

PRECIPITATION FRACTIONATION OF BLOCK COPOLYMERS

Zdeněk TUZAR, Antonín SIKORA, Dagmar STRAKOVÁ, Jiří PODEŠVA,
Jaroslav STEJSKAL and Pavel KRATOCHVÍL

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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Dedicated to Dr B. Sedláček on the occasion of his 60th birthday.

Possibilities offered by classical precipitation fractionation in the preparative separation of polymer admixtures from block copolymers and in an estimate of the polydispersity in molar mass and of the heterogeneity in chemical composition of block copolymers have been examined. A mixture of a two-block copolymer, polystyrene-block-polyisoprene, with polystyrene was separated in the systems cyclohexane/1-propanol and 1,4-dioxan/1-propanol, and a mixture of three two-block styrene-isoprene copolymers having different chemical composition was fractionated in the system benzene/methanol. In the cyclohexane/1-propanol system, two commercial samples of three-block copolymers polystyrene-block-poly(ethene-co-butene)-block-polystyrene and their mixture were fractionated. The results showed that the polydispersity and chemical heterogeneity thus estimated are much lower than the real ones, especially due to the colloid properties of block copolymers.

The molar mass polydispersity and heterogeneity in chemical composition of block copolymers are often *a priori* regarded as negligibly small. Depending on the polymerization conditions, however, one may expect more or less perceptible polydispersity and chemical heterogeneity due to the contamination of the given block copolymer by copolymers containing a lower number of blocks, and by one or both of the parent homopolymers¹. However, the interpretation of, *e.g.*, chromatographic data on industrial block copolymers is not unequivocal²⁻⁴.

Polymer admixtures are not the single source of chemical heterogeneity of block copolymers. Model calculations predict pronounced heterogeneity also for isolated block copolymers with the same number of blocks in all macromolecules^{5,6}. Such composition heterogeneity has been observed with two- and three-block copolymers of styrene and methyl methacrylate by the methods of thin-layer chromatography⁷ and adsorption column chromatography⁸.

Chromatographic methods are probably best suited for the characterization of the heterogeneity of copolymers on an analytical scale. On a preparative scale, *e.g.*, when undesired polymer admixtures are to be removed from the copolymer, one always has to turn to phase-separation procedures. A complicating factor arising

in the fractionation of block copolymers is their colloidal behaviour which involves the formation of micelles and solubilization of homopolymers by the latter^{9,10}.

There are only few studies devoted to the precipitation fractionation of block copolymers, and they do not deal with the fractionation efficiency in greater detail. We regarded therefore as useful: *a*) To verify to what extent a homopolymer can be removed by the precipitation fractionation from its mixture with the block copolymer one block of which is chemically identical with the homopolymer and has a comparable molar mass; *b*) to try, by employing the precipitation fractionation, to separate into the original components a mixture of three block copolymers of the same type, but markedly different in their chemical composition; *c*) to find out what information on the distribution of molar mass and chemical composition can be obtained by the precipitation fractionation of industrially important commercial block copolymers.

EXPERIMENTAL

Polymers

Two-block copolymers polystyrene-block-polyisoprene coded SI were prepared by the anionic polymerization as described earlier¹¹. The GPC diagrams of all three samples showed narrow, insignificantly asymmetrical peaks¹¹. The osmotically determined molar masses and the chemical composition obtained by means of ¹H NMR spectroscopy are given in Table I.

Two three-block copolymers, polystyrene-block-poly(ethene-co-butene)-block-polystyrene, Shell products, labelled as Kraton G-1650 and G-1652, were freed from mechanical impurities by filtering their solutions in toluene ($c = 10^{-2} \text{ g cm}^{-3}$) through a bacterial glass filter (G 5, Jena). After reprecipitation into methanol, separation and drying, the samples were characterized (Table I). In addition to the main narrow and symmetrical peak, the GPC diagrams of both samples contained one more distinctly separated peak, which by the elution volume corresponded

TABLE I

Characteristics of the samples used. M_n is the number average molar mass, x is the mass fraction of styrene units in the polymer. For sample codes see the text

Code	$M_n \cdot 10^{-3}$ g mol^{-1}	x
SI-1	93	0.34
SI-2	114	0.59
SI-3	121	0.79
G-1650	62.5	0.30
G-1652	49	0.29
PS	52	1.00

to polystyrene with the number average molar mass M_n approx. $1 \cdot 10^4 \text{ g mol}^{-1}$; its amount in the sample was 1–2 mass % (Fig. 1).

Polystyrene (labelled PS) was prepared by anionic polymerization (Table I).

Solvents

All solvents were reagent grade (Lachema, Czechoslovakia). Xylene, toluene and tetrahydrofuran were rectified before use.

Fractionation

A mixture of the two-block copolymer SI-3 and PS (1 : 1 by mass) in the systems cyclohexane/1-propanol and 1,4-dioxan/1-propanol, and a mixture of SI-1, SI-2 and SI-3 (1 : 1 : 1 by mass) in the system benzene/methanol were subjected to successive precipitation fractionation at 25°C. The initial mass of each polymer mixture was 0.5 g and the initial concentration was $7 \cdot 10^{-3} \text{ g} \cdot \text{cm}^{-3}$. In view of the potential reactivity of double bonds in isoprene blocks, all operations, including the reprecipitation of fractions into methanol, were carried out under argon in oxygen-free solvents. The content of styrene monomer units in the fractions was determined by means of ^1H NMR spectroscopy.

Kratons G-1650, G-1652 and their mixtures (1 : 1 by mass) were fractionated in the system cyclohexane/1-propanol. The initial mass of the polymer was 10 g at the initial concentration $7 \cdot 10^{-3} \text{ g cm}^{-3}$. Each sample was first divided into two fractions, these were divided into further two, *etc.* The resulting fractions were reprecipitated into methanol; the M_n values were determined osmotically for all fractions, and their chemical composition was determined by a sensitive differential-refractometric method¹².

Results of the fractionations are presented as integral fractionation curves which demonstrate the dependence of the cumulative mass fraction of the i -th fraction $W_i = w_i/2 + \sum_{j=2}^{i-1} w_j$ (w_i being the mass fraction of the i -th fraction) on its molar mass M_i or on the mass fraction of styrene units, x .

Characterization of Copolymers and Their Fractions

The M_n values of all samples were determined osmotically in toluene solutions with a Hewlett-Packard High Speed Membrane Osmometer, Model 502, using cellulose membranes Schleicher and Schüll SS 08 at 25°C.

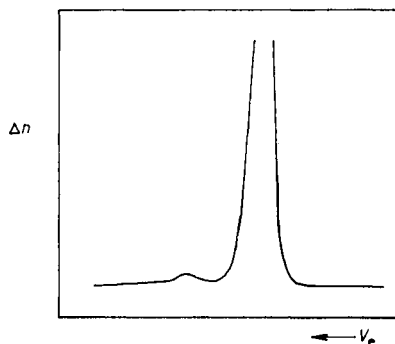


FIG. 1

The GPC diagram of Kraton G-1652 in tetrahydrofuran. V_e is the elution volume, Δn is the difference of refractive indices

The chemical composition of samples polystyrene-block-polyisoprene and of their fractions was determined by ^1H NMR spectroscopy (for details see¹¹). The chemical composition of the Kraton three-block copolymers and of their fractions was determined by the differential refractometry method with an internal standard¹². If the components of the copolymer differ markedly in their refractive index, this method is much more exact than the NMR method. Kraton G-1650 was chosen as the reference copolymer; its composition as given by the manufacturer ($x = 0.30$) agreed with the NMR data, and it is isorefractive with xylene (*cf.* Fig. 2) used as solvent. The concentrations of solutions taken for the measurements were $4 \cdot 10^{-2} \text{ g cm}^{-3}$. The composition of the samples was read off from the calibration plot (Fig. 2) obtained by means of a number of mixtures of polystyrene with the reference copolymer. The measurements were performed with a Brice-Phoenix BP 2000 V differential refractometer at 25°C and the wavelength of light *in vacuo* 546 nm.

The Kraton samples and their fractions were characterized by means of gel permeation chromatography, using an ALC/GPC-150 C (Waters) apparatus with a differential refractometer as detector, in tetrahydrofuran. Four columns packed with μ -Bondagel E-linear were used in series; 200 μl of solution at the concentration $5 \cdot 10^{-3} \text{ g cm}^{-3}$ was injected.

RESULTS AND DISCUSSION

Our aim in the fractionation of the mixture of the two-block copolymer SI-3 with polystyrene and of the mixture of three two-block copolymers was to find possibilities for the separation of the homopolymer, or for the mutual separation of block copolymers. For this reason, only the chemical composition of the fractions was studied at this stage. The resulting integral fractionation curves (Figs 3–5) are compared with the calculated distribution functions of chemical composition for which the chemical heterogeneity of the individual components was not considered for the sake of simplicity.

Although a considerable part of polystyrene could be separated by fractionation from its mixture with SI-3, the remaining part still contaminated the rest of the frac-

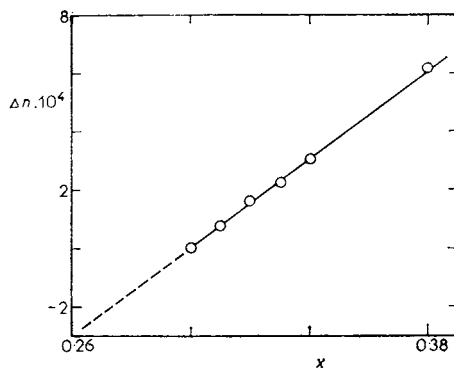


FIG. 2

Calibration dependence between the chemical composition of the copolymer, x , and the difference between the refractive indices, Δn , of xylene solutions of the given and reference copolymer; x is the mass fraction of styrene units. The polymer concentration used $c. 4 \cdot 10^{-2} \text{ g cm}^{-3}$, temperature 25°C , wavelength of light in vacuum 546 nm

tions. Figs 3 and 4 show that with the exception of one fraction, all the others have a higher polystyrene content than corresponds to the average composition of SI-3. Also, in the fractionation of the mixture of three copolymers (Fig. 5) the observed fractionation curve of chemical composition was steeper than the one predicted for this mixture.

The small efficiency of fractionation illustrated by Figs 3–5 is mainly due to the specific behaviour of block copolymers in selective solvents, *i.e.*, thermodynamically good solvents of one block and at the same time poor solvents of the other¹⁰. The addition of a precipitant in the course of fractionation usually results in that the given mixture becomes a precipitant, first of one type of blocks (in the benzene/methanol and 1,4-dioxan/1-propanol systems of the isoprene block, in the cyclohexane/1-propanol system of the styrene block). Microphase separation takes place, leading to the formation of spherical micelles, the cores of which consist of precipitated blocks and the shell is formed by the still soluble copolymer blocks. The micellar solution is thermodynamically stable, no macrophase separation of the copolymer takes place here. Such separation occurs only after the precipitant has been added

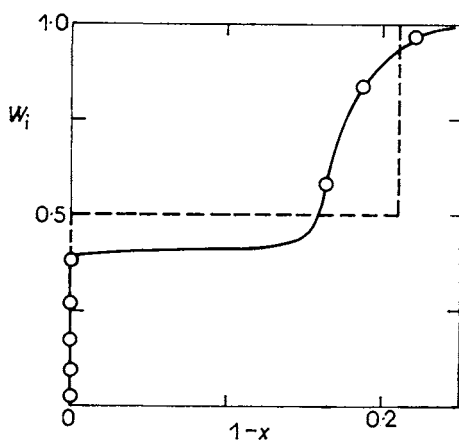


FIG. 3

Integral fractionation curve of chemical composition from fractionation data of a mixture of samples SI-3 and PS, 1 : 1 by mass, in the system cyclohexane/1-propanol. W_i is the cumulative mass fraction of the i -th fraction, x is the mass fraction of styrene units. ----- calculated distribution curve with neglected chemical heterogeneity of sample SI-3

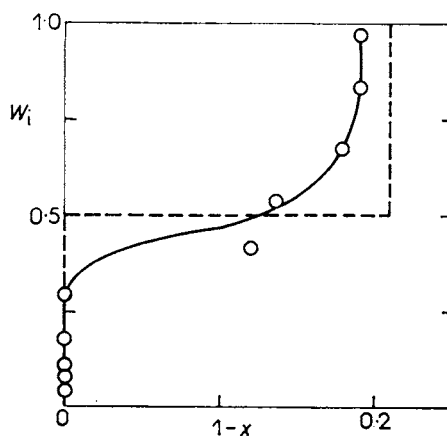


FIG. 4

Integral fractionation curve of chemical composition from fractionation data of a mixture of samples SI-3 and PS, 1 : 1 by mass, in the system 1,4-dioxan/1-propanol. W_i is the cumulative mass fraction of the i -th fraction, x is the mass fraction of styrene units. ----- calculated distribution curve with neglected chemical heterogeneity of sample SI-3

in such an amount that the mixture becomes poor solvent also for the other block. From what is known about the micellization of soaps, block copolymer micelles should have a much narrower distribution of chemical composition and molar mass than the given copolymer^{13,14}. Also, block copolymer micelles are able to solubilize a certain amount of the homopolymer chemically identical with blocks in the micellar core¹⁴.

The steeper course of the integral fractionation curve in Fig. 5 can therefore be explained by the existence of mixed micelles at the onset of macrophase separation. The higher styrene content in all fractions illustrated in Fig. 3 can be understood in the same way. Cyclohexane is a poorer solvent for polystyrene than for polyisoprene. By the addition of 1-propanol, polystyrene is precipitated preferentially, but to a certain extent it may be solubilized into the polystyrene cores of copolymer micelles; the macrophase separation of the latter occurs at a later stage.

Unlike cyclohexane, 1,4-dioxan is a thermodynamically poorer solvent for polyisoprene than for polystyrene. Hence, solubilization of polystyrene into micelles of the copolymer with the polyisoprene nucleus is out of question. Contamination

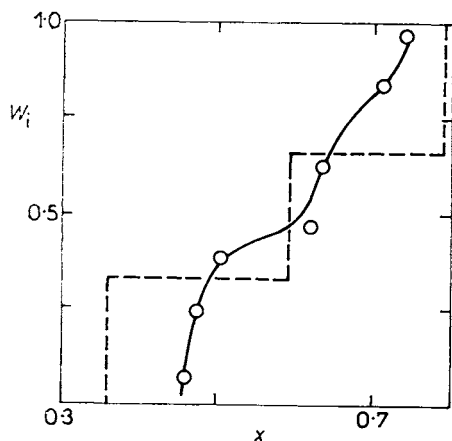


FIG. 5

Integral fractionation curve of chemical composition from fractionation data of a mixture of SI-1, SI-2 and SI-3, 1:1:1 by mass, in the system benzene/methanol. W_i is the cumulative mass fraction, x is the mass fraction of styrene units. ----- calculated distribution curve with neglected chemical heterogeneity of constituting copolymers

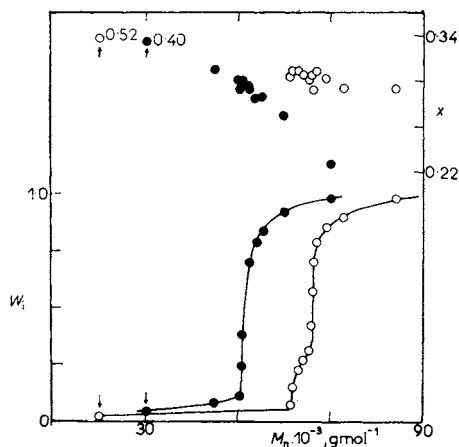


FIG. 6

Integral fractionation curves of molar masses and dependences of chemical compositions of fractions on their molar masses from the fractionation data of Kratons G-1650 (○) and G-1652 (●) in the system cyclohexane/1-propanol. W_i is the cumulative mass fraction of the i -th fraction, x is the mass fraction of styrene units and M_n is the number average molar mass of fractions

of copolymer fractions with polystyrene is brought about by some other mechanism. Also, it is surprising and difficult to explain that in the system 1,4-dioxan/1-propanol polystyrene undergoes macrophase separation earlier than copolymer micelles.

The aim of fractionation of Kratons G-1650 and G-1652 consisted in pointing out the possibilities of separation of these copolymers into fractions differing in their molar mass and chemical composition. Preliminary experiments showed that fractionation systems in which the central aliphatic block (*e.g.*, 1,4-dioxan/1-propanol) is preferentially precipitated are not suitable. First, the addition of 1-propanol gave rise to stable turbidity (micelles with an aliphatic core). The addition of a small amount of the precipitant or a small decrease of temperature then made almost all copolymer pass into the concentrated phase. We therefore used the cyclohexane/1-propanol system in which phase separation takes place without apparent difficulties.

The fractionation curves of molar mass and chemical composition of both Kratons are shown in Figs 6 and 7. The GPC diagrams of the fractions gave narrow and symmetrical peaks which within the limits of experimental error did not differ in the elution volume. The only exception was always the fraction with the lowest M_n denoted with an arrow in Figs 6 and 7. Chromatograms of these fractions had two separate peaks (Fig. 8). The elution volume of one peak was the same as that of the single peak of the other fractions; the elution volume of the second was identical with that of a very small peak which together with the main peak was recorded in the chromatograms of unfractionated Kratons (Fig. 1). As demonstrated by NMR

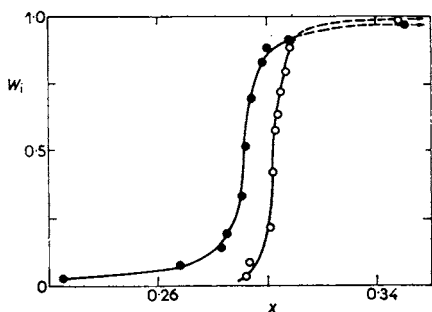


FIG. 7

Integral fractionation curves of chemical composition from the fractionation data of Kratons G-1650 (○) and G-1652 (●) in the system cyclohexane/1-propanol. W_i is the cumulative mass fraction of the *i*-th fraction, x is the mass fraction of styrene units

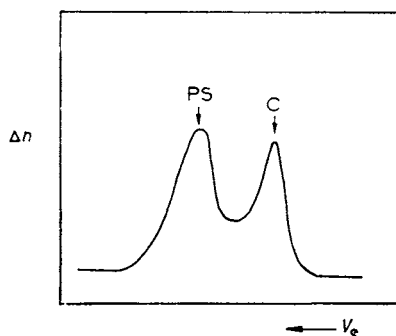


Fig. 8

GPC diagram of the Kraton fraction with the lowest molar mass. Peaks denoted with C and PS correspond to the copolymer and polystyrene, respectively

measurements and differential refractometry, this is due to polystyrene which according to the GPC calibration curve has $M_n 1 \cdot 10^4 \text{ g mol}^{-1}$. Its mass fraction in both Kratons is c. 0.015.

Thus, the experimentally proved decrease in the styrene content with increasing molar mass of the fraction (more pronounced for the sample G-1652, Fig. 6) cannot be explained by contamination of fractions with polystyrene. Neither could it be explained by the presence of the two-block copolymer in the sample. Compared with the three-block copolymer, the former should have a lower molar mass and at the same time a lower styrene content. As the fractions of the sample G-1650 with $M_n 60 - 65 \cdot 10^3 \text{ g mol}^{-1}$ also do not possess a lower styrene content than those with a higher M_n , the shoulder on the fractionation curve in Fig. 6 cannot be interpreted by the presence of the two-block copolymer.

The decrease in the styrene content in fractions with increasing molar mass of the latter as mentioned above, and the ensuing negative value of the heterogeneity parameter P , which is a measure of the mutual correlation of distribution of molar mass and chemical composition (for definition see, *e.g.*, ref.¹⁵), may be explained as a natural consequence of the polydispersity of the individual blocks. A theoretical analysis of the mechanism of formation of block copolymers^{6,16} shows that the parameter P assumes negative values if the polydispersity index of the individual polystyrene

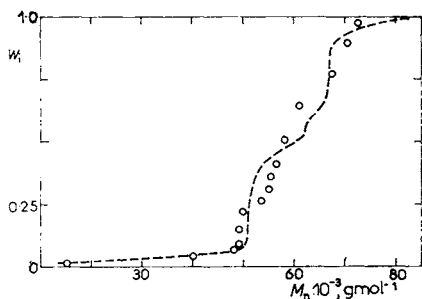


FIG. 9

Integral fractionation curve of molar mass from the fractionation data of a mixture of Kratons G-1650 and G-1652, 1:1 by mass, in the system cyclohexane/1-propanol. ----- distribution curve obtained by the weighted sum of distribution curves from Fig. 6. W_i is the cumulative mass fraction of the i -th fraction, M_n is the number average molar mass

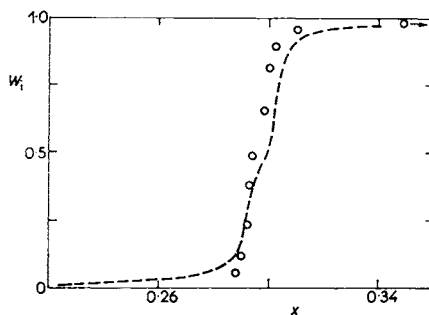


FIG. 10

Integral fractionation curve of chemical composition from the fractionation data of a mixture of Kratons G-1650 and G-1652, 1:1 by mass, in the system cyclohexane/1-propanol. ----- distribution curve obtained by the weighted sum of distribution curves from Fig 7. W_i is the cumulative mass fraction of the i -th fraction, x is the mass fraction of styrene units

blocks $(M_w/M_n)_S$ is higher than a certain minimal value. For both Kratons (mass fraction of styrene units, x , c. 0.3), *e.g.*, at the polydispersity of the aliphatic block $(M_w/M_n)_{AI}$ 1.1 or 1.2, it should be $(M_w/M_n)_S$ 1.02 or 1.04, respectively. In all likelihood, these conditions are satisfied for our copolymers.

In the fractionation of the mixture of both Kratons, we obtained integral fractionation curves of molar mass or chemical composition (Figs 9 and 10) which were however markedly narrower than those obtained by a weighted sum of experimental curves in Figs 6 and 7. One is justified to assume, therefore, that also the experimental fractionation curves of molar mass and chemical composition of both Kratons are narrower than the true ones. Thus, although the fractionation of Kratons in the given system was not very efficient, the homopolymer present in both samples and their mixture was completely removed (unlike the case of the mixture of SI-3 with PS, Figs 3 and 4).

It may be said, in conclusion, that the integral fractionation curves of block copolymers obtained by classical precipitation fractionation are steeper than the expected integral distribution curves of molar masses and chemical composition. In the case of statistical copolymers, this effect may be explained by the low efficiency of fractionation¹⁷; in the case of block copolymers, separation is impaired also due to the factor of colloidal behaviour which involves the formation of micelles, formation of mixed micelles and solubilization of the homopolymer by copolymer micelles.

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REFERENCES

1. Fetters L. J. in the book: *Block and Graft Copolymerization* (R. J. Ceresa, Ed.). J. Wiley and Sons, London 1973.
2. Fetters L. J., Meyer B. H., McIntyre D.: *J. Appl. Polym. Sci.* 16, 2079 (1972).
3. Inagaki H., Kotaka T., Min T.-I.: *Pure Appl. Chem.* 46, 61 (1976).
4. Enyiegbulam M., Hourston D. J.: *J. Appl. Polym. Sci.* 23, 2821 (1979).
5. Inagaki H., Tanaka T. in the book: *Developments in Polymer Characterization* (J. V. Dawkins, Ed.), Vol. III. Appl. Sci. Publishers Ltd., Essex, England 1982.
6. Stejskal J., Kratochvíl P.: *Polymer J.* 14, 603 (1982).
7. Kotaka T., Uda T., Tanaka T., Inagaki H.: *Makromol. Chem.* 176, 1273 (1975).
8. Tanaka T., Omoto M., Donkai N., Inakagi H.: *J. Makromol. Sci., Phys. B* 17, 211 (1980).
9. Tuzar Z., Kratochvíl P.: *Makromol. Chem.* 170, 177 (1971).
10. Tuzar Z., Kratochvíl P.: *Advan. Colloid Interface Sci.* 6, 201 (1976).
11. Podešva J., Špaček P., Sikora A., Podol'skii A. F.: *J. Polym. Sci., Polym. Chem. Ed.* 22, 3343 (1984).
12. Kratochvíl P., Straková D., Stejskal J.: *Polym. Commun.*, 26, 202 (1985).
13. Elias H.-G.: *J. Makromol. Sci., Chem. A* 7, 601 (1973).

14. Tuzar Z., Bahadur P., Kratochvíl P.: *Makromol. Chem.* 182, 1751 (1981).
15. Leng M., Benoit H.: *J. Polym. Sci.* 57, 253 (1962).
16. Kotaka T., Donkai N., Min T. I.: *Bull. Inst. Chem. Res., Kyoto Univ.* 52, 332 (1974).
17. Stejskal J., Kratochvíl P.: *Macromolecules* 11, 1097 (1978).

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