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Critical thin-layer chromatography as a novel method for the determination of the molecular weight and compositional inhomogeneity of block copolymers

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ABSTRACT

The mechanism of the fractionation of two-block AB copolymers (BC), consisting of polystyrene (PS) as block A and poly(*tert.*-butyl methacrylate) (PtBMA) as block B, was studied by thin-layer chromatography (TLC). It is shown that under the critical conditions for TLC [critical TLC (CTLC)], the PS blocks of BC are fractionated by the mechanism of exclusion TLC (ETLC) of the PS block (whereas the PtBMA block of BC is chromatographically invisible) and the PtBMA blocks of BC are fractionated by ETLC of the PtBMA block (whereas the PS block of BC is chromatographically invisible). The molecular weights (MW) of BC were determined by the ETLC method and those of PS and PtBMA blocks under the conditions of CTLC (PtBMA)–ETLC (PS) and CTLC (PS)–ETLC (PtBMA). The calculated compositions of the analysed BC correspond to the data calculated from the kinetics of copolymerization and microcolumn exclusion chromatography.

INTRODUCTION

The molecular weight distribution (MWD) and compositional inhomogeneity (CI) of block copolymers (BC) are the main characteristics that disclose the synthesis mechanism and make it possible to predict their properties.

The analysis of the CI of BC is considered in many investigations in which classical and chromatographic methods of fractionation have been used (for reviews see refs. 1–3).

When BC exhibit complex heterogeneity (with respect to MWD and CI), the only method for their reliable analysis is based on cross-fractionation [1]. When the compositional distribution of BC is narrow, their MWD may be determined relatively precisely by using one-dimensional fractionation, *e.g.*, by using dual-detector exclusion chromatography (with continuous determination of the fractional composition) [4].

The chromatographic cross-fractionation of BC may be carried out most effectively by using chromatography under critical conditions, which is the most selective type of polymer chromatography. On the basis of modern concepts of the theory of critical phenomena in the adsorption of macromolecules on porous adsorbents, a theory of liquid chromatography of polymers has been developed in recent years. This theory shows that exclusion (EC) and adsorption (AC) chromatography are separated from each other at a critical point at which the first-order phase transition takes place with a distribution coefficient $K_d = 1$ and the macromolecules pass from the adsorbed state into solution with a very slight change in eluent composition or temperature [5–9]. It has been shown theoretically [10,11] that conditions of critical chromatography (CC) exist under which heteropolymers (copolymers and functional oligomers) can differ only in the size (molecular weight, MW) of one of the components,

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whereas the second component is under the critical conditions and is chromatographically "invisible", *i.e.*, it is in the state in which its K_d is independent of MW. As applied to BC, CC may be used for separation according to the size (MW) of one of the blocks (chromatographically "visible"). The fractions obtained may be characterized according to the MWD with the aid of other chromatographic methods, *e.g.*, EC, which makes it possible to obtain a complete picture of BC heterogeneity (MWD and CI).

THEORETICAL

We shall now consider some theoretical aspects of BC chromatography. The composition of a two-block AB copolymer will be characterized by the fraction of component A:

$$\xi_A = \frac{N_A}{N_A + N_B} \tag{1}$$

where N is the unit number. Let us assume that the units of the B type are "tacky", *i.e.*, they are adsorbed on the pore surface, whereas those of the A type are adsorptionally inactive and, hence, are in the pore volume. The theory shows that at a fixed interaction energy between BC segments and the adsorbing surface, $-\varepsilon_A$ and $-\varepsilon_B$ in kT units (where k is Boltzmann's constant and T is the temperature in kelvin), a critical BC composition, ξ_A^{Cr}, exists at which all chains with $\xi_A < \xi_A^{Cr}$ are adsorbed and all chains with $\xi_A > \xi_A^{Cr}$ are in solution (in the mobile phase). In this instance the change in the Gibbs energy of BC with $\xi_A = \xi_A^{Cr}$ (in kT units), $-\Delta G_{BC}$, is equal to zero. Under these conditions, the distribution coefficient of the macromolecule is $K_d = \exp(-\Delta G) = 1$. The result of the change in $-\Delta G$ in chromatography is the chromatographic mobility, R_F:

$$R_F = \frac{1}{1 + (V_p/V_o)\exp(-\Delta G)} \tag{2}$$

where V_p and V_o are the pore and the interparticle volumes, respectively, of the sorbent.

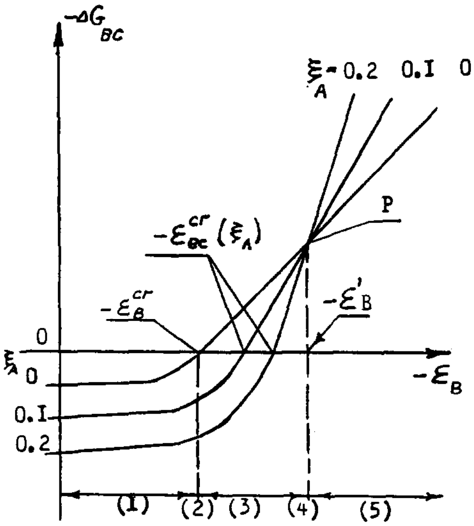

Fig. 1. Gibbs energy of BC adsorption ($-\Delta G_{BC}$) *versus* energy of interaction of a segment of block B with the adsorbent surface ($-\varepsilon_B$).

Fig. 1 shows the dependence of the Gibbs energy, $-\Delta G_{BC}$, of adsorption of BC that contain B blocks with the same dimensions (MW_B = constant) on the interaction energy (in kT units) with the surface of the segments of the more "tacky" block B, $-\varepsilon_B$ ($-\varepsilon_B > -\varepsilon_A$). BC differ in composition ξ_A (block A size). The curve for $\xi_A = 0$ corresponds to the homopolymer B, and the curves for $\xi = 0.1$ and $\xi_A = 0.2$ correspond to BC for which the MW of block A is 10% and 20% of that of block B, respectively. When $-\varepsilon_B$ is increased (by decreasing the displacer content in the eluent), the following successive chromatographic conditions may be distinguished (they are characterized in Fig. 1 by figures in parentheses):

(1) Exclusion chromatography of BC ($-\varepsilon_B < -\varepsilon_B^{Cr}$) with exclusion separation of BC according to the size of the macromolecule (proportional to $MW_{BC} = MW_A + MW_B$).

(2) Critical chromatography of block B ($-\varepsilon_B = -\varepsilon_B^{Cr}$) with exclusion separation of BC according to the size MW of block A (block B is chromatographically "invisible"[a]).

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[a] The conditions of pre-critical (PTLC) and near-critical (NTLC) TLC of block B [around point (2): $-\varepsilon_B = -\varepsilon_B^{Cr}$] could also be distinguished but they are not of interest from the analytical standpoint. The purpose of the present work was to carry out experimentally all the above chromatographic regimes of TLC and to apply these TLC variants to the determination of the polydispersity of the PS–PtBMA [polystyrene–poly(*tert.*-butyl methacrylate)] block copolymers.

(3) Pre-critical chromatography of block A ($-\varepsilon_B^{Cr} < -\varepsilon_B < -\varepsilon'_B$), where $-\varepsilon'_B$ is the energy that corresponds to eluent composition critical for block A ($-\varepsilon_A = -\varepsilon_A^{Cr}$). In this instance adsorption separation of block B according to length occurs with the exclusion effect for block A (with increasing MW_A the value of $-\Delta G_{BC}$ decreases and the R_F value of BC increases).

(4) Critical chromatography of block A ($-\varepsilon_A = -\varepsilon_A^{Cr}$ at $-\varepsilon_B > -\varepsilon_B^{Cr}$). In this instance the BC curves with different ξ_A intersect at point P, at which only adsorption separation according to the length of block B can occur (block A is chromatographically "invisible").

(5) Near-critical chromatography of block A ($-\varepsilon_A > -\varepsilon_A^{Cr}$, $-\varepsilon_B = -\varepsilon'_B$, $-\varepsilon_B \gg -\varepsilon_B^{Cr}$). In this instance separation according to the lengths of blocks A and B (with increasing MW_A the value of $-\Delta G_{BC}$ increases and the R_F value of BC decreases).

It can be seen from Fig. 1 that if the value of $-\varepsilon_B$ is varied from $+\infty$ to $-\varepsilon_B^{Cr}$ (by increasing the displacer content in the eluent), gradual desorption of BC will occur each time when we have $-\Delta G_{BC}$ (ξ_A) = 0 ($K_d = 1$) with a gradually increasing content of the "adhesive" block B (with decreasing ξ_A). The homopolymer B is desorbed last (at the point $-\varepsilon_B = -\varepsilon_B^{Cr}$). The selectivity of this process increases with decreasing pore size of the adsorbent [10,11].

EXPERIMENTAL

Preparation of block copolymers

PS–PtBMA block copolymers of the AB type were obtained by successive anionic polymerization in an all-sealed vacuum system (10^{-6} Torr) [12–14]. The PS precursors of BC were synthesized under conditions that make it possible to obtain linear narrow-disperse homopolymers [11]. After the completion of PS polymerization with tBMA, samples were collected from the reaction system. They were reference samples of PS blocks of each BC. According to the conditions of synthesis, BC can contain homo-PS as a result of the reaction of the "living" PS chains with possible impurities in the second monomer (tMBA), but should not contain homopolymers of the methacrylic monomer (PtBMA).

The MW of the PS precursors of BC were determined by microcolumn exclusion chromatography (MEC) [15].

Table I gives the MW of PS precursors of BC, PtBMA and BC according to the data from MEC

TABLE I

MW OF BLOCK COPOLYMERS; PC PRECURSORS, PtBMA; PS AND PtBMA BLOCKS OF BC

Method of determination	MW × 10^{-3}										
	Block copolymers					PS precursors of BC			PtBMA		
	BC-31	BC-21	BC-53	BC-41	BC-52	PS-30[a]	PS-50[a]	PS-20[a]	1	2	3
From polymerization conditions	130	95	75	65	27	64.5	13.5	80	20	80	200
TLC	127	97	78	69	30	66	15	83	24	81	250
PS block from polymerization conditions	64.5	80	13.5	5	13.5						
TLC	60	85	11	5	11						
PtBMA block from polymerization conditions	64.5	15	60	60	13.5						
TLC	60	13	60	60	13						

[a] Determined by microcolumn exclusion chromatography (MEC).

and TLC and those calculated from the polymerization conditions.

Thin-layer chromatography

TLC was carried out by using commercial plates on a glass support with KSKG silica gel (pore diameter 120 Å, 5–20-μm fraction) Reakhim (Moscow, Russia) [16] with silica sol [16] as binder, or plates prepared manually by the same procedure [16] with LiChrospher Si 300 silica gel (pore diameter 300 Å, 10-μm fraction) (Merck, Darmstadt, Germany). Prior to coating, the glass plates were washed in a dichromate–sulphuric acid mixture, then thoroughly washed with tap water and after coating they were activated at 120°C for 30 min. The samples were spotted from solutions (at a concentration of 5 mg/ml) of PS in carbon tetrachloride and of PtBMA and BC in chloroform in amounts of 2–3 μg for BC.

The plate with the samples was saturated in eluent vapour for 1 h, developed in the ascending mode in an appropriate eluent and dried in an oven at 180°C for 15–20 min. Detection was carried out by spraying the plates with a 3.3% solution of potassium permanganate in concentrated sulphuric acid with subsequent heating at 180°C for 15–20 min. The polymer zones developed as black spots on a white background.

PS standards from Waters (Milford, MA, USA) were used.

RESULTS AND DISCUSSION

Exclusion TLC. Evaluation of the MW of block copolymers, their PS pressures and PtBMA by ETLC

According to the ETLC data in methyl ethyl ketone (MEK), calibration dependences of R_F on log M were plotted for PS standards on silica gels with pore diameters of 120 Å (Si 120) and 300 Å (Si 300). These dependences were linear on silica gel Si 120 in the M range from $5 \cdot 10^3$ to $50 \cdot 10^3$ (exclusion limit $50 \cdot 10^3$) and on silica gel Si 300 in the M range from $50 \cdot 10^3$ to $500 \cdot 10^3$. By using these dependences, the MW of BC, the PS precursors of BC and PtBMA were determined with the aid of ETLC. The results are given in Table I. It is clear that the MW of BC obtained by ETLC, calculated from the polymerization conditions and obtained by the MEC are in good agreement.

Critical TLC for PtBMA–exclusion TLC for PS [CTLC(PtBMA)–ETLC(PS)]

For plates with silica gels Si 120 and Si 300, the conditions of CTLC of PtBMA (eluent composition) under which the PS samples undergo ETLC were established. Under these conditions of CTLC (PtBMA)–ETLC(PS), two pairs of BC with similar MW of the PS blocks but differing in the MW of the PtBMA blocks were chromatographed. Fig. 2 shows that on silica gel Si 120 PtBMA with different MW (points 1 and 2) have the same R_F values that

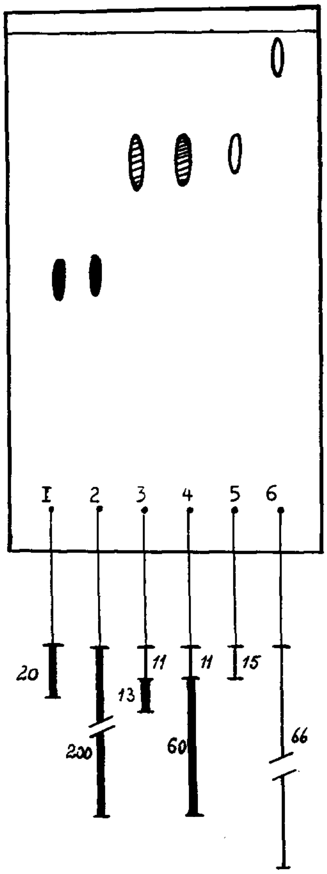

Fig. 2. CTLC(PtBMA)–ETLC(PS) on silica gel Si 120. Eluent: cyclohexane–toluene–MEK (9:1:2.3). (1,2) PtBMA with MW (1) $20 \cdot 10^3$ and (2) $200 \cdot 10^3$; (3) BC-52; (4) BC-53; (5) PS-50; (6) PS-30. Figs. 2–6 show schematically homopolymers and BC in the form of zones (open zones, PS; black zones, PtBMA; hatched zones, BC), and their compositions as lines, the length of which corresponds to the MW of polymers (figures indicate the MW of polymers and BC blocks according to TLC data): —— PS; ▬▬ PtBMA.

correspond to $K_d = 1$ (the proof of CTLC conditions for PtBMA). In this instance BC (points 3 and 4) with the same MW of the PS block ($13.5 \cdot 10^3$) and different MW of the PtBMA blocks ($13.5 \cdot 10^3$ and $60 \cdot 10^3$) have the same R_F values ($K_d < 1$) corresponding to the MW of the PS precursor (5) with MW $13.5 \cdot 10^3$. These results were confirmed by CTLC(PtBMA)–ELC(PS) on silica gel Si 300. In this instance BC with MW of the PS blocks equal to $64.5 \cdot 10^3$ and $80 \cdot 10^3$ and the MW of the PtBMA blocks equal to $64.5 \cdot 10^3$ and $15 \cdot 10^3$ have R_F values corresponding to those of PS precursors with MW of $64.5 \cdot 10^3$ and $80 \cdot 10^3$. These experiments showed that under the conditions of CTLC (PtBMA)–ETLC(PS) the MW of the PtBMA block does not affect the chromatographic behaviour of BC which undergo chromatography under conditions analogous to the ETLC of PS which correspond to the MW of their PS blocks. The MW of PS blocks of BC determined under the conditions of CTLC(PtBMA)–ETLC(PS) are given in Table I.

Critical TLC for PS and adsorption TLC for PtBMA

The conditions of CTLC(PS)–ATLC(PtBMA) for BC with the same MW of the PtBMA blocks correspond to point 4 in Fig. 1. However, under the CTLC conditions for PS on silica gel, even for relatively low MW PtBMA, we have $K_d \gg 1$, and the PtBMA zones remain at the start. Under these conditions, it is impossible to distinguish chromatographically BC differing in the MW of the PtBMA blocks. If pyridine, which has a high affinity for silanol hydroxyl groups, is added to the eluent, it is possible to perform dynamic modification of the silica gel, which converts it into an analogue of the phenyl silica gel. The affinity of the phenyl silica gel for PS exceeds that for PtBMA [3]. By varying the amount of pyridine, it is possible to achieve the conditions of CTLC(PS)–ATLC(PtBMA), whereas at a lower content, pre-critical TLC (PTLC) may be achieved and at a higher content near-critical TLC (NTLC) for PS and ATLC for PtBMA are achieved (Fig. 1, states 3, 4 and 5, respectively). Finally, by adding a still greater amount of pyridine to the eluent, it is possible to invert the chromatogram completely and to obtain CTLC(PS)–ETLC (PtBMA) conditions.

Conditions for CTLC(PS)–ATLC(PtBMA) and NCTLC(PS)–ATLC(PtBMA)

Figs. 3, 4 and 5 show the chromatograms corresponding to the conditions for CTLC(PS)–ATLC (PtBMA), PCTLC(PS)–ATLC(PtBMA) and NCTLC(PS)–ATLC(PtBMA), respectively, which are easily determined from the natural arrangement of the chromatographic zones of PS and BC with PS blocks of different MW. In Fig. 3 the PS zones with different MW are on the same level (CTLC of PS). Under these conditions BC with PS blocks of

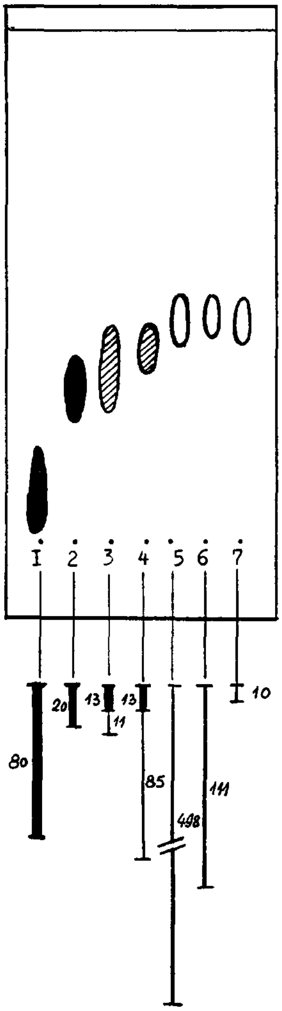

Fig. 3. CTLC(PS)–ATLC(PtBMA) on silica gel Si 120. Eluent: cyclohexane–toluene–MEK–pyridine (9:0.4:1.8:1). (1,2) PtBMA with MW (1) $80 \cdot 10^3$ and (2) $20 \cdot 10^3$; (3) BC-52; (4) BC-21; (5–7) PS with MW, (5) $498 \cdot 10^3$, (6) $111 \cdot 10^3$ and (7) $10 \cdot 10^3$.

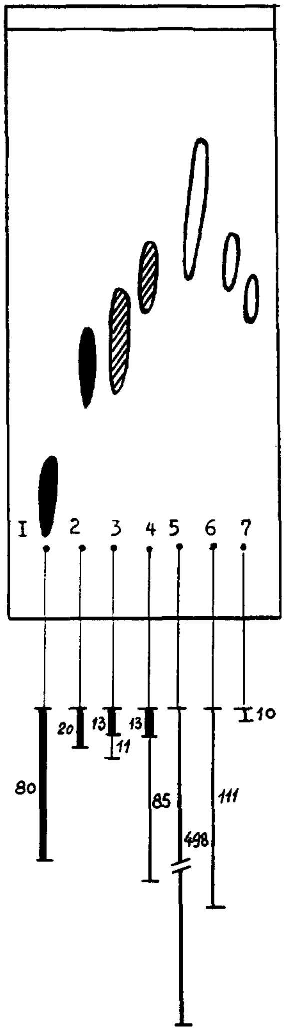

Fig. 4. PCTLC(PS)–ATLC(PtBMA) on silica gel Si 120. Eluent: cyclohexane–toluene–MEK–pyridine (9:0.4:1.7:1). For (1–7) see Fig. 3.

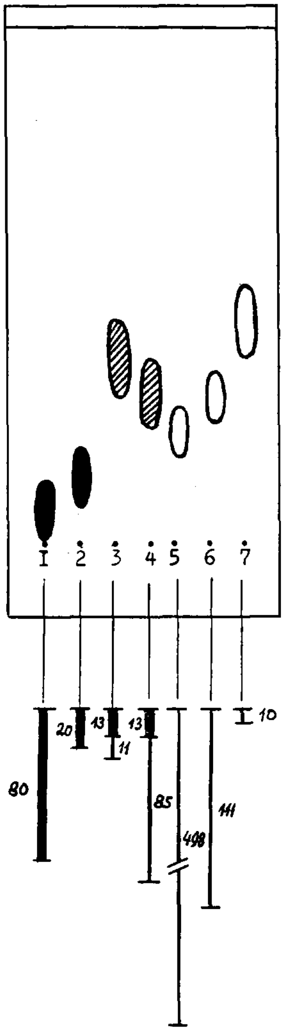

Fig. 5. NCTLC(PS)–ATLC(PtBMA) on silica gel Si 120. Eluent: cyclohexane–toluene–MEK–pyridine (9:0.4:1.3:1.2). For (1–7) see Fig. 3.

different MW and PtBMA blocks of the same MW are also on the same level (have identical R_F values). In Fig. 4 the R_F value of PS zones increases with increasing MW (PCTLC of PS). In this instance BC with the PS block of higher MW is placed higher (has a higher R_F value). Fig. 5 shows the decrease in the R_F value of PS with increasing MW because adsorption on silica gel increases (NCTLC of PS). Correspondingly, the R_F value for BC (MW_{PtBMA} = constant) depends on the length of the PS block; with increasing length of this block, R_F decreases.

Critical TLC for PS–exclusion TLC for PtBMA [CTLC(PS)–ETLC(PtBMA)]

Fig. 6 shows the TLC of BC under the conditions of CTLC(PS)–ETLC(PtBMA). It is clear that PS 1 and 2 of different MW migrate at the same level (the proof of CTLC for PS). The BC pairs 3–4 and 5–6

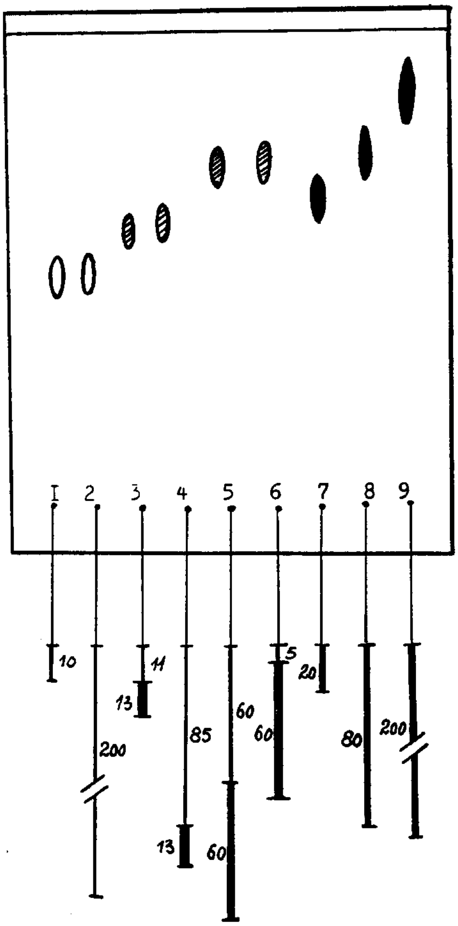

Fig. 6. CTLC(PS)–ETLC(PtBMA) on silica gel Si 300. Eluent: cyclohexane–toluene–MEK–pyridine (9:0.4:0.4:4). (1,2) PS with MW (1) 10 · 10^3 and (2) 200 · 10^3; (3) BC-52; (4) BC-21; (5) BC-31; (6) BC-41; (7–9) PtBMA with MW (7) 20 · 10^3, (8) 80 · 10^3 and (9) 200 · 10^3.

with similar MW of the PtBMA blocks (13.5 · 10^3, 15 · 10^3 and 64.5 · 10^3, 60 · 10^3, respectively) but with different MW of the PS block have the same R_F values values for each pair determined by the MW of the PtBMA blocks. This can be seen if these R_F values are compared with those for PtBMA with MW equal to 20 · 10^3 and 80 · 10^3.

Hence, in this instance the conditions of CTLC (PS)–ETLC(PtBMA) are observed, the PS block of BC is chromatographically invisible and the comparison with the ETLC of PtBMA makes it possible to evaluate the MW of the PtBMA block.

The values of MW for the investigated BC and their PS and PtBMA blocks obtained according to the TLC data (Table I) show that they are in good agreement with each other and with the data obtained from the polymerization conditions and MEC.

In many instances BC are inhomogeneous and contain homopolymer admixtures. They can be removed under the conditions of pre-critical TLC in which the impurities of a more "tacky" homopolymer are more intensively absorbed than BC (their R_F value is lower than that for BC). Homopolymer admixtures may be separated from BC by using stepwise TLC [17]. The authors separated PS from BC with the aid of ETLC on a dry plate in chloroform. Under the chosen polymerization conditions, the investigated BC dit not contain homo-PtBMA admixtures. If necessary, PtBMA may be separated from BC with the aid of precipitation TLC by using an appropriate solvent.

It may be assumed that the proposed method of analysis of composition inhomogeneity of BC is universal, and the mechanism of carrying out the analysis under the conditions described here by normal-phase and reversed-phase (with dynamic modification of the silica gel) TLC is relatively easy. A procedure for the determination of BC compositional inhomogeneity on the basis of this method may be proposed.

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