EFFECT OF LITHIUM *tert*-ALKOXIDES ON ANIONIC POLYMERIZATION OF BUTADIENE INITIATED WITH A BIFUNCTIONAL INITIATOR

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Polymerization of buta-1,3-diene initiated by bifunctional dilithium initiator in *tert*-butyl methyl ether, hexane and hexane–toluene mixtures was studied in the presence of Li *tert*-butoxide, 2-methylpentan-2-olate, 3-methylpentan-3-olate or 2,3-dimethylbutan-2-olate. The alkoxides lower the overall polymerization rate and affect, to a certain extent, microstructure of formed polymers. When applied in a concentration equal to that of the initiating centres, they lower the content of vinyl structures in polybutadiene by 10–12%. Increasing concentration of the alkoxide has no perceptible effect and, if used in 12-fold excess over the initiator, the content of 1,2-structures even increases. Polymers prepared in the presence of an alkoxide mostly have unimodal and narrow MWDs.
**Key words**: Anionic polymerization; Polybutadiene; *tert*-Alkoxides; Microstructure; Polymers.

Microstructure of polybutadiene (PB) prepared anionically is determined mainly by polarity of the solvent used and by the counterion type[1,2]. The active polymerization centre with the character of allylic ionic pair can have *cis* or *trans* configuration (Scheme 1), their relative contents depending on polarity of the solvent and temperature[3–7]. In a non-polar solvent, the *cis* centre reacts prevailingly in α-position giving *cis*-1,4-polymer,
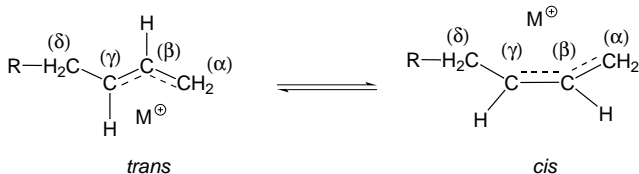
SCHEME 1

whereas in a polar medium, the charge is located rather on the γ-carbon atom so that mainly 1,2-polymer is formed[8–10]. In aliphatic hydrocarbons, the 1,4-PB is a mixture of *cis* and *trans* configurations, the composition of which depends on the monomer : initiator mole ratio[11]. A simple mechanistic explanation[12] is based on competition between addition of the monomer onto *cis* centre and its isomerization into a more stable *trans* centre (Scheme 2). In hydrocarbon, PB-Li as well as polyisoprene-lithium are aggregated[13,14] so that the polymerization kinetics is most probably more complex[15,16].
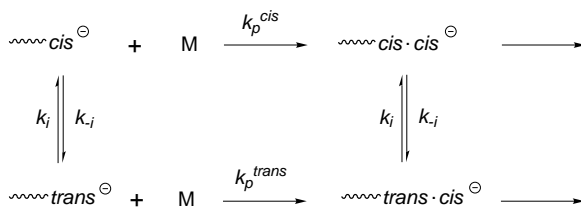

SCHEME 2

In polar media, the self-aggregates are assumed to be dissociated down to unimer centres[2], the negative charge on the γ-C atom increasing at the expense of α-C position[5,17–19]. It is assumed that 1,2-units are mostly formed on the *trans*-type centre[20] and that the highly solvated Li counterion is located near the α-carbon atom forming steric hindrance for the monomer addition at this site[21]. Addition of Lewis bases, such as *N,N,N′,N′*-tetramethylethane-1,2-diamine (TMEDA) or 1,2-dipiperidinoethane (DIPIP), leads to completely dissociated species and causes charge localization on the γ-carbon atom increasing distinctly the content of vinyl structures in polydienes[22].
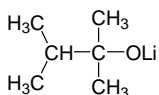
When initiated with bifunctional initiators, polymerization offers a way to triblock copolymers, *e.g.*, of dienes and styrene; however, common bifunctional initiators (*e.g.*, Li naphtalenide) are not well soluble in hydrocarbons or form various self-aggregates which leads to a polymer with a broad or even bimodal MWD (ref.[23]). This was found, for instance, in the polymerization initiated by a product of addition of BuLi onto 1,3-bis(1-phenylethenyl)benzene[24–26]. To avoid this, a small amount of a polar solvent (TMEDA, *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine – PMDETA, or anisole) has to be added into the polymerization mixture[27,28]; polymer with a narrow unimodal MWD is formed having, however, a high content of 1,2-microstructure units. Similar results were obtained when the adduct of *sec-* or *tert*-BuLi onto 1,3-diisopropenylbenzene was used as an

initiator[29,30]. In a mixture cyclohexane–diethyl ether (100 : 5, v/v), the initiator is completely bifunctional and the product contains 40–50% of 1,2-units. Lithium alkoxides, if used in concentrations from 0.1 to 1.01 mol per mol of the Li initiator, also enhance the functionality of initiator, but, in contrast to Lewis bases, they do not perceptibly change the microstructure of the formed polymer[31]. Methoxide, ethoxide, isopropoxide and *tert*-butoxide were tested and it was found that, except methoxide, all of them have a very similar favourable effect[26].

Owing to the lack of information about the effect of alkoxides on the butadiene polymerization in polar solvents and, moreover, because complexes of BuLi with Li *tert*-alkoxide can be used for polymerization of styrene[32], the following Li *tert*-alkoxides were studied as additives in polymerization of butadiene in polar *tert*-butyl methyl ether (MTBE) or in non-polar hydrocarbons, initiated by a bifunctional Li initiator.
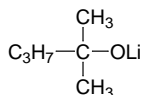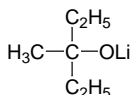
$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OLi$$
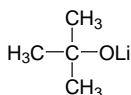
Li *tert*-butoxide
(*t*-BuOLi)

$$\underset{H_3C}{\overset{H_3C}{>}}CH-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OLi$$

Li 2,3-dimethylbutan-2-olate
(2,3-DMBOLi)

$$C_2H_5-\overset{\overset{\displaystyle C_2H_5}{|}}{\underset{\underset{\displaystyle C_2H_5}{|}}{C}}-OLi$$
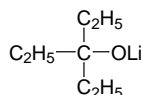
Li 3-ethylpentan-3-olate
(3-EPOLi)

$$C_3H_7-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OLi$$

Li 2-methylpentan-2-olate
(2-MPOLi)

$$H_3C-\overset{\overset{\displaystyle C_2H_5}{|}}{\underset{\underset{\displaystyle C_2H_5}{|}}{C}}-OLi$$

Li 3-methylpentan-3-olate
(3-MPOLi)

EXPERIMENTAL

Butadiene (Kaučuk, Inc., Czech Republic) was predried in ampoules with solid KOH for several days, then condensed into flame-dried thick-wall ampoules with CaH_2. Just before use, a required amount of the monomer was transferred into a dry calibrated dosing ampoule equipped with a valve and stainless steel capilary. MTBE, toluene and hexane were distilled with CaH_2 on a column under argon, transferred into a circulation apparatus, kept there with CaH_2 (MTBE and hexane) or with sodium benzophenone ketyl (toluene) and freshly distilled before use. Dilithium bifunctional initiator (DLB) is a fine dispersion of 1,4-dilithiobutane in MTBE prepared by Kaučuk, Inc. (ref.[33]) and was used as received; content of Li was determined by acidic titration. For the experiments in nonpolar solvents (toluene or hexane, see Table I), MTBE from the initiator was evaporated at sub-zero temperature almost to dryness, replaced by hexane which was again evaporated; the procedure was repeated three times. Finally, hexane was added and, after vigorous stirring of the formed suspension, Li content was determined by acidimetric titration. Li *tert*-alkoxides were prepared and purified in a described way[34] and used as MTBE or hexane solutions.

Polymerizations were performed in a glass reactor Büchi; typically, into MTBE (or another solvent) in the reactor, a calculated amount of DLB was added at 0–5 °C and stirred for 5 min. Then, a solution of the alkoxide was dosed and the mixture was stirred again for 5 min at the same temperature. A first part of the butadiene (about 20% of the total amount) was added quickly at 0–5 °C and stirred under at the same temperature for 10 min, the residual amount of butadiene being dosed slowly at 45 °C. The polymerization time was about 45–120 min in dependence on the presence of an alkoxide in a mixture. Then, the reaction mixture was poured into a methanol–water mixture, MTBE solution of PB was separated and the oily product isolated and dried.

TABLE I
Effect of Li *tert*-alkoxides on microstructure of polybutadiene prepared by DLB

Run	Solvent	Solvent for DLB	Lithium alkoxide	Z^a	SEC		NMR, % triads		
					M_n	M_w/M_n	1,4-*cis*	1,4-*trans*	1,2-
1	MTBE	MTBE	–	–	2 740	1.11	19.2	18.9	61.9
2	MTBE	MTBE	–	–	3 080	1.07	20.2	20.2	59.6
3	hexane	hexane	–	–	1 810	1.16	33.3	22.7	44.0
4	toluene	hexane	–	–	3 100	1.15	65.4		34.6
5	MTBE	MTBE	*t*-BuLi	1 : 1	1 870	1.19	22.2	25.6	52.2
6	MTBE	MTBE	*t*-BuLi	3 : 1	1 550	1.47	20.3	21.7	58.0
7	MTBE	MTBE	*t*-BuLi	12 : 1	3 720	1.90^b	16.9	13.8	70.2
8	hexane	hexane	*t*-BuLi	3 : 1	1 760	1.15	31.7	20.6	47.7
9	toluene	hexane	*t*-BuLi	1 : 1	3 000	1.06	23.5	28.3	48.2
10^c	toluene	hexane	*t*-BuLi	1 : 1	3 430	1.20	28.3	27.8	43.9
11	MTBE	MTBE	3-MPOLi	1 : 2	3 450	1.05	21.5	24.5	54.0
12	MTBE	MTBE	3-MPOLi	1 : 1	3 200	1.11	22.9	26.5	50.6
13	MTBE	MTBE	3-MPOLi	2 : 1	5 300	1.20^d	22.6	28.4	48.9
14	MTBE	MTBE	3-EPOLi	1 : 1	2 000	1.07	23.1	27.2	49.7
15	MTBE	MTBE	3-EPOLi	2 : 1	2 300	1.19^d	22.9	29.3	47.8
16	MTBE	MTBE	2-MPOLi	1 : 1	3 600	1.06	23.6	26.8	49.6
17	MTBE	MTBE	2-MPOLi	2 : 1	3 200	1.06	22.6	25.6	51.8
18	MTBE	MTBE	2,3-DMPOLi	1 : 1	3 400	1.07	23.0	27.0	50.0
19	MTBE	MTBE	2,3-DMPOLi	2 : 1	4 300	1.05	23.0	27.2	49.8

^{a} Mole ratio [alkoxide]$_0$: [centre]$_0$; ^{b} bimodal MWD; ^{c} polymerization performed at 45 °C without cooling in the starting phase; ^{d} hint of bimodality, [But]$_0$ = 1.98–3.81 mol/l, [DLB]$_0$ = 0.065–0.150 mol/l.

Molecular weights were measured by SEC on a Labora apparatus (Czech Republic), equipped with refractometric and UV detectors and with either a wide-range column PL MIXED (Polymer Laboratories, G.B.) or two columns (PSS, Germany) with porosities 10^5 and 10^3 Å at 25 °C with THF as a mobil phase. PL MIXED column was calibrated with PL polystyrene standards, PSS columns were calibrated with PMMA standards of PSS. For treatment of eluograms, the following constants of Mark–Houwink–Sakurada equation[35] were used: $K = 4.57 \cdot 10^{-4}$, $a = 0.693$. They are valid for PBs with low contents of vinyl structures, however, in a wide range of molecular weights ($1–81 \cdot 10^3$). Both the systems gave comparable results. The calculated M_n values are presented in Table I without additional corrections.

Microstructures of the polymers were determined from ^{1}H NMR spectra measured in $CDCl_3$ with a Bruker DPX-300 spectrometer at 300.1 MHz and at room temperature with hexamethyldisiloxane as an internal standard. The contents of 1,2- and 1,4-structures were determined from the region 4.8–5.7 ppm by comparing integrated intensities of vinyl methylidene protons at 4.9 ppm with those at 5.3–5.8 ppm where signals of vinyl methine protons of 1,2-units (5.5–5.8 ppm) and CH=CH protons of 1,4-units appear. The peak at 5.30 ppm corresponds to 1,4-*cis* and that at 5.34 ppm to 1,4-*trans* microstructures. These two peaks are not well separated in the spectrum showing, however, the same linewidth, so that the 1,4-*cis*/1,4-*trans* ratio is determined from their heights, in accordance with literature[36]. The relevant part of ^{1}H NMR spectrum is demonstrated in Fig. 1.

RESULTS AND DISCUSSION

The results of polymerization experiments are summarized in Table I. As expected, in neat polar MTBE, PB with a high content of vinyl structures (61.9%, run 1) and a narrow MWD is formed in accordance with the literature[2]. Addition of one equivalent of *t*-BuOLi with respect to the concentration of Li in the initiator lowers the content of vinyl arrangement in the
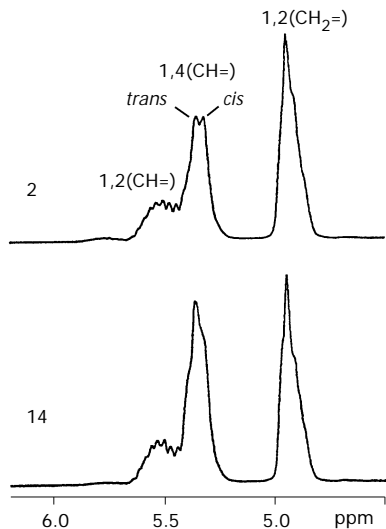

FIG. 1
Parts of ^{1}H NMR spectra of polybutadienes prepared with DLB initiator in MTBE in the presence and absence of alkoxide (curve numbers correspond to the runs in Table I)

formed polymer to 52.2% (see run 5). MWD of this polymer remains narrow and unimodal as that of the product prepared in the absence of the alkoxide (Fig. 2). Three-fold excess of the alkoxide has a less pronounced effect and the system gives a polymer with 58% of 1,2-structure; however, its MWD is broader (run 6). If the content of *t*-BuOLi is high (run 7, twelve-fold excess of the alkoxide over the initiator), the behaviour of the system distinctly changes. The product in this case has a high content of vinyl structures, even higher than the polymer prepared in the absence of the additive, and its MWD is clearly bimodal (Fig. 3). The bimodality of the molecular weight distribution indicates multiplicity of active species in the intiator and/or in the growing chains which is probably caused by formation of different complexes between the alkoxide and the active species. It is well known from the results of foregoing studies[37] that *tert*-alkoxides form self-aggregates in polar solvents. Consequently, if the self-aggregates themselves act as the ligands in the complex of the active centre and alkoxide, they can form steric hindrance to addition of the monomer onto the α-carbon atom of the allylic-type carbanion at the end of growing chain in the sense of Bywater's idea[20]. Thus, addition of butadiene onto γ-carbon atom is preferred leading to formation of 1,2-structure (Scheme 1). Also, some of the complexes containing a high part of the alkoxide can have distinctly lowered reactivity and, thus, the initiator and/or growing chain be-
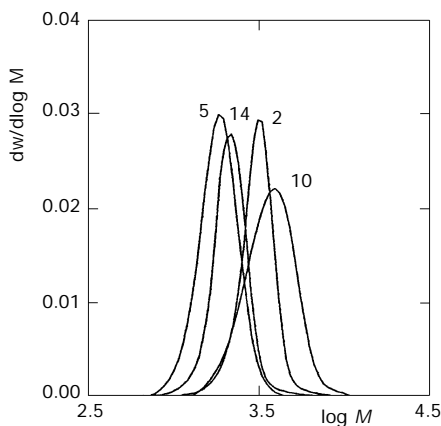

FIG. 2
MWD curves of polybutadienes prepared with DLB initiator in MTBE with and without alkoxide addition (curve numbers correspond to the runs in Table I)
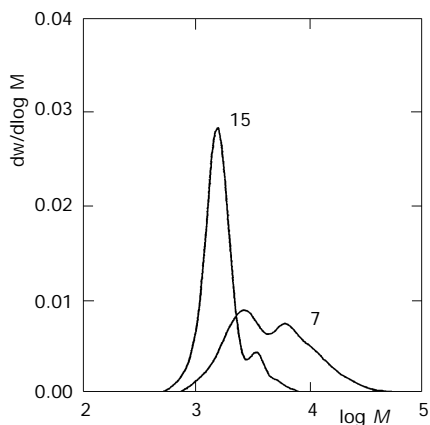
FIG. 3
MWD curves of polybutadienes prepared with DLB initiator in MTBE with and without alkoxide addition (curve numbers correspond to the runs in Table I)

have in such case as monofunctional. The efect of the increasing content of *t*-BuOLi on microstructure of PB prepared in MTBE is also seen in Fig. 4. Polymerizations in toluene (run 4) or in hexane (run 3) initiated by DLB transferred into hexane (see Experimental) give products with lowered contents of 1,2-microstructure which are, surprisingly, lower in toluene than in hexane. Nevertheless, in both the cases, the content of vinyl structures is higher than that found earlier for polymerizations initiated by Li initiators in non-polar hydrocarbons[31]. This difference can originate in the transfer of DLB from MTBE into hexane (see Experimental) because evaporation can probably hardly ensure complete replacement of the ether by hydrocarbon and even small and various amounts of MTBE can affect the microstructure of the prepared polymer. In the polymer, prepared in hexane (run 3), *cis* configuration distinctly prevails in the 1,4-structure. Addition of *t*-BuOLi has no perceptible effect on polymerizations in hydrocarbons; the contents of vinyl structures are almost the same, just slightly higher than in polymerization without the additive. Again, in the product from hexane, the content of 1,4-*cis* structure is about 50% higher than that of 1,4-*trans* (run 8). In runs 9 and 10, the effect of reaction temperature can be seen because in run 10, polymerization was performed at 45 °C without cooling in the starting phase (see Experimental), so that the content of vinyl structures is slightly lower than that in run 9, which is in agreement with literature data[10]. The mentioned polymers, prepared in hydrocarbons, have narrow and unimodal MWD curves (Fig. 2), indicating that the processes are controlled by one type of active centres, probably bifunctional. This is corroborated by the fact that MWD curves of the polymers are symmetrical without any hint of bimodality which would indicate the co-existence of mono- and bifunctional centers; this is in contrast to the results of Teyssié[38] who
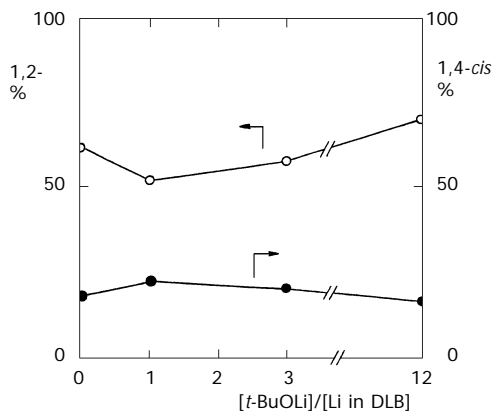

FIG. 4

Dependence of microstructure of polybutadienes prepared with DLB initiator in MTBE on the content of *t*-BuOLi; [*t*-BuOLi] : [Li in DBL] represents mole ratio of *t*-BuOLi to active centres of polymerization

observed non-symmetrical MWDs for PBs prepared by bifunctional initiator in hydrocarbon medium in the presence of *t*-BuOLi. The traces of residual MTBE in the hydrocarbon polymerization systems can also play a favourable role in this sense. In our study, hints of bimodality were observed in two experiments which were performed in neat MTBE in the presence of two-fold excess of 3-EPOLi (Fig. 3, MWD curve 15) or two-fold excess of 3-MPOLi (run 13); surprisingly, this was not observed in the polymerization performed in the presence of two-fold excess of 2,3-DMBOLi (run 19). To explain the fact, further investigation is needed; one can again only speculate about formation of various complexes between the growing centre and *tert*-alkoxide in dependence on chemical structure and concentration of the alkoxide. If this is the case, some of the complexes could have a very low reactivity toward the monomer and the growing chains behave as monofunctional, similarly to the polymerization in the presence of high excess of *t*-BuOLi (run 7). As to the microstructures of polymers prepared in the presence of 3-MPOLi, 3-EPOLi, 2-MPOLi and 2,3-DMBOLi, they are almost the same as that of PB prepared in the presence of one equivalent of *t*-BuOLi (see runs 11–19 in Table I). The contents of vinyl structures are only 2–4% lower and, in 1,4-structure, *trans* configuration slightly prevails.

Thus, in polymerization of But in MTBE, initiated with a bifunctional initiator the effect of the polar solvent on the stereospecific efficiency of propagation remains dominating even in the presence of Li *tert*-alkoxides. Consequently, the microstructure of the prepared polymers is affected by complexation of growing centres with the alkoxides only to a small extent.

REFERENCES

1. Morton M., Rupert J. R. in: *Initiation of Polymerization* (F. E. Bailey, Jr., Ed.). *ACS Symp. Ser.* **1983**, *212*.
2. Bywater S., Firat Y., Black P. E.: *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22, 669*.
3. Schué F., Worsfold D. J., Bywater S.: *J. Polym. Sci., Polym. Lett. Ed.* **1969**, *7*, 821.
4. Glaze W. H., Jones P. C.: *J. Chem. Soc., Chem. Commun.* **1969**, 1434.
5. Bywater S., Worsfold D. J.: *J. Organomet. Chem.* **1978**, *159, 229*.
6. Bywater S.: *Prog. Polym. Sci.* **1994**, *19*, 287.
7. McDonald R. T., Bywater S.: *Organometallics* **1986**, *5*, 1529.
8. Guantai J., Ligun F., Wei Y.: *J. Polym. Mater.* **1987**, *4*, 215.
9. Salle R., Pham Q. T.: *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15, 1799*.

10. Antkowiak T. A., Oberster E. A., Halasa A. F., Tate D. P.: *J. Polym. Sci., Part A-1* **1972**, *10*, 1319.
11. Gerbert W., Hinz J., Sinn H.: *Makromol. Chem.* **1971**, *144*, 97.
12. Young R. N., Quirk R. P., Fetters L. J.: *Adv. Polym. Sci.* **1984**, *56*, 1.
13. Hsieh H. L., Quirk R. P. (Eds): *Anionic Polymerization. Principles and Practical Applications*, Chap. 9. Dekker, New York 1996.
14. Fetters L. J., Balsara P. N., Huang J. S., Jeon H. S., Almdal K., Lin N. Y.: *Macromolecules* **1995**, *28*, 4996.
15. Bywater S., Worsfold D. J., Hollingsworth G.: *Macromolecules* **1972**, *5*, 389.
16. Young R. N., Fetters L. J., Huang J. S., Krishnamorti S.: *Polym. Int.* **1994**, *33*, 217.
17. Brownstein S., Bywater S., Worsfold D. J.: *Macromolecules* **1973**, *6*, 715.
18. Lachance P., Worsfold D. J.: *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 2295.
19. Glaze W. H., Hanicak J. E., Chaudhuri J., Moore M. L., Duncan D. P.: *Organomet. Chem.* **1973**, *51*, 13.
20. Bywater S. in: *Recent Advances in Anionic Polymerization* (T. E. Hogen-Esch and J. Smid, Eds), p. 187. Elsevier, New York 1987.
21. Bywater S. in: *Anionic Polymerization. Kinetics, Mechanisms and Synthesis* (J. E. McGrath, Ed.). *ACS Symp. Ser.* **1981**, *166*, 71.
22. Werbowyj R., Bywater S., Worsfold D. J.: *Eur. Polym. J.* **1986**, *22*, 707.
23. Tung L. H., Lo G. Y. S.: *Macromolecules* **1994**, *27*, 2219.
24. Bredeweg C. J., Gatzke A. L, Lo G. Y. S., Tung L. H.: *Macromolecules* **1994**, *27*, 2225.
25. Gatzke A. L., Green D. P.: *Macromolecules* **1994**, *27*, 2249.
26. Lo G. Y. S., Otterbacher E. W., Gatzke A. L., Tung L. H.: *Macromolecules* **1994**, *27*, 2233.
27. a) Lo G. Y. S., Otterbacher E. W., Bezoari M. D., Walther B. W.: U.S. 5,057,583 (1991); b) Tung L. H. Griggs J. A.: Eur. 210016 (1987); *Chem. Abstr.* **1992**, *106*, 157044.
28. Fetters L. J., Morton M.: *Macromolecules* **1969**, *2*, 453.
29. Yu Y. S., Dubois Ph., Jérome R., Teyssié Ph.: *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2221.
30. Yu Y. S., Dubois Ph., Jérome R., Teyssié Ph.: *Macromolecules* **1996**, *29*, 2738.
31. Hsieh H.: *J. Polym. Sci., Part A-1* **1970**, *8*, 533.
32. Vlček P., Otoupalová J., Kříž J., Composto R. J., Oslanec R.: *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38*(*1*), 446.
33. Seyček O., Čermák J., Pleska A., Sufčák M.: Czech. 223252 (1980); *Chem. Abstr.* **1986**, *105*, 44497.
34. Trekoval J., Lím D.: *J. Polym. Sci., Part C: Polym. Symp.* **1963**, *4*, 333.
35. a) Kraus G., Stacy C. J.: *J. Polym. Sci., Part A-2* **1972**, *10*, 657; b) ASTM D 3593-80 (Polymer Supply and Characterization Centre, Rubber and Plastics Assn., Shawbury, Shrewbury, Great Brittain).
36. Santee E. R., Chang R., Morton M.: *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 449.
37. Lochmann L., Pospíšil J., Vodňanský J., Trekoval J., Lím D.: *Collect. Czech. Chem. Commun.* **1965**, *30*, 2187.
38. Yu Y. S., Dubois Ph., Jérome R., Teyssié Ph.: *Macromolecules* **1997**, *30*, 7356.