

CHROM. 8153

## USE OF COMBINED CHROMATOGRAPHIC METHODS INCLUDING THIN-LAYER CHROMATOGRAPHY FOR ANALYSIS OF COMPLEX POLYMER SYSTEMS

### DETERMINATION OF THE POLYDISPERSITY OF BLOCK COPOLYMERS OF STYRENE AND METHYL METHACRYLATE BY GEL PERMEATION, THIN-LAYER AND PYROLYSIS GAS CHROMATOGRAPHY

B. G. BELENKII, E. S. GANKINA, P. P. NEFEDOV, M. A. LAZAREVA, T. S. SAVITSKAYA  
and M. D. VOLCHIKHINA

*Institute of Macromolecular Compounds, Academy of Sciences of the U.S.S.R., Leningrad (U.S.S.R.)*

(First received March 26th, 1974; revised manuscript received December 19th, 1974)

---

#### SUMMARY

A combination of gel permeation chromatography (GPC), thin-layer chromatography (TLC) and pyrolysis gas chromatography (PGC) has been used for investigations of a polymethyl methacrylate-polystyrene-polymethyl methacrylate block copolymer. Continuous distribution of the polymer (40-mg sample) was attained according to the content of the styrene and methyl methacrylate units and of the block copolymer and according to the composition of the copolymer as functions of the hydrodynamic radius of the macromolecules.

The polymer was subjected to a preliminary fractionation with an analytical gel chromatograph. The fractions were investigated by TLC, which permitted the separation of the block copolymer and the homopolymers. The composition of the fractions obtained by GPC and TLC was determined by PGC. As a result, it was possible to establish the composition of the block copolymer and its ratio to polymethyl methacrylate in each fraction.

This investigation was based on a combination of highly effective fractionation by chromatographic methods with precise quantitative ratios obtained from Benoit's universal calibration graph and from determinations of the composition of the polymer fractions by PGC.

The mechanism of the TLC of polymers, including the appearance of artefacts that distort the results of analysis, is also discussed.

---

#### INTRODUCTION

The determination of the polydispersity of block copolymers includes an analysis of their molecular-weight distribution based on composition and on admixtures of homopolymers. Classical methods for the determination of the polydispersity of

copolymers by fractionation based on the different solubilities of polymers of different chemical compositions do not permit the preparation of distinct fractions that are homogeneous in one or several respects, especially for a sample that is polydisperse in molecular weight (MW)<sup>1</sup>. Methods such as sedimentation, diffusion and turbidimetric titration are complicated and unsatisfactory for the determination of the continuous distribution of copolymers<sup>2</sup>.

Chromatographic methods involving fractionation of macromolecules according to their size (gel permeation chromatography, GPC<sup>3</sup>) and chemical composition (thin-layer chromatography, TLC<sup>4</sup>) provide new possibilities for the analysis of block copolymers. GPC can be used not only for the fractionation of polymers but also for the determination of the size of macromolecules (the hydrodynamic radius) on the basis of the unit calibration graph of Benoit *et al.*<sup>5</sup>.

Depending on the composition of the solvent, four versions of the TLC separation of polymers can be carried out:

(1) Adsorption TLC based on the use of a solvent with small additions of an adsorption-active component proposed for the separation of copolymers according to their composition by us<sup>6-8</sup> and by Inagaki *et al.*<sup>9</sup> and for the separation of polymers according to their MW<sup>10</sup>. Adsorption TLC has been used successfully for the separation of syndiotactic and atactic polymethyl methacrylate (PMMA)<sup>11</sup>, the determination of the MW of PMMA<sup>4,12,13</sup>, polyethylene oxide<sup>4</sup> and polystyrene (PS)<sup>14</sup>, the separation of linear and branched PS<sup>15</sup>, the identification of block copolymers<sup>4,16,17</sup> and alternating copolymers<sup>16</sup> and the separation of copolymers according to composition<sup>18,19</sup>.

(2) Precipitation TLC with the use of a mixture of the solvent and the precipitant. Either one of them or both should be adsorption-active and should be present in an amount that prevents polymer adsorption. Under these conditions, the separation of polymers is based on a change in the dissolving properties of the eluent along the chromatographic plate. This change arises as a consequence of the following measures: (a) an eluent with a varying composition is applied to the plate (extraction version of precipitation TLC<sup>20</sup>), or (b) the composition of the eluent changes owing to evaporation and/or decreasing phase ratio,  $r$  (ratio of the weight of the eluent to the weight of the adsorbent)<sup>13</sup>. Precipitation TLC has been proposed by Kamiyama and Inagaki<sup>13</sup> for the separation of homopolymers and by Kotaka and White<sup>19</sup> for the separation of copolymers by MW. The mechanism of precipitation TLC has been investigated by Kamiyama and Inagaki<sup>13</sup> and Otocka and co-workers<sup>21-23</sup>.

(3) Extraction TLC in a single-component solvent proposed by Inagaki and co-workers<sup>24,25</sup> for the separation of syndiotactic and atactic PMMA from isotactic PMMA, based on selective dissolution of polymers of different structures in the zone of the starting spot (this method has also proved effective for the separation of block copolymers from the accompanying homopolymers<sup>4</sup>).

(4) Gel permeation TLC (TLGPC). We have shown<sup>4,10</sup> that in the TLC of polymers, both the adsorption and the molecular sieve effect may be observed, depending on the composition of the eluent. The latter is observed when the adsorption is suppressed and the pore spaces of the adsorbent have previously been filled with the solvent by exposing the plate to the solvent vapour<sup>4,10</sup> or by pre-elution<sup>25,26</sup>. TLGPC has been shown to be useful for suppressing the effect of MW on the adsorption capacity of random copolymers in adsorption TLC<sup>4</sup>.

A combination of chromatographic methods is of particular interest<sup>15,27</sup>. Thus, one might suggest the following sequence of chromatographic operations for block copolymers. After a preliminary fractionation of macromolecules according to size (by GPC), the fractions are subjected to a second chromatographic separation according to composition by TLC in which the block copolymer is separated from admixtures of homopolymers. Finally, the composition of the fractions obtained by using GPC and TLC is determined by pyrolysis gas chromatography (PGC). This combination is advantageous because it permits large fractionation capacities of chromatography to be used and the fractions to be characterized according to rigorous quantitative relationships: the size of macromolecules is estimated from the universal calibration graph derived by Benoit *et al.*<sup>5</sup> and the composition of the fractions is determined by PGC after an appropriate calibration of the instrument<sup>28</sup>. This sequence of chromatographic operations should be used because of the different scales of fractionation (10–40 mg in GPC, 10–100  $\mu\text{g}$  in TLC). Moreover, an amount of only 3–5  $\mu\text{g}$  of a copolymer is sufficient for the composition of the fractions to be determined by PGC to within 1–3%. In this work, the PGC method was perfected: the sensitivity was increased 10–15-fold and the precision of analysis attained previously<sup>28</sup> was retained. A 40-mg amount of a block copolymer of the ABA type in which A is PMMA and B is PS was fractionated by GPC into 34 fractions with a common analytical gel chromatograph. The fractions were analyzed by TLC in which the homopolymers were separated from the block copolymer and, finally, the composition of the fractions was determined by PGC. These results in combination with data on the composition of fractions obtained by GPC permitted us to obtain very precise continuous distributions of the block copolymer according to several features: the overall composition of the polymer fractions and the composition of the block copolymer, and the presence of homopolymers as a function of the hydrodynamic radius of the polymer fraction. By using some approximations that correlate the hydrodynamic size of the molecules of the block copolymer with their MW and composition<sup>29</sup>, it is possible to obtain a final distribution according to MW rather than hydrodynamic size. However, this procedure was not used in our work.

## EXPERIMENTAL

### *Gel permeation chromatography*

GPC experiments were carried out with a KhZh-1302 liquid chromatograph for polymer analysis (Special Design Office of Analytical Instruments of the Academy of Sciences of the U.S.S.R.) using five Waters Ass. (Framingham, Mass., U.S.A.) chromatographic columns:  $10^5$ ;  $3 \cdot 10^4$ ;  $10^4$ ;  $10^3$ ;  $5 \cdot 10^2$  Å. Dimethylformamide (DMF) was used as eluent. The sensitivity of the refractometer,  $n$ , was  $10^{-6}$ – $2 \cdot 10^{-6}$  refractive index unit.

### *Thin-layer chromatography*

Silica gel KSK with a mean pore diameter of 80 Å, a specific pore volume of 0.9 ml/g and a particle diameter of 20–40  $\mu\text{m}$  was used. The plates,  $6 \times 6$  and  $6 \times 10$  cm, with an adsorbent layer 200 or 500  $\mu\text{m}$  thick (for analytical and preparative TLC, respectively) were prepared with an automatic applicator. Samples of volume 3  $\mu\text{l}$  were applied manually with a calibrated capillary and samples of volume 100–200  $\mu\text{l}$  (for preparative TLC) were applied in a streak with an automatic dosimeter.

The solvents for TLC were of "chemically pure" and "pure for analysis" grades.

For developing the spots, the plates were sprayed with a 1% solution of potassium permanganate in concentrated sulphuric acid and heated at 160° for 10–15 min. The polymer zones were developed as black spots.

In preparative TLC, in order to remove the polymer from the plate, the sorbent layer in the polymer zones was scraped off and packed into a micro-column 1.5–2 mm in diameter and 40 mm in length. The polymer was eluted with acetone (PMMA and the block copolymer). Instruments from the set KTKh-01 (Special Design Office of Analytical Instruments of the Academy of Sciences of the USSR) were used for TLC.

### *Pyrolysis gas chromatography*

For analyzing the composition of the block copolymer, we used a Tsvet-4 chromatograph equipped with a flame ionization detector, a pyrolytic reactor described elsewhere<sup>28</sup> and also a pyrolytic reactor with a Curie point control unit. The pyrolytic reactor described earlier<sup>28</sup> is a flow reactor. A previously heated platinum wire with the polymer sample was introduced into it; the amount of the sample was 3–5  $\mu\text{g}$  and it was applied to the wire from a 0.5% dichloroethane solution. The pyrolysis temperature was 500° and the time of pyrolysis was 10 sec. The products of pyrolysis were separated on a chromatographic column (100  $\times$  0.3 cm) packed with Chromosorb P (100 mesh) with 2% of 1,2,3-tris-(2-cyanoethoxy)propane. The column temperature was 70° and the flow-rate of the carrier gas (helium) was 40 ml/min.

For analyzing small samples of the copolymer, a Pye 104 gas chromatograph (Pye Unicam, Cambridge, Great Britain) was used with a pyrolytic reactor and a Curie point control unit. The pyrolysis temperature was 610° and the time of pyrolysis was 10 sec. The products of pyrolysis were separated on a chromatographic column (100  $\times$  30 cm) packed with Chromosorb P (100 mesh) with 2% of 1,2,3-tris-(2-cyanoethoxy)propane. The column temperature was 70° and the flow-rate of the carrier gas (argon) was 40 ml/min. The polymer samples (0.1–0.3  $\mu\text{g}$ ) were applied to the pyrolyzer wire from a 0.05% solution in dichloroethane.

### *Materials*

*Reference polymers.* Standard polystyrene samples ("high pressure.") with a narrow fractionation range,  $M_w/M_n \leq 1.1$ –1.2, were used. ( $M_w$  = weight-average molecular weight;  $M_n$  = number-average molecular weight).

*Polymer samples.* The block copolymer (PMMA-PS-PMMA) was synthesized by using a bifunctional "triperoxide" initiator<sup>30</sup>.

An "active" PS was prepared by polymerization of styrene (St) with "triperoxide" at 75° and heating at 100° in the presence of methyl methacrylate (MMA) to yield the desired block copolymer. The latter was purified from homopolymer admixtures by selective dissolution in acetonitrile (PMMA) or diethyl ether (PS of MW *ca.* 30,000). PMMA was synthesized from benzoyl peroxide (1–3%) in a benzene solution.

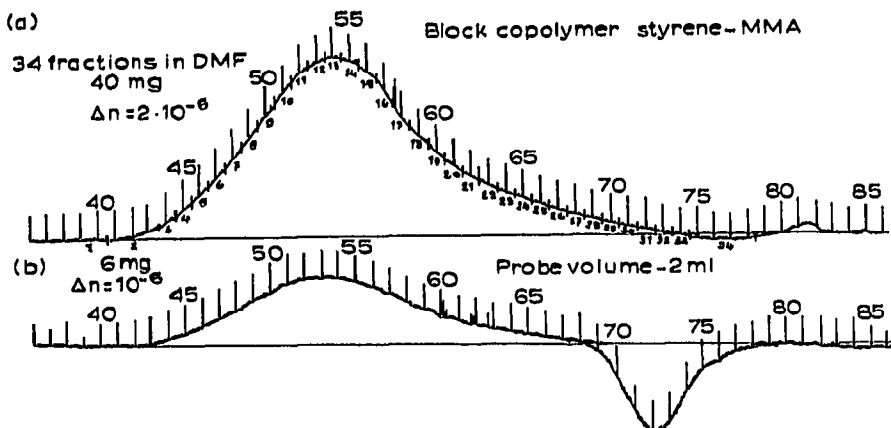


Fig. 1. Gel chromatogram of the PMMA-PS-PMMA block copolymer in DMF (the figures under the curve denote fraction) numbers. (a) Preparative chromatogram (40 mg of polymer); (b) analytical chromatogram (6 mg of polymer).

## RESULTS AND DISCUSSION

### *Gel permeation chromatography of block copolymers of the ABA type*

Fig. 1 shows chromatograms obtained with a KhZh-1302 gel chromatograph. The block copolymer (40 mg) was micro-preparatively fractionated into 34 fractions. An analytical chromatogram of this block copolymer (a sample of 6 mg) is shown for comparison. It is clear that the shapes of both chromatograms are identical; hence, no great deformation of the chromatogram due to increasing concentrations takes place in the micro-preparation. It can be seen from Fig. 2, which shows the results of a control fractionation, that the separation of the block copolymer into fractions is satisfactory. According to Bly<sup>31</sup>, the values of the  $M_w/M_n$  ratios for the fractions are close to 1.4.

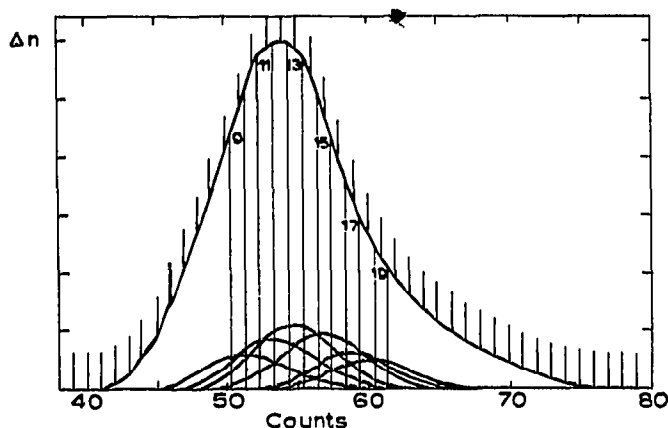


Fig. 2. Chromatogram of the initial block copolymer and of some of its fractions obtained by control fractionation.

The KhZh-1302 chromatograph was calibrated by using reference samples of PS. The Marc-Kuhn constants obtained by us for PS in DMF are obtained from the equation

$$[\eta] = K_{\eta} M^a = 3.96 \cdot 10^{-4} M_w^{0.588} \quad (1)$$

and enable us to transform Moore's calibration dependence<sup>32</sup>:

$$V = C_1 - C_2 \log M \quad (2)$$

into the universal calibration graph developed by Benoit *et al.*<sup>5</sup>:

$$V = D_1 - D_2 \log \{M[\eta]\} \quad (3)$$

where

$$D_2 = C_2/1.588 \quad (4a)$$

and

$$D_1 = C_1 - 2.142C_2 \quad (4b)$$

Fig. 3 shows Moore's experimental curve.

By using the Benoit dependence (eqn. 3) and the expression for the hydrodynamic radius of the macromolecule,  $R_s$ , related to rotary diffusion<sup>33</sup>:

$$R_s = \left( \frac{3[\eta] M}{10\pi N_A} \right)^{1/3} \quad (5)$$

where  $N_A$  is Avogadro's number, we obtain the retention volume,  $V$ , as a function of  $\log R_s$ :

$$V = B_1 - B_2 \log R_s \quad (6)$$

where

$$B_2 = 2D_2 \quad (7a)$$

and

$$B_1 = D_1 - D_2 \log \left( \frac{10\pi \cdot 6.06 \cdot 10^{23}}{3 \cdot 10^{26}} \right) = D_1 + 1.19 D_2 \quad (7b)$$

Fig. 3 also shows the calibration dependence (eqn. 6). It permits the establishment of the distribution of macromolecules according to hydrodynamic radius on the basis of GPC.

GPC was used for fractionating not only the block copolymer but also PMMA in order to compare the TLC behaviour of samples of these polymers obtained with a

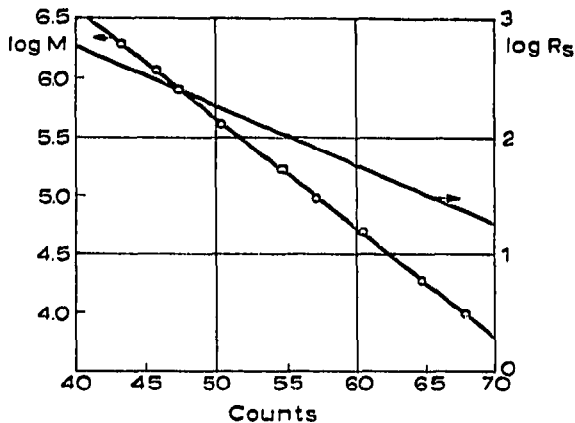


Fig. 3. Retention volume ( $V$ ) versus MW and hydrodynamic radius of macromolecules ( $R_s$ ) determined from eqn. 6.

gel chromatograph by using equal retention volumes. This procedure permitted the precise identification of the PMMA admixture in fractions of the block copolymer and the selection of optimum systems for the chromatographic separation of PMMA and the block copolymer over a wide range of MW.

#### *Pyrolysis gas chromatography of polymers*

Fig. 4 shows pyrograms of the block copolymer obtained with Tsvet-4 and

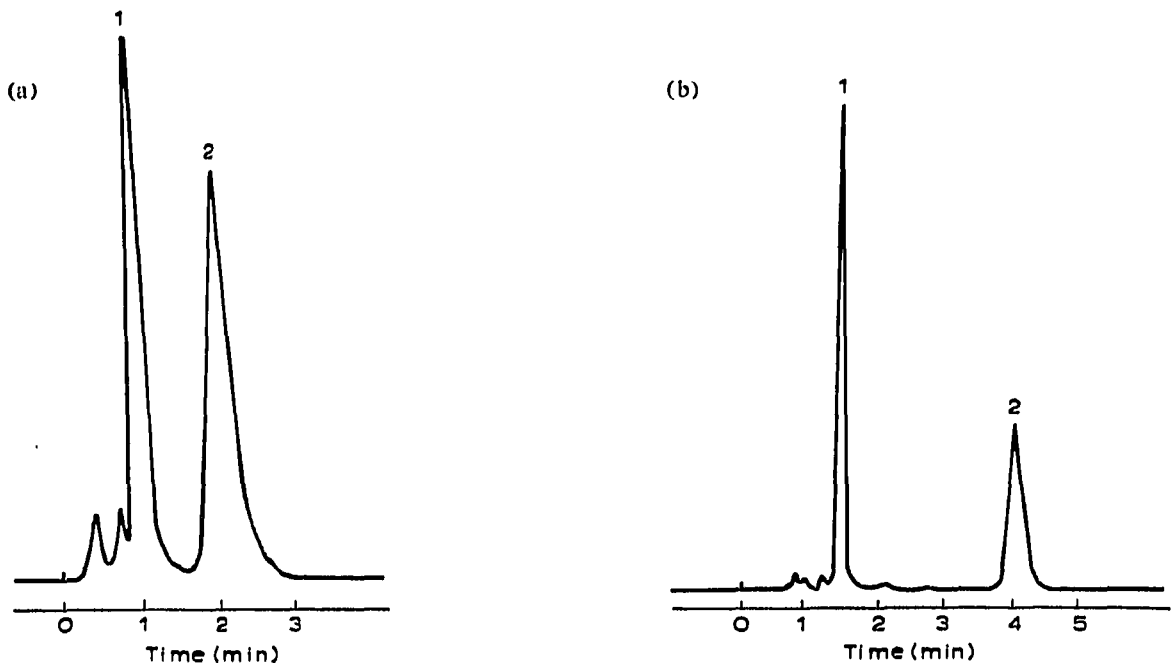


Fig. 4. Pyrograms of the PMMA-PS-PMMA block copolymer obtained with (a) Tsvet-4 and (b) Pye 104 chromatographs. 1, MMA; 2, St.

Pye 104 gas chromatographs. Both chromatograms show good separations of the chromatographic peaks of MMA and St. The time of the analysis was 4 min with the former instrument and 5 min with the latter, excluding the time required for the introduction of the sample into the pyrolytic reactor (for a Pye chromatograph it is much longer than for a Tsvet-4 chromatograph with the pyrolytic reactor described previously<sup>28</sup>). The reproducibility of the pyrograms obtained with both instruments is the same (1–3 %). As already mentioned, the sensitivity of analysis with a Pye chromatograph is higher.

It is known<sup>28,34</sup> that, depending upon the characteristics of a polymer (MW, composition), its pyrolysis proceeds differently. However, conditions of pyrolysis can be chosen such that these differences do not affect the chromatogram<sup>28</sup>. It is clear that only under these conditions PGC is suitable for our purposes, *i.e.*, for investigation of the polydispersity of the block copolymer. Fig. 5 shows the ratio of the areas under the chromatographic peaks for St and MMA in the pyrogram as a function of the ratio of the proportions of these monomers in the sample. It is evident that, irrespective of the MW of PMMA\* and the type of the sample (mixture of homopolymers, random or block copolymer), under the conditions of pyrolysis used all of the experimental points fall on a straight line, which can be used as a calibration graph for determining the overall composition of the block copolymer (if the gas chromatograph is calibrated by using mixtures of PS and PMMA).

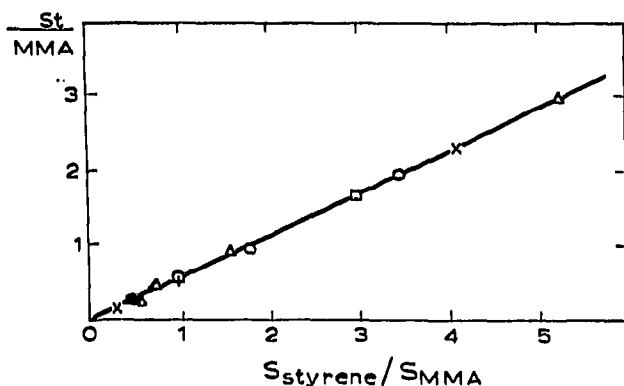


Fig. 5. Ratios of peak areas for St and MMA ( $S_{St}/S_{MMA}$ ) versus ratios of the residues of these monomers ( $q_{St}/q_{MMA}$ ) in polymers of different types. Random copolymer of St–MMA (+); block copolymer of St–MMA (●); mixtures of PS with MW = 51,000 and PMMA with different MW: 30,000 (○); 60,000 (×); 100,000 (□); and 200,000 (△).

#### TLC of block copolymers of St and MMA

Inagaki and co-workers<sup>17</sup>, in investigations on the hydrodynamics of block copolymers in solvents of different thermodynamic strength, found that adsorption TLC is very sensitive to conformational changes in the block copolymers of the AB and ABA types<sup>35</sup>. Thus, if a solvent is a poor solvent for PS and a good solvent for

\* For PS, it is known that the character of its thermal decomposition is virtually independent of its MW.



PMMA (*e.g.*, the nitroethane–acetone system), it follows that when the MW of the block copolymer increases, the PS block collapses and a compact helical PS domain is formed, surrounded by a PMMA envelope. Owing to this intramolecular phase separation, as the MW increases the AB or the ABA block copolymer becomes increasingly similar to pure PMMA in its adsorption properties. Conversely, the greatest differences in the adsorption characteristics between PMMA and a copolymer of St and MMA that contains a small percentage of St will be observed in a system of solvents equally good for PS and PMMA, such as benzene–butanone.

Proceeding from Inagaki and co-workers' concepts, it might be assumed that the greatest difference in the adsorption properties of PMMA and a block copolymer of the ABA type that contains little St (in particular, for a block copolymer of high MW) should be observed in a solvent system that is thermodynamically good for PS and poor for PMMA. However, they did not study such a system.

In the separation of block copolymers of the ABA type according to composition, we can use the precipitation mechanism rather than the adsorption mechanism. In this case, in a system that is poor solvent for one of the homopolymers that constitutes the block copolymer, the block copolymer enriched with this homopolymer may be selectively precipitated. In principle, under these conditions the separation of the homopolymer and the block copolymer that contains a small amount of the second component may take place. It is based on selective dissolution of the homopolymer, whereas the block copolymer remains insoluble in the starting spot. In this connection, it would be of interest to develop a chromatographic system the composition of which changes as the solvent migrates along the plate and the thermodynamic strength with respect to the homopolymer decreases. Then the homopolymer separated from the block copolymer would not move with the solvent front but would stop near the centre of the plate. This change in the composition of the chromatographic system might be achieved, for example, by the evaporation from the plate of a more volatile component of the solvent that is a good (selective) solvent for the homopolymer.

Chloroform–methanol (*ca.* 1:3) exhibits these properties. As this system contains large amounts of adsorption-active methanol, it follows that PMMA and the block copolymer will not be adsorbed on silica gel. Also, chloroform, a selective solvent for PMMA, is more volatile than methanol, and it will therefore be the first to be evaporated from the plate in the chromatographic chamber unsaturated with the solvent vapour.

Fig. 6 shows the chromatograms of PMMA in the chloroform–methanol (4.5:16) system. The chromatograms were obtained in a common chromatographic chamber unsaturated with the solvent vapour. As the PMMA samples applied along the plate are located along a straight line parallel to the line of the position of their starting points, it may be inferred that an elution gradient exist on the plate<sup>4</sup>. Under these conditions in TLC the block copolymer with an MW equal to the MW of PMMA remained at the start. These properties of our chromatographic system show that it is suitable for separating PMMA and the block copolymer of equal MW and gives an  $R_f$  value of 0.5–0.7 for PMMA. Thus, this system permits the separation of PMMA from both the block copolymer and PS and also from various admixtures moving with the solvent front.

It should be noted that as the chloroform content in the system decreases, precipitation of PS takes place first, which is followed by precipitation of PMMA

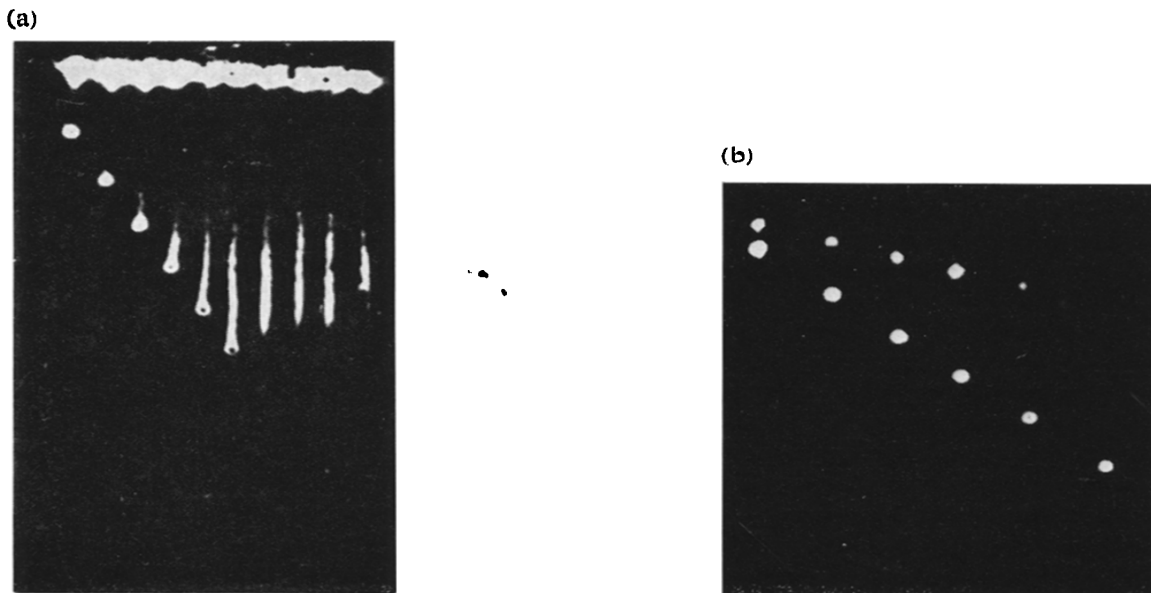


Fig. 6. Thin-layer chromatogram of PMMA (MW = 500,000) (a) in chloroform-methanol (6:16) in an unsaturated chamber and (b) in chloroform-methanol (4.5:16) in a chamber with preliminary saturation.

(Fig. 7). As a result, a block copolymer of the ABA type with a low content of St collapses in the region of the B block and, acquiring solubility properties similar to those of PMMA, moves with it along the plate. This leads to difficulties in separating the block copolymer and PMMA by this method. In order to ensure a better separation of the block copolymer and PMMA, it was necessary to vary the composition of the chromatographic system depending on the MW ( $R_f$ ) of the polymer, as shown in Table I. As expected, the results in Table I indicate that with increase in the MW of PMMA (decrease in the fraction number), systems that contain a smaller amount of precipitator (methanol) should be used.

By eluting the zones of the block copolymer and of PMMA with acetone and determining their composition by PGC, we can estimate the ratio of PMMA to the block copolymer in a sample (in a fraction obtained by GPC).

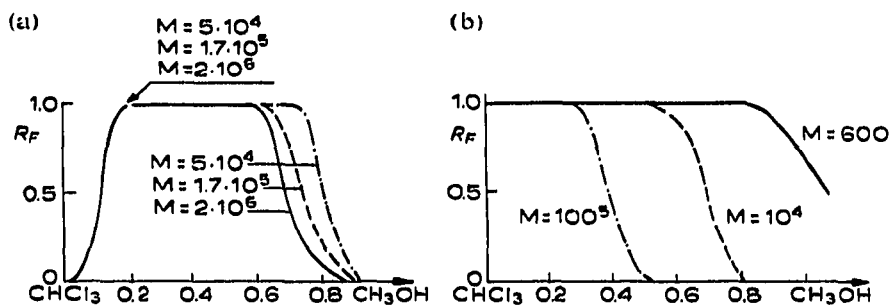


Fig. 7.  $R_f$  for (a) PMMA and (b) PS versus the composition of the chloroform-methanol system in the TLC of polymers of different MW.

TABLE I  
COMPOSITION OF BLOCK COPOLYMER AND RATIO OF PMMA TO BLOCK COPOLYMER IN FRACTIONS OBTAINED BY GPC (Fig. 1) (ACCORDING TO TLC AND PGC)

V or fraction in chromatogram (Fig. 1)	Composition of TLC solvent system (chloroform:methanol, v/v)	Overall composition of the fraction, $z = \frac{m''_{PS}}{m''_{PMMA}}$	Overall composition of the lower spot (block) copolymer, $x = \frac{m'_{PS}}{m'_{PMMA}}$	Overall composition of the middle spot (PMMA), $y = \frac{m''_{PS}}{m''_{PMMA}}$	MMA content of the block copolymer (%)	Ratio of PMMA to block copolymer in a fraction, $\omega = \frac{q_{PMMA}}{q_{block}}$
	6:16	0.23	0.32	0.024	75.7	0.34
5	6:16	0.03	0.04	0.009	96	0.464
7	6:16	0.04	0.08	0.018	92.2	1.72
9	0:06	0.06	0.12	0.026	89.4	1.62
11	5.5:16	0.09	0.14	0.005	88	0.522
14	5.5:16	0.16	0.24	0.005	80.9	0.42
15	5:16	0.18	0.31	0.007	76.6	0.58
17	5:16	0.28	0.49	0.013	67.3	0.535
19	4.2:16	0.55	0.77	0.014	56.4	0.234
20	4.2:16	0.80	0.88	0.008	53.3	0.054
23	4:16	2.36	1.13	0.051	47	0.26
24	4:16	3.34	1.33	0.043	43	0.27

Determination of the weight ratio of the polymer fractions obtained by TLC based on analysis of their overall composition (by PGC)

Determination of the content of the block copolymer in the sample and of its composition. It is easy to show that if the chemical composition (the ratio of the monomer units) of the two polymer components

$$m'_1/m'_2 = x; m''_1/m''_2 = y \quad (8)$$

and the chemical composition of the mixture

$$m'''_1/m'''_2 = Z \quad (9)$$

are known, it is possible to determine the ratio of weight components  $q(i)$  in this mixture,  $\omega = q''/q'$ :

$$\omega = \frac{(z-x)(1+1/y)}{(1+x)(1+z/y)} = \frac{(z-x)(1+y)}{(1+x)(y-z)} \quad (10)$$

In the case when the first component is a pure or an almost pure homopolymer, ( $m'_1 \rightarrow 0$ ,  $m'_2 \rightarrow q'$ ), eqn. 10 becomes

$$\omega = \frac{1+y}{(y/z)-1} \quad (11)$$

Thus, for estimating the ratio of the components in a mixture, it is sufficient

to determine its chemical composition  $z$  and the composition of separated components ( $x$ ,  $y$ ) and to use eqn. 10 or 11 to calculate  $\omega$ .

This method of calculation was checked by using model mixtures of PS and PMMA. Two mixtures were prepared with weight ratios of PS to PMMA of 1:2 and 1:20. These mixtures were considered as components and were used for preparing new mixtures; their composition and the composition of the initial mixtures were determined by PGC. The precision of the determinations was 6–7%.

The results of the analysis of fractions of the block copolymer with determination of  $x$ ,  $y$  and  $z$  are shown in Table I.

*Formation of artificial chromatographic zones in the TLC of PMMA*

In the TLC of PMMA in the S-chamber when the chloroform–methanol system (3.5:16) was used as eluent, we observed an interesting phenomenon associated with the separation of the chromatographic spot into two parts. The chromatogram of PMMA obtained under these conditions and with the starting spot applied along the diagonal of the plate is shown in Fig. 8. It is evident that the PMMA samples the starting points of which are located near the line of the immersion remain at the starting spot while the upper PMMA spots move from the start and migrate with the solvent front. It is characteristic that the larger the amount of the polymer that remains at the starting spot, the lower is the amount of the polymer in the polymer zone near the solvent front. It seems that the explanation of this interesting phenomenon, which can lead to erroneous conclusions concerning the amount of the components in the PMMA samples under analysis, is as follows. As seen from Fig. 7, the chloroform–methanol system exhibits two ranges of concentrations in which the  $R_F$  value for PMMA changes from 0 to 1. This is the zone with a methanol content of 0–5% and the zone that contains over 70% of methanol.

When this chromatographic system migrates along the plate, frontal separation of the methanol zone and the chloroform zone should be observed (when meth-

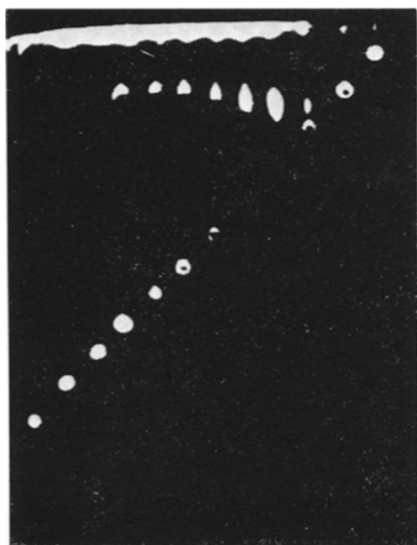


Fig. 8. Thin-layer chromatogram of PMMA (MW = 500,000) in an S-chamber in the chloroform–methanol (3.5:16) (contact photo).

anol is in excess, the fronts of these zones should be located relatively near each other). Hence, when the spreading front of the methanol zone with low methanol concentration comes into contact with the chromatographic spot, it should dissolve a certain part of the polymer which moves along the plate in this range of methanol concentrations according to the laws of adsorption chromatography, *i.e.*, the rear boundary of the polymer zone becomes sharper because it is accelerated by the concentration gradient of methanol.

As a result, the upper spots of the polymer are parallel to the solvent front. However, when the flow-rate of the solvent greatly exceeds the rate of polymer dissolution, the region of the starting spot is rapidly occupied by that part of the solvent front in which the concentration of methanol exceeds 70%, and the PMMA that has not dissolved by this stage can no longer be dissolved.

As a result, the polymer zone is divided into two parts, one of which moves with the solvent front and the other remains at the start. Apparently, there should be no difference in the properties of the polymer in these zones\*: hence, the formation of two chromatographic spots is an artefact resulting from specific conditions of polymer chromatography in a binary solvent system when the polar component in high concentrations is a precipitator for the polymer. Evidently, the longer the time for polymer dissolution, *i.e.*, the slower the migration of the solvent along the plate, the greater is the part of the polymer in the spot that moves with the solvent front and the smaller is the amount of PMMA that remains in the starting zone. Hence, it is clear that the higher the location of the starting spot of the polymer along the plate, the smaller is the amount of it that remains in the starting zone as the flow-rate of the solvent decreases as it rises up the plate.

An interesting result is observed in the TLC of PMMA in a chamber saturated with the solvent vapour when the same chromatographic system is used (chloroform-methanol, 4.5:16; Fig. 8c). Here, the upper spots of the polymer are at an angle to the line of the solvent front, which indicates that gradient conditions on the plate are absent. Thus, part of the polymer in one solvent remains at the start whereas the other part migrates along the plate according to the laws of elution chromatography. This may occur when the concentration of methanol in the eluent that ensures that the precipitation TLC of PMMA occurs is higher than the concentration that permits the dissolution of this polymer in the zone of the starting spot. The passing of the polymer from the solid phase adsorbed on the plate into solution takes place through the formation of the gel phase. In this case, the first stage of dissolution requires a stronger solvent (containing less methanol) than the second stage, corresponding to an elementary act in precipitation TLC. This agrees with Otocka *et al.*'s observation<sup>23</sup> that the threshold of the polymer solubility decreases in the presence of the adsorbent and that the quality of the solvent affects the desorption rate.

When the eluent contains methanol in an amount greater than that necessary for the transition of the polymer from the solid state into the gel phase, dissolution of the polymer in the region of the starting spot occurs only if the solvent front (in which the concentration of methanol decreases) passes through it. In this case, as in TLC in unsaturated chambers (Fig. 8a and b), the shorter the time during which the solvent

\* Nevertheless, some difference in the MW of PMMA in both spots is possible as the time of dissolution is limited and low-molecular-weight components are eluted from the starting spot first.

front is in contact with the starting spot (the closer is this spot to the line of immersion of the plate into the solvent), the smaller is the part of the polymer that passes into solution and is developed as the upper spot.

*Continuous distribution of the overall composition of the content of the block copolymer and of its composition plotted as functions of the hydrodynamic radius of the polymer fraction,  $R_s$*

As a result of the investigation of the block copolymer fractions obtained by GPC (Fig. 1), it is possible to determine by PGC and TLC the weight ratio of PS to PMMA in each fraction,  $z$ :

$$z = m_{\text{PS}}/m_{\text{PMMA}} \quad (12)$$

where  $m$  is the amount of the substance, and, by using eqn. 11 the weight ratio of PMMA to the block copolymer in these fractions,  $\omega$ :

$$\omega = q_{\text{PMMA}}/q_{\text{block}} \quad (13)$$

Evidently, the ratios  $z$  and  $\omega$  are also valid for the corresponding concentrations of the polymer solutions in the fractions obtained with a gel chromatograph. Now, if we know the refractive index increments for PS and PMMA,  $(\partial n/\partial c)_{\text{PS}}$  and  $(\partial n/\partial c)_{\text{PMMA}}$ <sup>\*</sup>, and the change in the refractive index of the solution with respect to the solvent,  $\Delta n$ , it is possible to determine from chromatograms the ratio of PS to PMMA and to the block copolymer in a fraction, depending on its hydrodynamic size,  $R_s$ .

For this purpose, using the rule of additivity of refractive index increments for the components of a copolymer in solution<sup>36</sup>, we can write

$$\left(\frac{\partial n}{\partial c}\right)_{\text{PS}} \cdot C_{\text{PS}} + \left(\frac{\partial n}{\partial c}\right)_{\text{PMMA}} \cdot C_{\text{PMMA}} = \Delta n \quad (14)$$

Solving this equation in combination with eqn. 12, we obtain

$$C_{\text{PMMA}} = \frac{\Delta n}{\left(\frac{\partial n}{\partial c}\right)_{\text{PS}} \cdot z + \left(\frac{\partial n}{\partial c}\right)_{\text{PMMA}}} \quad (15)$$

If we replace  $\Delta n$  by  $n/l/l_0$ , where  $n$  is the limit of measurement of the refractive index on the complete scale of a recorder of length  $l_0$  and  $l$  is the deviation of the pointer of the recorder corresponding to  $\Delta n$ , we have

$$C_{\text{PMMA}} = \frac{n/l/l_0}{\left(\frac{\partial n}{\partial c}\right)_{\text{PS}} \cdot z + \left(\frac{\partial n}{\partial c}\right)_{\text{PMMA}}} \quad (16)$$

Using the value of  $C_{\text{PMMA}}$  in eqn. 16, we obtain  $C_{\text{PS}}$  with the aid of eqn. 12

\* For DMF,  $(\partial n/\partial c)_{\text{PS}} = 0.173 \text{ ml/g}$  and  $(\partial n/\partial c)_{\text{PMMA}} = 0.064 \text{ ml/g}$ .

and, summing these values, we can estimate the total amount of the polymer in a given fraction of the solution,  $C_i$ , corresponding to  $R_{s,i}$ :

$$C_i = C_{PS_i} + C_{PMMA_i} \quad (17)$$

Eqn. 13 makes it possible to determine the concentration of the block copolymer,  $C_{\text{block}}$ . As shown above, the ratios of the concentrations,  $C_{PS}/C_{PMMA}$  and  $C_{PMMA}/C_{\text{block}}$ , can be replaced by the weight ratios of the respective components in the polymer contained in a given fraction.

The final results of the calculations are summarized in Fig. 9, which shows the distribution of the overall composition of the polymer sample, the amount of the block copolymer present in it and the latter's composition as a function of  $R_s$ . It is clear that an increase in the  $R_s$ (MW) of the sample leads to a decrease in the content of PS and an increase in the content of PMMA. This is understandable as the synthesis of the block copolymer proceeds in two stages and PMMA is attached to the PS block. Naturally, under these conditions, the MW of the polymer increases with the increasing content of PMMA.

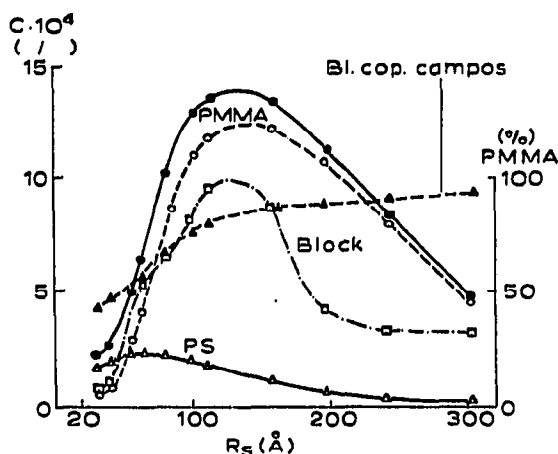


Fig. 9. Distribution of the PMMA-PS-PMMA block copolymer depending on  $R_s$ . Unfractionated polymer (●); PS (▲); PMMA (○); block copolymer (□); content of PMMA in the block copolymer (△) according to GPC.

It should be noted that the results of our investigation do not permit precise conclusions to be drawn concerning the mechanism of the preparation of the block copolymer, as we studied a sample with partially washed-off homopolymers.

## CONCLUSIONS

This work clearly demonstrates the considerable analytical possibilities of the combined use of chromatographic methods in investigations of complex polymer systems. The distributions obtained for block copolymers of the ABA type are very detailed and continuous. Moreover, the results are not obtained by using arbitrary

TABLE II  
RESULTS OF ANALYSES OF BLOCK COPOLYMER BY GFC, TLC AND PGC

Fraction No. (Fig. 1)	Counts in chromatogram (start and finish)	$R_s$ (Å)	Overall composition of fraction (z)	PMMA: block copolymer ratio in a fraction <sup>13</sup>	MMA content in block copolymer (%)	PMMA <sup>16</sup>	PS <sup>12</sup>	Block copolymer <sup>13</sup>	Overall <sup>17</sup>
						Polymer concentration $\times 10^4$ (g/100 ml)			
5	45-46	302	0.03	0.46	96	4.75	0.14	3.34	4.89
7	47-48	340	0.04	1.72	99.2	8.2	0.33	3.1	8.53
9	49-50	195	0.06	1.62	89.4	10.8	0.65	4.3	11.45
11	51-52	155	0.09	0.52	88	12.3	1.11	8.8	18.41
14	54-55	109	0.16	0.42	80.9	11.8	1.89	9.6	13.69
15	55-56	98	0.18	0.58	76.6	11	1.98	8.2	12.98
17	57-58	79.5	0.28	0.54	67.3	7.98	2.24	6.6	10.22
19	59-60	63	0.55	0.23	56.4	4.18	2.3	5.3	6.48
20	60-61	55	0.80	0.05	53.3	2.94	2.35	5.1	5.29
23	60-64	39.8	2.36	0.26	47	0.8	1.89	1.1	2.69
24	64-65	35.5	3.34	0.27	43	0.51	1.7	0.73	2.21



assumptions but are based on reliably established physical relationships: the fractionation of macromolecules according to their size by GPC, the Benoit universal calibration graph, the fractionation of polymers according to composition by TLC and the quantitative determination of the copolymer composition by PGC. In addition, only 40 mg of polymer are required for the analysis, so that it can be concluded that the use of combined chromatographic methods in analytical studies of high-molecular-weight compounds provides excellent possibilities for investigation of complex polymer systems.

#### ACKNOWLEDGEMENTS

The authors thank T. A. Sokolova, G. D. Rudkovskaya and L. D. Ovsianikova for supplying samples of block copolymers and PMMA and for helpful discussions.

#### REFERENCES

- 1 O. Fuchs and W. Schmieder, in M. Y. R. Cantow (Editor), *Polymer Fractionation*, Academic Press, New York, London, 1967.
- 2 S. Ya. Frankel, *Vvedenie v Statysticheskuyu Teoriju Polimerizatsii*, Nauka, Moscow, Leningrad, 1965.
- 3 J. Johnson and R. Porter, *Progr. Polym. Sci.*, 2 (1971) 000.
- 4 B. G. Belenkii and E. S. Gankina, *J. Chromatogr.*, 53 (1970) 3.
- 5 H. Benoit, Z. Grubisic, P. Rempp, D. Decker and J. Zilliox, *J. Chim. Phys.*, 63 (1966) 1507.
- 6 B. G. Belenkii, E. S. Gankina and L. D. Turkova, v kn. *Lektsii 2-Oi Shkoly po Metodam Ochistki i Otsenki Chistoty Monomerov i Polimerov*, Chernogolovka, 1968, p. 216.
- 7 I. A. Baranovskaya, B. G. Belenkii, E. S. Gankina and V. E. Eskin, v kn. *Sintez, Struktura i Svoistva Polimerov*, Moscow, Leningrad, Nauka, 1970, p. 77.
- 8 B. G. Belenkii and E. S. Gankina, *Dokl. Akad. Nauk SSSR*, 186 (1969) 857.
- 9 X. Inagaki, H. Matsuda and F. Kamiyama, *Macromolecules*, 1 (1969) 520.
- 10 B. G. Belenkii and E. S. Gankina, *Dokl. Akad. Nauk SSSR*, 194 (1970) 573.
- 11 H. Inagaki and F. Kamiyama, *Macromolecules*, 6 (1973) 107.
- 12 X. Inagaki, F. Kamiyama and T. Jagi, *Macromolecules*, 4 (1971) 133.
- 13 F. Kamiyama and H. Inagaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, 49 (1971) 53.
- 14 F. Kamiyama, H. Matsuda and H. Inagaki, *Polym. J.*, 1 (1970) 518.
- 15 B. G. Belenkii, E. S. Gankina, P. P. Nefedov and M. A. Kuznetsova, *J. Chromatogr.*, 77 (1973) 209.
- 16 F. Kamiyama, H. Matsuda and H. Inagaki, *Makromol. Chem.*, 125 (1969) 286.
- 17 F. Kamiyama, H. Inagaki and T. Kotaka, *Polym. J.*, 3 (1972) 470.
- 18 D. O. Quisenberry, *Tenn. Eng.*, (1971/72) 5.
- 19 T. Kotaka and J. L. White, *Macromolecules*, 7 (1974) 106.
- 20 E. P. Otocka and M. J. Hellman, *Macromolecules*, 3 (1970) 362.
- 21 E. P. Otocka, *Macromolecules*, 3 (1970) 691.
- 22 E. P. Otocka, P. M. Muglia and H. Z. Frisch, *Macromolecules*, 4 (1971) 512.
- 23 E. P. Otocka, M. J. Hellman and P. M. Muglia, *Macromolecules*, 5 (1972) 227.
- 24 T. Miamoto and H. Inagaki, *Macromolecules*, 2 (1969) 554.
- 25 H. Inagaki, T. Miyamoto and F. Kamiyama, *J. Polym. Sci., Part B*, 7 (1969) 329.
- 26 N. Donkai and H. Inagaki, *J. Chromatogr.*, 71 (1972) 473.
- 27 T. Taga and H. Inagaki, *Angew. Makromol. Chem.*, 33 (1973) 129.
- 28 L. D. Turkova and B. G. Belenkii, *Vysokomol. Soedin., Ser. A*, 12 (1970) 467.
- 29 J. R. Runyon, D. E. Barnes and J. F. Tung, *J. Appl. Polym. Sci.*, 13 (1969) 2359.
- 30 T. A. Tolpyshka, V. I. Galibei and S. S. Ivanchev, *Vysokomol. Soedin., Ser. A*, 14 (1972) 1027.
- 31 D. D. Bly, *J. Polym. Sci., Part C*, 21 (1968) 13.

- 32 J. C. Moore, *J. Polym. Sci., Part A*, 2 (1964) 835.
- 33 V. N. Tsvetkov, V. E. Eskin and S. Ya. Frenkel, *Struktura Makromolekul v Rastvorakh*, Nauka, Moscow, Leningrad, 1964.
- 34 B. G. Belenkii, L. D. Turkova and G. A. Andreeva, *Vysokomol. Soedin., Ser. B*, 14 (1972) 349.
- 35 H. Ohnuma, T. Kotaka and H. Inagaki, *Polym. J.*, 1 (1970) 716.
- 36 H. Benoit and W. Bschuk, *Can. J. Chem.*, 36 (1958) 1616.