreyfuss, M. P.; Dreyfuss, P. In *Oxetane Polymers in Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Kroschwitz, J. I., Eds.; Wiley: New York, 1987, 2nd ed., Vol. 10, p. 653.
36. Penczek, S.; Kubisa, P. In *Cationic Ring-opening Polymerization: Ethers in Comprehensive Polymer Science*; Alen, G., Ed.; Pergamon Press: Oxford, 1989, Vol. 3, p. 751.
37. Desai, H. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: New York, 1996, Vol. 11, p. 8268.
38. Vandenberg, E. J.; Mullis, J. C.; Juvet, R. S. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3083.
39. Vandenberg, E. J.; Mullis, J. C.; Juvet, R. S.; Miller, T.; Nieman, R. A. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 3113.
40. Magnusson, H.; Malmstron, E.; Hult, A. *Macromolecules* **2001**, *34*, 5786.
41. Magnusson, H.; Malmstron, E.; Hult, A.; Johansson, M. *Polymer* **2002**, *43*, 301.
42. Sikder, A. K.; Reddy S. *Propellants, Explos., Pyrotech.* **2013**, *38*, 14.
43. Malik A. A.; Manser G. E.; Archibald T. G. US Patent 1995/5650483.
44. Sanderson, A. J.; Edwards, W. WO Patent 2000034350 A2.
45. Chugunov, P. A.; Chinarev, A. A.; Tuzikov, A. B.; Formanovsky, A. A.; Prokhorov, V. V.; Gambaryan, A. S.; Bovin, N. V. *Mendeleev Commun.* **2009**, *19*, 62.
46. Tan, W. Q.; Zhao, X. D.; Yu, Z. K. *J. Organomet. Chem.* **2007**, *692*, 5395.
47. Soga, T.; Kudo, H.; Nishikubo, T.; Sato, S. *Polym. J. (Tokyo, Jpn.)* **2008**, *40*, 832.
48. Larkin, P. *Infrared and Raman Spectroscopy*; Elsevier: Oxford, 2011, p. 74.
49. Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Vyvyan, J. A. *Introduction to Spectroscopy*; Brooks Cole: Boston, 2008, p. 50.
50. Lipatov, Yu. S.; Shilov, V. V.; Gomza, Yu. P.; Kruglyak, N. E. *X-ray Methods for the Study of Polymeric Systems* [in Russian]; Nauk. dumka: Kiev, 1982, p. 3.

51. Svergun, D. I.; Feigin, L. A. *Small-angle X-ray and Neutron Scattering* [in Russian]; Nauka: Moscow, 1986, p. 154.
52. Carraher, C. E., Jr. *Carraher's Polymer Chemistry*; Taylor&Francis: Boca Raton, 2011, 8th ed., p. 55.
53. Sharnin G. P.; Falyakhov I. F. *Chemistry of Energetic Compounds. Volume 2: N-, O-Nitrocompounds, Furoxans, Furazans, Azides, Diazo Compounds* [in Russian]; KNITU: Kazan, 2011, p. 246.
54. Blaskovich, M. A.; Evindar, G.; Rose, N. G. W.; Wilkinson, S.; Luo, Y.; Lajoie, G. A. *J. Org. Chem.* **1998**, *63*, 3631.
55. Barbieri, U.; Polacco, G.; Paesano, E.; Massimi, R. *Propellants, Explos., Pyrotech.* **2006**, *31*, 369.
56. Overberger, C. G.; Okamoto, Y.; Bulacovschi, V. *Macromolecules* **1975**, *8*, 31.
57. Wilson, E. R.; Frankel, M. B. *J. Org. Chem.* **1985**, *50*, 3211.