POLY(AMIDE-IMIDE)S CONTAINING POLYBUTADIENE BLOCKS

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Poly(amide-imide)s containing polybutadiene blocks were prepared by reaction of 4,4'-methylenedi(phenyl isocyanate) with trimellitic anhydride and α,ω-diisocyanatopoly-butadiene. The polymers were characterized by spectroscopic methods and X-ray diffraction. Incorporation of 5 wt.% of polybutadiene structures into polyimide decreases the temperature of 10% weight loss in nitrogen by 90 °C. Glass transition temperature of the polymer also decreases with the increasing content of soft polybutadiene segments, but the decrease is moderate for the contents higher than 20 wt.%. Broad amorphous halo dominates wide-angle X-ray diffractograms of all the samples, but sharper peaks of a more ordered structure were observed in definite concentration range of polybutadiene blocks. The copolymers are soluble in N-methylpyrrolidone.
Key words: Copolymers; Polyimides; Poly(amide-imide)s polybutadiene blocks; Thermal stability; X-ray diffraction; Synthesis.

Polycondensation reaction of low-molecular-weight polyamides, polyurethanes, polyethers *etc.*, containing isocyanate end-groups, with aromatic diisocyanates and aromatic dianhydrides is a well-tried synthetic route leading to variety of block copolymers containing polyimide structure[1–3]. The attractivity of such modification of various polymers by imide cyclic structures consists in excellent thermal and mechanical properties of polyimides[4,5]. Aromatic polyimides generally show high relaxation transition temperatures, compared with most commercially available polymers, which make it possible to preserve their high modulus and tensile strength at exceptionally high temperatures. Therefore, incorporation of imide moieties among polymer segments of an other chemical structure by the above mentioned polycondensation reaction is motivated by the effort to increase thermal and high-temperature mechanical properties without the danger of macroscopic demixing typical of polymer blends[6–13].

An interesting way of molecular reinforcement of a soft polymer with stiff segments seemed to be preparation of poly(butadiene-imide)s containing oligobutadiene blocks of definite length. Suitable telechelic oligomers can be prepared by application of organodilithium-based initiator to living anionic polymerization of butadiene and subsequent proper termination and chemical modification of chain ends. This procedure leads to preparation of an isocyanate-end-capped oligobutadiene having definite molecular weight and low index of polydispersity[14]. Previously we used such telechelic oligomers in the reaction with 3,3′,4,4′-benzophenone-tetracarboxylic acid dianhydride (BTDA) and 4,4′-methylenedi(phenyl isocyanate)[15] (MDI). Unfortunately, such poly(butadiene-imide)s are suitable just for preparation of elastomers with relatively low contents of polyimide structures since a higher concentration of imide moieties makes the copolymer insoluble in common solvents.

In this work, related poly(butadiene-amide-imide)s were synthesized by replacing BTDA with trimellitic anhydride (TMA). Poly(amide-imide)s are more soluble than polyimides and therefore they might be more suitable for modification of polybutadiene with high concentration of stiff segments containing imide structures. This communication describes our effort to develop the above mentioned copolymers and to show some of their basic physicochemical and physical properties.

EXPERIMENTAL

Materials

The α,ω-diisocyanato-polybutadiene LBD-3000 was obtained from Kaučuk Co., Kralupy. M_n of individual samples was 3 500 ± 300, with concentration of isocyanate groups 730 mmol/g (samples 2, 3) and 719 mmol/g (samples 4–7), respectively, because of different concentration of the free MDI. The polydispersity index of the main fraction was M_w/M_n = 1.3, but minor peak in the range of short retention times was also observed. The oligomers contained 60% of 1,2-, 25% of 1,4-*trans*, and 15% of 1,4-*cis* structure units.

Trimellitic anhydride (TMA, Aldrich) was purified by sublimation and 4,4′-methylenedi(phenyl isocyanate) (MDI, Aldrich) was purified by pressure filtration at 60 °C (ref.[16]). Anhydrous *N*-methylpyrrolidone (NMP, Aldrich, water content <0.01 wt.%) was used as received.

Synthesis

4-(Phenylcarbamoyl)phthalimide (**1**) was synthesized by the reaction of chloride of TMA (9.5 mmol) with aniline (19 mmol) and pyridine (2 ml) in NMP (35 ml) at 160 °C for 3 h. The crude product was isolated by precipitation into water and crystallized twice from nitromethane. Yield 83%, m.p. 208 °C. FTIR (KBr): 3 476, 3 344 (NH, amide); 3 060 (CH,

arom.); 1 780 (C=O, imide); 1 646 (C=O, amide); 1 600 (C=C, arom.); 1 540 (NH, amide). ^{1}H NMR (DMSO-d_6): 10.57 s (CONH); 7.07–8.49 m (arom.). For $C_{21}H_{14}N_2O_3$ (342.8) calculated: 73.57% C, 4.12% H, 8.17% N; found: 73.49% C, 4.32% H, 8.25% N.

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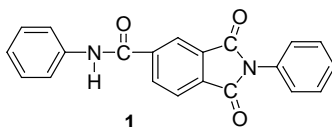
Synthesis of Poly(butadiene-amide-imides)

Diisocyanates (MDI, LBD-3000) were dissolved in NMP in a glass reactor equipped with a nitrogen inlet and $CaCl_2$ drying tube. Then an equimolar amount of solid TMA was added into the reaction mixture and the reactor was heated in an oil bath at 70 °C for 90 min. The solid content (including LBD-3000) was 15 wt.%. Then the temperature 90 °C was maintained for 90 min, 130 °C for 120 min, 150 °C for 180 min, and 180 °C for 60 min. The polymer was then precipitated into water and washed with THF.

Measurements

Infrared spectra of samples in the form of KBr pellets were measured using a Bruker IFS 55 FTIR spectrometer. ^{1}H NMR spectra were recorded on a Bruker ACF-300 spectrometer at 25 °C in DMSO-d_6. Viscometric measurements were carried out in an Ubbelohde viscometer at 25 °C in *m*-cresol. Concentration of samples was 0.001 g/cm^3. Wide-angle X-ray diffractograms were measured with a HZG4A automatic powder goniometer. CuKα radiation was registered with scintillation counter and monochromatized with Ni filter and pulse-height analyzer. The diffractograms were performed in θ/2θ scan in the scattering angle range 2θ 4–40°. Small-angle X-ray scattering curves were measured using a Kratky camera in the region of the scattering vector q = 0.1–2.0 nm^{-1}. The scattering vector is defined as q = $(4\pi/\lambda)/\sin\theta$, where λ is the wavelength and 2θ is the scattering angle. CuKα radiation was registered using a position-sensitive detector[17] (Joint Institute for Nuclear Research, Dubna, Russia). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out using Perkin–Elmer DSC-7 and TGA-7 instruments, respectively, with a heating rate 10 °C/min in both cases.

RESULTS AND DISCUSSION

Poly(amide-imide)s containing polybutadiene blocks, poly(amide-imide) TMA/MDI and poly(α,ω-diisocyanato-polybutadiene-*co*-trimellitic anhydride), were synthesized by a well-tried method consisting in reaction of TMA with aromatic diisocyanates[18] (Scheme 1). This reaction is based on the reactivity of –N=C=O groups both with anhydride group, resulting in the formation of cyclic imide[19], and with carboxylic group, leading to amide structures[20]. Traces of water are necessary for a quantitative imide ring formation[21]. Therefore, no further drying of commercially available

pre-dried solvent was used. Moreover, numerous organometallic compounds (alkali metal alkoxides, phenoxides, naphthoxides, lactamates, *etc.*) are known to catalyse the amide bond formation[20]. On the other hand, basic catalysts, in particular sodium alkoxides, promote undesirable cyclotrimerization of isocyanate groups[22]. Since organometallics and traces of water would deactivate each other, we did not add any special catalyst into the reaction system and carried out the reaction at high temperatures (up to 177 °C), in spite of the fact that a few side reactions can take place under such condition, as it is published in literature (in particular, the reaction of isocyanate end-goups with solvent – NMP, ref.[18]).
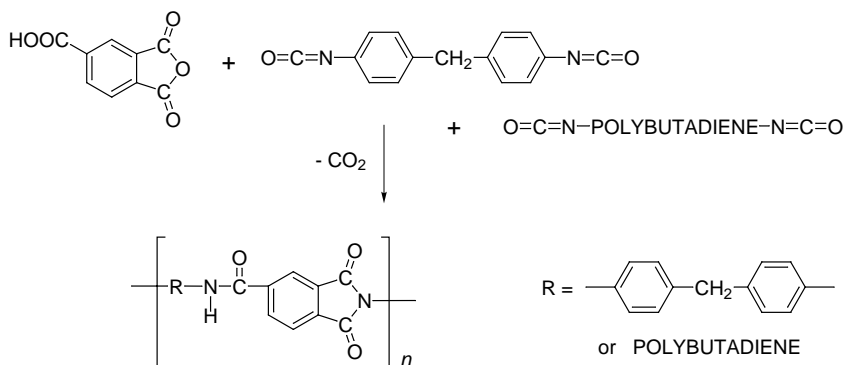
SCHEME 1

Basic characteristics and composition of (co)polymers are shown in Table I. The yields and inherent viscosities are comparable with those of related poly(butadiene-imide)s and other high-performance polymers. But in contrast to related poly(butadiene-imide)s, the (co)polymers in question are well soluble in NMP even at low or zero contents of butadiene blocks.

In Fig. 1, FTIR spectra of poly(amide-imide) TMA/MDI (*a*) and copolymer sample 6 (*b*) are shown. The spectrum of neat poly(amide-imide) (sample 1) contains absorption bands which are typical of macromolecules containing amide and imide groups. Characteristic absorption bands of the amide moiety[23] appear at 1 778 [ν_s(C=O)], 1 722 [ν_{as}(C=O)], 1 376 [ν(C=N], 726 [δ(C=O)], and those of amide group[24] can be seen at 1 660 [ν(C=O)] and 1 540 cm^{-1} [δ(N–H)]. The same absorption bands are also obvious in the spectrum of copolymer (*b*). In addition, absorptions of polybutadiene occur[25]. The strong absorption in the region 1 640–1 665 cm^{-1} indicates the presence of bands corresponding to C=C stretching vibrations of both 1,2- and *trans*-1,4-polybutadiene structures. Weaker absorption bands in the range

994–1 000 cm^{-1} are located in the range of the C–H out-of-plane vibrations of both mentioned polybutadiene isomers.

^{1}H NMR spectra are too complex to give an evidence of any side reactions. On the other hand, strong singlet of amide proton (at 10.4 ppm for the copolymer and 10.5 ppm for poly(amide-imide)s, several overlapping multiplets in the range 7.0–8.5 ppm (corresponding undoubtedly to aromatic protons) confirm the aramide-type structures in the (co)polymer.

TABLE I
Content of LBD-3000, yield, inherent viscosity, and glass transition temperature of poly-(amide-imide)s containing polybutadiene (LBD-3000) blocks

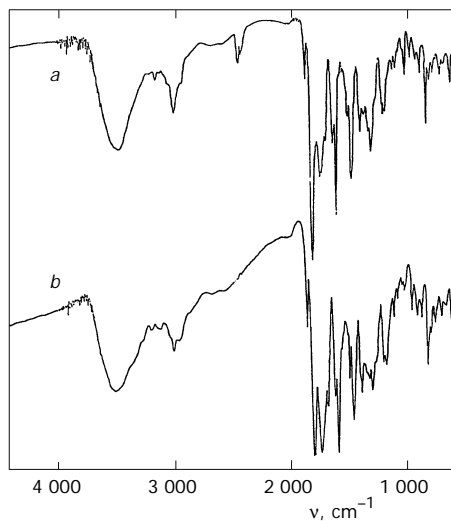| Sample	LBD-3000 content wt.%	Yield, %	η_{mn}, dL/g	T_g, °C
1	0	94	0.89	255
2	5	89	0.80	–
3	8	89	0.90	211
4	16	91	1.22	206
5	18	82	0.54	202
6	42	96	1.05	193
7	94	92	0.39	–

FIG. 1
FTIR spectra of poly(amide-imide) TMA/MDI (sample 1) (a) and sample 6 (b)

Thermal stability of (co)polymers was characterized by temperatures of 10% (T_{10}) and 20% (T_{20}) weight loss. As can be seen in Fig. 2, incorporation of 5 wt.% of polybutadiene into the poly(amide-imide) chain leads to a decrease in thermal stability by 90 °C. However, further increase of polybutadiene content in copolymers causes relatively smaller drop of the respective initial decomposition temperature (Fig. 2). Further increase of polybutadiene content in copolymers does not decrease decomposition temperatures (T_{loss}). On the other hand, as follows from Fig. 3, total weight loss for poly(butadiene-amide-imide)s at temperatures up to 550 °C considerably
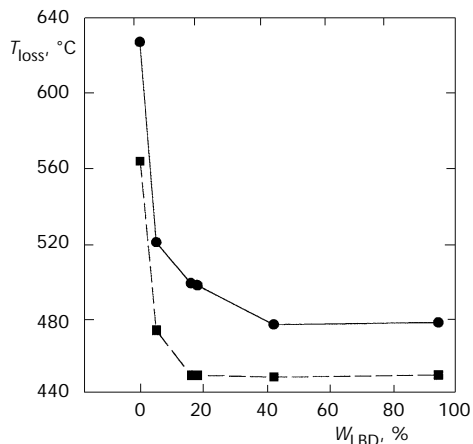

FIG. 2

The dependence of 10% weight loss (■) and 20% weight loss (●) on the weight fraction of LBD-3000, W_{LBD}, in TGA experiments in nitrogen
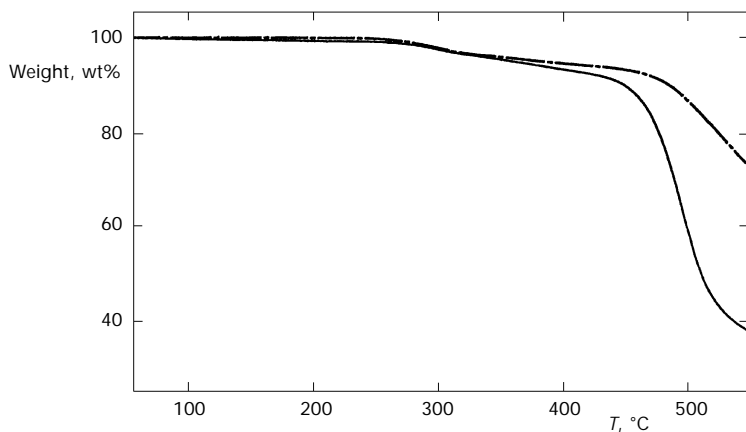

FIG. 3

TGA curve in nitrogen for poly(amide-imide) (sample 1, – – –) and poly(butadiene-amide-imide) containing 5 wt.% polybutadiene (sample 2, ——)

exceeds the value corresponding to T_{20}, strongly reflecting the effect of thermally labile polybutadiene blocks.

Polubutadiene segments flexibilize copolymer chains, so that just an addition of 8 wt.% of these soft blocks leads to a decrease in the glass transition temperature T_g by 45 °C, as it can be seen from Table I. Further increase in the concentration of polybutadiene does not influence T_g considerably, probably due to the limited miscibility of soft polybutadiene, and hard poly(amide-imide) blocks.

Wide-angle X-ray diffraction (WAXD) patterns of the (co)polymers are shown in Fig. 4. All samples exhibit a broad amorphous halo, the maximum of which is slightly shifted to lower values of 2θ with increasing polybutadiene content. While the neat poly(amide-imide) (sample 1) has maximum at 2θ = 20°, which corresponds, according Bragg's law, to the average interchain distance d = 4.4 Å, sample 7 showed the maximum at 2θ = 18° corresponding to the interchain distance d = 4.9 Å. Difractograms of samples 4 and 6 (sample 5 was not measured since its composition is almost the same as that of sample 4) show one additional, relatively sharp but very weak peak demonstrating appearance of an ordered structure. From the position of this peak at the diffraction angle 2θ = 25°, the corresponding Bragg's distance d = 3.5 Å was calculated. These peaks might reflect intersegmental distance of rigid TMA-related segments, since in some
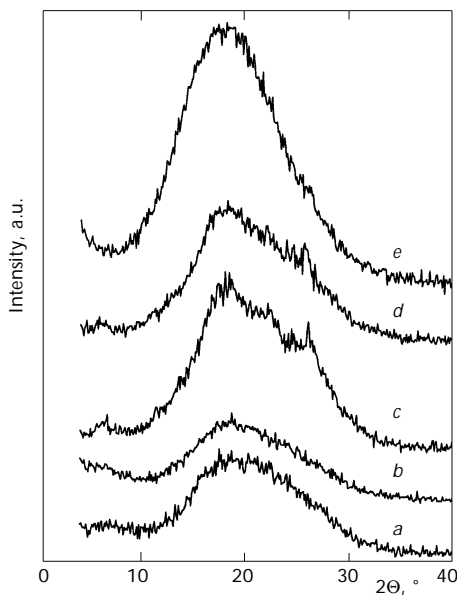

FIG. 4
Wide-angle X-ray diffractograms of (co)polymers: sample 1 (*a*), sample 2 (*b*), sample 4 (*c*), sample 6 (*d*), sample 7 (*e*)

BTDA-based polyimides[26], intersegmental distances between two diimide structures were observed by means of WAXD.

The existence of a partially ordered structure only in a discrete range of polybutadiene content can be explained by the flexibilizing effect of such soft segment. Since steric hindrance of rigid poly(amide-imide) chains, composed dominantly from heterocyclic and aromatic rings and intermolecular H-bond-forming amide structures, prevents reorganization in the (co)polymer, there are no sharp peaks in samples 1 and 2 (*i.e.*, those with no or very low contents of polybutadiene). An increase in the content of soft segment flexibilizing macromolecules might enable partial ordering of TMA-related structures and therefore sharp peaks in Fig. 4, diffractograms *b* and *c* (samples with 18 and 42 wt.% of polybutadiene) were observed. Further increase in polybutadiene concentration leads to dilution of such stiff segments so that they cannot approach each other to form a more compact structure. This assumption is supported by the absence of the ordering in sample 7 (Fig. 4, diffractogram *e*).

In order to get more information about the origin of the ordering in some samples, the TMA-related model compound, 4-(phenylcarbamoyl)phthalimide (**1**), was synthesized and its WAXD pattern was measured. The diffractogram (Fig. 5) is clearly more complicated and the peaks are much sharper in comparison with those in copolymers because of the
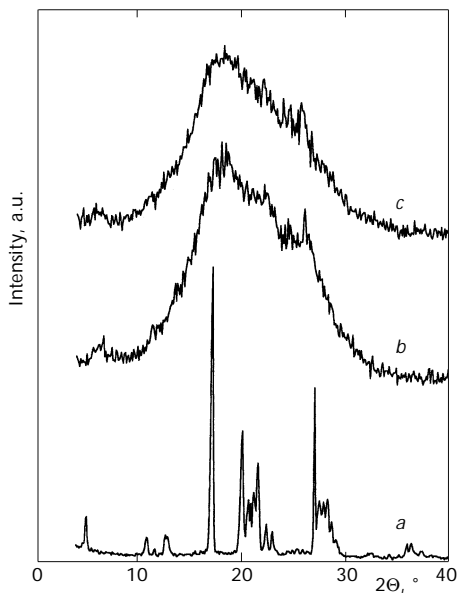

Fig. 5

Wide-angle X-ray diffractograms of 4-(phenyl-carbamoyl)phthalimide (*a*), sample 4 (*b*), sample 6 (*c*)

low-molecular-weight nature of the crystalline model compound. Two distances, d = 4.1 and 3.3 Å, are close to those in WAXD patterns of the copolymers, which indicates the possibility that sharp peaks in Fig. 4 (diffractograms b and c) originate from stiff TMA-related structures similar to the model. On the other hand, some distances (in particular the intensive sharp peak corresponding to d = 5.2 Å) are not presented in the diffractogram of the model. This fact can be explained either by not exactly the same orientation of the model and the stiff TMA-related segments in copolymers or by non-identical structure of copolymer segments in question and 4-(phenylcarbamoyl)phthalimide (the real stiff TMA-related segment in the copolymer is larger than in a case of model compound).

Small angle-X-ray scattering (SAXS) patterns of the same (co)polymer samples are shown in Fig. 6. Curves of scattering intensity, I, vs scattering vector, q, show a relatively sharp increase in the intensity for $q \rightarrow 0$ (even the sample 1 – neat polyamid-imide). Therefore, we believe that microvoids of air (commonly present in polymers like polyimides) are present. Besides, SAXS curves of the copolymers exhibit a slight shoulder in the range of the scattering vector q = 0.2–0.4 nm^{-1}. This faint maximum can be attributed to the formation of the supermolecular structure typical of copolymers.

FIG. 6
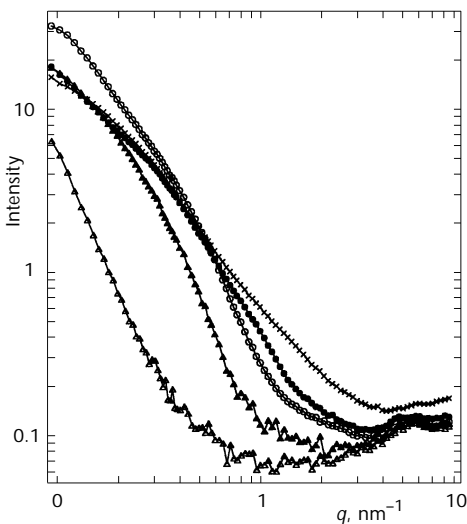Small-angle X-ray scattering curves: sample 1 (△), sample 2 (▲), samle 4 (○), sample 6 (●), sample 7 (×)

REFERENCES

1. Wang H.-H., Su C.-C.: *J. Appl. Polym. Sci.* **1996**, *61*, 1087.
2. Jeon J. Y., Tak T.-M.: *J. Appl. Polym. Sci.* **1996**, *62*, 763.
3. Sendijarević A., Sendijarević V., Frisch K. C., Korug-Lazarević B., Torlić E. J.: *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3603.
4. Sroog C.-E., Endrey A. L., Abramo S. V., Berr C. E., Edwards W. M., Olivier K. L.: *J. Polym. Sci., Part A-3* **1965**, 1371.
5. Jordan R.: *Seifen-Öle-Fette-Wachse* **1988**, *114*, 825.
6. Tsutsumi N., Tsuji A., Horie C., Kiotsukuri T.: *Eur. Polym. J.* **1988**, *24*, 834.
7. Nishi S., Sasaki S., Hasuda Z.: *ACS Polym. Prep.* **1987**, *28*, 175.
8. Scola D. A., Brunette C. M.: *Sampe J.* **1987**, *23*, 41.
9. Alonso M. A., Shaw M. T.: *Polym. Mater. Sci. Eng.* **1988**, *59*, 1182.
10. Tieke B., Gabriel W.: *Polymer* **1990**, *31*, 20.
11. Kareka R. J., Porter R. S.: *Polymer* **1992**, *33*, 4866.
12. Jo W. H., Lee M. R., Liu G. B., Lee M. S.: *Polym. Bull. (Berlin)* **1994**, *33*, 113.
13. Spontak J. R., Williams M. C.: *Polym. J.* **1988**, *20*, 649.
14. Čermák J.: *Plasty Kauc.* **1995**, *32*, 360.
15. Marek M., Holler P., Schmidt P., Schneider J., Kovářová J., Kelnar I., Pytela J., Sufčák M.: *Polym. Int.*, submitted.
16. Yu X. H., Okoma A. Z., Cooper S. L.: *J. Appl. Polym. Sci.* **1990**, *41*, 1977.
17. Chernenko S. P., Cherekhina G. A., Fateev O. V., Smykov L. P., Vasilev S. E., Zanevsky Yu. V., Kheiker D. M., Popov A. N.: *Nucl. Instrum. Methods Phys. Res., Sect. A* **1994**, *348*, 261.
18. Terney S., Keating J., Zielinski J., Hakala J., Sheffer H.: *J. Polym. Sci., Part A-1* **1970**, *8*, 683.
19. Sillion B. in: *Comprehensive Polymer Science* (G. Allen and J. C. Bevington, Eds; A. Ledwith, S. Russo and P. Sigwalt, Vol. Eds), Vol. 5, p. 499. Pergamon Press, Oxford 1989.
20. Onder K. B., Andrewa P. S., Farissey W., Tilled J. N.: *ACS Polym. Prepr.* **1980**, *21*, 132.
21. Carleton P. C., Farrissey W. J., Jr., Rose J. S.: *J. Appl. Polym. Sci.* **1972**, *16*, 2983.
22. Kresta J. E., Hsien K. H.: *ACS Polym. Prepr.* **1980**, *21*, 126.
23. Ishida H., Wellinghoff S. T., Baer E., Koenig J. L.: *Macromolecules* **1980**, *13*, 826.
24. Schneider B., Schmidt P., Marek M., Straka J., Bednář B., Králíček J.: *Eur. Polym. J.* **1990**, *26*, 941.
25. Schmidt P., Roda J., Nováková V., Pastor J. M.: *Angew. Makromol. Chem.* **1997**, *245*, 113.
26. Wakelyn N. T., Platt J. R.: *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 2833.