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THIN-LAYER CHROMATOGRAPHY OF POLYMERS

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CONTENTS

I. INTRODUCTION

In 1968, the first investigations on the thin-layer chromatography (TLC) of random copolymers were carried out simultaneously in our laboratory[1] and by Inagaki at Kyoto University, Japan[2]. Since then, the main trends developed have been investigations of the heterogeneity of polymers [their molecular-weight distribution (MWD) and inhomogeneities of composition] and the identification of polymers with various microstructures[3–5]. The following investigations became possible with the aid of TLC: separation of random copolymers according to their composition[6–9]; determination of molecular weight (MW) and MWD of homopolymers (PS[2,10–14], PEO[3,12] and PMMA[15,16])*, identification and separation of stereoregular PMMA[16–18], separation of poly-1,4-*cis*-, -1,4-*trans*- and -1,2-vinylbutadiene[19], identification of block and graft copolymers of St and MMA and St and PEO, determination of the presence of homopolymers in these copolymers[3,20–22], identification of linear and branched-chain PS[23] and PS with carboxylic end-groups[24], and identification of random, block and alternating copolymers of St–MMA[25,26] and two- and three-block copolymers[27,28]. Later, two groups of American scientists, Otocka and co-workers[12–14,29,30] and White and co-workers[31,32], began to investigate the TLC of polymers. The first group developed a method for the determination of the MWD of PS and studied the mechanism of the TLC of polymers, while the second group investigated the TLC of PS, PBD, polyisoprene and their copolymers and developed a method for the determination of the MWD and compositional homogeneity of copolymers of St and BD. An important trend in the TLC of polymers is the use of this method for the determination of the MWD and the functionality of oligomers[33,34].

Depending on the character of the interactions involved, the following types of TLC of polymers can be carried out:

(a) Adsorption TLC (ATLC). This method was proposed first for the separation of copolymers[1,2,6] and was later used for the analysis of homopolymers[10,12,13]. This type of TLC is based on differences in the adsorption activities of polymers, which increase with the MW and with the percentage of adsorption-active polar groups in a copolymer (oligomer). A peculiarity of ATLC is the use of solvents that contain a small amount of the polar adsorption-active component, the displacer, an increasing content of which leads to an increase in R_F value.

(b) Thin-layer gel-permeation chromatography (TLGPC)[3,6,35]. TLGPC is based on the molecular-sieve effect, *i.e.*, the distribution of polymers between the mobile phase and the porous adsorbent determined from the ratio of the size of the macro-

* The following abbreviations for compounds and polymers are used: St = styrene; PS = polystyrene; MMA = methyl methacrylate; PMMA = poly(methyl methacrylate); EO = ethylene oxide; PEO = poly(ethylene oxide); BD = butadiene; PBD = polybutadiene; P-α-MS = poly(α-methylstyrene); $CHCl_3$ = chloroform; CCl_4 = carbon tetrachloride; MEK = methyl ethyl ketone (2-butanone); THF = tetrahydrofuran; DMF = dimethylformamide; Ch = cyclohexane; Bz = benzene; Ac = acetone.

molecules to the pore size. Polymer adsorption is suppressed and the volume within the pores of the adsorbent is previously filled with the solvent.

(c) Precipitation TLC (PTLC). This method was suggested by Inagaki and co-workers[15,36]. The eluent consists of a polar or a non-polar solvent and a large amount of an adsorption-active precipitant for the polymer. Under these conditions, the adsorption activity of the chromatographic layer is completely suppressed and the separation of polymers is based on changes in the properties of the eluent on the plate effected as follows: (a) by introducing on to the plate an eluent of varying composition (extraction-type PTLC) or (b) by changing the eluent composition on the plate by evaporation and/or decreasing the phase ratio, r (the ratio of the weight of eluent to that of the adsorbent).

(d) Extraction TLC (ETLC)[3,17]. ETLC is based on the selective dissolution of polymers in the region of the starting spot according to the "all or nothing" principle. This method permits the separation in a starting spot of polymers of different types according to their affinities for the solvent.

Combined types of TLC are often used for the separation of polymers. For example, the separation of polymers at the starting spot is carried out according to the mechanism of selective dissolution (desorption) with subsequent fractionation on the basis of ATLC or PTLC.

It is advisable to separate the above four types of TLC into two groups:

(1) Chromatographic methods based on adsorption: ATLC and TLGPC, in which the positive and negative adsorption, respectively, of polymers are carried out on a porous adsorbent.

(2) Chromatographic methods related to the solubility of polymers: PTLC and ETLC, based on the different solubilities of polymers and their different rates of desorption in the region of the starting spot.

At present, TLC is used extensively for investigations of MWD, compositional inhomogeneity and structural peculiarities of widely different classes of polymers and oligomers (Table 1).

II. THIN-LAYER CHROMATOGRAPHY OF POLYMERS BASED ON ADSORPTION

1. Adsorption TLC of copolymers

ATLC was the first type of TLC of polymers to be developed[1,2,6,7] for the fractionation of copolymers according to composition. Investigations on the ATLC of copolymers were related to investigations of random copolymers of St with MA and MMA. For the TLC of the St–MMA copolymers[1,6,7], the elution systems consisted of solvents (chlorinated hydrocarbons) and displacers (adsorption-active oxygen-containing compounds). The dependence of the R_F values of copolymers C-10 (31% St) and C-5 (54% St) on the nature of the solvent and the displacer on a plate coated with silica gel is shown in Table 2.

Table 2 shows that the solvents and the displacers for the St–MMA copolymers can be arranged in the following eluotropic series: diethyl ether $<$ MEK $<$ Ac $<$ THF $<$ dioxan; chlorobenzene $<$ dichloroethane $<$ $CHCl_3$.

The chromatography of copolymers was carried out in an S-chamber in which the displacer gradient was achieved by gradual evaporation of the eluent into the air

TABLE 1

USES OF TLC IN POLYMER ANALYSIS

Quantitative analysis		*Diagnostics*		*Investigations of complex polymer systems (in combination with other chromatographic methods)*
MWD	*Composition homogeneity*	*Branching*	*Microstructure*	
1. Homopolymers (ATLC, PTLC)	1. Random copolymers (ATLC)	1. Homopolymers (ATLC)	1. Random, alternating and block copolymers (ATLC)	1. Analysis of mixtures of linear and branched-chain homopolymers (GPC, ATLC)
2. Random copolymers (PTLC)	2. Block copolymers (ATLC)	2. Oligomers (ATLC)	2. Two- and three-block copolymers (ATLC)	2. Analysis of mixtures of block copolymers and corresponding homopolymers (GPC, PTLC, PGC*)
3. Oligomers (ATLC)	3. Functionality of oligomers (ATLC)		3. Block and graft copolymers and admixtures of homopolymers in these copolymers (ATLC, PTLC and ETLC) 4. Separated side-chains of graft copolymers (ATLC) 5. Regularity of polybutadienes (ATLC, ETLC) 6. Stereoregularity (ATLC, PTLC, ETLC) 7. Carboxylic end-groups of polymers (ATLC)	3. Analysis of graft copolymers, MWD of branched chains (GPC, ATLC)

* Pyrolytic gas chromatography.

TABLE 2

R_F VALUES OF COPOLYMERS WITH 31% (C-10) AND 54% (C-5) OF St IN CHROMATOGRAPHIC SYSTEMS CONTAINING 12 ml OF SOLVENT AND 2.4 ml OF DISPLACER ON PLATES COATED WITH KSK SILICA GEL

Solvent	*Displacer*									
	Diethyl ether		*MEK*		*Ac*		*THF*		*Dioxan*	
	C-10	*C-5*	*C-10*	*C-5*	*C-10*	*C-5*	*C-10*	*C-5*	*C-10*	*C-5*
Dichlorobenzene	0	0	0	0	0	0.52	0	0.71	0	0.83
Dichloroethane	0	0	0	0	0	0.70	0.69	0.92	0.77	0.92
Chloroform	0	0.17	0	0.32	0.49	0.85	0.70	0.90	0.88	0.95

space during its movement up the plate. As the adsorption activities of the St and MMA groups in chlorinated hydrocarbons differ widely, strong gradients were used to separate copolymers of widely differing compositions. These gradients were obtained by mixing the solvent with a small amount of an adsorption-active displacer (such as Ac) or with a large amount of a weak displacer (diethyl ether) (Fig. 1). For the separation of copolymers of similar compositions, chromatographic systems of high resolution with a weak gradient were used, prepared from a solvent containing a small amount of a weak displacer (diethyl ether, MEK).

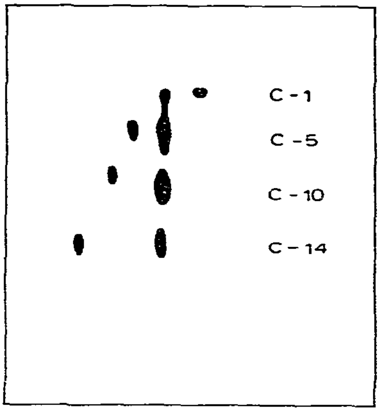


Fig. 1. TLC of random copolymers of St and MMA on KSK silica gel in $CHCl_3$–Ac (12:2.2) in an S-chamber: C-14 (22% St, $M_w = 2.3 \cdot 10^5$), C-10 (31% St, $M_w = 8.7 \cdot 10^4$), C-5 (54% St, $M_w = 8 \cdot 10^4$), C-1 (80% St, $M_w = 1.2 \cdot 10^5$).

Fig. 2 shows chromatograms of copolymers with virtually indistinguishable elemental compositions. However, High-resolution TLC makes it possible to show distinctly that the C-2 copolymer consists of two fractions identical with copolymers C-1 and C-3. The effectiveness of high-resolution TLC for copolymer separations is so great that it permits the determination of differences in the polydispersity of copolymers of azeotropic composition (with 54 mole-% of St) obtained at various extents of conversion (Fig. 3).

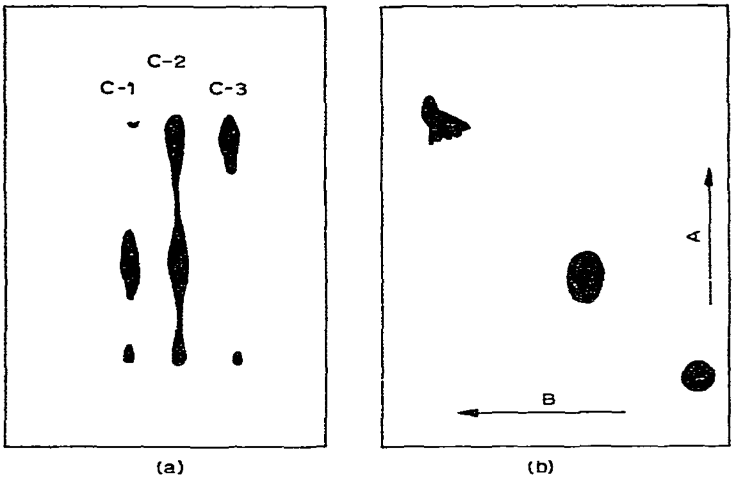


Fig. 2. High resolution TLC: (a) copolymers of St–MMA containing 80% of St (C-1, C-2, C-3) in $CHCl_3$–MEK (12:0.6) in an S-chamber; (b) two-dimensional chromatogram of C-2 in the same solvent system.

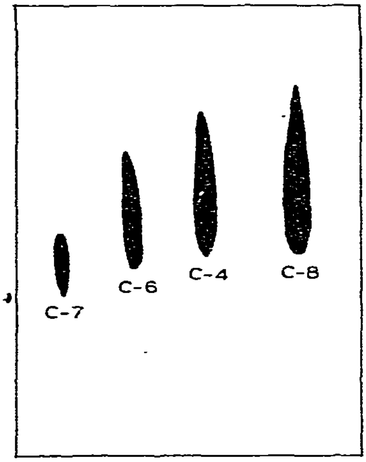


Fig. 3. TLC of azeotropic copolymers of St–MMA containing 54% of St with various degrees of conversion [C-7 (0.5%), C-6 (11.7%), C-4 (33.8%), C-8 (70.6%)] on KSK silica gel in $CHCl_3$–diethyl ether (12:4.2).

A two-dimensional chromatogram (Fig. 4) shows that elongated spots in a one-dimensional chromatogram of azeotropic polymers are produced by the polydispersity of the samples rather than by chromatographic spreading due to concentration effects.

Similar results in the ATLC of random copolymers of St–MMA and St–MA have been obtained by Inagaki *et al.*[2], who has used gradient TLC in which methyl and ethyl acetate were added to $CHCl_3$. They used densitometry of the plates to determine the distribution of the St–MMA copolymer according to composition. This distribution agreed with the theoretical distribution, whereas the mean value of the molar

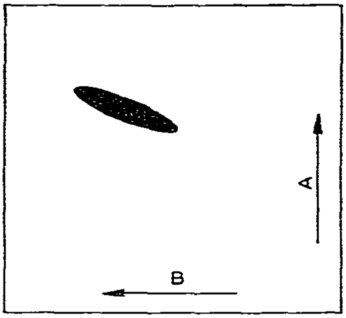


Fig. 4. Two-dimensional chromatogram of the C-4 copolymer (see Fig. 3) in the same solvent system.

fraction of St in the copolymer (0.355) agreed well with the value of 0.342 determined by elemental analysis.

Our investigations[3,6] have shown that the R_F value of the copolymer depends not only on its composition but also on its MW, the strongest dependence being observed at MW $\approx 10^5$ (Fig. 5).

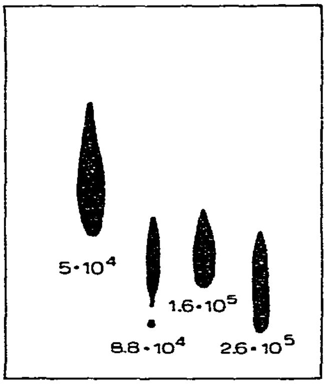


Fig. 5. TLC of random copolymers of St–MMA containing 31 % of St of various MW (M_w) on KSK silica gel in $CHCl_3$–Ac (12:2.2).

Inagaki found[26] that the chromatographic mobility of St–MMA copolymers is related not only to their composition but also to their structure (the block length). Thus, in the $CHCl_3$–ethyl acetate system copolymers containing 49 % of St behave as follows: the block copolymer remains at the start, the alternating copolymer is located in the middle of the plate and the random copolymer migrates at the highest rate. Recently, Donkai *et al.*[28] showed that the R_F value for St–MMA block copolymers varies, depending on the number of blocks present. Thus, in the MEK–CCl_4 gradient systems the R_F value increases in the following order: the two-block, the three block and the random copolymer of St and MMA. At first, Inagaki[26] ascribed these differences (in a similar manner to differences in the adsorption of stereoregular PMMA) to different extents of adsorption of triads of monomer units, considering them as adsorption units of the polymer chain. The nearest neighbours of the adsorbed groups are probably responsible for the extent of polymer adsorption but the triad model of the adsorption of macromolecules suggested by Inagaki[26] is too simple and was later rejected[28].

2. *Adsorption TLC of homopolymers*

The possibilities of using ATLC for the separation of homopolymers according to MW were first demonstrated by Belenkii and Gankina[10]. Fig. 6 shows chromatograms of narrow-disperse PS ($M_w/M_n < 1.1$) obtained on plates coated with KSK silica gel using the Ch–Bz–Ac system; the first two components are solvents for PS and the third is a precipitant. As adsorption-active Ac is present in small amounts in chromatographic systems, ATLC of PS takes place in which Ac acts as a displacer.

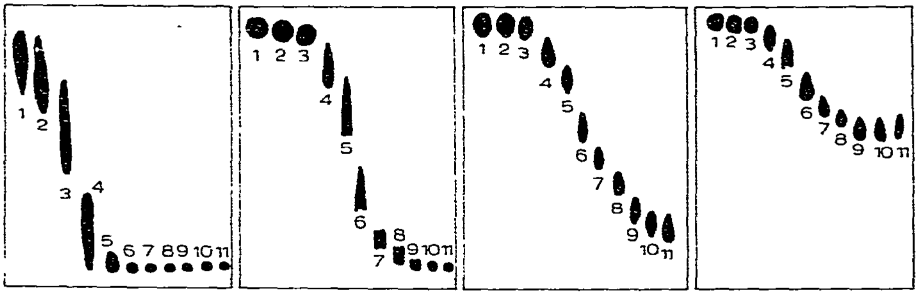


Fig. 6. TLC of narrow-disperse ($M_w/M_n < 1.1$) PS samples on KSK silica gel in Ch–Bz–Ac: (a) 13:3:1; (b) 12:4:0.4; (c) 12:4:0.7; (d) 12:4:1. M_n values of PS samples (1) 900; (2) $2.3 \cdot 10^3$; (3) $4.5 \cdot 10^3$; (4) $9.7 \cdot 10^4$; (5) $1.96 \cdot 10^4$; (6) $4.9 \cdot 10^4$; (7) $9.62 \cdot 10^4$; (8) $1.64 \cdot 10^5$; (9) $3.92 \cdot 10^5$; (10) $8.67 \cdot 10^5$; (11) $1.78 \cdot 10^6$.

Fig. 6 shows that the R_F value of PS increases with increasing content of acetone and, when the system contains over 10% of Ac (Fig. 6d), even polymers with the highest MW cease to be adsorbed. If the plate has previously been saturated with the solvent vapour, PS is separated according to the molecular-sieve effect, low-molecular-weight PS migrating more slowly than high-molecular weight PS.

On the basis of ATLC, it was possible to separate PS in systems that contained only solvents for this polymer with different adsorption activities with respect to silica gel, such as CCl_4–$CHCl_3$ and Ch–Bz. Fig. 7 shows the separation of PS in Ch–Bz systems. It is clear that polymers of low and medium MW are adequately separated and that the chromatography of PS with MW $> 4 \cdot 10^5$ is not effective, probably owing to the low rate of the adsorption–desorption processes for polymers of high molecular weight in these systems.

By using ATLC, it was also possible to separate PEO according to MW in the systems pyridine–water and ethylene glycol–methanol on silica gel and methanol–DMF on aluminium oxide[13] and PMMA in the system $CHCl_3$–methanol on silica gel[22].

As Fig. 7 shows, the ATLC of PS permits its fractionation with high resolution over relatively narrow ranges of MW. It is possible to change these ranges by two methods: by using gradient TLC with a gradual increase in the Ac content of the

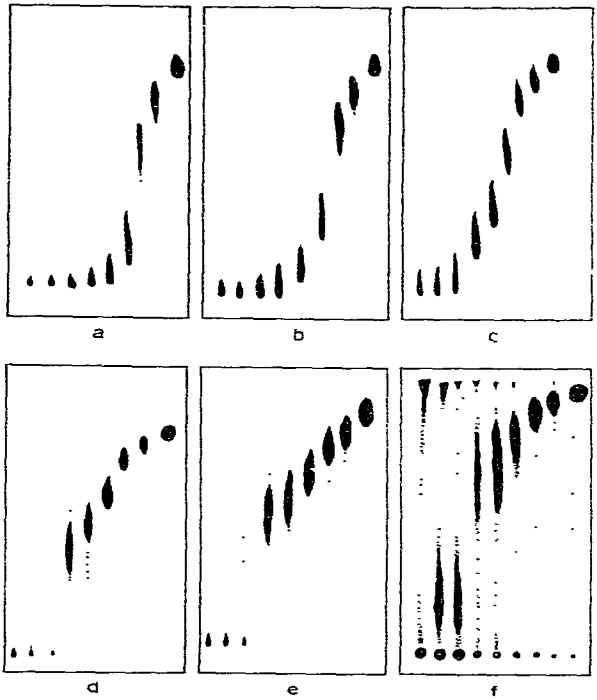


Fig. 7. TLC of PS samples 3–11 (see Fig. 6) from right to left on KSK silica gel in Bz–Ch: (a) 15:7, (b) 15:6.5; (c) 15:6, (d) 15:5.5, (e) 15:5.3; (f) 15:5.

eluent, or by varying the composition of the eluent in such a way as to change the energy of interaction of the polymer unit with the adsorption surface (see p. 26). Thus, Fig. 6 shows that PS of low and medium MW are separated in an eluent containing 2.4% of acetone and, when the acetone content increases to 4.2%, the separation of PS on the plate takes place over the entire range of MW from 10^3 to 10^6.

3. Thin-layer gel-permeation chromatography (TLGPC) of polymers

The possibility of effecting polymer separations by TLC based on the molecular-sieve mechanism has been reported[3,10]. Donkai and Inagaki[35] and Otocka and co-workers[30] have also investigated this type of TLC of polymers. Two conditions are required for the appearance of the molecular-sieve effect in TLC: the suppression of the adsorption activity of silica gel and the filling of the pores of the adsorbent with the solvent before elution. The latter can be achieved by two methods: by pre-elution, *i.e.*, by the passage of the solvent up the plate before spotting of the sample[35], and by capillary condensation, *i.e.*, by preliminary saturation of the plate with the solvent vapour[3,10]. Inagaki[35] found that for the appearance of the molecular-sieve effect the level of pre-elution (the distance between the solvent front and the starting spot at the moment of its application) should attain a certain value (Fig. 8). Fig. 8 shows the differences between ascending and descending TLGPC related to the higher saturation of the inter-particle space by the eluent in the ascending mode. Fig. 9 shows that the

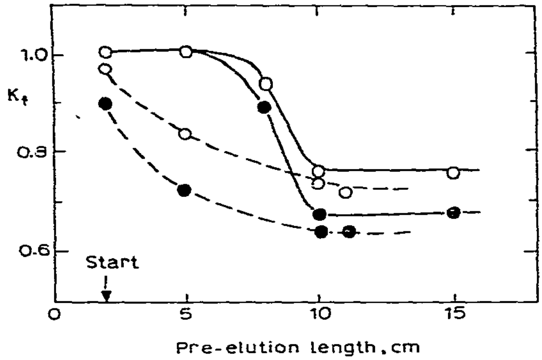


Fig. 8. K_f (ratio of length of development on a plate of the polymer being studied to that of the polymer completely excluded from the sorbent) *versus* pre-elution length for PS with $M_w = 4000$ (●) and $M_w = 10{,}000$ (○) in ascending (solid line) and descending (broken line) TLGPC in THF on silica gel with pore diameter $\varnothing_p = 300$ Å.

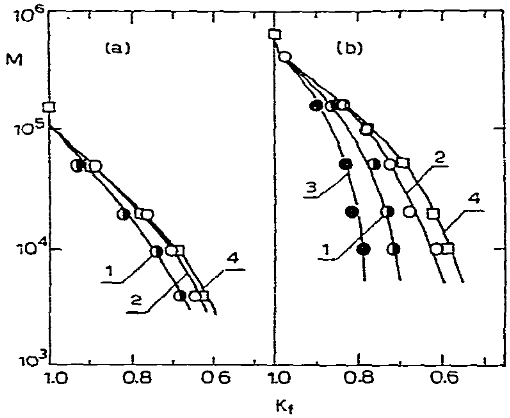


Fig. 9. K_f *versus* log M for PS in TLGPC in THF on silica gels with pore diameter $\varnothing_p$ = (a) 300 Å and (b) 700 Å. Layer thickness in TLGPC: (1) 0.5 mm; (2) 1 mm; (3) 0.25 mm; (4) column GPC.

molecular-sieve effect is less pronounced in TLGPC than in the column GPC and decreases with decreasing thickness of the adsorbent layer. These results indicate that the efficiency of GPC is affected not only by the extent of filling of the inter-particle volume with the solvent, but also by the magnitude of this volume, which is smaller for columns than for plates owing to the denser packing of the adsorbent. The influence of the thickness of the adsorbent layer on the efficiency of TLGPC is probably also related to a decrease in the packing density with decreasing thickness of the layer. Naturally, the pore size of the adsorbent also affects the efficiency of TLGPC (Fig. 9).

4. *Principal relationships in the adsorption TLC of polymers*

Consideration of theoretical studies[37–45] on the peculiarities of the adsorption of macromolecules makes it possible to elucidate the main relationships observed in the adsorption chromatography of polymers on macroporous adsorbents[46]. The change in the free energy of macromolecules in adsorption

$$\Delta F_M = \Delta H_M - T\Delta S_M \tag{1}$$

is related to the formation of the segment–adsorbent contacts, which is accompanied by changes in enthalpy, ΔH_M, and changes in entropy, ΔS_M, of macromolecules when they pass from solution into the adsorbed state. The passage of macromolecules from solution into the pore space of the adsorbent is accompanied by changes in the configurational entropy of solution, ΔS_c, owing to the redistribution of macromolecules and solvent molecules between the solution and the adsorbent. At the equilibrium distribution of macromolecules, the change in ΔF of the system accompanied by a change in ΔS_c of solution is precisely equal to changes in $N_A \Delta F_M$ for adsorbed macromolecules:

$$\Delta F = -T\Delta S_c = N_A \Delta F_M = N_A \Delta H_M - N_A T \Delta S_M \tag{2}$$

where N_A is Avogadro's number. The changes in the enthalpy and energy of the solvent molecules during the adsorption–desorption which accompanies the adsorption of polymer molecules may be included in the value of ΔH_M

The chromatographic mobility, R_F, which is the ratio of the rate of movement of the polymer zone to that of the eluent zone ($R_F = v/u$), is proportional to the probability of the residence of macromolecules in the mobile phase, $w = n/(n + n')$, where n and n' are the numbers of macromolecules in the mobile and the stationary phase, respectively:

$$R_F \equiv \frac{V}{u} = \frac{n}{n+n'} = \frac{1}{1+\frac{V_p}{V_0}\cdot\frac{c'}{c}} = \frac{1}{1+\frac{V_p}{V_0}\cdot K_d} \tag{3}$$

Here V_p and V_o are the volumes of the pore space of the adsorbent and the mobile phase, respectively, c' and c are the corresponding concentrations of macromolecules and $K_d = c'/c$ is the distribution coefficient, which, according to eqn. 2, is given by

$$K_d = \exp\left(-\frac{\Delta F}{RT}\right) = \exp\left(-\frac{\Delta H_M}{kT} + \frac{\Delta S_M}{k}\right) \tag{4}$$

where k is Boltzmann's constant.

It is evident that when enthalpy changes predominate over entropy changes in eqn. 1, we obtain

$$-\Delta F > 0 \tag{5}$$

and K_d is greater than unity. When the entropy changes predominate, we have

$$-\Delta F < 0 \tag{6}$$

and K_d is less than unity. Finally, when ΔH_M is equal to $T\Delta S_M$, we obtain

$$\Delta F = 0 \tag{7}$$

and K_d is unity.

In the first case (eqn. 5) we have adsorption chromatography, in the second (eqn. 6) GPC (molecular-sieve effect) and in the third (eqn. 7) the macromolecules are not influenced by the porous structure of the adsorbent and are distributed as if the adsorbent consisted of one large cavity of volume V_p. Di Marzio[39] considers that this state when the macromolecule in which part of segments is in contact with the adsorbent surface is characterized by the same free energy, ΔF, as in solution, is related to the second-order phase transition. Di Marzio and Rubin[40] have shown that this situation is observed in the adsorption of macromolecules both on a plane surface and in pores, *i.e.*, in the system under consideration*. The energy of interaction of a macromolecular unit with the absorbtion surface, $\varepsilon = -\Delta H_M/N_a kT$ (where N_a is the number of adsorbed units of the macromolecule), which corresponds to the phase transition (at $\Delta H_M = T\Delta S_M$), was called the critical energy, ε_{cr}. Fig. 10 shows the dependence of $-\Delta F_M/NkT$ (where N is the number of segments in the macromolecule) on ε as calculated by Di Marzio and Rubin[40]. It can be seen that, in the adsorption of macromolecules, when ε changes the macromolecule passes through several states, which can be divided into states characteristic of the molecular-sieve effect to the left of ε_{cr}, where K_d is less than unity, and adsorption states to the right of ε_{cr}, where K_d is higher than unity.

In the range where the molecular-sieve effect applies, entropy changes predominate and $-\Delta F$ is less than zero, whereas in the adsorption range enthalpy changes prevail and $-\Delta F$ is greater than zero. If ε is changed, for example by varying the solvent composition or the temperature, then the dependence of the R_F value on MW, characteristic of GPC in which the R_F value increases with increasing MW, changes into the adsorption MW dependence of R_F, the R_F value decreasing with increasing MW. In this instance a state will occur when the R_F value of the polymer does not depend on its MW; this state corresponds to ε_{cr} *i.e.*, to the phase transition of the adsorbed macromolecule.

Hence, by observing the MW dependence of the R_F value during changes in the eluent composition it is possible to determine ε_{cr} (at the point at which the R_F value is independent of MW) and, by using the R_F value at ε_{cr}, to find the V_p/V_0 ratio because in this instance K_d is unity and, consequently, according to eqn. 3

$$\frac{V_p}{V_0} = \left(\frac{1 - R_F}{R_F}\right)_{\varepsilon=\varepsilon_{cr}} \tag{8}$$

The range of the molecular-sieve effect (to the left of ε_{cr} in Fig. 10) is interesting in that here the influence of adsorption energy (ε) on the value of $-\Delta F_M/NkT$ is very pronounced, *e.g.*, in GPC K_d depends not only on the ratio of the size of the macromolecule in the free state to the pore size but also on the interaction of macromolecular segments with the pore surface. Evidently, this should lead to a change in the exclusion limit of macromolecules from the pores of the adsorbent, depending on ε (the eluent composition).

The transition from molecular-sieve chromatography to adsorption chromatography when the interaction energy, ε, changes has been described in the literature, including the literature on TLC[35,47]. Nevertheless, many peculiarities of this process,

* Phase transition of the first order in pores.

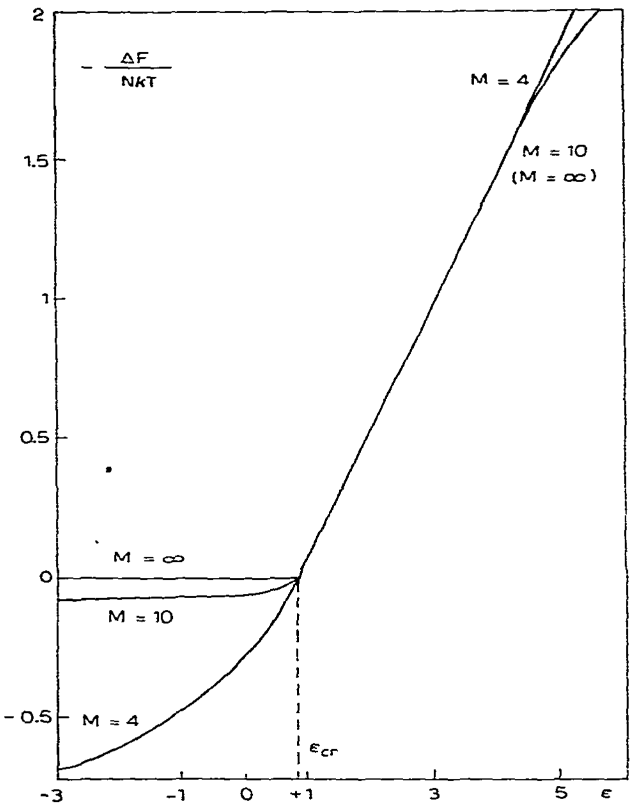


Fig. 10. $-\Delta F/NkT$ *versus* energy of interaction of the segment of macromolecule with the adsorbent surface ($\varepsilon = -\Delta H/N_a kT$) ($M$ is the slit width in segment length units).

in particular the fact that during changes in ε a transition is observed through the state characterized by the critical energy, have not been considered before.

These effects may be observed in the TLC of polymers (*e.g.*, in the TLC of PS with MW = $1\cdot10^4$–$5\cdot10^5$) on KSK silica gel (the mean pore diameter of which is 100 Å) in the Ch–Bz–Ac system (140:16:γ) (with preliminary saturation of plates in solvent vapour, Fig. 11). For correct treatment of the results obtained, it should be shown that in these experiments, when the plates are saturated with the solvent vapour, adsorption chromatography takes place and that polymer desorption in the region of the starting spot does not affect the chromatographic separation of polymers. If the desoprtion time is represented by t_d, it follows that when the starting points of the polymer are applied along the diagonal of the plate, their development time will be $t - t_d$. Hence, during slow desorption, *i.e.*, when t_d increases, the line of the end spots will intersect the line of the solvent front and the line of starting spots at the same point. As all of these three lines intersect precisely at one point in the TLC of PS in the Ch–Bz–Ac system (Fig. 12), it can be concluded that t_d tends to zero. It is clear from Fig. 11 that when the Ac content (γ) decreases and, consequently, the adsorption energy of a polymer segment, ε, increases, macromolecules of higher and higher MW enter the pores (their R_F value corresponds to MW = $2\cdot10^4$). At γ = 1.7, the interaction

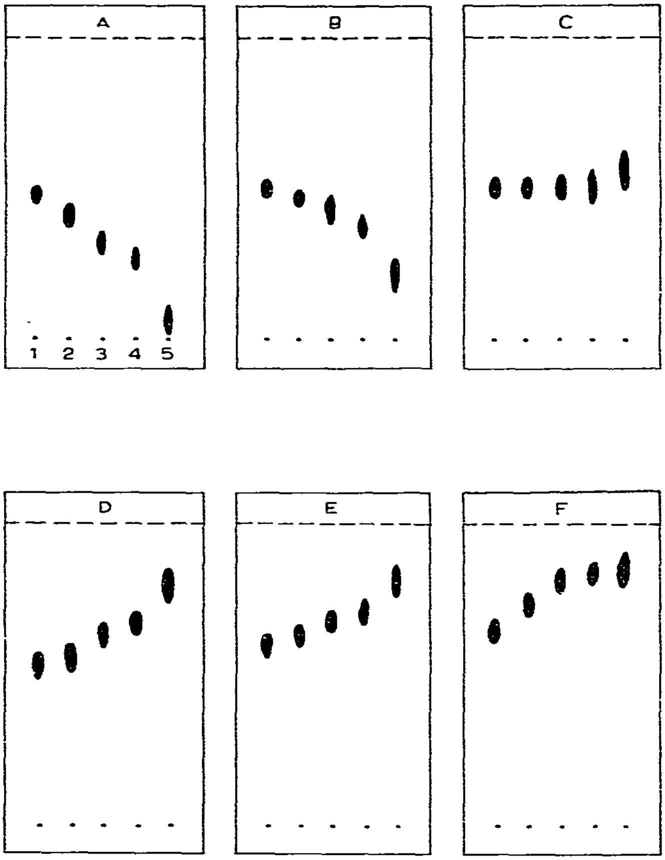


Fig. 11. TLC of PS samples 5–9 (see Fig. 6) from left to right on KSK silica gel in Ch–Bz–Ac (40:16:γ), where γ = (A) 1.5, (B) 1.8, (C) 2, (D) 2.2, (E) 2.5 and (F) 2.8, with preliminary saturation of the plate in solvent vapour for 2 h.

of PS with the adsorbent surface corresponds to the critical energy, ε_{cr}. When the Ac content becomes lower than $\gamma = 1.7$, TLGPC changes into ATLC, in which polymers of the highest MW exhibit the lowest R_F value.

The R_F values in the chromatogram can be converted into the $-\Delta F_M/kT$ values according to the equation obtained from eqns. 3, 4 and 8:

$$\frac{\Delta F_M}{kT} = \ln\left(\frac{1-R_F}{R_F}\right) + \ln\left(\frac{V_0}{V_p}\right) = \ln\left(\frac{1-R_F}{R_F}\right) - \ln\left(\frac{1-R_F}{R_F}\right)_{\varepsilon=\varepsilon_{cr}} \quad (9)$$

It follows from Fig. 11 that

$$\ln\left(\frac{V_0}{V_p}\right) = -\ln\left(\frac{1-R_F}{R_F}\right)_{\varepsilon=\varepsilon_{cr}} = 0.06$$

Fig. 13 shows the dependences of $-\Delta F_M/kT$ on ε obtained in this manner. This energy (ε) was determined in kT units per elementary area of 8.5 Å^2 as the value of

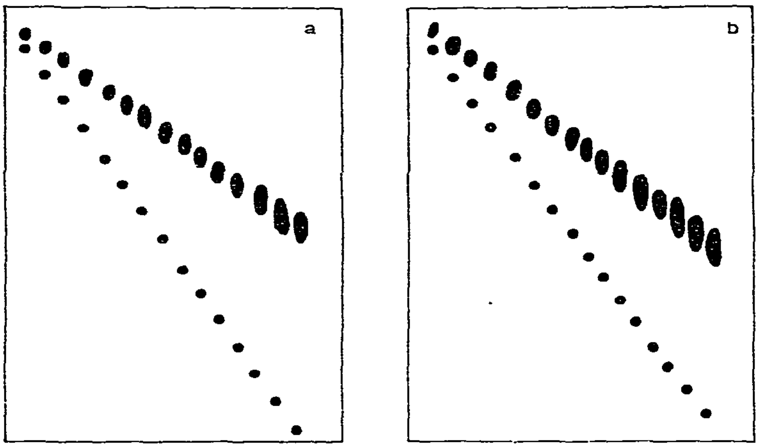


Fig. 12. TLC of PS samples (a) 5 and (b) 6 (see Fig. 6) on KSK silica gel in Ch–Bz–Ac (40:16:2.5) with preliminary saturation of the plate in solvent vapour for 2 h (samples were spotted along the diagonal of the plate).

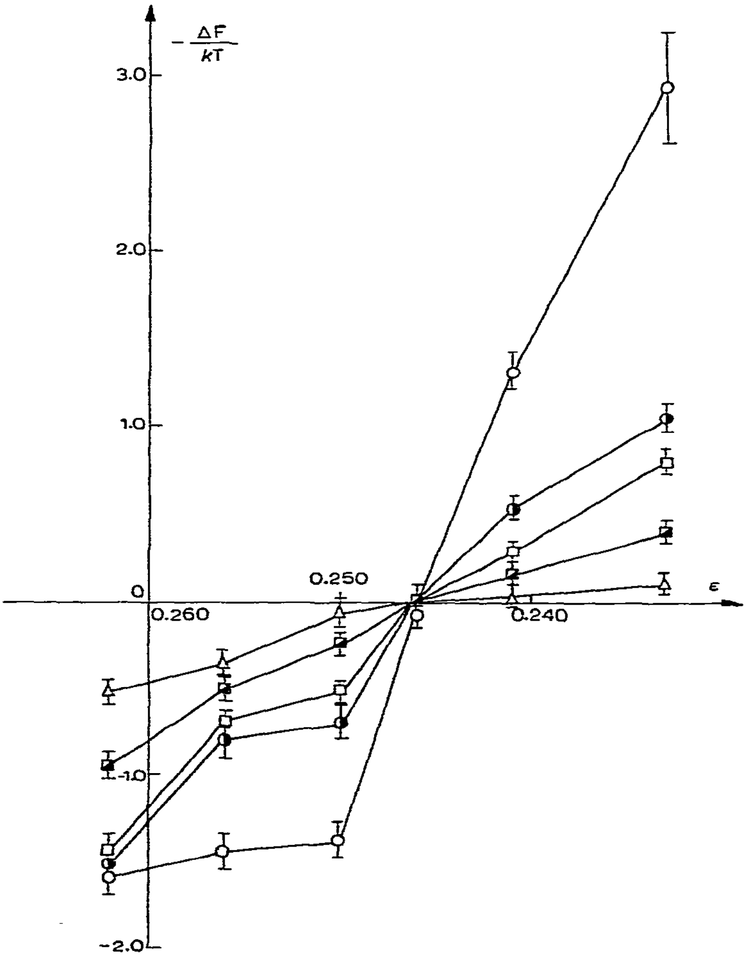


Fig. 13. Experimental dependence of $-\Delta F/kT$ on the energy of interaction of the segment with the adsorbent surface obtained by TLC (see Fig. 11). PS samples (see Fig. 6): △, 5; ◪, 6; □, 7; ◑, 8; ○, 9.

$\Delta\varepsilon = \varepsilon_{pa} - \varepsilon_{sa}$, where the subscripts *pa* and *sa* refer to polymer–adsorbent and the solvent–adsorbent contacts, respectively. The value of ε_{sa}, the adsorption potential of the solvent, can be determined according to Snyder's method[48]. First, $\varepsilon^0{}_{ab}$ is calculated for the Ch (*a*)–Bz (*b*) binary system from the equation

$$\varepsilon^0_{ab} = \varepsilon^0_b - \frac{\log N_b}{a n_b} \tag{10}$$

where N_b is the molar fraction, a is the adsorption potential of the adsorbent (for silica gel it is unity in Snyder's units) and n_b is the molecular area of Bz: $n_b = 6$ (in the 8.5 Å^2 units). Then one calculates the value of $\varepsilon^0_{abc} = \varepsilon_{sa}$, where the subscript c refers to Ac:

$$\varepsilon^0_{abc} = \varepsilon^0_{ab} + \frac{\log (N_c\, 10^{a n_c (\varepsilon^0_c - \varepsilon^0_{ab})} + 1 - N_b)}{a n_c} \tag{11}$$

The values of ε^0 used in these calculations were 0.4 for Ac, 0.25 for Bz and 0.04 for Ch; n_c for Ac is 4.2.

As it is impossible to calculate ε_{pa} (because the configuration of the adsorbed polymer unit is unknown), the value ε_{sa} is used instead of ε. It should be borne in mind that the higher ε_{sa} is, the lower is the value of ε.

As can be seen from Fig. 13, the dependence of $-\Delta F_M/kT$ on ε obtained in experiments on the TLC of polymers is in good agreement with the theoretical dependence shown in Fig. 10. Fig. 13 shows that the dependences for polymers of all molecular weights intersect the abscissa at one point, where $\varepsilon = \varepsilon_{cr}$ (ε_{cr} is 0.246 kT units). It is noteworthy that with PS of MW $5 \cdot 10^5$ a very slight change in ε causes a pronounced change in $-\Delta F_M/kT$ near the critical point, ε_{cr}. This effect results from the phase transition during the adsorption of macromolecules. As can be seen, this transition is distinctly observed from the experimental data; it is much less pronounced when the MW decreases.

It is not surprising that the theoretical relationships obtained for the adsorption of single macromolecules and the experimental relationships obtained by TLC are in good agreement, as the concentration range used in the TLC experiments corresponds to dilute solutions of polymers in which macromolecules behave as single macromolecules.

In TLC, adsorption effects can be observed only at adsorption energies close to ε_{cr}, because when the energy increases further the adsorption capacity of the macromolecules increases sharply and this effect prevents their migration up the plate ($R_F \rightarrow 0$).

Of particular interest is the influence of the molecular-sieve effect on the adsorption of macromolecules in pores in adsorption chromatography, *i.e.*, to the right of ε_{cr} in Fig. 10. It has been reported[49–51] that the molecular-sieve effect limits the adsorption of macromolecules in small pores. On the other hand, it follows directly from the Di Marzio–Rubin theory[40] (see Fig. 10) that the adsorption of macromolecules in narrow pores is more pronounced ($-\Delta F_M/kT$ is higher) than in large pores. It was necessary to check the agreement between this theory and the experimental data as the Di Marzio–Rubin theory was developed for a freely jointed chain (without taking into account the excluded volume) and it was not clear whether it agreed with experimental data concerning absorption of macromolecules on adsorbents with a truly porous structure. TLC was therefore carried out for PS of MW 600, 2000, 4000, $20\cdot10^3$ $50\cdot10^3$, $100\cdot10^3$ and $173\cdot10^3$ on silica gels of different porosity: KSM-6 (pore diameter $\varnothing_p = 30$ Å), KSK ($\varnothing_p = 120$ Å) and Silochrome S-80 ($\varnothing_p = 500$ Å). For an adequate comparison of the adsorption of PS on these silica gels, it was necessary to prepare silica gels of identical chemical structure. For this purpose, silica gels were treated with dilute hydrochloric acid (1:1) in order to destroy the Lewis centres. The number of Lewis centres is proportional to the aluminium content in the silica gel[52] and can vary between batches, whereas the concentration of silanol hydroxyl groups that remain after the acid treatment is the same for silica gels of all types (*ca.* 5 per 100 Å)[53]. On the other hand, we could show that in the chromatographic system under consideration even variations in the contents of Lewis adsorption centres do not affect the adsorption of PS, as chromatograms of PS obtained on the Na form (without acid treatment) and on the H form of silica gel of the same type were identical.

TLC was carried out in cells with preliminary saturation of the plate with the eluent vapour for 2 h in a Ch–Bz-Ac system (40:16:γ). The composition of the system was selected such that the adsorption interaction of PS segments with the surface of the silica gel corresponded to the critical energy ($\gamma = 2.0$) and to energy above the critical energy ($\gamma = 1.7$).

The chromatograms are shown in Fig. 14. It is clear that when the K_d of PS is unity, irrespective of its MW, the critical energy (ε_{cr}) for KSK silica gel with large pores and for S-80 macroporous silica gel is attained in eluents of the same composition and, hence, its value is the same. Nevertheless, for the KSM microporous silica gel the value of ε_{cr} is higher than for silica gels with large pores. This result is inexplicable from the standpoint of the Di Marzio–Rubin theory[40] and is probably caused by the excluded volume of the macromolecules, which is not taken into account in this

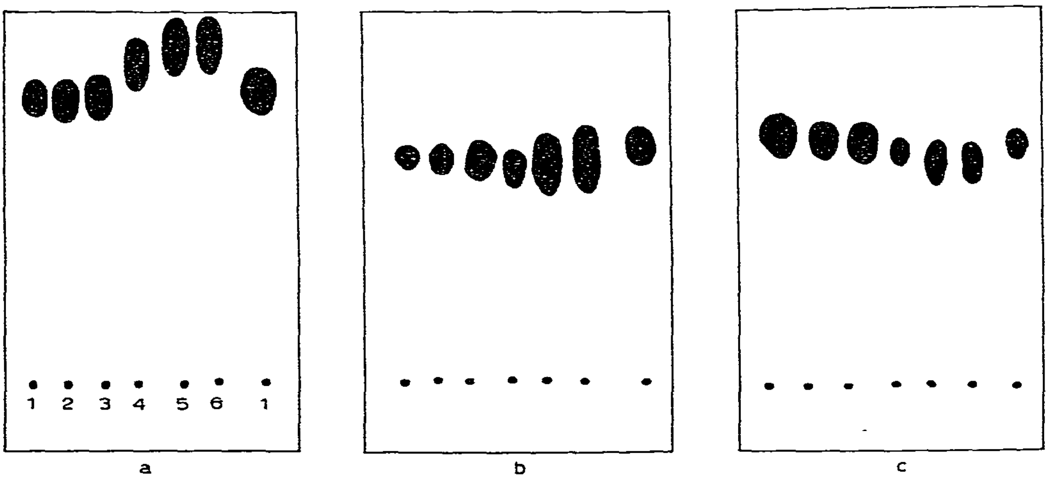


Fig. 14. Effect of pore size of silica gels (a) KSM ($\varnothing_p = 30$ Å), (b) KSK ($\varnothing_p = 120$ Å) and (c) S-80 ($\varnothing_p = 500$ Å) (H form) on the R_F value of PS with M_n = (1) 600, (2) $2\cdot10^3$, (3) $4\cdot10^3$, (4) $1.96\cdot10^4$, (5) $9.62\cdot10^4$, (6) $1.64\cdot10^5$ in TLC in Ch–Bz–Ac (40:16:2).

theory. If it is taken into account, it follows that the molecular-sieve effect should influence adsorption near ε_{cr} when the sizes of the polymer molecules and of the adsorbent pores differ widely [the coil size, $(\overline{h^2})^{\frac{1}{2}}$, exceeds 10^2 Å for PS with MW = 10^4 and the pore size, $\varnothing_p$, of KSM silica gel, is 30 Å]. However, when the energy of interaction, ε, is relatively high (Fig. 15), PS macromolecules enter the pores of KSM silica gel up to MW = $1.73 \cdot 10^5$ and the result predicted by the theory is observed: the smaller the pore size of the adsorbent ($\varnothing_p$ for KSM < $\varnothing_p$ for KSK < $\varnothing_p$ for S-80) the greater is the adsorption of macromolecules (the higher is $-\Delta F_M/kT$).

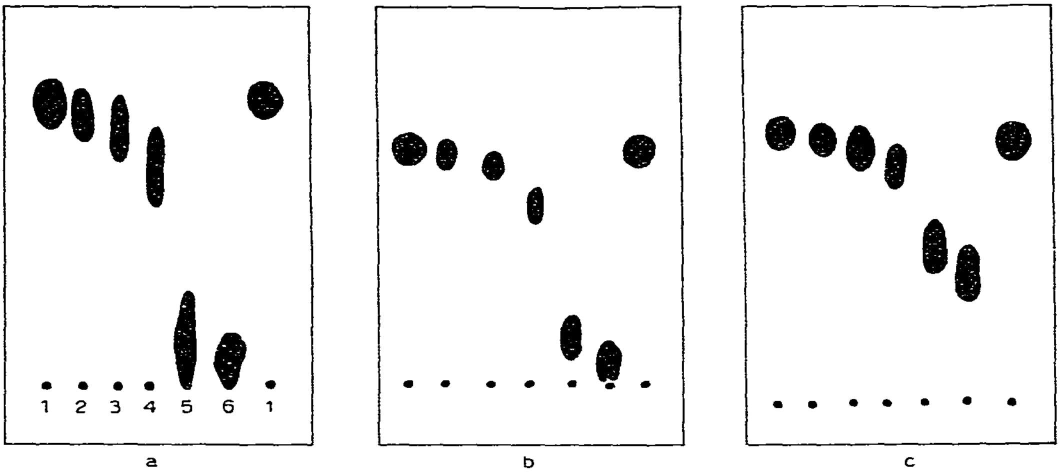


Fig. 15. Effect of pore size of silica gels (a) KSM, (b) KSK and (c) S-80 on the R_F value of PS with M_n values as in Fig. 14 in TLC in Ch–Bz–Ac (40:16:1.7).

This observation makes it possible to formulate the relationship between the molecular-sieve effect (the effect of the ratio of the size of macromolecules to the pore size upon their adsorption) and the adsorption in gel-permeation and adsorption chromatography. In GPC ($\varepsilon < \varepsilon_{cr}$; $K_d < 1$) K_d for silica gels with large pores is higher than for those with narrow pores and adsorption favours the entrance of large macromolecules into narrow pores and increases the limit of exclusion from the pore space of the adsorbent. In adsorption chromatography ($\varepsilon > \varepsilon_{cr}$; $K_d > 1$), the molecular-sieve effect favours the adsorption of macromolecules in pores, and on adsorbents with narrow pores K_d is higher than on those with large pores. At $\varepsilon = \varepsilon_{cr}$ the molecular-sieve effect is absent and macromolecules are not influenced by the porous structure of the adsorbent (K_d is unity irrespective of the MW of the polymer). These results show that the modern theory of adsorption of macromolecules is suitable for describing adsorption chromatography and that the critical energy, the principal parameter of this process, actually exists.

The above relationships can be considered as fundamental relationships for the adsorption chromatography of polymers (GPC and adsorption chromatography proper).

Fig. 13 shows that the dependence of $-\Delta F/kT$ and, hence, of K_d, on energy (ε) when $\varepsilon > \varepsilon_{cr}$ is linear. It should be noted that the dependence of $-\Delta F_M/kT$ on the number of monomer units in a macromolecule, N, is also linear, as can be seen from Fig. 16, which shows the dependence of $-\Delta F_M/kT \approx \ln[(1-R_F)/R_F]$ on N.

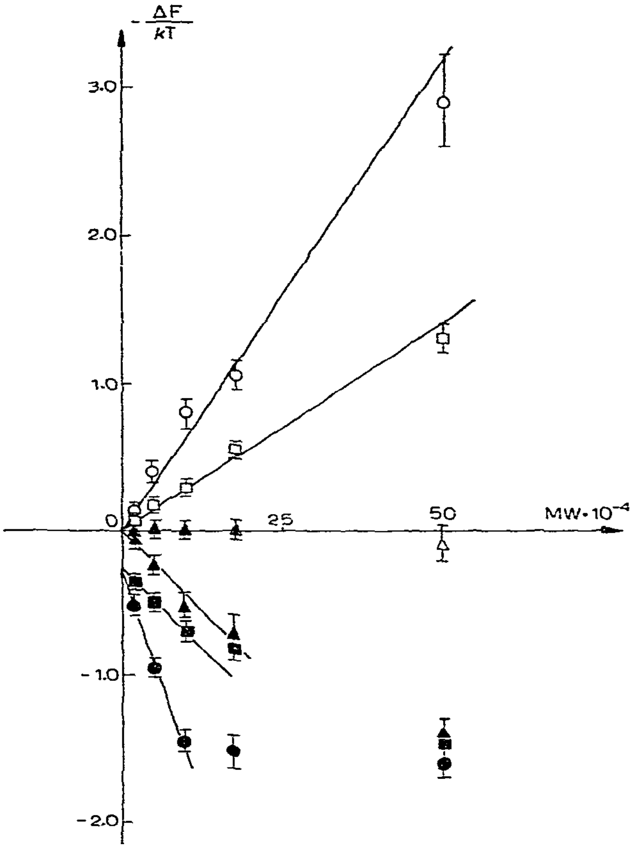


Fig. 16. Experimental dependence of $-\Delta F/kT$ on the number of segments N (MW) of PS at various interaction energies (ε). Dependence ○, □, △, ▲, ■ and ● correspond to solvent systems A, B, C, D, E and F, respectively, in Fig. 11.

This experimental dependence follows from the dependence predicted by the theory:

$$K_d = \exp(-\lambda_\varepsilon N) \tag{12}$$

where $-\lambda_\varepsilon$ is the change in the free energy of the macromolecule per unit.

By using eqn. 12, one can write the expression for R_F for the TLC of polymers as

$$R_F = \frac{1}{1 + \frac{V_p}{V_0} \cdot K_d} = \frac{1}{1 + \frac{V_p}{V_0} \cdot \exp(-\lambda_\varepsilon N)} \tag{13}$$

If eqn. 13 is differentiated with respect to N and λ_ε, it becomes clear that the sensitivity of R_F to the MW of the polymer, $\partial R_F/\partial N$, decreases with increasing N, whereas the dependence of $\partial R_F/\partial N$ on λ_ε is maximal near ε_{cr}. For each MW a particular maximum exists for λ_ε (for a particular eluent composition). This dependence is confirmed experimentally in the TLC of PS (Fig. 6), which shows that for the effective separation of these polymers according to MW it is necessary to select an eluent of a specific composition. The value of λ_ε is also determined by the chemical composition of the polymer. In this instance, the dependence of $\partial R_F/\partial \lambda_\varepsilon$ on N passes through a maximum. It has been shown experimentally[3] that the sensitivity of R_F to the copolymer composition is retained at least up to an MW of *ca.* $5 \cdot 10^5$.

Inagaki and co-workers[35,36,54] and Kotaka and White[32] maintain that in ATLC, polymers are readily fractionated according to their chemical composition rather than according to MW, and the fractionation by MW proceeds only when binary solvents that have components with similar dielectric permittivities are used. This conclusion is based on experiments in which it was shown that PMMA samples with $M_v = 4.12 \cdot 10^5$ and $1.65 \cdot 10^5$, which are not separated in any pure solvent (Bz, isopropyl, ethyl and methyl acetate, methyl formate and Ac; in the first three solvents $R_F = 0$ for both polymers and in the last three solvents $R_F = 1$), are readily separated according to MW in binary mixtures of these solvents. The effectiveness of separation, ΔR_F, increases in a series of equi-eluotropic mixtures (*i.e.*, mixtures that give identical mean R_F values of samples) with decrease in the difference in dielectric permittivities of the components: $CHCl_3$–methanol (29:71) < Bz–Ac (2:8) < isopropyl acetate–methyl formate (10:6.2) < ethyl acetate–methyl acetate (10:2.3). As Inagaki justly pointed out, these relationships do not follow from Snyder's theory of adsorption chromatography[48], although this theory can be used to describe other peculiarities of the adsorption chromatography of polymers if the adsorption potential of a polymer is considered to be the sum of the adsorption potentials of monomer units.

Inagaki[54] proved this as follows. According to Snyder's theory, K_d in TLC is determined by the ratio of the volumes of the solvent in the stationary and the mobile phases (V_p/V_0) and by the adsorption potentials of the adsorbent (α), of the substance being investigated (S°) and of the solvent (ε°), referred to the area of the component being investigated (A_s):

$$\log K_d = \log (V_p/V_o) + \alpha (S^\circ - A_s\varepsilon^\circ)$$

A number of polymers were subjected to TLC in CCl_4–MEK mixtures of various compositions selected in such a way that their R_F values were identical. According to the above equation, this can be accomplished only if there is a linear relationship between S° and A_s for these solvents and polymers. In fact, the values of S° and A_s calculated for monomer units[48] and the value of ε° obtained according to the interpolation scheme for the CCl_4–MEK system of an appropriate composition showed the existence of a linear relationship between S°/A_s and ε° in these experiments.

It has been reported[54] that the impossibility of separating polymers according to their MW by using ATLC in a single solvent is caused by the difficulty of selecting a solvent in which polymers of different MW would have a value of exp $(-\Delta F/kT)$ between 0 and 3 (for example, for PS with MW from $2 \cdot 10^4$ to $5 \cdot 10^5$, as shown in Fig. 14).

In many instances it is impossible to find a solvent that would ensure the required value of ε^{o}. The only solution to the problem is to use binary or ternary systems of solvents, among which it is not difficult to select a solvent composition that exhibits a value of ε necessary for polymer separations over the required range of MW. As Kamiyama and Inagaki[54] pointed out, the most suitable components for these mixtures are solvents in which the R_F value for polymers of all MW is zero for one solvent and unity for the other. Nevertheless, similar dielectric permittivities of these solvents are of no importance as a criterion for their selection.

It should be noted that the adsorption chromatography of polymers is also complicated by the slow kinetics of the adsorption–desorption process.

It can be seen from Fig. 7, which shows chromatograms of PS in the Ch(ε^{o} = 0.04)–Bz(ε^{o} = 0.25) system, that for PS of MW $> 10^5$ the chromatographic process does not occur because the adsorption–desorption kinetics are too slow. Part of the polymer remains at the start and another part migrates with the solvent front. The addition of adsorption-active acetone (ε^{o} = 0.40) to the system changes the situation (Fig. 6).

Hence, the most effective chromatographic separation of substances can be carried out over the range $\varepsilon_m > \varepsilon > \varepsilon_{cr}$ in which K_d attains a value of *ca.* 2–3. At the energy of interaction $\varepsilon > \varepsilon_{cr}$, chromatography does not proceed owing to strong adsorption of macromolecules. In the region of ε_{cr} chromatography is not effective for polymer separation according to MW, whereas in the range $\varepsilon < \varepsilon_{cr}$ its effectiveness increases with decreasing ε, attaining a maximum at $\varepsilon = -\infty$. As over the entire range of changes in ε the dependence of K_d on the MW of the polymer is of the character described by eqn. 12, this dependence can be suggested as a calibration dependence for all chromatographic systems:

$$K_d = \exp(-\gamma \, \mathrm{MW}) \quad (14)$$

The parameter γ, determined for any polymer of a given homologous series, characterizes the whole series if the solvents used and the temperature conditions are identical. This permits the determination of the MWD of polymers under conditions of adsorption chromatography with more effective separation of the components of a polymer sample according to MW than, for example, in GPC.

III. THIN-LAYER CHROMATOGRAPHY BASED ON DIFFERENCES IN POLYMER SOLUBILITIES

Inagaki and co-workers[15,36] proposed precipitation TLC as the principal method for polymer separations based on MW. PTLC has been used successfully by Inagaki and other workers for the following processes: fractionation of homopolymers[12,15,20,36] and random copolymers[32] by MW, separation of atactic and syndiotactic PMMA[16], fractionation of block copolymers of St–MMA[20] and separation of block copolymers of this type and PMMA[22].

1. Peculiarities of precipitation and extraction TLC of polymers

The elementary process of PTLC is related to the separation of a polymer solution into a dilute phase and a concentrated gel phase that is precipitated on the surface of the adsorbent grains. The dilute phase is transported with the solvent flow and thus chromatography is effected. In order to carry out PTLC, polymer adsorption should be suppressed and the eluents used should therefore meet two requirements: they should be adsorption-active (they should exhibit a comparatively high adsorbability, *i.e.*, the adsorbability characterized by ε^0 according to Snyder[43]) and should be poor solvents for the polymer. The latter property can be evaluated by using the Flory–Huggins interaction parameter[55], χ, which is the change in the free energy (in kT units) observed when the solvent molecules are transported from the pure solvent to the polymer. At $\chi > 0.5$ the solubility of the polymer decreases and the gel phase begins to be formed.

According to the Flory–Huggins theory[55], the phase separation of the polymer solution (if the temperature is kept constant) can occur in two cases (at $\chi > 0.5$ and at $\chi \approx 0.5$), when the volume concentration of the polymer in solution increases. The increase in χ can be achieved by increasing the content of the precipitant in the eluent and the increase in ψ_p by changing the phase ratio, r (the ratio of the volume of eluent to the weight of adsorbent). A simple equation can be written characterizing the phase separation of the polymer solution. If the fraction of molecules (with a degree of polymerization N) in the gel phase in designated by $f'(N)$ and in the dilute phase by $f(N)$ and if the volume ratio of these phases is $R = v'/v$, then the following expression for the distribution coefficient, $K_d = f'(N)/f(N)$, is obtained:

$$K_d = R_F \exp (\sigma_s^0 N) \tag{15}$$

where σ_s^0 is the fractionation factor, which is a function of volume fractions of the polymer and the solvent and also a function of the interaction parameter, χ.

As the value of σ_s^0 is positive and its dependence on MW (or N) is very slight, it follows that when the MW increases the polymer will pass into the concentrated phase. The distribution coefficient also increases with increasing volume concentration of the polymer, ψ_p. Eqn. 15 can easily be transformed into a dependence for TLC:

$$\ln \left(\frac{1 - R_F}{R_F}\right) = R + \sigma_s^0 N \tag{16}$$

In principle, the PTLC of polymers can be carried out under non-gradient conditions (Fig. 25). Nevertheless, when polymers with widely different solubilities are to be separated, gradient TLC should be used. It can be carried out by mixing a solvent and a precipitant for the polymer; both compounds, or at least one, should be more adsorption-active than the polymer. The eluent should contain the adsorption-active component at a concentration that precludes polymer adsorption.

In PTLC, the polymer can be either selectively dissolved at the starting zone or selectively precipitated during its migration up the plate. In the first instance, the composition of the eluent introduced on to the plate should be varied by the gradual addition of solvent to the precipitant. In the second instance, the concentration of the precipitant in the eluting solution moving up the plate should be increased, *e.g.*, by evaporating the solvent near the eluent front when TLC is carried out in a non-saturated

S-chamber. In both instances the precipitant gradient in the direction of development will be positive. Consequently, the corresponding distribution of polymer zones should be observed on the plate when the most soluble polymer fractions, such as those which contain polymer homologues of the lowest MW, have the highest R_F values.

The first method for obtaining a gradient is related to selective dissolution of the polymer in the zone of the starting spot, and should be called the extraction type of PTLC. The second method, in which a gradient of polymer solubility appears on the plate owing to solvent evaporation and to a decreasing phase ratio, r, may be called precipitation TLC proper. Examples of the extraction type of PTLC are the separation of PS according to MW by adding Ac–$CHCl_3$ and Ac–toluene mixtures to the precipitant, Ac[12]. The separation of PMMA in the methanol–$CHCl_3$ system (71:29) with methanol as precipitant (Fig. 17) and the separation of PS in the benzene–MEK–Ac–ethanol system (5:3:6:4) are examples of precipitation TLC proper. The first two components in the last system are solvents for PS and the last two are precipitants. A distinction should be made between the type of PTLC in which a solvent–precipitant gradient is applied to the plate and fine fractionation of the polymer according to MW is possible, and the extraction TLC proper carried out according to the "all or nothing" principle (a non-gradient system). In the latter instance, selective separations can be achieved of polymer fractions that differ widely in solubility, such as isotactic and atactic PS (Fig. 18) or St–PEO block copolymer from PS and PEO homopolymers (Fig. 19).

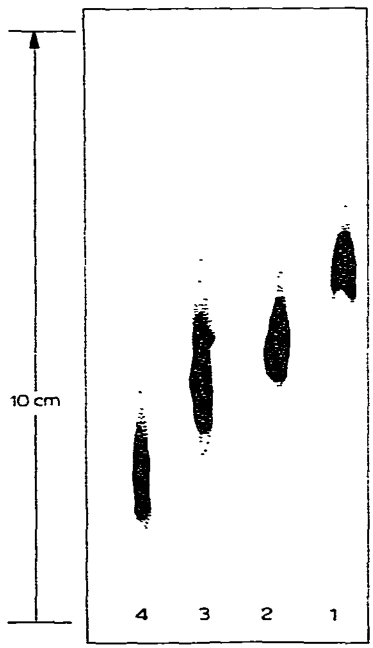
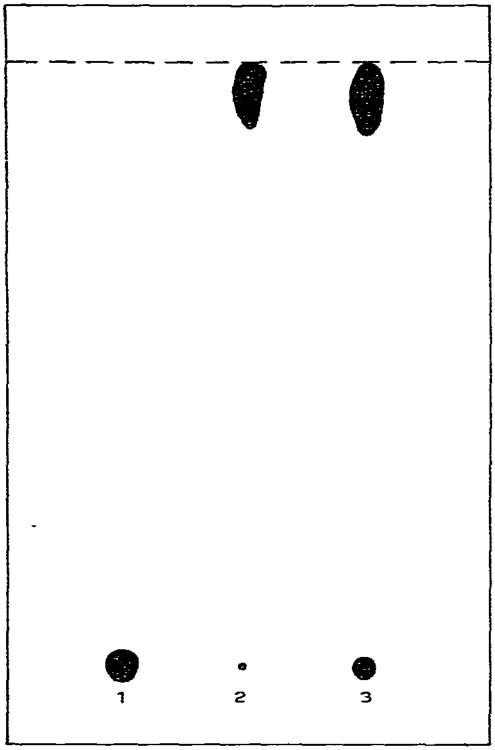


Fig. 17. TLC of PMMA with M_w = (1) $4.3 \cdot 10^4$, (2) $1.14 \cdot 10^5$, (3) $1.65 \cdot 10^5$ and (4) $4.12 \cdot 10^5$ on silica gel in $CHCl_3$–methanol (29:71).



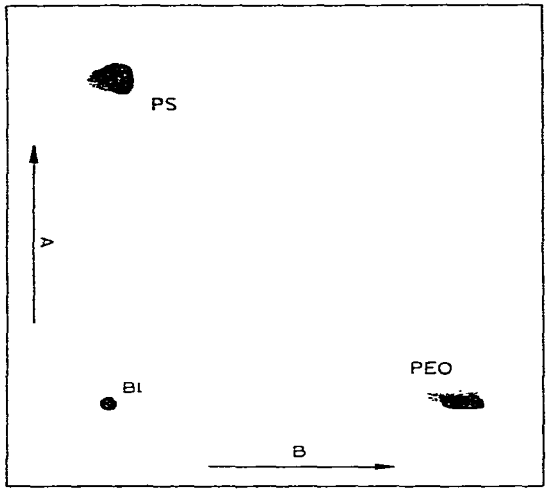


Fig. 18. TLC of (1) isotactic PS, (2) atactic PS and (3) their mixture in Bz on KSK silica gel.

Fig. 19. Two-dimensional TLC of St–EO block copolymer (B1) (50:50) on KSK silica gel in Ch–Bz–Ac (12:4:2) in direction A and in pyridine–water (3:7) in direction B.

Fig. 20 shows the MW (M) dependence of R_F for PS obtained in the benzene–MEK–acetone–ethanol system (curve b). This dependence obeys the linear equation $R_F = A + B\log M$, where A and B are constants. If this dependence is compared with

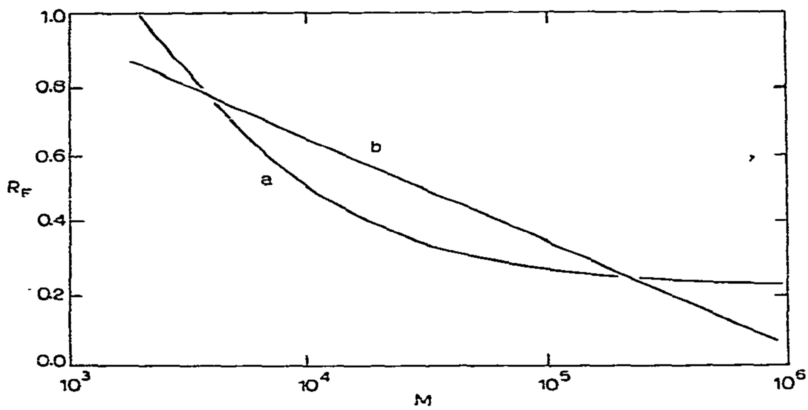


Fig. 20. R_F *versus* log M of PS in TLC on silica gel in the following systems: (a) polar and non-polar solvent (MEK–Ch); (b) good solvent and precipitant (Bz–MEK–Ac–ethanol).

a similar dependence for the ATLC of PS in the cyclohexane-MEK system (curve a), it is clear that at MW $< 10^5$ the MW dependence of adsorption is stronger and at MW $> 10^5$ it is weaker than the precipitation dependence. However, when an appropriate solvent is used in ATLC on silica gel with large pores, a relatively strong MW dependence of R_F can also be observed for polymers with MW $> 10^5$ (Fig. 21). Otocka and Hellman[12] also observed a high efficiency of ATLC in polymer separations according to MW when the ATLC of PS in a tetrachloromethane–THF system was compared with PTLC in acetone–toluene and acetone–$CHCl_3$ systems. According to these relationships, Kotaka and White[32] used PTLC in a THF–methanol system for the determination of the MWD of random copolymers of St and DVB and ATLC in a $CHCl_3$–CCl_4 system for the determination of the inhomogeneity of composition of these polymers.

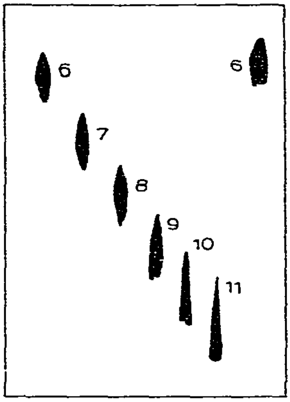


Fig. 21. TLC of PS samples 6–11 (see Fig. 6) on MSA-1 silica gel ($\varnothing_p$ = 500 Å) in Ch–Bz–Ac (13:3:1.1).

As already mentioned, the phase separation of the polymer solution occurs not only with increasing χ but also with increasing volume concentration of the polymer, ψ_p, related to a decrease in the phase ratio, r. A peculiar mechanism is known to exist on a thin-layer plate, decreasing r close to the eluent front; it is related to the finite rate of wetting of the adsorbent with a liquid. Kamiyama and Inagaki[36] measured the distribution of r along the plate (Fig. 22) and determined the volume concentration of the polymer in the chromatographic zone (precipitation zone), ψ_p, to be 0.01. This corresponds approximately to the beginning of the phase separation in similar experiments without an adsorbent ($\psi_p = 0.03$). On the other hand, Otocka *et al.*[30] calculated that the limit of the solubility of PS of MW of 160,000 is $\psi_p = 0.007$, whereas in turbidimetric titration the precipitation of PS cannot be detected even at $\psi_p = 0.02$. It was concluded that in PTLC the adsorbent plays a certain role in decreasing the concentration threshold of the polymer precipitation.

A characteristic peculiarity of PTLC is that the porous structure of the adsorbent is of minor importance in polymer separations. Thus, Otocka *et al.*[30] showed that in a θ-solvent (dioxan–methanol, 72:28) the R_F values for PS on adsorbents with different chemical natures and porosities are approximately equal. It can be concluded

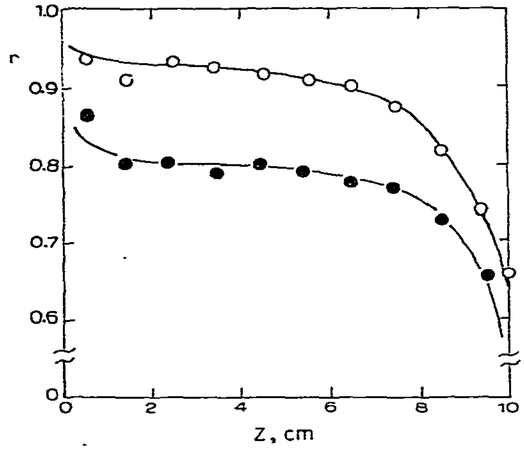


Fig. 22. Profile (r) of the solvent (DMF) on a plate in ascending (○) and descending (●) TLC on silica gel. z = length of the plate.

that the precipitation of the gel phase of the polymer occurs on the outer surface of the adsorbent grains.

2. Formation of artificial chromatographic zones in the precipitation TLC of polymers

Depending on the solvent–precipitant ratio, either ATLC or PTLC of polymers may be observed when the precipitant exhibits adsorption activity and the solvent does not. Fig. 23 shows that in the TLC of PMMA in a system of this type ($CHCl_3$–methanol at two concentration ranges in which the methanol content is below 5% and above 70%), the R_F value changes from 0 to 1. The first range corresponds to the ATLC and the second to the PTLC of PMMA. This peculiarity makes it possible to explain the formation of artificial chromatographic spots in the TLC of PMMA in

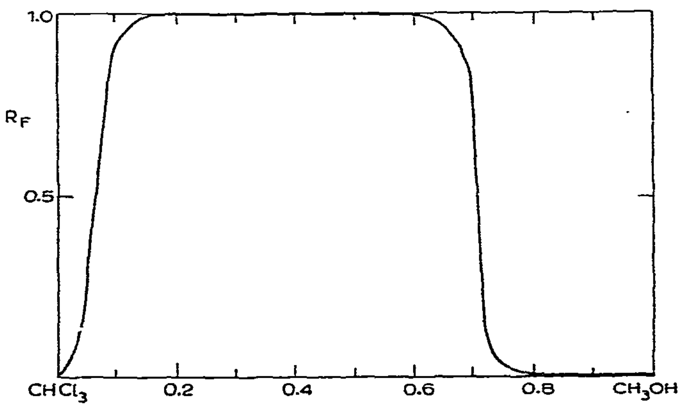


Fig. 23. R_F value of PMMA with $M_w = 4.1 \cdot 10^4$ *versus* composition of the $CHCl_3$–methanol mixture in TLC on silica gel.

$CHCl_3$–methanol (3.5:16). The nature of this phenomenon becomes understandable when the starting spots of PMMA are applied along the diagonal of the plate. Fig. 24 shows that under these conditions, as the height of the starting zone increases, the substance seems to be redistributed from the lower spot (at the starting point) to the higher spot, migrating with the eluent front. This phenomenon can be explained as follows. When the mixture of $CHCl_3$ and methanol moves up the plate, frontal separation of the eluent into the $CHCl_3$ and the methanol zones occurs (when methanol is present in excess, the fronts of these zones should be relatively close to each other). As a result, the spreading eluent front with a low methanol concentration coming into contact with the spot dissolves a certain part of the polymer which, at this range of methanol concentrations, will migrate up the plate according to the conditions of adsorption chromatography.

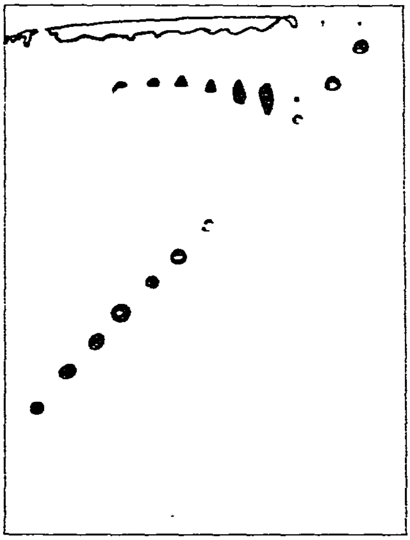


Fig. 24. TLC of PMMA with $M_w = 5 \cdot 10^5$ in $CHCl_3$–methanol (3.5:16) on KSK silica gel in an S-chamber (samples were spotted along the diagonal of the plate).

Hence, the back edge of the polymer zone becomes sharper. This effect is induced by the concentration gradient at the front of the methanol zone, the rate of which determines the rate of migration of the polymer zone. As gradient conditions of chromatography exist, the upper polymer spots are located parallel to the eluent front (to the line of immersion of the plate in the eluent). If the rate of the eluent movement is greater than the rate at which the polymer dissolves, the polymer will dissolve (desorb) in the zone of the starting spot until the spot is reached by that part of the eluent front in which the methanol concentration is higher than 70% and the PMMA that has not yet dissolved will be unable to dissolve further. As a result, the polymer zone is divided into two parts, one of which migrates close to the eluent front and the other remains at the start. Hence, the formation of two spots is an artefact due to specific conditions of the chromatography of the polymer in a binary solvent system in which the adsorption-active polar component at high concentrations is a precipitant for the polymer. Evidently, the higher the starting spot on the plate, the slower is the movement of the solvent front in this region and the greater is the amount of the polymer that is desorbed from the silica gel and passes into the moving chromatographic zone.

An interesting result is obtained in the TLC of PMMA carried out in a cell saturated with the solvent vapour when the same chromatographic system is used, *i.e*,. $CHCl_3$–methanol (4.5:16) (Fig. 25). Here the upper spots of the polymer are located at an angle to the eluent front; this result indicates that gradient conditions in the plate do not exist. Hence, it is observed that in a non-gradient eluent a part of the polymer remains at the start while the other part migrates up the plate according to the conditions of elution chromatography. This situation can occur if the concentration of methanol in the eluent ensuring the PTLC of PMMA is too high and does not permit the transition of the polymer from the solid phase adsorbed on the plate into solution. The first stage of polymer dissolution requires a thermodynamically "better" solvent (containing a smaller amount of methanol) than the second stage, which corresponds to the elementary act of PTLC. This requirements agrees with the observation of Otocka and co-workers[29,30] that the threshold of the polymer solubility becomes lower in the presence of the adsorbent and that the quality of the solvent affects the desorption rate. If the eluent contains methanol in an amount that prevents the transition of the polymer from the solid state into the gel phase, the dissolution of the polymer in the starting zone occurs only when the eluent front in which the methanol concentration is low passes through it. In this instance, as in TLC in an unsaturated S-chamber (Fig. 24), the longer the time of contact between the solvent front and the starting spot, the greater is the proportion of the polymer that passes into solution and is developed under conditions of non-gradient PTLC.

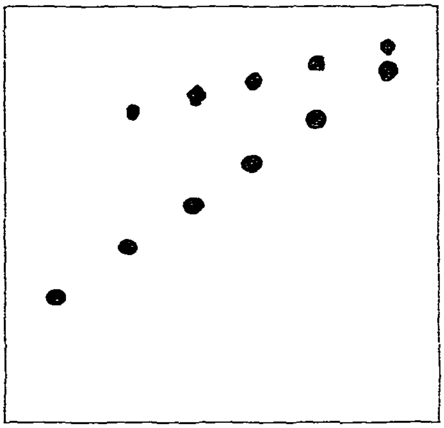


Fig. 25. TLC of PMMA ($M_w = 5 \cdot 10^5$) in $CHCl_3$–methanol (4.5:16) in a chamber with preliminary saturation of the plate in solvent vapour (samples were spotted along the diagonal of the plate).

IV. DEPENDENCE OF SPOT SHAPE ON CONCENTRATION IN THE TLC OF POLYMERS

The shape of the spot is determined by the type of adsorption isotherm. Weak adsorption ($R_F \rightarrow 1$) is characterized by a concave adsorption isotherm. In this in-

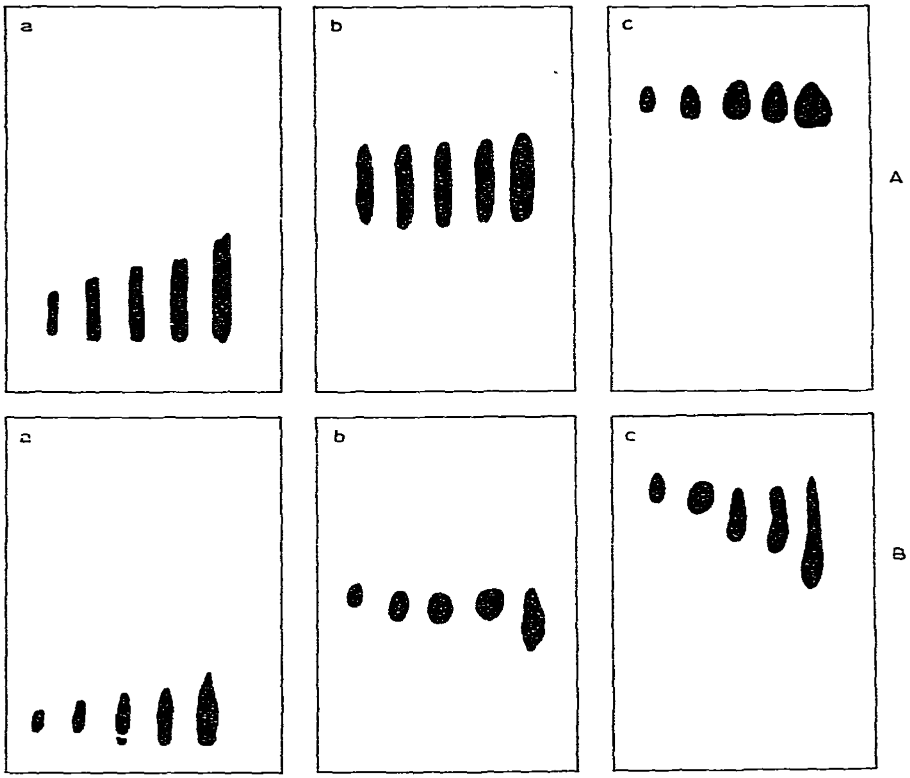


Fig. 26. Concentration dependence of the spot shape in TLC. (A) PS with $M_w = 2 \cdot 10^4$ in Ch–Bz–Ac: (a) 12:4:0.25; (b) 12:4:0.5; (c) 12:4:1. (B) PS with $M_w = 4 \cdot 10^5$ in Ch–Bz–Ac: (d) 12:4:0.25; (e) 12:4:0.5; (f) 12:4:1. Amounts of PS (left to right): 2, 5, 10, 20 and 40 μg.

stance, when the concentration increases the spot becomes elongated. A convex adsorption isotherm is characteristic of high adsorption capacity ($R_F \to 0$). In this instance, when the concentration increases the spot becomes elongated upwards. At $R_F \approx 0.5$, the adsorption isotherm is close to the linear isotherm and the concentration dependence of the shape of the spot is very slight (Fig. 26). Two-dimensional spreading in TLC leads to additional concentration effects. In the side parts of the chromatographic zone the concentration of the substance decreases and the rate of its migration is therefore determined by a distribution coefficient different from that in the central zone. As a result, the spot becomes tapered at the front when the adsorption isotherm is convex and at the rear when it is concave (Fig. 27).

There are other concentration effects that are specific to polymers and determine the shape of the spot. One effect is related to the precipitation of polymer that takes place if an eluent gradient exists on the plate with a gradual decrease in the solvent–precipitant ratio. As a result, the higher the concentration of the polymer in the spot, the lower is the concentration of the precipitant corresponding to the threshold of the polymer solubility and the more elongated the spot becomes in the direction opposite to that of migration of the polymer up the plate (Fig. 28). This effect is similar to the influence of the concave adsorption isotherm on the shape of

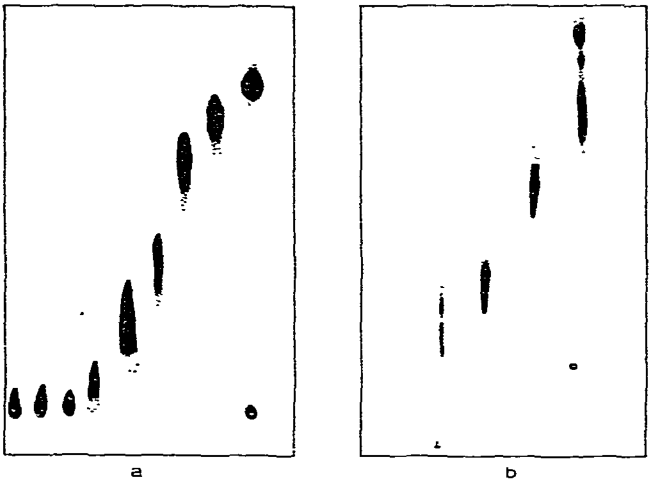


Fig. 27. TLC of PS on KSK silica gel. Spot shape: (a) adsorption TLC (convex adsorption isotherm) in Ch–Bz–Ac (12:4:0.7); (b) precipitation TLC (convex adsorption isotherm) in Ac–Bz (15:15). Samples from right to left: (a) PS samples 3–11; (b) PS samples 2–5 (see Fig. 6).

Fig. 28. Concentration dependence of the spot shape in the precipitation TLC of PS ($M_w = 5.1 \cdot 10^4$) in Bz–Ac (3:40). Amounts of PS (left to right): 40, 30, 20 and 10 μg.

the spot, although it results from other causes related to precipitation of the polymer under conditions of gradient TLC.

The spot shape in the TLC of polymers also depends on the peculiarities of the viscous flow of a polymer solution up a plate. In the centre of the spot, where the polymer concentration is high, the eluent rate is at a minimum. At the periphery it increases and attains a maximum in the spaces between the spots, and the spot acquires a drop-like shape (Fig. 29) that is characteristic of streams formed when a viscous liquid flows past obstacles[56]. In this instance the rear edge of the spot is additionally sharpened by the liquid flow, which prevents the diffusion spreading of the spot, while in the front part of the zone the velocity of diffusing molecules and the flow velocity are combined[57]. These processes lead to instability of the chromatographic zone, which may acquire an irregular shape or may even be divided into several spots that move separately.

V. INVESTIGATIONS OF THE MICROSTRUCTURE OF POLYMERS BY TLC

1. Investigations of the stereoregularity of polymers

As Inagaki and Kamiyama showed[16], the separation of stereoregular polymers may be based on differences in their solubility which increase if the dissolution of the

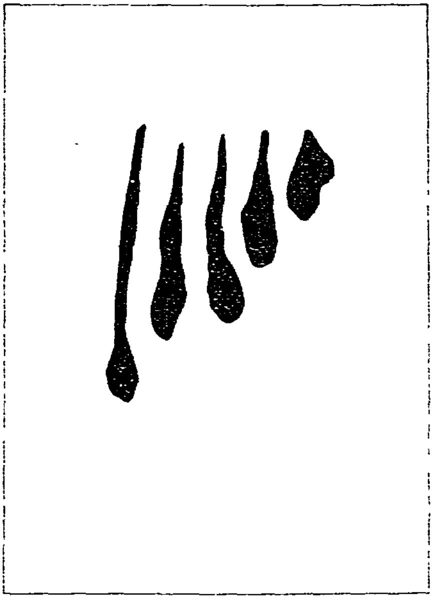


Fig. 29. Viscosity shape of the spot of PS ($M_w = 8.7 \cdot 10^5$) in TLC on KSK silica gel in Bz. Amounts of PS (left to right): 40, 30, 20 and 10 μg.

polymer is combined with its desorption from the adsorbent surface. Thus, by using ETLC with ethyl acetate as the eluent, it has been possible to separate isotactic (i) PMMA, which remains at the start, from syndiotactic (s) and atactic (a) PMMA, which migrate with the solvent front[17]. If the elution is carried out in acetone[18], i-PMMA is also desorbed but the stereo-complex of i-PMMA and s-PMMA (1:1) remains at the start and mixtures of these polymers in the proportions of 2:1 and 1:2 are developed as two spots, at the start and close to the solvent front. The lower spot is a stereo-complex (1:1) and the upper spot is either i-PMMA or s-PMMA. It should be noted that if the starting spot has not been previously wetted with a drop of $CHCl_3$, the stereo-complex is not formed. TLC also permits the separation of stereo-block PMMA with a high content of isotactic and syndiotactic triads[17].

Similar results have been obtained in the TLC of PS[3]. Crystalline isotactic PS does not dissolve in Ch–Bz–Ac (12:4:1.5) in which samples of atactic PS of the highest molecular weight migrate with the solvent front, whereas samples of isotactic PS remain at the start (Fig. 18). a-PMMA and s-PMMA can be separated[18] by ATLC in ethyl acetate–isopropyl acetate (Fig. 30a) and by PTLC in acetonitrile–methanol (Fig. 30b). In this instance, if single solvents are used it is not possible to obtain an R_F value intermediate between 0 and 1 for i-PMMA, a-PMMA and s-PMMA. Thus, for TLC in pure ethyl acetate, $R_F(\text{i}) \approx 0$, $R_F(\text{s}) \approx 1$ and $R_F(\text{a}) \approx 1$. However, when the less polar isopropyl acetate is added, these PMMA samples are separated: $0 \approx R_F(\text{i}) < R_F(\text{s}) < R_F(\text{a}) < 1$.

When these systems are used, the R_F value depends not only on the content of syndiotactic triads (T_s) but also on the MW. Thus, for the acetronitrile–methanol system:

$$R_F = 1.73\, T_s - 0.51 \log \text{MW} - 2.2 \qquad (17)$$

and for the ethyl acetate–isopropyl acetate system:

$$R_F = 1.74\, T_s - 0.08 \log \text{MW} + 6.0 \tag{18}$$

Hence, in the TLC of PMMA in these systems of solvents it is possible to determine the T_s and MW values of the polymers being investigated to within 10% by substituting the R_F values into eqns. 17 and 18.

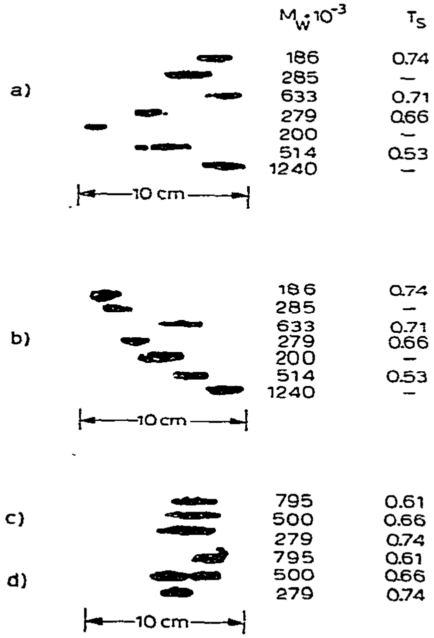


Fig. 30. TLC of stereoregular PMMA. (a) s-PMMA and a-PMMA of various M_w and T_s in isopropyl acetate–ethyl acetate (8:25); (b) the same samples in gradient TLC in the acetonitrile–methanol system; (c) and (d) TLC of PMMA in systems (a) and (b), respectively.

As the MW dependence of R_F in both systems of solvents is direct whereas the dependence of R_F on T_s is inverse, both systems should be used to investigate the stereoregularity of PMMA samples of unknown but differing MW. This is shown in Fig. 30c and 30d, in which PMMA 74MB (MW $= 7.95 \cdot 10^5$; $T_s = 0.61$) and MB20 (MW $= 2.79 \cdot 10^5$; $T_s = 0.74$) could be separated only in acetonitrile–methanol. In this instance it was found that sample 74MB20 (MW $= 5.00 \cdot 10^3$; $T_s = 0.66$) prepared by varying the polymerization conditions during the experiment consisted of two components[18].

2. Investigations of the regularity and isomerism of polybutadienes

With the aid of TLC, *trans*-1,4-, *cis*-1,4- and 1,2-polybutadienes (PBD) could be separated[19]. Table 3 gives the R_F values of isomeric PBD in various solvents.

Table 3 shows that *trans*-1,4- and *cis*-1,4-PBD can be separated by using TLC on silica gel and aluminium oxide with CCl_4 and amyl chloride. In the first solvent,

TABLE 3

R_F VALUES OF ISOMERIC PBD IN TLC ON SILICA GEL AND ALUMINIUM OXIDE

Solvent	*Dielectric constant*	*ε^0 (Al_2O_3) according to Snyder*	*R_F*					
			SiO_2			*Al_2O_3*		
			Trans-1,4-PBD	*Cis-1,4-PBD*	*1,2-PBD*	*Trans-1,4-PBD*	*Cis-1,4-PBD*	*1,2-PBD*
Cyclohexane	2.0	0.04	0	0	0	0	0	0
CS_2	2.64	0.15	0	0	0	0	0	0
CCl_4	2.2	0.18	0.8–0.9	0	1	1	0–0.1	1
Amyl chloride	6.6	0.26	0	1	1	0	1	1
p-Xylene	2.27	0.26	1	1	1	1	1	1
Benzene	2.28	0.32	1	1	1	1	1	1
$CHCl_3$	4.8	0.40	1	1	1	1	1	1
THF	7.42	0.45	1	1	1	1	1	1

cis-1,4-PBD remains at the start and *trans*-1,4-PBD and 1,2-PBD migrate together, whereas in the second *trans*-1,4-PBD remains at the start and 1,2-PBD and *cis*-1,4-PBD migrate together.

The separation of PBD in CCl_4 and amyl chloride is based on different mechanisms. As CCl_4 is a good solvent for all types of PBD, when it is used they are separated on the basis of ATLC. In amyl chloride, only *cis*-1,4- and 1,2-PBD dissolve at temperatures below 40°; hence in this instance PBD is separated according to the mechanism of ETLC.

On this basis, it is possible to separate by one-dimensional TLC any binary mixture of PBD by using both solvents and passing them various distances up the plate (Fig. 31). For the separation of a ternary mixture of *cis*-1,4-, *trans*-1,4- and 1,2-PBD, two-dimensional TLC in these solvents should be used (Fig. 32).

This method can be used to investigate the homogeneity of the so-called "equibinary" PBD in which units of *cis*-1,4- and 1,2-butadiene are present. In TLC with CCl_4, equibinary PBD migrate with the solvent front just as *cis*-1,4-PBD, and when the polymer is a mixture of *cis*-1,4- and 1,2-PBD, they are separated on the plate into the corresponding zones.

3. *TLC of block copolymers*

On the basis of hydrodynamic investigations of block copolymers in solvents of different thermodynamic strength, Kamiyama *et al.*[20], established that ATLC is very sensitive to conformational changes of St and MMA block copolymers of the A–B and A–B–A types. Thus, in a solvent poor for PS and good for PMMA (*e.g.*, nitroethane–acetone), the PS block collapses with the formation of a dense helix-like PS domain surrounded by the PMMA "coating". Owing to this intramolecular phase separation, as the MW and, therefore, the ability for intramolecular aggregation to occur increase, the adsorption properties of the block copolymer approach those of pure PMMA. On the other hand, PMMA and the block copolymer containing a small percentage of St differ widely in their adsorption characteristics in a solvent

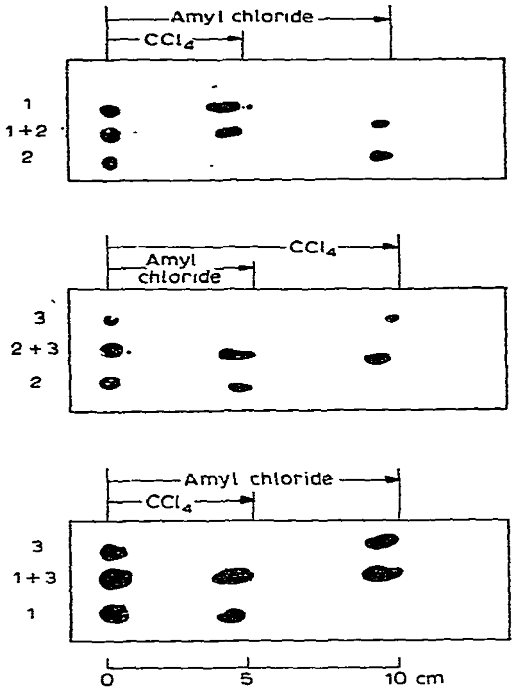


Fig. 31. Separation of PBD by two-stage TLC in CCl_4 and amyl chloride. (1) *trans*-1,4-PBD; (2) *cis*-1,4-PBD; (3) 1,2-PBD.

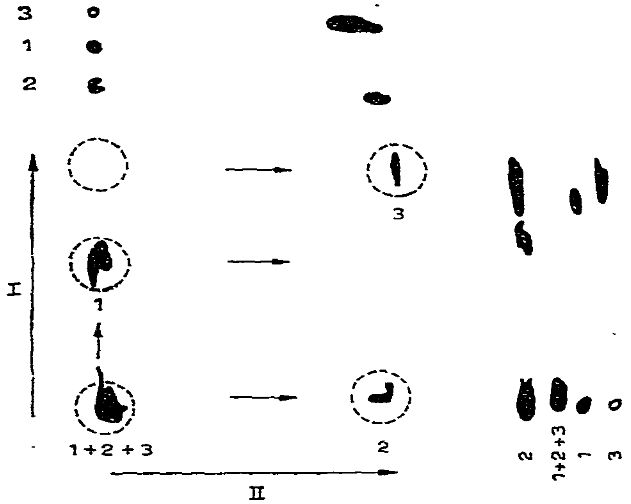


Fig. 32. Separation of (1) *trans*-1,4-PBD, (2) *cis*-1,4-PBD and (3) 1,2-PBD by two-dimensional TLC in CCl_4 (direction I) and amyl chloride (direction II).

equally good for PS and PMMA, such as benzene–MEK, in which these polymers exhibit the random-coil conformation.

Proceeding from this concept, it might be suggested that the greatest changes in the adsorption properties of PMMA and block copolymers with a low content of St (in particular, for a block copolymer of high MW) should be observed in a solvent which, being a weak displacer, is thermodynamically "good" for PS and "poor" for PMMA.

The possibility of separating two- and three-block copolymers of St and BD and two- and three-block copolymers of St and MMA by ATLC has been demonstrated[28,29].

In order to separate block copolymers of St and MMA, the CCl_4–MEK system is used, in which random two- and three-block copolymers of St and MMA are separated on silica gel plates. For this purpose, as the solvent front rises to a height of 10 cm, 125 ml of MEK are gradually added to 50 ml of CCl_4. The rate of addition is varied and thus gradients of three types, as shown in Fig. 33, are obtained. In this instance, the MW of copolymers does not affect their chromatographic behaviour (R_F values). Under these conditions, it is possible to separate random and block AB and ABA copolymers of the same composition (Fig. 34). As seen from Fig. 34, the R_F values for St and MMA copolymers of the same composition increase in the order random < three-block < two-block copolymers.

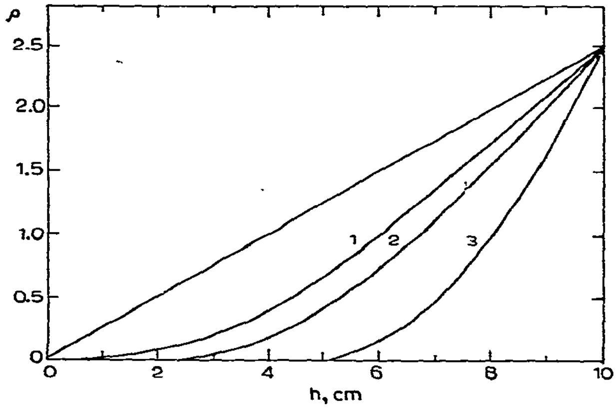


Fig. 33. MEK–CCl_4 gradients used to separate block copolymers of St–MMA by TLC. ϱ = MEK:CCl_4 (v/v) ratio; h = distance from the front.

TLC was used to investigate block copolymers of St and BD. In the Ch–$CHCl_3$ system, the R_F values of St–BD copolymers increase in the order two-block (St–BD) < three-block (St–BD–St) copolymers (*i.e.*, two- and three-block copolymers of St and BD migrate up the plate in an order which differs from that of analogous copolymers of St and MMA). In this chromatographic system (ATLC), the R_F values of St–BD copolymers do not depend on their MW. When PTLC was used in the $CHCl_3$–methanol system (3:2) with addition of methanol, St–BD copolymers could be separated according to their MW. Two-dimensional TLC with the use of both systems

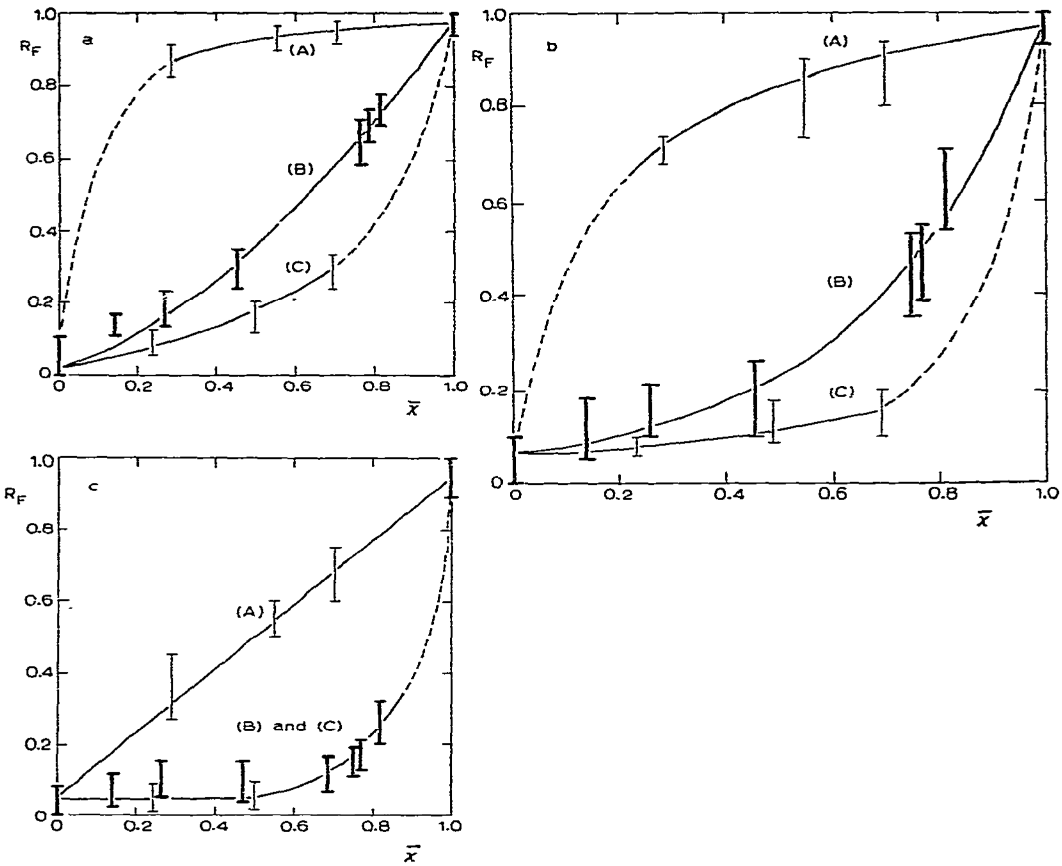


Fig. 34. Separation of (A) random, (B) three-block MMA–St–MMA and (C) two-block St–MMA copolymers by using gradients (a) 1, (b) 2 and (c) 3 shown in Fig. 33. $\bar{\chi}$ = Fraction in the copolymer.

made it possible to establish that the commercial St–BD copolymer Kraton 1101 contains two three-block copolymers of St–BD–St with similar compositions but different MW and an admixture of PS of MW = 10^4.

These conditions for the TLC of St–MMA copolymers, under which the R_F value depends only on the composition of the copolymer and not on its MW, permitted Kotaka *et al.*[27] to propose a method for the determination of the heterogeneity of the composition of copolymers (see p. 59) based on the densitometry of thin-layer chromatograms at two wavelengths: 225 nm, where both St and MMA units absorb, and 265 nm, where only St units absorb. In this instance, for the determination of the composition it is not necessary to calibrate plates by using copolymers of known composition (the "absolute" method for the determination of the heterogeneity of composition). The distribution of composition for two- and three-block copolymers of St and MMA found by this method was in complete agreement with the distribution obtained by cross-fractionation and calculated with the assumption of a random mechanism of block coupling in anionic polymerization.

In the TLC of block copolymers, the precipitation mechanism can be used instead of the adsorption mechanism. In this instance, in a solvent poor for one of the blocks, selective precipitation of the block copolymer rich in this block is observed. Under these conditions, it is possible to separate the homopolymer and the block copolymer with a low content of the second component.

In this instance, if gradient chromatography is used, in which the content of the solvent selective for the homopolymer decreases as the eluting liquid moves up the plate, the block copolymer remains at the start and PMMA migrates with the eluent. For this purpose, the chloroform–methanol system can be used in the S-chamber, in which chloroform, the solvent selective for PMMA, is more volatile and evaporates from the plate. As can be seen from Fig. 35, as the methanol content in this system increases, PS is precipitated before PMMA. Hence, at a certain methanol concentration, it is possible to carry out ETLC and to separate PMMA from the block copolymer. In this instance, as the MW of PMMA increases, the percentage of methanol in the solvent should be decreased from 80 to 72%.

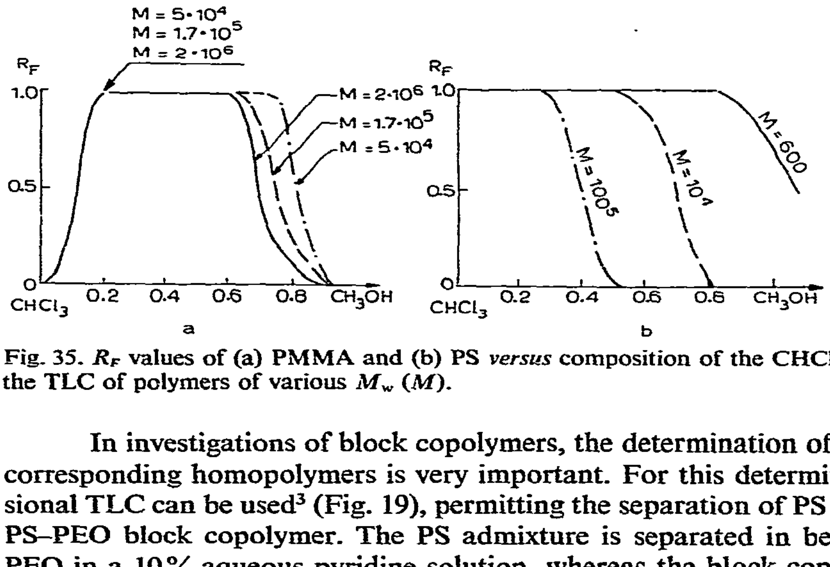


Fig. 35. R_F values of (a) PMMA and (b) PS *versus* composition of the $CHCl_3$–methanol system in the TLC of polymers of various M_w (M).

In investigations of block copolymers, the determination of admixtures of the corresponding homopolymers is very important. For this determination two-dimensional TLC can be used[3] (Fig. 19), permitting the separation of PS and PEO from the PS–PEO block copolymer. The PS admixture is separated in benzene and that of PEO in a 10% aqueous pyridine solution, whereas the block copolymer remains at the start. The separation of a block copolymer of PS–PEO and corresponding homopolymers on microcrystalline cellulose by one-dimensional TLC in ethyl acetate–methanol has been described by Wesslen and Nansson[21].

Under these conditions, PS migrates with the solvent front, the block copolymer is located in the centre of the plate and PEO remains at the start. On this basis, Wesslen and Nansson[21] developed a preparative method for the separation of the block copolymer by column chromatography. PS was separated by elution with ethyl acetate, while the block copolymer was eluted with a mixture of ethyl acetate and methanol. The column chromatography was controlled by TLC. The block copolymer and PS were detected from the extinction of luminescence of a luminophore introduced into the cellulose after the plate had been irradiated with UV light at 254 nm and PEO was detected in iodine vapour.

VI. THIN-LAYER CHROMATOGRAPHY OF OLIGOMERS

1. Principal relationships in the TLC of oligomers

The thin-layer chromatography of oligomers is of great interest both in their analysis and from the standpoint of peculiarities of the adsorption chromatography of polyfunctional compounds with different chemical structures of the central and end-units of the chain. The TLC of many classes of oligomers has been described: polyols[34,58–67], polyesters[68–72], polyolefins[73] and polyamides[74]. In most papers the possibility was demonstrated of separating oligomers with different numbers and structure of the end-groups. Many workers[34,63,64,67,70] have demonstrated that the chromatographic behaviour of oligomers is independent of their MW when the differences in R_F values are determined only by the number of functional groups present in these oligomers. Thus, it becomes possible to carry out a very important type of polymer analysis: the analysis of their functionality[75], which is responsible for the quality of high polymers obtained from these oligomers, such as polyurethanes. On the other hand, substituted polyoxyethylenes can be separated on the basis of their MW with the isolation of single-polymer homologues of up to 12–15-mers, as has been reported by Favretto *et al.*[66]. They showed that the efficiency of the separation of polyols on the basis of the MW depends on the type of substituent blocking the hydroxyl group of the end-units. The more hydrophobic the substituent (probably, the more bulky its hydrocarbon radical and, hence, the lower the adsorption of the end-units), the greater is the efficiency of the separation of the oligomer into single-polymer homologues.

Peculiarities of the adsorption of oligomers are related to the presence of functional end-groups. As a rule, the adsorption activity of these end-groups exceeds that of the central oligomer units and the change in the free energy of the oligomer in adsorption is mainly induced by the change in the free energy of the adsorbed end-groups. It is clear that the greater the difference in the adsorption activity of central and end-units, the smaller is the contribution of the central units to the change in the free energy of adsorption and, hence, the less pronounced is the MW dependence of the R_F values of the oligomer in ATLC.

We shall now consider these relationships in the TLC of oligomers in greater detail.

The change in the free energy (ΔF) in oligomer adsorption, as in the adsorption of high polymers (see above), is related to an increase in the enthalpy of the system when oligomer units come into contact with the adsorbent surface and to a decrease in the entropy caused by a decreasing number of possible conformations of the oligomer in adsorption. This change in the free energy of the system (ΔF), equal to the change in the configurational entropy of the oligomer solution in the mobile phase ($-T\Delta S_c$), is equivalent to a change in ΔH_M and ΔS_M in the adsorption of oligomer molecules passing from the mobile into the stationary phase:

$$\Delta F = -T\Delta S_c = N_A \Delta H_M - N_A T \Delta S_M \tag{19}$$

The change in enthalpy in the adsorption of the oligomer (the N-mer) is determined by the formation of N_e contacts of end-units of oligomers with energy $kT\,\varepsilon_e$

and of $N-N_e$ central units with energy $kT\,\varepsilon_c$, where ε_c and ε_e are the energies of interaction of the central and end-units, respectively, of the oligomer with the adsorption surface in kT units. If the concept of critical energy (ε_{cr}) in oligomer adsorption is used and it is assumed that at this energy $\Delta H_M = T\Delta S_M$ and hence the contact of an oligomer unit with the adsorption surface is not related to changes in the free energy, then ΔF in oligomer adsorption is given by

$$\Delta F = -T\Delta(\Delta S_c) \approx N_A kT[(\varepsilon_e-\varepsilon_{cr})N_e + (\varepsilon_c-\varepsilon_{cr})(N-N_e)] \tag{20}$$

where $\Delta(\Delta S_c)$ is the change in the configurational entropy of solution from the state $\Delta S_c = 0$ (at $K_d = 1$) to ΔS_c in adsorption (at $K_d > 1$). In eqn. 20, a term describing the entropy change ($-T\Delta S_M$) has been omitted as it is lower than ΔH_M. Here we consider the case when ε_e is greater than ε_c; hence, in oligomer adsorption ε_e is always greater than ε_{cr} and ε_c may be greater or less than ε_{cr}. Depending on the ratio of ε_c to ε_{cr}, the following three cases of the dependence of ΔF on the number of oligomer units (N) may be observed:

$$\left.\begin{array}{ll}(1) & \varepsilon_c > \varepsilon_{cr};\ -\Delta F \approx N_A kT(\varepsilon_e-\varepsilon_{cr})\,N_e + N_A kT(\varepsilon_c-\varepsilon_{cr})N \\ (2) & \varepsilon_c < \varepsilon_{cr};\ -\Delta F \approx N_A kT(\varepsilon_e-\varepsilon_{cr})\,N_e - N_A kT(\varepsilon_c-\varepsilon_{cr})N \\ (3) & \varepsilon_c = \varepsilon_{cr};\ -\Delta F \approx N_A kT(\varepsilon_e-\varepsilon_{cr})N_e\end{array}\right\} \tag{21}$$

Three types of dependence of the distribution coefficient $K_d \approx \exp(-\Delta F/kT)$ corresponding to eqn. 21 can be written:

$$\left.\begin{array}{ll}(1) & \varepsilon_c > \varepsilon_{cr};\ K_d \approx \exp\{-[(\varepsilon_e-\varepsilon_{cr})N_e + (\varepsilon_c-\varepsilon_{cr})N]\} \\ (2) & \varepsilon_c < \varepsilon_{cr};\ K_d \approx \exp\{-[(\varepsilon_e-\varepsilon_{cr})N_e - (\varepsilon_c-\varepsilon_{cr})N]\} \\ (3) & \varepsilon_c = \varepsilon_{cr};\ K_d \approx \exp\{-[(\varepsilon_e-\varepsilon_{cr})N_e]\}\end{array}\right\} \tag{22}$$

Thus, in the first case the dependence of K_d on N is positive, in the second case it is negative and in the third case K_d is independent of N and is determined only by the number of functional groups in the oligomer, N_e. In accordance with this, in the first case the R_F value of the oligomer decreases with increasing MW, in the second case it increases with increasing MW and in the third case the R_F value is independent of MW and is determined by the functionality of the oligomer.

These relationships in the adsorption chromatography of oligomers can also be obtained by using the correlation theory of Snyder[48]:

$$R_m = \log K_d = \log\left[\left(\frac{1-R_F}{R_F}\right)\frac{V_0}{V_p}\right] = \log(V_a\,W/V^0) + a\sum_i(Q_i^0 - a_i\,\varepsilon^0)$$

where V_a is the volume of the adsorption layer, W is the adsorption weight, V^0 is the volume of the mobile phase, Q_i^0 is the adsorbability of the functional group of the oligomer, a_i is their molecular area (in 8.5 Å^2 units) and ε^0 represents the eluent strength. As the oligomer consists of N units of adsorbability Q_N^0 and of N_e end-groups of adsorbability Q_e^0, the above equation becomes

$$R_m = \log(V_a\,W/V^0) + aN_e(Q_e^0 - a_e\,\varepsilon^0) + aN(Q_N^0 - a_N\,\varepsilon^0)$$

It follows from this equation that, depending on the ratio of Q_N^0 to a_N^0 (Q_i^0 is always greater than $a_e\varepsilon^0$), the following three cases of the dependence of R_m on N can be observed:

(1) at $Q_N^0 > a_N\,\varepsilon^0$; $R_m = A + B\,N_e + C\,N$

(2) at $Q_N^0 < a_N\,\varepsilon^0$; $R_m = A + B\,N_e - C\,N$

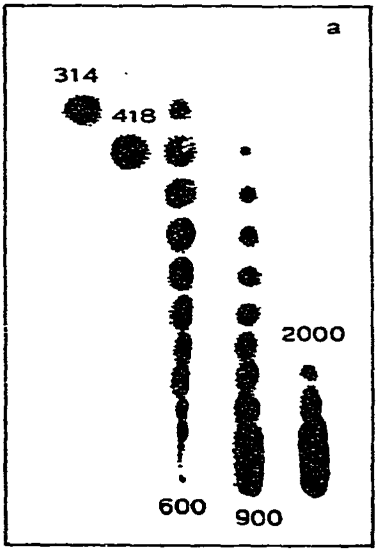
(3) at $Q_N^0 = a_N\,\varepsilon^0$; $R_m = A + B\,N_e$

where $A = \log V_a\,W/V^0$, $B = \alpha\,(Q_e^0 - a_e\,\varepsilon^0)$ and $C = \alpha\,(Q_N^0 - a_N\,\varepsilon^0)$.

It should be noted that although these results follow from the Snyder theory, they are not formally strict as this theory does not consider negative and zero adsorption (types 2 and 3).

It is noteworthy that in the absence of functional groups ($N_e = 0$), only the first type of dependence can occur as in the second type of dependence all oligomers move with the solvent front.

Fig. 36 shows chromatograms of these functionless oligomers of PS and of poly(α-methylstyrene) in which the MW dependences of the first type can be clearly seen.



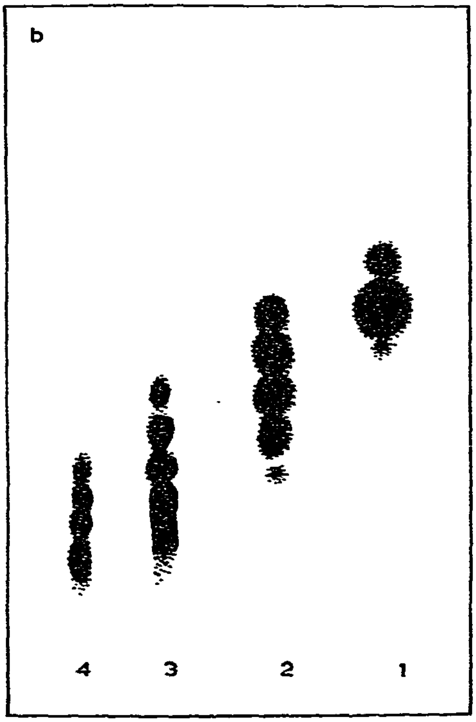


Fig. 36. TLC of oligomers: (a) PS with M_n = 314, 418, 600, 900 and 2000 in Ch–Bz (14:3); (b) poly(α-methylstyrene) fractions [(1) tetramer, (2) hexamer, (3) octamer, (4) decamer] in CCl_4–n-heptane (2:1) on KSK silica gel.

It is evident that with functionless oligomers the MW dependence of R_F (type 1 dependence) is the strongest. When the oligomers contain a functional group, as the difference between ε_e and ε_c increases the MW dependence of R_F becomes weaker. This becomes clear if we consides eqn. 22 (case 1). In order to obtain a strong MW (N) dependence of R_F, the multiplier of N ($\varepsilon_c - \varepsilon_{cr}$) should be relatively high. However, differences in R_F value depending on MW may be observed on the plate only at $K_d <$ 3–5, and for this it is necessary that the first term, $(\varepsilon_e - \varepsilon_{cr})N_e$, should be as small as possible. This can be accomplished only at $\varepsilon_e \approx \varepsilon_c$. When the difference between ε_e and ε_c is great, it follows that when the value of the multiplier $(\varepsilon_e - \varepsilon_{cr})$ is decreased (in order to decrease the value of K_d to $<$ 3–5), ε_c can become smaller than ε_{cr} and the second type of MW dependence of the R_F value of the oligomer will be observed.

It is possible to obtain experimentally all three types of the above MW dependences of R_F values for oligomers containing functional groups, such as polyols.

Fig. 37 shows the TLC of PEO with M_n = 300, 400 and 600 in chromatographic systems in which MW dependences of R_F values of the first, second and third types are observed. It is noteworthy that R_F values of polymer homologues in PEO of various MW correspond to each other. The MW dependence of the R_F value for PEO shown in Fig. 37b is characteristic of the molecular-sieve effect. However, in this instance the TLC mechanism is different as it has been established that in GPC the oligomers under investigation begin to be excluded from the pore volume of silica gel and aluminium oxide when their MW exceeds 10,000, *i.e.*, at a much higher MW than for PEO in the experiment described. The moon-like shape of the spots is related to a peculiar manifestation of the influence of concentration on the adsorption of polyols in TLC which is characterized by a convex adsorption isotherm. With a convex adsorption isotherm, the R_F value increases with concentration (see p. 41). Consequently, the R_F value will be lower for the sides of the spot in which the concentration of the substance decreases than for the central part of the polymer zone, and the spot acquires a peculiar shape with a sharp "nose". The difference between the R_F value for the

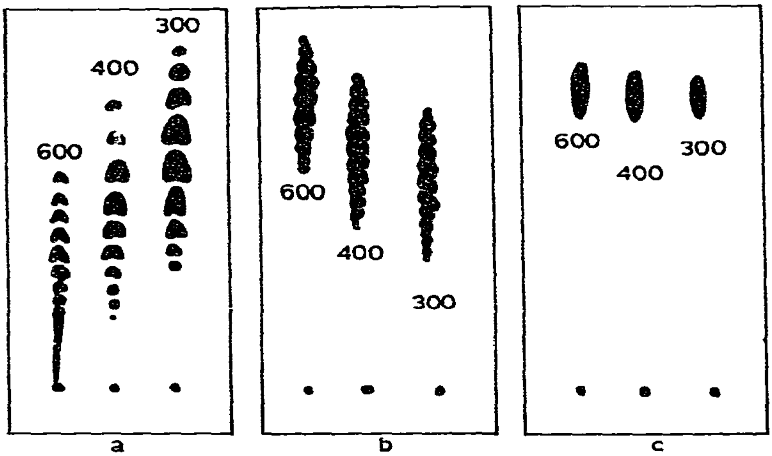


Fig. 37. TLC of PEO with M_n = 300, 400 and 600: (a) on KSK silica gel in pyridine–water (0.1:10); (b) on aluminium oxide in $CHCl_3$–ethanol (10:1); (c) on KSK silica gel in $CHCl_3$–pyridine (5:7).

"nose" of a spot and that of its sides, or the R_F value for a spot with a low polyol content, can be used to determine the amount of polyols present in the spot.

It is noteworthy that when the hydroxyl end-groups of PEO are replaced with less adsorption-active groups, it is easier to obtain a positive MW dependence of adsorption ($-\Delta F$) and, hence, a negative MW dependence of the R_F value.

If oligomers with weak adsorption activity of the central units such as polydimethylsiloxanediols, are investigated, it is impossible to achieve a highly effective separation of these oligomers according to MW unless the end-groups are blocked (Fig. 38). Nevertheless, even after blocking hydroxyl end-groups, *e.g.*, with a residue of dinitrobenzoic acid, only an MW dependence of the R_F value of the second type can be obtained: the R_F value of the oligomer increases with increasing number of weakly adsorbed siloxane units.

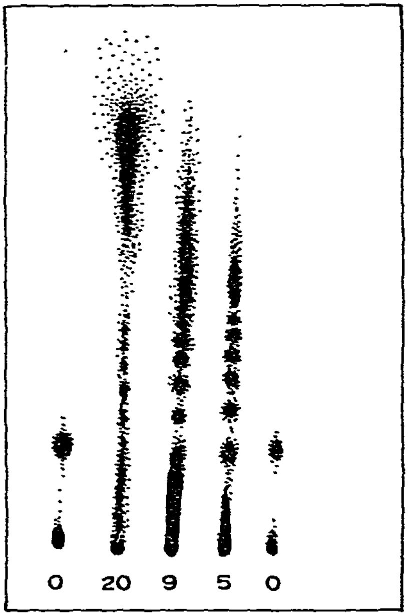


Fig. 38. TLC of 3,5-dinitrobenzoate poly(dimethylsiloxane) diols with $n = 0, 5, 9$ and 20 on KSK silica gel containing 0.007% of fluoresceine in Bz–ethyl acetate (10:0.1). TLC was performed twice (luminescent photography).

The above results indicate that the peculiarities of the TLC of oligomers are related to the ratio of the adsorption activities of the central and end-units. Hence it is possible to carry out various types of TLC with positive and negative MW dependences of the R_F value or, in the absence of an MW dependence of the R_F value, with oligomer separation by functionality. The last two types of TLC can be used to determine the MWD of oligomers.

2. *Separation of oligomers according to functionality*

The separation of oligomers according to functionality in the absence of an

MW dependence of the R_F value is of great practical interest. The possibilities of using TLC for the determination of functionality can be shown by taking as an example poly(propylene oxide) polyols (POPP). It is clear from Fig. 39 that the TLC of POPP in ethyl acetate saturated with water, with the addition of 5–10% of MEK, permits the separation of monools, diols, triols and pentaols over a wide range of MW. A slight MW dependence of R_F values of the first type is observed, which is not superimposed on the effect of the functionality of POPP on R_F. It is interesting that the MW dependence of POPP can be suppressed or changed when the adsorption activity of silica gel decreases. Fig. 40 compares chromatograms of diols and triols on standard KSK silica gel and on KSK silica gel with a low specific adsorption activity induced by its treatment with NaOH and NaCl[53]. In the latter instance, the R_F value increases with increasing MW of the polyol, which is characteristic of an MW dependence of the second type. However, even in this instance the chromatographic behaviours of polyols of different functionality remain very different. Hence, these conditions of TLC permit the determination of the functionality of POPP irrespective of MW[75]. This method for the determination of oligomer functionality makes it possible to separate linear and branched-chain oligomers that differ in the number of functional end-groups. Thus, in benzene–ethanol (3:1), complete separation is possible of linear and branched-chain complex oligoester polyols of the same MW (Fig. 41). In this system, the MW dependence on R_F value is very slight but it increases with decreasing ethanol content in the eluent. The system consisting of benzene and THF (1:1) was also found to be suitable for the separation of linear and branched-chain oligoester polyols. TLC with this system can be used to analyse oligoesters that contain, in addition to linear macro-

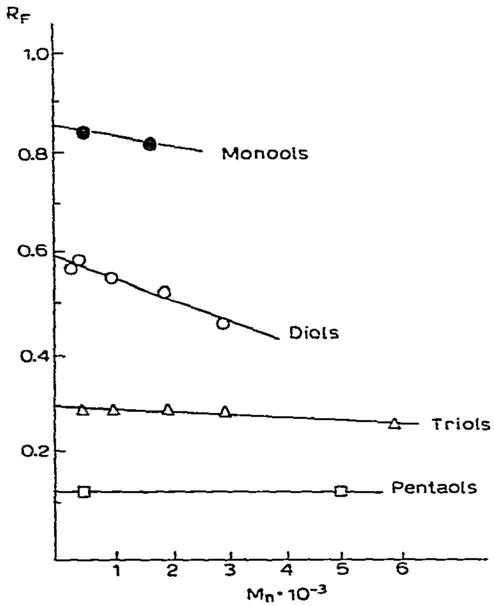


Fig. 39. TLC of poly(propylene oxide) polyols (PPOP) on KSK silica gel in ethyl acetate saturated with water containing 5–10% of MEK.

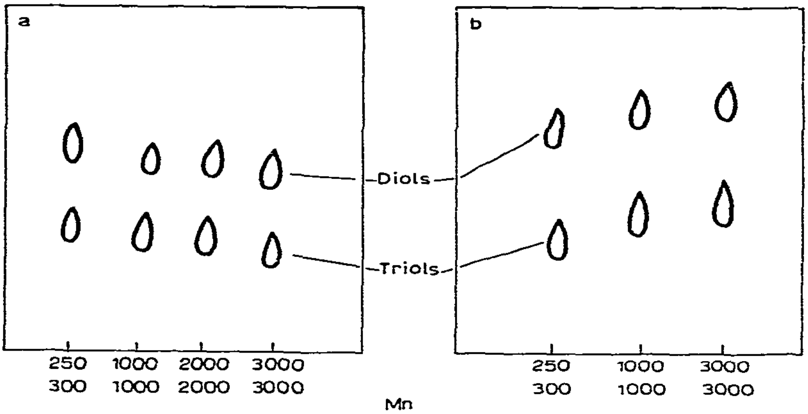


Fig. 40. TLC of PPOP of various M_n on (a) KSK silica gel and (b) KSK-2 silica gel treated with NaOH and NaCl in the solvent (as in Fig. 39).

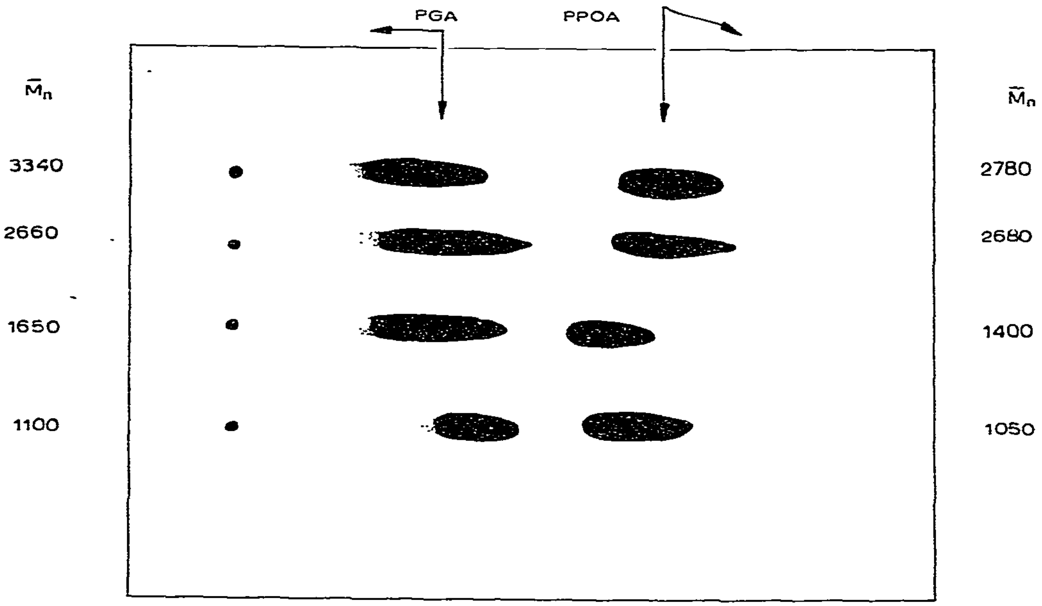


Fig. 41. TLC of linear poly(propylene oxide) adipates (PPOA) and branched-chain poly(glycerol) adipates (PGA) of polyesters of similar MW in Bz–ethanol (3:1) on KSK-2 silica gel.

molecules, 10% of branched chains (Fig. 42). These differences between linear and branched-chain oligoesters of the same MW are of great analytical interest because, as we have found[76] in GPC, they are eluted from the column at the same retention volume. Hence, data on the MWD of oligoesters obtained from GPC can be usefully supplemented by information on the MW dependence of the distribution of branched-chain polyfunctional oligoesters in the sample.

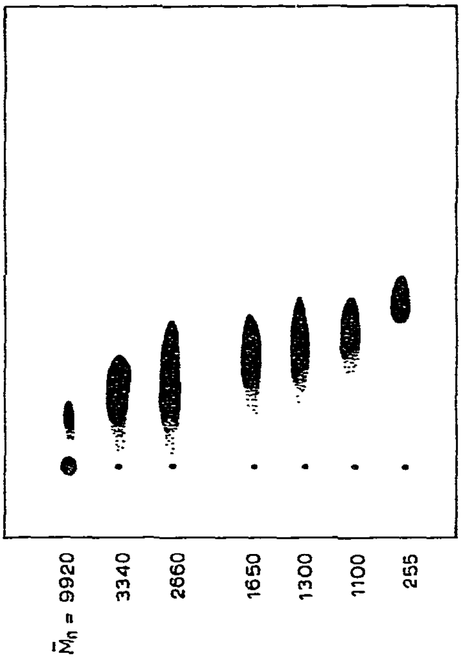


Fig. 42. Separation of branched-chain polyesters (PGA) on KSK-2 silica gel in Bz–ethanol (85:15).

VII. DETERMINATION OF MOLECULAR WEIGHT AND COMPOSITIONAL DISTRIBUTION OF POLYMERS FROM TLC DATA

1. Photometric method for the quantitative TLC of polymers

In order to plot the MW or the compositional distribution from TLC data, the following steps are necessary:

(a) To render visible (to stain) the polymer zone on the chromatogram. The most common procedures involve the use of a 1% solution of iodine in methanol[2], a saturated solution of thymol blue with subsequent treatment with 3*N* H_2SO_4[11], a 5% solution of $KMnO_4$ in concentrated H_2SO_4[3] and the Dragendorff reagent for oxygen-containing polymers[3].

(b) To determine the dependence of R_F value or the fractionating factor, Z, on MW or the polymer composition.

(c) To measure the sensitivity of detection as a function of R_F: $(\mathrm{d}Q/\mathrm{d}I)R_F$.

(d) To measure the distribution of the substance stained, $I(R_F)$, in the spot.

(e) By using $(\mathrm{d}Q/\mathrm{d}I)R_F$ and $I(R_F)$, to determine the polymer distribution in the spot:

$$Q\,(R_F) = I\,(R_F)\left(\frac{\mathrm{d}Q}{\mathrm{d}I}\right)_{R_F} \tag{23}$$

(f) Knowing the dependence $R_F(Z)$, to obtain the MWD or the compositional distribution, $P(Z)$:

$$P\,(Z) = Q\,(R_F)\,\frac{\mathrm{d}R_F}{\mathrm{d}Z} \tag{24}$$

When narrow-disperse polymers are investigated, it is also necessary to correct the distribution $Q(R_F)$ for chromatographic spreading, *e.g.*, by using two-dimensional chromatography (Fig. 43)[3]. In this instance, the chromatogram of the polymer obtained by elution in the first direction shows the MWD or the compositional distribution. This spot is then used as a starting zone for development in the second direction. The difference between the dispersions of the zones obtained after the first (σ_1^2) and second (σ_2^2) developments is the dispersion of the chromatographic spreading (σ_{chr}^2). A correction for the spreading of polymer (σ^2) can be made simply by subtracting the dispersion (σ_{chr}^2), or by a more complex but more accurate procedure, as in the analysis of the MWD of polymers by GPC[77].

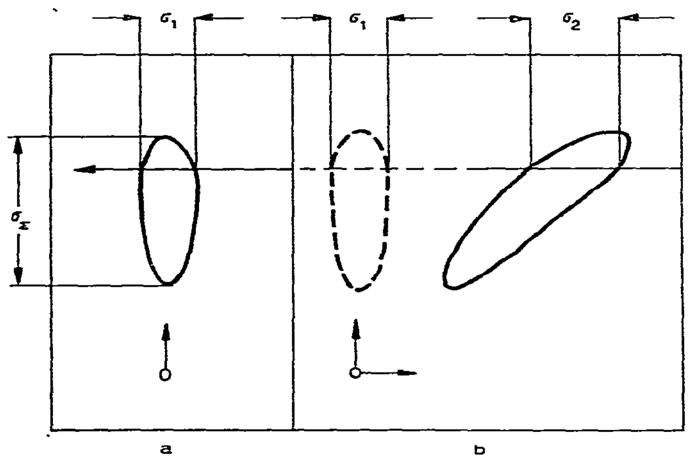


Fig. 43. Determination of chromatographic spreading in TLC: (a) chromatogram in the first direction; (b) two-dimensional chromatogram. $\sigma_{chr}^2 = \sigma_2^2 - \sigma_1^2$; $\sigma^2 = \sigma_\Sigma^2 - \sigma_{chr}^2$.

The chromatographic distribution is usually determined by photometric scanning of the spot along the direction of development (x) with a high slit, the height of which corresponds to the width of the spot[5,12,13,32]. This densitometric method is not precise and suffers from errors due to irregular filling of the high slit with light.

In order to obtain accurate photometric results, multi-step scanning should be used with point-light detection and with integration of the signal in the y-direction normal to the axis of development. These integral values represent the distribution $I(R_F)$, which is calculated with a precision inversely proportional to the step value Δx.

A simple but precise method for measuring the polymer distribution in the chromatographic zone is based on the preparation of images of polymer chromatograms with equal density (see below). Knowing the polymer distribution by weight, $P(x)$, it is possible to derive the normalized integral distribution:

$$\int P(Z) = \int_0^{Z'} dP(Z) \Big/ \int_0^{\infty} dP(Z) \qquad (25)$$

the corresponding differential distribution:

$$dP(Z) = P(Z) \Big/ \int_0^\infty dP(Z) \tag{26}$$

and the weight-average value of Z:

$$\bar{Z} = \int_0^\infty Z \, dP(Z) \tag{27}$$

A method has been proposed for the determination of the compositional distribution of copolymers (under the condition that the R_F value of the copolymer is independent of its MW) based on scanning the plate at two wavelengths[25] at which the molar extinctions of the components of the copolymer differ greatly. For this purpose, a dual-wavelength scanning spectrodensitometer (CS-900, Shimadzu Seisakusho Co., Tokyo, Japan), which is similar to the Schoeffel SO 3000 scanning spectrodensitometer (Schoeffel Instrument Co., Westwood, N.J., U.S.A.), can be used. The adsorption, I, at a point x corresponding to the content, Z, of St in the copolymer is given by the following equations:

$$\text{at } \lambda_1 = 265 \text{ nm: } I'(x) = Z\,\varepsilon'_{St} \cdot W(x) \tag{28}$$

$$\text{at } \lambda_2 = 225 \text{ nm: } I''(x) = [Z\,\varepsilon''_{St} + (1 - Z)\,\varepsilon''_{MMA}]\,W(x) \tag{29}$$

where $W(x)$ is the amount of the polymer in the range $x \pm dx/2$ and ε is the molar extinction. If the area under the chromatogram of the copolymer, A, is determined, then by obtaining $I'(x)$ and $I''(x)$ and knowing relative extinctions $\varepsilon''_{St}/\varepsilon''_{MMA}$ and $\varepsilon'_{St}/\varepsilon''_{MMA}$, it is possible to calculate the following characteristics of the copolymer:

(a) the weight distribution of the copolymer, $P(Z)$:

$$P(Z) = \frac{W(x)}{W_t} = \frac{[1 - (\varepsilon''_{St}/\varepsilon''_{MMA})]\,I'(x) + (\varepsilon'_{St}/\varepsilon''_{MMA})\,I''(x)}{[1 - (\varepsilon''_{St}/\varepsilon''_{MMA})]\,A' + (\varepsilon'_{St}/\varepsilon''_{MMA})\,A''} \tag{30}$$

(b) the dependence of the composition (Z) on the position on the chromatogram (x):

$$Z(x) = \frac{1}{[1 - (\varepsilon''_{St}/\varepsilon''_{MMA})]\,I'(x) + (\varepsilon'_{St}/\varepsilon''_{MMA})\,I''(x)} \tag{31}$$

(c) the average composition of the copolymer, $\bar{Z}$:

$$\bar{Z} = \frac{1}{[1 - (\varepsilon''_{St}/\varepsilon''_{MMA})]\,A' + (\varepsilon'_{St}/\varepsilon''_{MMA})\,A''} \tag{32}$$

Thus, by using eqns. 30–32, TLC makes it possible to determine the values of $W(x)/W_t$, $Z(x)$ and $\bar{Z}$ without using reference samples of copolymers. When dual-wavelength photometry is used to determine the heterogeneity of the composition of copolymers in which one of the components does not absorb UV light in the spectral range of the spectrodensitometer (*e.g.*, a copolymer of St–Bd), it is possible to stain the polymer zones on the plate. However, in this instance it is difficult to determine

$\varepsilon'_{St}/\varepsilon''_{MMA}$ owing to the poor reproducibility of chemical staining. This parameter can be obtained from eqn. 32 if the value of $\varepsilon''_{St}/\varepsilon''_{MMA}$ and the average copolymer composition, $\bar{Z}$ (which is determined by an independent method), are known.

2. Analysis of distribution of polydisperse polymers throughout the width of the chromatographic zone

In TLC, the distribution of a substance along the y-axis normal to the eluent movement along the x-axis always has a Gaussian shape. Therefore, by measuring the width of the zone at a certain limiting (lowest detectable) concentration, C_l, it is possible to determine the amount of substance in this (the ith) section of the polymer zone on the plate. Let C_l be given by

$$C_l = C_{m\,i} \exp\left[-\frac{(\Delta y_i)^2}{8\sigma^2_{y,i}}\right] \tag{33}$$

where $C_{m,i}$ is the polymer concentration at the maximum, $\sigma^2_{y,i}$ is the dispersion of distribution in the ith (along the x-axis) section of the zone and Δy_i is the distance along the y-axis between the points of C_l (the width of the B zone in the ith section). Then, the amount of the substance, q_i, in the ith section of width Δx is expressed by the distribution parameters (eqn. 33) as follows:

$$q_i = \sqrt{2\pi}\, \bar{C}_{m,i}\, \bar{\sigma}_{y,i}\, \Delta x = \sqrt{2\pi}\, C_l\, \bar{\sigma}_{y,i}\, \Delta x \exp\left[\frac{(\overline{\Delta y_i})^2}{8\bar{\sigma}^2_{y,i}}\right] \tag{34}$$

where the zone width, $\overline{\Delta y_i}$, and the dispersion, $\bar{\sigma}_{y,i}$, were selected averages over Δx.

In photographic recording of chromatograms, a certain optical density, D_l, should correspond to C_l, $C_l = kD_l$, where k is a coefficient that is constant for the homopolymer and depends on the composition in the case of a copolymer:

$$q_i = \sqrt{2\pi}\, k_i\, D_l\, \bar{\sigma}_{y,i}\, \Delta x \exp\left[\frac{(\overline{\Delta y_i})^2}{8\bar{\sigma}^2_{y,i}}\right] \tag{35}$$

In order to use eqn. 35, it is necessary to determine the value of $\bar{\sigma}_{y,i}$, expressing it in terms of the width of the chromatographic zone, $\overline{\Delta y_i}$, measured experimentally. This can be accomplished by two methods:

(a) by the separation of two chromatograms of the polymer containing different amounts of the substance, Q_1 and Q_2; then in each section of these two chromatographic zones the ratio of the amounts of the substance, q_i'/q_i'', will be equal to the known ratio Q_1/Q_2; and

(b) by taking the photograph of the chromatogram of the polymer at two exposures in order that the contour of the spot will correspond to different $C_l(D_l)$ values and determining the ratio D'_l/D''_l.

By using eqn. 34, the first method permits the following equations to be written:

$$\left.\begin{aligned} q_i' &= \sqrt{2\pi}\, C_l\, \bar{\sigma}_{y,i}\, \Delta x \exp\left[\frac{(\overline{\Delta y_{i,1}})^2}{8\bar{\sigma}^2_{y,i}}\right] \\ q_i'' &= \sqrt{2\pi}\, C_l\, \bar{\sigma}_{y,i}\, \Delta x \exp\left[\frac{(\overline{\Delta y_{i,2}})^2}{8\bar{\sigma}^2_{y,i}}\right] \end{aligned}\right\} \tag{36}$$

By combining eqns. 36, the expression for $\bar{\sigma}_{y,i}$ can be obtained:

$$\bar{\sigma}_{y,i} = \frac{1}{2} \sqrt{\frac{(\overline{\Delta y}_{i,1})^2 - (\overline{\Delta y}_{i,2})^2}{2 \ln (Q_1/Q_2)}} \tag{37}$$

By using eqn. 35, the second method permits the following equations to be written:

$$\left.\begin{aligned} q &= \sqrt{2\pi}\, k_i\, D'_i\, \bar{\sigma}_{y,i}\, \Delta x \exp \left[\frac{(\overline{\Delta y}'_i)^2}{8\bar{\sigma}^2_{y,i}} \right] \\ q &= \sqrt{2\pi}\, k_i\, D''_i\, \bar{\sigma}_{y,i}\, \Delta x \exp \left[\frac{(\overline{\Delta y}''_i)^2}{8\bar{\sigma}^2_{y,i}} \right] \end{aligned}\right\} \tag{38}$$

Eqns. 38 yield an expression for $\bar{\sigma}_{y,i}$:

$$\bar{\sigma}_{y,i} = \frac{1}{2} \sqrt{\frac{(\overline{\Delta y}'_i)^2 - (\overline{\Delta y}''_i)^2}{2 \ln (D'_i/D''_i)}} \tag{39}$$

By substitution of eqns. 37 and 39 into eqn. 35, it is possible to obtain equations for the polymer distribution, $W_i = q_i/\sum_i q_i$, expressed in terms of the width of the chromatographic zone, $\Delta \bar{y}_i$, and of the known ratios Q_1/Q_2 or D'_i/D''_i and k_i:

$$\text{(a)}\quad W_i = \left. \frac{\left\{ k\, [(\overline{\Delta y}_1)^2 - (\overline{\Delta y}_2)^2]^{\frac{1}{2}} \left(\frac{Q_1}{Q_2}\right)^{\frac{(\overline{\Delta y}_1)^2}{(\overline{\Delta y}_1)^2 - (\overline{\Delta y}_2)^2}} \right\}_i}{\sum_i \left\{ k\, [(\overline{\Delta y}_1)^2 - (\overline{\Delta y}_2)^2]^{\frac{1}{2}} \left(\frac{Q_1}{Q_2}\right)^{\frac{(\overline{\Delta y}_1)^2}{(\overline{\Delta y}_1)^2 - (\overline{\Delta y}_2)^2}} \right\}_i} \right|_{Q_1/Q_2 = e} =$$

$$= \frac{\left\{ k\, [(\overline{\Delta y}_1)^2 - (\overline{\Delta y}_2)^2]^{\frac{1}{2}} \exp \left[\frac{(\overline{\Delta y}_1)^2}{(\overline{\Delta y}_1)^2 - (\overline{\Delta y}_2)^2} \right] \right\}_i}{\sum \left\{ k\, [(\Delta y_1)^2 - (\Delta y_2)^2]^{\frac{1}{2}} \exp \left[\frac{(\overline{\Delta y}_1)^2}{(\overline{\Delta y}_1)^2 - (\overline{\Delta y}_2)^2} \right] \right\}_i} \tag{40}$$

$$\text{(b)}\quad W_i = \frac{\left\{ k\, [(\overline{\Delta y}')^2 - (\overline{\Delta y}'')^2]^{\frac{1}{2}} \left(\frac{D'_i}{D''_i}\right)^{\frac{(\overline{\Delta y}')^2}{(\overline{\Delta y}')^2 - (\overline{\Delta y}'')^2}} \right\}_i}{\sum_i \left\{ k\, [(\overline{\Delta y}')^2 - (\overline{\Delta y}'')^2]^{\frac{1}{2}} \left(\frac{D'_i}{D''_i}\right)^{\frac{(\overline{\Delta y}')^2}{(\Delta y')^2 - (\Delta y'')^2}} \right\}_i} \tag{41}$$

If method (a) is adopted for obtaining W_i, it is convenient to use chromatograms in which the polymer is applied at the $Q_1/Q_2 = e$ ratio, then the expression for W_i (eqn. 41) is simplified.

As already mentioned, in the TLC of homopolymers or copolymers of narrow-disperse composition, k_i is constant, and it is then possible to omit these coefficients in eqns. 40 and 41. When copolymers of a polydisperse composition are analyzed, it is necessary to take into account the dependence of k_i on the composition of the copolymer (or on the R_F value) and the values of W_i should be found from eqns. 40 and 41.

Of the above equations for W_i, eqn. 41 is of the greatest interest as only one chromatogram is necessary for it to be used. Hence, no errors arise due to the inaccurate application to the plate of calculated amounts of the polymer (Q_1 and Q_2) or to concentration effects distorting the shape of the spot. In order to use eqn. 41 it is necessary to know D_t. For this purpose, the "equidensity" method was developed for obtaining images of the spot. This method is based on the well known Sabatier phenomenon in photography[78], which consists of total or partial reversion of an image developed for a short time under the effect of secondary illumination. This method, which allows the preparation of a system of iso-photes of an elongated object without complicated equipment[79], has been widely used in astronomy[80–82]. An "equidensity" image ("equidensity" means a curve joining points on the negative with the same density of darkening) is obtained if a print from an object (a negative, *i.e.* a TLC plate) is made on a contrasting photographic material at an exposure t_b. This print is developed for a short time and, without fixing, is exposed for a second time under uniform lighting. After the second exposure, the zones of the image (the equidensities corresponding to the density of the object, $D + \Delta D$, become light on a dark background. The optical density of the object, D, distinguished by this equidensity is determined by the time of the first exposure. By varying this time it is possible to obtain equidensities corresponding to various optical densities, D_t, which can easily be determined if a photograph of a graduated optical wedge is taken together with the photograph of the object. In order to increase the contrast of the image, it is advisable to take a photographic copy of the equidensity image on a super-contrasting material, obtaining a black equidensity on a light background. The value of the equidensity method based on the Sabatier effect lies in the possibility of taking photographic copies. If a photograph of the chromatogram is taken in such a way that the image is a continuous spot, the dimensions of the photographic copy of this image depend on the exposure made when obtaining the copies and, hence, cannot be used to determine W_i from the size of the chromatographic zone.

The precision of this equidensity method of quantitative analysis was checked by determining from the chromatogram (Fig. 44) the ratio of the amounts of two polymers in a mixture that was applied to the plate in the ratio Q'/Q''. The ratios attained (2.48 and 0.592) are in good agreement with the ratio (Q'/Q'') of these polymers in the sample (2.5 and 0.6).

Fig. 45 shows an example of the analysis of polymer distribution according to MW by the equidensity method.

It should be noted that this method is less precise than methods of quantitative analysis based on densitometric scanning because the width of the spot is not very sensitive to the amount of the substance present in it. The precision of the equidensity method can be increased if the determination of D'_t and of the spot width, y (*i.e.*, of the quality of iso-photographs) is more precise and if the amount of the measured equidensity images of the spot is increased because the mean square error of the dis-

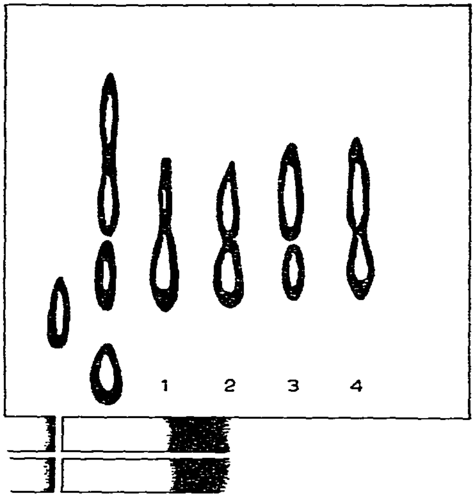


Fig. 44. "Equidensity" image of chromatograms of a mixture of PS with $M_n = 2\cdot 10^4$ and $3.3\cdot 10^4$ in the ratios (1) 0.1:1, (2) 0.6:1, (3) 2.5:1 and (4) 1:1 and reference PS (left) in Ch–Bz–Ac (12:4:0.7). Below: image of the optical wedge.

tribution obtained is inversely proportional to the square root of the number of measurements. On the other hand, as the dependence of y on q is characteristic of a Gaussian distribution, this method is very sensitive in determinations of micro-impurities. This can be seen if eqn. 34 is differentiated:

$$\frac{\mathrm{d}\,(\overline{\Delta y})}{\mathrm{d}q} = \frac{2\,\bar{\sigma}_y}{q_i\,\{2\ln\,[q/(2\pi)^{\frac{1}{2}}\,C_i\,\bar{\sigma}_y\,\Delta x]\}^{\frac{1}{2}}} \tag{42}$$

Eqn. 42 shows that the sensitivity of the method is inversely proportional to the amount of substance present in a spot section. Actually, it can be seen from Fig. 46 that the spot is detected with the greatest sensitivity when small amounts of a substance are present.

3. *Determination of molecular-weight distribution of oligomers by using equidensity images of thin-layer chromatograms*

A peculiarity of the TLC of oligomers is the discrete character of the chromatographic zones of single polymer homologues up to $N \leqslant 10$–12. Polymer homologues of higher MW are developed as a continuous zone, which can be analyzed by the same method as for chromatograms of polymers. When the amount of a substance present in discrete zones is determined, it is necessary to take into account its distribution along both the y- and x-axes[83], which can be effected as follows. The equation of the ellipse forming the boundary of the spot (x_i, y_i) is given by

$$C_i = C_m \exp\left[-\frac{1}{2}\left(\frac{x_i^2}{\sigma_x^2} + \frac{y_i^2}{\sigma_y^2}\right)\right] \tag{43}$$

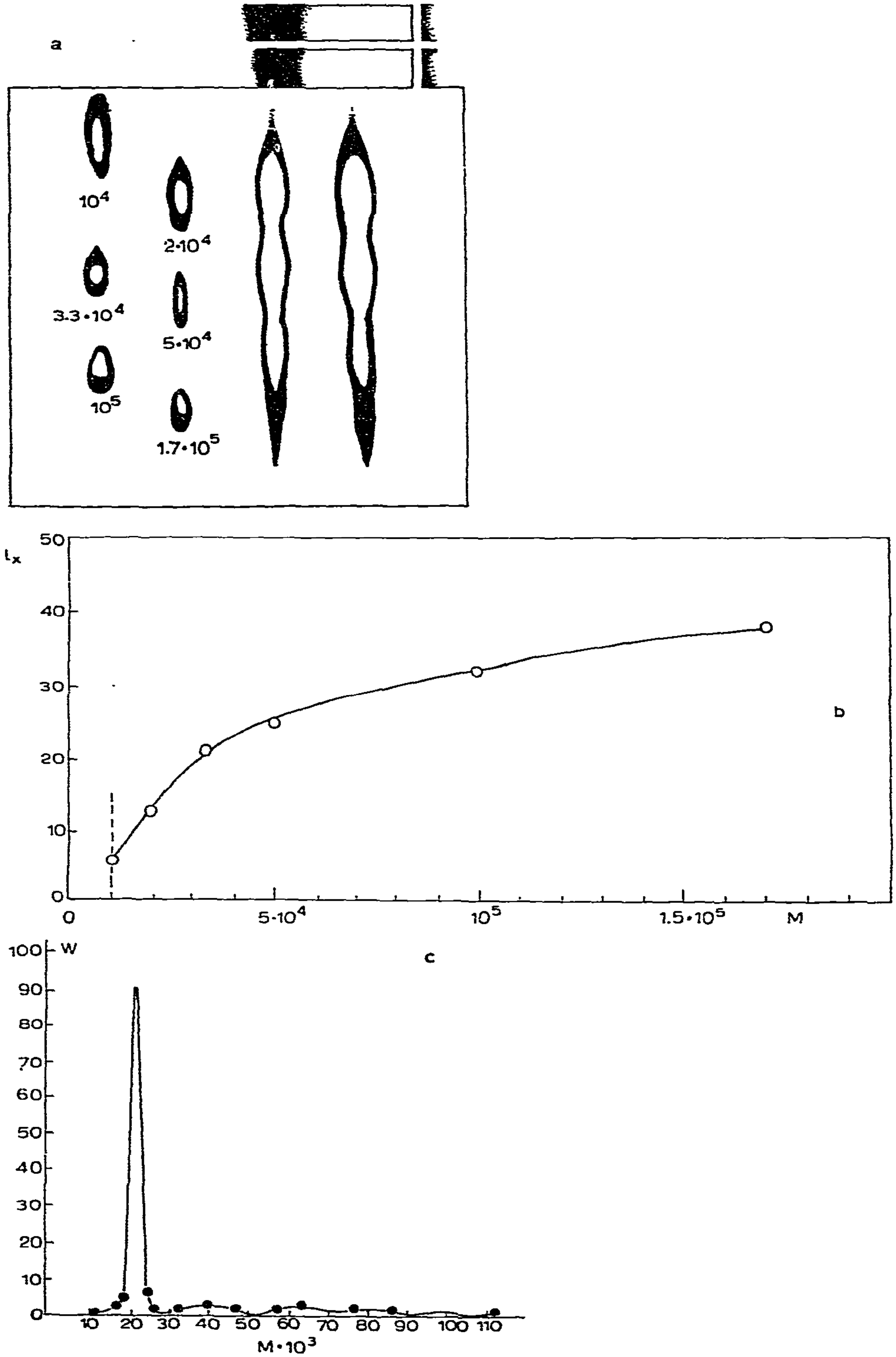


Fig. 45. Determination of MWD of PS by the "equidensity" method. (a) "Equidensity" image of chromatogram of the PS sample at two concentrations in Ch–Bz–Ac (12:4:0.9): left, chromatograms of reference PS; above, image of the optical wedge. (b) Distance from the front (l_x) *versus* MW (M) of PS in TLC under the same conditions as in (a). (c) MWD of PS. It was found that $M_n = 2.18\cdot 10^4$, $M_w = 2.39\cdot 10^4$ and $M_w/M_n = 1.10$.

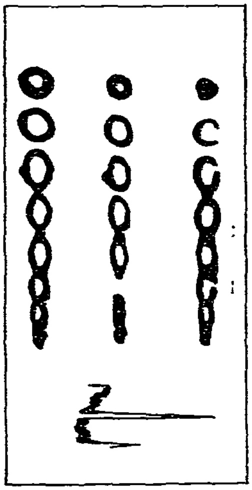


Fig. 46. Equidensity images (with printed optical wedge, below) of thin-layer chromatogram of PS with $M_n = 600$ on KSK silica gel in Ch–Bz (14:3).

where C_m is the concentration at the spot maximum. If we designate the semi-axes of this ellipse by x_0 and y_0, eqn. 43 gives

$$C_l = C_m \exp\left[-\frac{1}{2}\left(\frac{x_0^2}{\sigma_x^2}\right)\right] = C_m \exp\left[-\frac{1}{2}\left(\frac{y_0^2}{\sigma_y^2}\right)\right] \tag{44}$$

and, hence,

$$\frac{x_0}{\sigma_x} = \frac{y_0}{\sigma_y} \tag{45}$$

The amount of a substance present in the chromatographic zone, q, can be determined by integrating eqn. 43:

$$q = 2\pi C_m \sigma_x \sigma_y \tag{46}$$

Substitution into eqn. 46 of the expressions for C_m (eqn. 43) and σ_y (eqn. 45) gives

$$q = 2\pi\, C_l\, \sigma_x^2 \frac{y_0}{x_0} \exp\left(+\frac{1}{2}\cdot\frac{x_0^2}{\sigma_x^2}\right) \tag{47}$$

If C_l is replaced with the optical density, D_l, of the contour of the equidensity image of the chromatographic zone, $C_l = kD_l$, where k is a constant, we can write

$$q = 2\pi\, k\, D_l\, \sigma_x^2 \frac{y_0}{x_0} \exp\left(\frac{1}{2}\cdot\frac{y_0}{x_0}\right) \tag{48}$$

If two equidensity images of the chromatogram with densities D_l' and D_l'' are used to calculate the chromatogram, then it is possible to write two equations of the type of eqn. 48:

$$\left.\begin{aligned} q &= 2\pi\, k\, D_i'\ \sigma_x^2 \frac{y_0'}{x_0'} \exp\left(\frac{1}{2}\cdot\frac{y_0'}{x_0'}\right) \\ q &= 2\pi\, k\, D_i''\ \sigma_x^2 \frac{y_0'}{x_0'} \exp\left(\frac{1}{2}\cdot\frac{y_0'}{x_0'}\right) \end{aligned}\right\} \quad (49)$$

It follows that

$$\sigma_x^2 = \frac{(x_0'')^2 - (x_0')^2}{2 \ln\left(\dfrac{D_i'}{D_i''}\cdot\dfrac{y_0'/x_0'}{y_0''/x_0''}\right)} \quad (50)$$

The final expression for q has the following form:

$$q = 2\pi\, k\, D_i' \frac{(x_0'')^2 - (x_0')^2}{2 \ln\left(\dfrac{D_i'}{D_i''}\cdot\dfrac{y_0'/x_0'}{y_0''/x_0''}\right)} \cdot \frac{y_0''}{x_0''} \cdot \left(\frac{D_i'}{D_i''}\cdot\frac{y_0'/x_0'}{y_0''/x_0''}\right)^{\frac{(x_0')^2}{(x_0'')^2-(x_0')^2}} \quad (51)$$

The weight-average MWD (differential MWD, $\mathrm{d}f_i$, and integral MWD, $\int f_i$) are found from the equations

$$\left.\begin{aligned} \mathrm{d}_{fi} &= \frac{q_i}{\sum_{i=1}^{N} q_i} \\ \int_{fi} &= \frac{\sum_{i=1}^{j} q_i}{\sum_{i=1}^{N} q_i} \end{aligned}\right\} \quad (52)$$

where i is the degree of polymerization and N is the maximum degree of polymerization of the separated spots.

The number-average MWD ($\mathrm{d}g_i$ and $\int g_i$) is calculated from the equations

$$\left.\begin{aligned} \mathrm{d}g_i &= \frac{q_i/i}{\sum_{i=1}^{N} q_i/i} \\ \int g_i &= \frac{\sum_{i=1}^{j} q_i/i}{\sum_{i=1}^{N} q_i/i} \end{aligned}\right\} \quad (53)$$

It is also possible to find the amount of the substance in these spots which is not separated on the chromatogram (with $i > N$). By using the calibrating dependence $R_F(i)$ as a polynomial of the second power:

$$R_F(i) = a + bi + ci^2$$

where the a, b and c are obtained by the least-squares method, it is possible to find the values of R_F at $i > N$. Further, by the method of linear extrapolation (valid at R_F 1/3) one obtains the values of x_i', x_i'', y_i' and y_i'' at $i > N$ by using their values at $i = N$ and $i = N - 1$.

Fig. 46 shows equidensity images of a thin-layer chromatogram of PS with $M_n = 600$. The results of measurements of $x'_{0,i}$ and $x''_{0,i}$ are given in Table 4.

Fig. 47 shows differential MWD of the PS investigated. M_n was found to be 574.

TABLE 4

RESULTS OF MEASUREMENTS OF EQUIDENSITY IMAGES OF THIN-LAYER CHROMATOGRAMS FOR PS WITH $M_n = 600$

Parameter	*i*						
	3	*4*	*5*	*6*	*7*	*8*	*9*
R_F	0.73	0.60	0.49	0.36	0.25	0.16	0.1
$x'_{0,i}$	1.28	3.04	2.69	2.43	2.27	1.75	1.35
$y'_{0,i}$	2.45	3.24	3.93	4.16	3.53	3.30	2.68
$x''_{0,i}$	5.37	4.8	4.27	3.57	3.27	2.67	2.40
$y''_{0,i}$	5.17	5.48	5.60	6.05	5.30	4.75	3.75

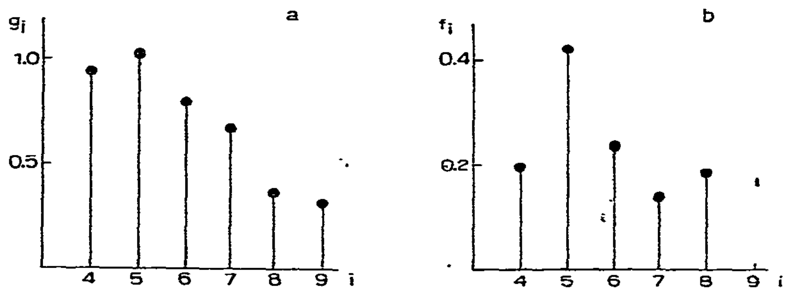


Fig. 47. Differential MWD of PS with $M_n = 600$ according to number (a) and weight (b) obtained from the chromatogram in Fig. 46.

4. Quantitative determination by TLC of impurities of low functionality in poly(propylene oxide) polyols

It is possible to carry out quantitative determinations of components with low functionality in poly(propylene oxide) polyols (PPOP) by a method based on the dependence of the mobility of the spot on the content of the oligomer[74]. Fig. 48 shows that the spots of POPP have a "nose" with a sharp edge tapered to the front, whereas

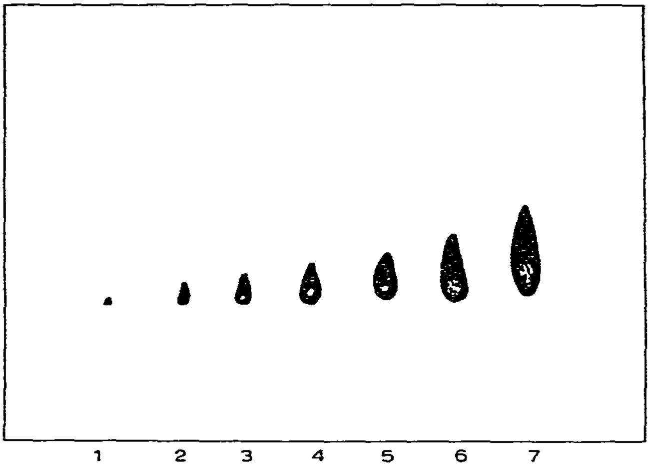


Fig. 48. TLC of poly(propylene oxide) diols (PPOD) with $M_n = 1000$ in ethyl acetate saturated with water containing 2% of MEK. Amounts of PPOD: (1) 6; (2) 20; (3) 30; (4) 35; (5) 50; (6) 65; (7) 100 μg.

the rear part of the spot is spread out. As mentioned above, this shape of the chromatographic zone is caused by specific concentration effects in oligomer adsorption due to the convex adsorption isotherm. It is natural to use the chromatographic mobility of the "nose" of the spot related to the polymer concentration because the R_F value of the nose can be measured precisely in order to determine the amount of POPP present in it. The chromatographic homogeneity of the substance being investigated is an indispensable condition for using this method of quantitative analysis. Under our experimental conditions, the R_F value of the oligomer does not depend on its MW (MW dependence of the third type) and therefore POPP samples of the same functionality are chromatographically homogeneous. Experimental checking showed that this dependence exists, is linear and remains constant over a concentration range of two orders of magnitude. The slope of this dependence is related to the MW of POPP and to the length of development (Fig. 49). This dependence can be obtained from the following simplified model of the ATLC of oligomers.

It is known that the R_F value of the spot maximum containing an amount q of the substance, R_{Fq}, is related to its concentration at the spot maximum by

$$R_{Fq} = \frac{l_q}{l_s} = \frac{1}{1 + \frac{m_c}{c}} \tag{55}$$

where l_q and l_s are the lengths of development of the maximum of the spot and of the solvent front on the plate, respectively, and c and m_c are the concentrations of the substance at the spot maximum for the mobile and the stationary phase (throughout the thickness of the whole chromatographic layer).

The ratio of m_c to c can be determined by using the Freundlich equation which, in many instances, adequately describes polymer adsorption[84]:

$$m_c = \alpha c^{\beta} \tag{56}$$

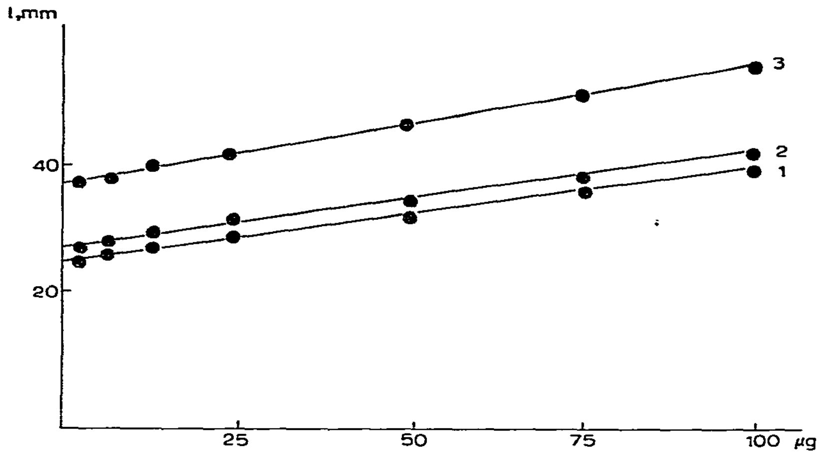


Fig. 49. Spot length (l) *versus* amount of PPOD with M_n = (1) 1000, (2) 425 (the same system as in Fig. 48) and (3) 1000 (with 40% of MEK).

where α and β are constants ($\beta < 1$).

The concentration of the polymer in the mobile phase, c, can be related to the amount of the substance in the spot, q, by the equation

$$c = kR_F q \tag{57}$$

where k is a constant ($k \ll 1$). Substitution of eqns. 56 and 57 into eqn. 55 gives

$$R_{Fq} = \frac{1}{1 + \alpha\,(k\,R_{Fq}\,q)^{\beta-1}} \tag{58}$$

For a limitingly small but still detectable amount of the substance, q_0 ($R_{Fq_0} = l_{q_0}/l_s$), we have

$$R_{Fq_0} = \frac{1}{1 + \alpha\,(k\,R_{Fq_0}\,q_0)^{\beta-1}} \tag{60}$$

Assuming that $kR_{Fq}q$ and $kR_{Fq_0}q_0 \ll 1$, after simple transformations the desired dependence is obtained:

$$\Delta l = \gamma q \tag{61}$$

where $\Delta l = l_q - l_{q_0}$ and $\gamma = \alpha(1-\beta)^2 k l_{q_0} R_{Fq_0}/(1-\alpha)$.

Eqn. 61 shows that the value of Δl is linearly related to q, as follows from the experimental data. It shows also that the sensitivity of quantitative analysis based on measurements of the spot length (Δl) increases as β decreases and R_{Fq} increases. In this instance, the slope of the dependence $\Delta l/q = \gamma$ increases.

The proposed method for the quantitative analysis of thin-layer chromatograms is very simple and fairly accurate (σ_q/q = 2–3%), and can be recommended for practical use. It permits the determination of admixtures of monool and diol in POPP samples (present in amounts of 1–2%) with this precision.

VIII. COMBINED CHROMATOGRAPHIC METHODS OF ANALYSIS OF COMPLEX POLYMER SYSTEMS INVOLVING THIN-LAYER CHROMATOGRAPHY

In the synthesis of complex polymer systems, such as block and graft copolymers and branched homopolymers, apart from the main products characterized by the polydispersity of the MW and composition (the type of branching), corresponding linear homopolymers are also formed. So far, the investigation of these polydisperse systems has been very complicated and laborious and often could not be carried out by classical methods of polymer analysis. Important results can be obtained by using combined chromatographic methods of polymer analysis, such as GPC for the micro-preparative fractionation of polymers with determination of the hydrodynamic radius (R_s) of the fractions obtained, TLC for the qualitative and quantitative analysis of the structural and chemical heterogeneity of fractions and pyrolytic gas chromatography (PGC) for the determination of their overall composition. PGC is the most sensitive (only several micrograms of sample are required) and precise method for the determination of the composition of copolymers with proportions of the components of less than 1/20–1/50[85]. It can also be used to determine the average MW of some homopolymers (such as PMMA)[86], the stereoregularity of polymers (polypropylene)[87] and their short-chain branching (polyethylene)[88].

1. Investigations of mixtures of linear and branched-chain polymers by gel-permeation and thin-layer chromatography

Classical methods for the fractionation of macromolecules, as well as GPC, do not permit the effective separation of linear and branched-chain macromolecules with similar dimensions. This problem can be solved by using ATLC, which permits the fractionation of linear and branched-chain PS of the same hydrodynamic size.

(a) TLC of linear and branched-chain polystyrene

It has been established[23] that the dependence of R_F on γ, the content of acetone (the adsorption-active component) in the eluent, is more pronounced for linear than for branched-chain PS*. As a result, linear and branched-chain PS with similar R_F values are well separated on the plate (Fig. 50) and can be identified by comparing them with reference samples of linear PS with respect to the R_F–γ dependence (Fig. 51).

Although the theory of adsorption of linear polymers is well developed[37–46], the adsorption of branched-chain macromolecules has not been considered theoretically. However, it might be suggested that differences in the adsorption capacity of linear and branched-chain PS are related to the following peculiarities of their adsorption behaviour. At high interaction energies (at low acetone contents in the eluent), linear polymers become much flatter than branched-chain polymers and therefore more of their units come into contact with the adsorbent. As a result, their adsorption capacity is higher than that of branched-chain polymers. On the other hand,

* It cannot be ruled out that the branched-chain PS investigated in this work bear, at the end of branches, adsorption-active functional groups (such as OH) that cannot be detected spectroscopically because of their low content.

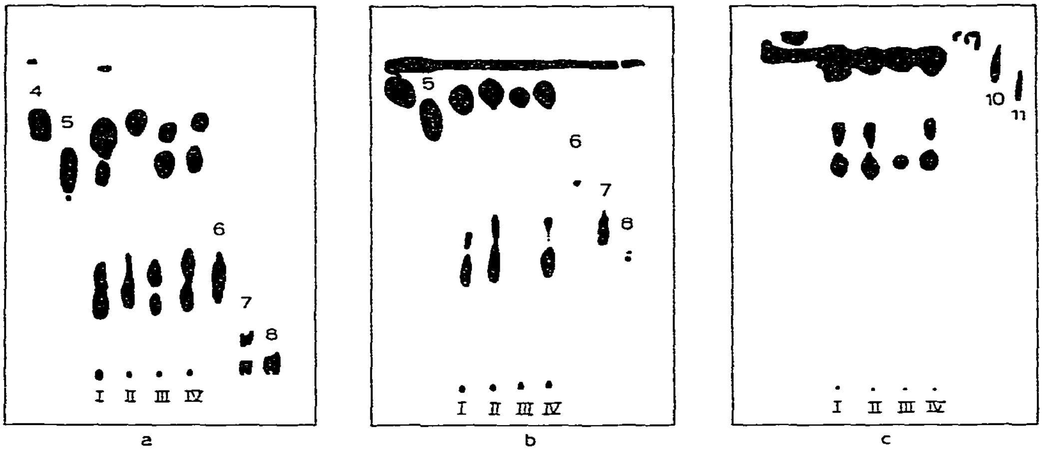


Fig. 50. TLC of PS (samples I, II, III and IV) containing linear and branched-chain components and standard PS samples 4–11 (see Fig. 6) in Ch–Bz–Ac (12:4:γ) where γ = (a) 0.4, (b) 0.8 and (c) 1.5.

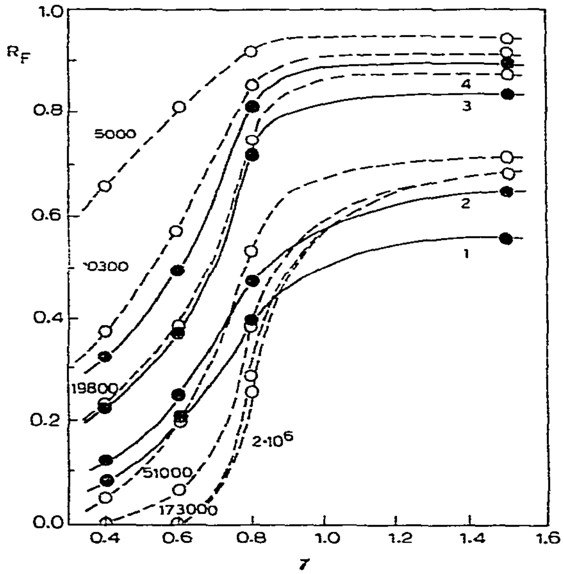


Fig. 51. R_F *versus* acetone content (γ) in TLC in Ch–Bz–Ac (12:4:γ) for linear and branched-chain components of sample 1 (full lines) and linear standard PS samples of various M_w (broken lines).

with weak interactions (when the acetone content in the eluent is high; $\gamma > 0.1$), branched-chain macromolecules in which the segment density per unit area is greater than for linear chains are adsorbed more strongly. If this hypothesis is assumed, it can be concluded that the dependence of $-\Delta F/kT$ on ε should be more pronounced for linear than for branched-chain PS and differences in the adsorption capacities of linear and branched-chain macromolecules should increase with increase in the degree of branching. If the experimental results (Fig. 50) are evaluated from this standpoint, it can be inferred that components 1 and 2 of the samples being analysed are branched, component 1 being branched to a greater extent, and components 4 and 5 are linear. Although the chromatographic behaviour of component 3 is similar to that of the corresponding linear PS with an MW of 19,750, there is some difference between them, possibly associated with a slight branching of component 3.

(b) Micro-fractionation of polymer samples by GPC and subsequent TLC of the fractions obtained

The analysis of polymer samples consisted in their separation into 12–14 fractions by GPC with a KhZh 1302 chromatograph (Special Design Office of Analytical Instruments, Academy of Sciences, Leningrad, U.S.S.R.) by using a system of Styragel columns. These fractions were investigated by TLC, including densitometry of the chromatograms.

Fig. 52 shows the densitograms obtained from fractions of one sample. In the upper part, a densitogram of an unfractionated polymer sample is shown and a method for the separation of densitometric peaks into components is illustrated. These data made it possible to represent the gel chromatogram of a polymer sample as a superposition of elution curves of linear and branched-chain PS constituting these samples (Fig. 53). By using this procedure, it was possible to determine the content of linear and branched-chain components in a PS sample and, by means of calibration against PS standards, to obtain the MW of linear components by GPC or TLC. The

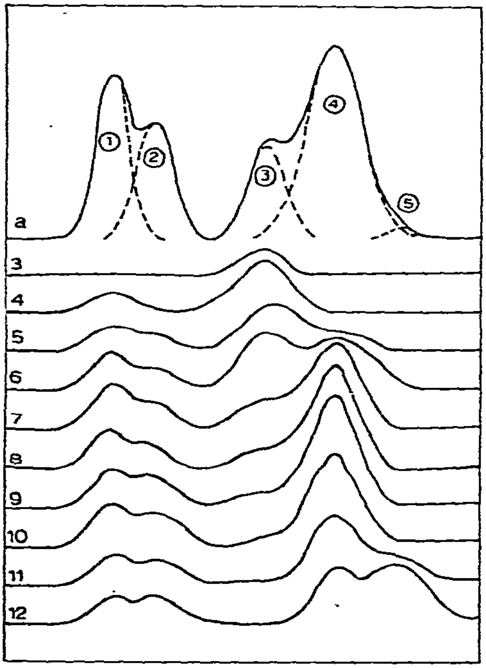


Fig. 52. Densitograms of thin-layer chromatograms of sample 1 and its fractions obtained by GPC (3–12).

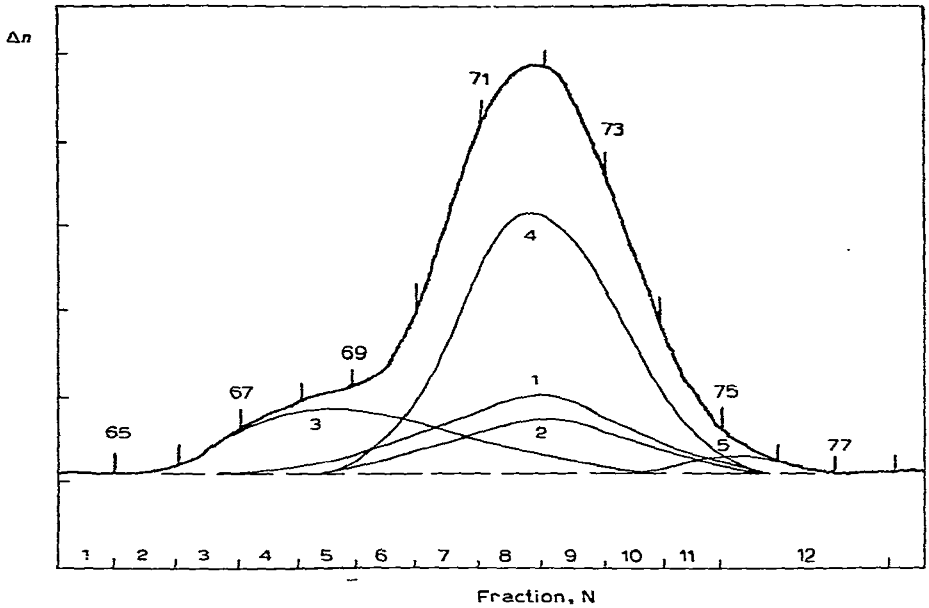


Fig. 53. Elution curve of GPC analysis of sample 1 and distribution of components 1–5 in this sample (from TLC data). Numbers on the upper curve refer to elution volumes (counts).

results obtained by both methods are in good agreement. A combination of GPC and TLC made it possible to detect and characterize a minor component in linear PS (component 5), the content of which was 1–4%.

(c) Determination of the molecular weight of branched-chain polystyrene

According to Coll[89], chromatographic columns for GPC were calibrated in values of the hydrodynamic radius, R_s:

$$R_s = \left(\frac{3}{10\pi} \cdot \frac{[\eta]\,M}{N_A}\right)^{\frac{1}{3}} \tag{62}$$

where N_A is Avogadro's number, $[\eta]$ is intrinsic viscosity and M is molecular weight.

Fig. 54 permits the determination of the value of R_s corresponding to the maximum of each component. As the components are very narrow polymer fractions ($M_w/M_n < 1.1$), these values correspond to their average hydrodynamic radii, R_s. According to Tsvetkov *et al.*[90], the hydrodynamic radius is related to the number of statistical segments, N, the segment length, b, and the branching factor, h, and in this instance, for PS, to h and M, by the following equation:

$$R_s = 0.78 \cdot \frac{h}{\sqrt{6}} \cdot bN^{\frac{1}{2}} = 0.255\,M^{\frac{1}{2}} \tag{63}$$

where $h = (R_s)_b/(R_s)_l$ is the ratio of the hydrodynamic radii of branched-chain and linear macromolecules with the same number of segments. On the basis of these data, the distribution of components 1–5 in sample 1 of PS is plotted against R_s (Fig. 54).

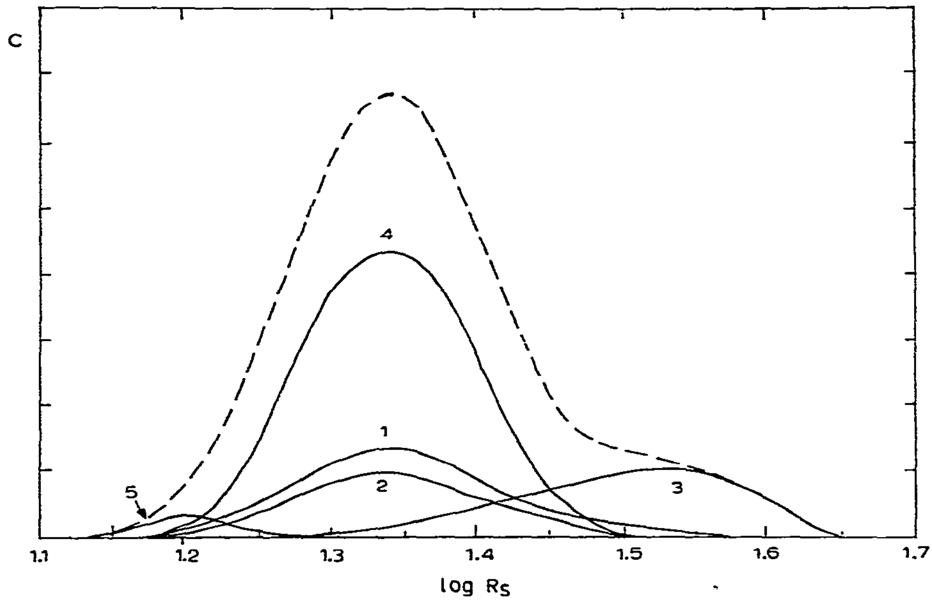


Fig. 54. Concentration curves of distribution of sample 1 (broken line) and its components (solid lines) as a function of the logarithm of the hydrodynamic radius (log R_s). C = concentration.

Hence, if R_s is known and an assumption is made concerning the value of h, it is possible to determine the MW of branched-chain PS. When polystyryl-lithium is used as initiator in the synthesis of PS[91], a comb-like structure of the polymer chain with various numbers of branches is possible. Consequently, it is possible to ascribe to the components of these PS samples the structures shown in Table 5, where the h values for these samples are selected in accordance with Grechanovsky[92]*. It is assumed that component 5 was formed from an unreacted initiator of polystyryl-lithium.

The data in Table 5 permit the determination of the MW of the branched-chain component by using eqn. 63 and also (assuming that the linear component 5 is the backbone of the macromolecule) the determination of the length of the branch. It is clear that in this instance the MW of the polymer exhibits only a slight dependence on the selected model of branching, whereas the length of its branches exhibits a strong dependence.

Table 6 shows as an example the results of a complete analysis of one of the PS samples.

This investigation shows that, by using a combination of GPC and TLC, it is possible to characterize in detail a complex narrow-disperse polymer system containing linear and branched-chain PS. Thus, for a sample with a weight of 2 mg it was possible to obtain the following characteristics: to determine the percentage of components, their branching, MW and MWD of linear components and, within the scope of the

* Calculations in the paper by Grechanovsky[92] are made for θ-solvents, but in accordance with other workers[93–97], for polymers with MW $5 \cdot 10^5$ they can be extended to good solvents.

TABLE 5

MODELS OF BRANCHING OF COMB-LIKE TYPE FOR COMPONENTS OF PS IN SAMPLE 2 AND CORRESPONDING VALUES OF THE BRANCHING FACTOR, *h*

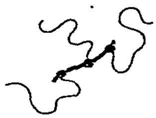
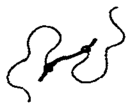
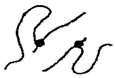
Component	*Type of branching according to TLC data*	*Models of branching*	*h*	
			Statistical distribution of branch length	*Fixed branch length*
1	Branched		0.916	0.888
2	Branched		0.931	0.903
3	Slightly branched		0.950	0.922
4	Linear		0.972	0.947
5	Linear		1.0	1.0

TABLE 6

RESULTS OF ANALYSIS OF SAMPLE 2 OF PS (COMB-LIKE MODEL)

Parameters of the component	*Component*				
	Branched-chain			*Linear*	
	1	*2*	*3*	*4*	*5*
R_s (Å)	20.5	21.5	32.5	22.5	16.5
MW of the polymer	10,500	10,600	19,500	10,500	5500
MW of the backbone	5000	5000			
MW of branches	1400	1900			
Content of the component (%)	23	15	16	42	4

theory used, to determine the parameters of branched-chain macromolecules (their MW, MW of the backbone and branches). A component present in an amount of 1–4% was detected and characterized.

2. *Determination of the polydispersity of block copolymers of styrene and methyl methacrylate by gel-permeation, thin-layer and pyrolytic gas chromatography*

The determination of the polydispersity of block copolymers includes the analysis of their distribution according to MW, composition and content of the corresponding homopolymers. Classical methods for the determination of the polydispersity of block copolymers by fractionation based on the different solubilities of polymers of different chemical composition do not permit the preparation of distinct fractions that are homogeneous in one or several properties, in particular, for a sample polydisperse according to MW[98]. Methods of sedimentation, diffusion and turbidimetric titration are complicated and are also insufficiently effective for the determination of the continuous distribution of copolymers[99]. The polydispersity of block copolymers can be investigated effectively by using a combination of several chromatographic methods with the following sequence of chromatographic operations. After a preliminary fractionation of macromolecules according to size by GPC, a second separation of the fractions according to composition is carried out by TLC, with separation of the block copolymer from admixtures of homopolymers. Finally, the compositions of the GPC and TLC fractions are determined by PGC[85]. This method was used to investigate a block copolymer of the A–B–A type synthesized by using a triperoxide[100], in which A is PMMA and B is PS.

(a) Gel-permeation chromatography of block copolymers

Fig. 55 shows gel chromatograms obtained with a Kh Zh-1302 chromatograph. A 40-mg amount of the block copolymer was subjected to micro-preparative fractionation and was separation into 34 fractions. A comparison with an analytical chromatogram of this block copolymer (a sample of 6 mg) shows the absence of concentration distortions on the chromatogram in micro-preparative fractionation of narrow-disperse fractions ($M_s/M_n < 1.4$ according to Bly[101]).

On the basis of the universal calibration graph and the values of the Mark–Kuhn constants (K_η, a) for PS and DMF:

$$[\eta] = K_\eta M^a = 3.96 \cdot 10^{-4} M^{0.588} \tag{64}$$

the retention volumes dependence $V_R = V_R(R_s)$ was found from eqn. 62. The PMMA fractions were also obtained by GPC in order to compare their R_F values with those of GPC fractions of block copolymers obtained at the same elution volume. This method permitted the accurate identification of the PMMA admixtures in the block copolymer and the selection of optimal systems for the chromatographic separation of PMMA and block copolymers of different MW.

(b) Pyrolytic gas chromatography

Fig. 56 shows pyrograms of a block copolymer obtained (a) with a Tsvet-4 gas chromatograph equipped with a pyrolytic cell described previously[85] and (b)

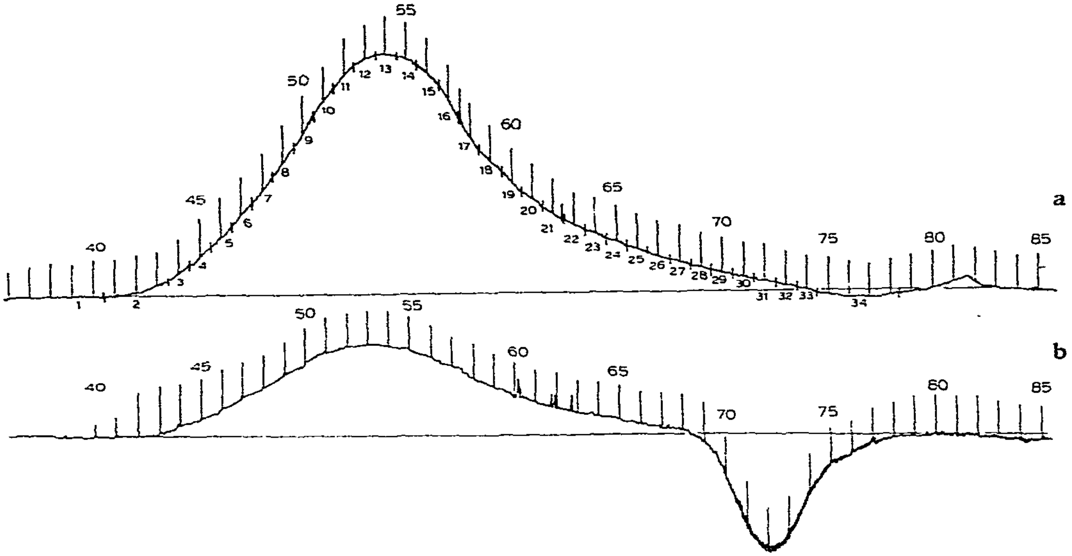


Fig. 55. Gel chromatogram of block copolymer PMMA–PS–PMMA in DMF on columns with Styragel $5 \cdot 10^2$, 10^3, 10^4, $3 \cdot 10^4$ and 10^5 Å. (a) Preparative chromatography (40 mg of polymer); (b) analytical chromatogram (6 mg of polymer). The numbers under the curve are fraction numbers, the numbers above the curves are elution volume counts.

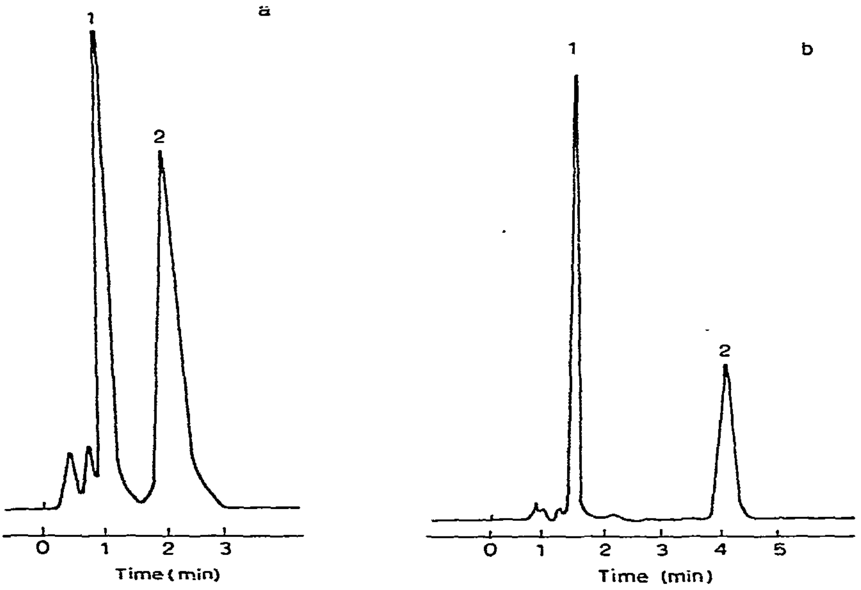


Fig. 56. Pyrograms of the PMMA–PS–PMMA block copolymer obtained with (a) a Tsvet-4 and (b) a Pye Series 104 chromatograph on columns packed with 2% of 1,2,3-tris-(2-cyanethoxy)propane on Chromosorb P at a pyrolysis temperature of (a) 500° and (b) 610°. 1 = MMA; 2 = St.

with a Pye Series 104 chromatograph equipped with a cell in which the pyrolysis temperature is controlled by a Curie-point control unit. The reproducibility of the pyrograms obtained with both instruments is 1–3%. However, the sensitivity of analysis is higher with the Pye chromatograph, which permits the determination of the composition of a copolymer by using 0.2 mg of sample.

It is known[85,102] that, depending on the structural properties of polymers (MW, composition, etc.), their pyrolysis proceeds differently. Nevertheless, it is possible to select conditions of pyrolysis under which these differences do not affect the chromatogram[85]. It is clear that only under these conditions is PGC suitable for determining the overall composition of block copolymer fractions. Fig. 57 shows the ratio of the areas under the chromatographic peaks for St and MMA in the pyrogram *versus* the ratio of the weights of PS and PMMA in the sample. It is clear that, irrespective of the MW of PMMA and the type of sample being analysed (a mixture of homopolymers, random or block copolymers) under these conditions of pyrolysis, all experimental points fall on the same straight line and the dependence obtained can therefore be used to determine the overall composition of the block copolymer (if the instrument is calibrated against a mixture of PS and PMMA).

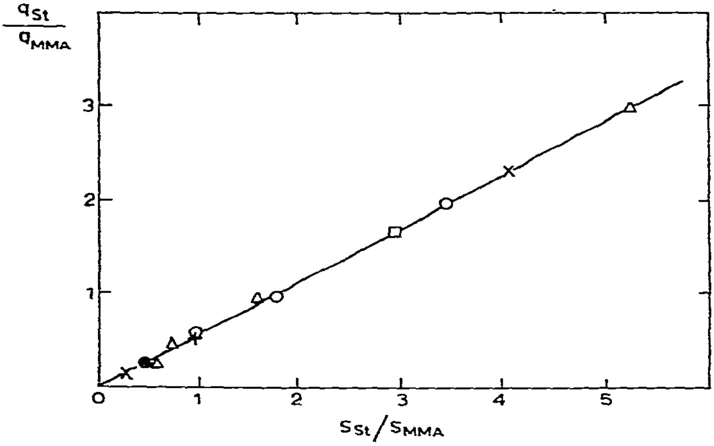


Fig. 57. Ratios of peak areas for St and MMA (S_{St}/S_{MMA}) *versus* weight ratios of these monomers (q_{St}/q_{MMA}) in polymers of various types. +, Random copolymer of St–MMA; ●, block copolymer of St–MMA; mixtures of PS with MW = $5.1 \cdot 10^4$ and PMMA of MW = (○) $3 \cdot 10^4$, (×) $6 \cdot 10^4$, (□) 10^5 and (△) $2 \cdot 10^5$.

(c) Separation of poly(methyl methacrylate) and the block copolymer of polystyrene–poly(methyl methacrylate) by TLC and determination of their ratios and of the block copolymer composition by PGC

Precipitation TLC as described on p. 49 was used to separate the ST–PMMA block copolymer and the accompanying PMMA. The plates were chromatographed in a mixture of $CHCl_3$ and methanol, the composition of which was varied (Table 7), depending on the MW of the block copolymer and PMMA (PGC fraction number). Fractions obtained with a gel chromatograph at the same retention volumes as the block copolymer fractions were used as reference PMMA. The relative contents of PMMA and the block copolymer were determined from the overall composition of GPC fractions containing the block copolymer and PMMA and of TLC fractions extracted from the plate with acetone. The overall composition of the fractions was determined by PGC under conditions excluding the effect of the micro-structure of the copolymer on the character of pyrolysis (Fig. 57). It can easily be shown that if the chemical compositions (the ratio of monomer units) of two polymer components of TLC fractions of the block copolymer (x) and of the PMMA admixture (y):

$$\left.\begin{aligned} \frac{m_1'}{m_2'} &= x \\ \frac{m_1''}{m_2''} &= y \end{aligned}\right\} \tag{65}$$

and the chemical composition of their mixture (GPC fraction) (z):

$$\frac{m_1'''}{m_2'''} = z \tag{66}$$

are known, it is possible to determine the ratio of these components in the mixture ($\omega = q_1/q_2$) from the equation

$$\omega = \frac{q_1}{q_2} = \frac{(z - x)(1 + 1/y)}{(x + 1)(1 - z/y)} = \frac{(z - x)(1 + y)}{(1 + x)(y - z)} \tag{67}$$

When the first component is a pure or almost pure homopolymer ($m_1' \to 0$, $x \to 0$), eqn. 67 is simplified to

$$\omega = \frac{z(1 + y)}{y - z} \tag{68}$$

Hence, in order to determine the weight ratio of components in the mixture, it is sufficient to analyse by PGC its chemical composition, z, and also the composition of the separated components, x and y, and to use the corresponding equations for calculating ω. The precision of these determinations is 5–10%.

The results obtained for the composition of the GPC fractions (the contents of PMMA and the block copolymer) and the composition of the block copolymer are given in Table 7.

(d) Compositional distribution of the block copolymer depending on R_s

As a result of investigations of GPC fractions of the block copolymer (Fig. 55) by PGC and TLC, it is possible to determine from eqns. 66 and 68 and values of x, y and z and the weight ratio of the block copolymer to PMMA ($\omega = q_{PMMA}/q_{block}$) in each fraction. Now, knowing the increments of the refractive index [$(\partial n/\partial c)_{PS}$ = 0.173 ml/g and $(\partial n/\partial c)$ = 0.064 ml/g] and by using for copolymers the rule of the additivity of increments of refractive index in solution[103], it is easy to obtain from the gel chromatogram $\Delta n = \Delta n(V_R)$, the ratio of PS, PMMA and the block copolymer in GPC fractions.

The results of the calculations are given in Fig. 58, which shows the distribution of the overall composition of the polymer sample, the amount of the block copolymer in it and its composition *versus* hydrodynamic radius (R_s) calculated from that for PS according to eqn. 62.

Fig. 58 shows that as R_s (MW) of the block copolymer increases, the content of PS in it decreases while that of PMMA increases. This result becomes understandable if one takes into account that the synthesis of the A–B–A block copolymer pro-

TABLE 7

COMPOSITION OF FRACTIONS OBTAINED BY GPC AND TLC AND COMPOSITION OF THE BLOCK COPOLYMER

Composition of fractions in a chromatogram (Fig. 55a)	*Composition of eluent for TLC ($CHCl_3$–methanol, v/v)*	*Mean composition of GPC fractions, $z = m'''_{PS}/m'''_{PMMA}$*	*Mean composition of the lower spot in TLC (block copolymer), $x = m'_{PS}/m'_{PMMA}$*	*Mean composition of the middle spot in TLC (PMMA), $y = m''_{PS}/m''_{PMMA}$*	*Content of MMA in the block copolymer (%)*	*Ratio of amounts of PMMA and block copolymer in GPC fractions, $\omega = q_{PMMA}/q_{block}$*
Unfractionated	6:16	0.23	0.32	0.024	75.7	0.34
5	6:16	0.03	0.04	0.009	96.0	0.464
7	6:16	0.04	0.08	0.018	92.2	1.72
9	6:16	0.06	0.12	0.026	89.4	1.62
11	5.5:16	0.09	0.14	0.005	88.0	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	0.26
24	4:16	3.34	1.33	0.043	43.0	0.27

ceeds in two stages when a triperoxide is used as initiator[100]: PMMA is bonded to the PS backbone. It is natural that under these conditions an increase in the MW of the polymer takes place owing to its increasing PMMA content.

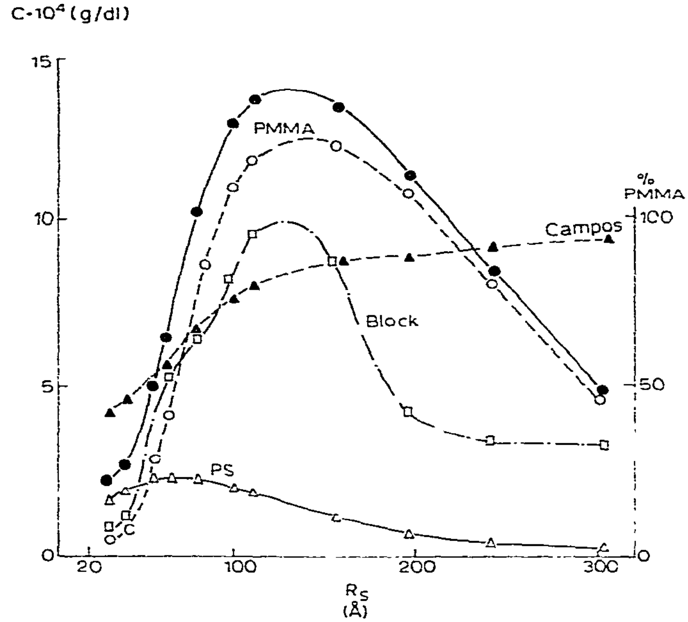


Fig. 58. Distribution of the PMMA–PS–PMMA block copolymer as a function of R_s according to GPC, TLC and PGC data. ●, Unfractionated polymer; ○, PMMA; △, PS; □, block copolymer; ▲, PMMA content in the block copolymer.

The distributions obtained for the block copolymer of St and MMA are continuous and, moreover, they are not based on any arbitrary assumptions. Their basis is provided by such reliable physical relationships and processes as fractionation of macromolecules according to size by GPC, the Benoit universal calibration graph and fractionation of copolymers according to composition by TLC with quantitative determination of the composition of the copolymer by PGC.

3. *Investigations of graft copolymers of cellulose by gel-permeation and thin-layer chromatography*

Usually, in investigations of graft copolymers it is necessary to establish the presence of the corresponding homopolymers, and methods of fractionation involving extraction, precipitation[103,104], and centrifugation in density gradient have been used for this purpose. The solubility of the graft copolymer of cellulose has been ensured by chemical modification of the cellulose backbone or by a special selection or solvents[105]. In principle, TLC can be used for the separation of the graft copolymef and corresponding homopolymers, as was shown by Stannett and co-workers[106–108], taking as an example the graft copolymer of PS–PMMA.

Another trend in studies of cellulose graft copolymers is based on the decomposition of the cellulose backbone by acid hydrolysis[109–111] or acetolysis[112] and the determination of the molecular characteristics of the liberated graft copolymer. However, it is difficult to separate the products obtained.

Taga and Inagaki[113] proposed a variation of this method for investigations of the cellulose–styrene graft copolymer, involving acid hydrolysis of the copolymer, separation of free and grafted PS by adsorption TLC and determination of the MWD of this PS by GPC. The polystyrene chains that are split off by acid hydrolysis bear polysaccharide end- residues, the presence of which in PS in confirmed by the bending vibrations at 3620 cm^{-1} in the IR spectra. PS with polysaccharide end-residues exhibits a high adsorption activity, which correlates with an increase in the adsorption capacity of PS with an MW of 10^5 when carboxylic end-groups are introduced into it[114]. On this basis, free and grafted PS can be separated by TLC on silica gel plates in THF. Grafted PS is located in the lower (starting) spot and free PS moves with the solvent front. If the chromatogram is developed by spraying successively with a saturated solution of thymol blue in 50% aqueous ethanol and 3 N sulphuric acid, the intensity of blacking of the upper and lower spots allows the determination of the fraction of grafted PS–P_{gr} in the total amount of PS.

The upper and lower spots of PS were extracted from the plate and their MWD determined by GPC on Styragel columns ($10^7 + 10^6 + 10^4$ Å). The values of M_w and M_n for PS found by this method are given in Table 8.

Taga and Inagaki[113] reported that the value of M_w obtained by GPC is higher than its value determined by sedimentation and viscometry. The data in Table 8 permit the checking of the material balance of fractionation of PS by TLC:

$$M_w(PS_{tot}) = P_{gr} \times M_w(PS_{gr}) + (1 - P_{gr}) \times M_w(PS_{fr}) \tag{69}$$

$$M_n(PS_{tot}) = M_n(PS_{gr}) \times M_n(PS_{fr}) \times [P_{gr} \times M_n(PS_{fr}) + (1 - P_{gr}) \times M_n(PS_{gr})]^{-1} \tag{70}$$

where P is the molar fraction, and the subscripts tot, gr and fr refer to the total amounts of PS, graft and free PS, respectively. The values of $M_w = 12.4 \cdot 10^5$ and $M_n = 2.9 \cdot 10^5$ for PS_{tot} are in good agreement with experimental values (Table 8) for this PS.

TABLE 8

RESULTS OF ANALYSIS OF PS BY GPC

Sample	$M_n \cdot 10^{-5}$	$M_w \cdot 10^{-5}$	M_w/M_n
PS after hydrolysis — PS_{tot}	2.8	13.0	4.6
Grafted PS–PS_{gr} (lower spot in TLC)	1.9	5.8	3.0
Free PS–PS_{fr} (upper spot in TLC)	4.9	17.0	3.5

This method of analysis permits the determination of the index of the degree of grafting (F_g) for the graft copolymer:

$$F_g = \frac{\text{average number of PS chains in the graft copolymer}}{\text{average number of cellulose chains in the graft copolymer}} = \left(\frac{A \cdot P_{gr}}{M_n\,(PS_{gr})}\right) \cdot \left(\frac{100}{M_n\,(\text{cellulose})}\right)^{-1} \tag{71}$$

where A (%) is the increase in the weight of cellulose during grafting.

IX. CONCLUSIONS

Thin-layer chromatography was developed later than gel-permeation chromatography and attention was drawn to this method primarily because it provided the possibility of studying the compositional homogeneity of copolymers and other types of polydispersity of polymers not related to differences in the hydrodynamic radii of macromolecules on which GPC analysis is based.

Later, TLC was used to investigate other polymers and at present it permits the investigation of virtually all types of polydispersity of polymers: in molecular weight, chemical composition, regularity and stereoregularity. It is also used to determine the MWD and functionality of oligomers and admixtures of homopolymers in block and graft copolymers. Simple qualitative methods have been developed for the determination of all of these peculiarities of chemical structure of polymers, including the characterization of such hardly distinguishable polymers as two- and three-block copolymers with the same compositions. Quantitative methods for the TLC of polymers are more complicated. In this instance, quantitative analysis based on dual-wavelength densitometry requires expensive instrumentation. Nevertheless, when computers are used in this method, its efficiency permits the mass analysis of the MWD and compositional homogeneity of polymers. The same problems can be solved, but with lower accuracy, by methods related to the determination of the dimensions of the chromatographic zones on a thin-layer plate, including the method based on the equidensity technique. The advantage of these methods is that they do not require complex instrumentation.

In the TLC of polymers, all advantages of this type of chromatography are combined: simple instrumentation, high sensitivity, speed of analysis and relative simplicity of the selection of separating systems. However, the TLC of polymers has certain limitations. First, it requires reference samples of the polymers being analysed and, secondly, its reproducibility is not high and it is necessary to develop on the same plate reference samples for comparison in each experiment. Nevertheless, the high sensitivity of TLC makes it possible to use only a few micrograms of the polymer for the analysis and hence only small amounts of reference samples are consumed.

Virtually all types of mechanisms of the distribution of polymers between liquid and solid phases have been used in the TLC of polymers. Consequently, further development of these methods will be related to the use of new types of adsorbents, such as cellulose and inorganic adsorbents with adsorption characteristics that differ fundamentally from those of silica gel (such as magnesium oxide or silicate).

Further progress in the TLC of polymers will also be related to the standardization of the analytical technique, primarily in quantitative analysis. TLC should also be more widely applied to different classes of polymers and different types of polydispersity.

The application of a combination of TLC and GPC to polymers is particularly promising, as GPC permits the fractionation of macromolecules according to their hydrodynamic size and TLC allows the investigation of the chemical structures and compositions of the fractions obtained. It is also possible to obtain by GPC polymer samples characterized according to MW and to use them as reference polymers in TLC.

The current state of development of the TLC of polymers makes it possible to use this technique effectively both in the analysis of newly synthesized polymers and in the industrial control of commercial polymer materials.

X. APPENDIX

TABLE A1

USES OF ATLC IN POLYMER ANALYSIS

Symbols: PI = polyisoprene; TAcC = triacetate cellulose; VAc = vinyl acetate; PVAc = polyvinyl acetate; ETPh = ethylene terephthalate; PETPh = polyethylene terephthalate; MeOH = methanol; EtOH = ethanol; EtOAc = ethyl acetate; iPrOAc = isopropyl acetate; MeOAc = methyl acetate; $C_2H_2Cl_2$ = dichloroethylene; HCOOH = formic acid; CH_2Cl_2 = dichloromethane; DMF = dimethylformamide; iPrOH = isopropanol; MeOOCH = methyl formiate; Ch = cyclohexane; Bz = benzene; Ac = acetone; CCl_4 = tetrachloromethane; $CHCl_3$ = chloroform; THF = tetrahydrofuran; MEK = methyl ethyl ketone; → shows changes in the solvent by the gradient elution technique; b and g in the polymer symbols signify block and graft copolymers, respectively. Heterogeneity and MWD show that compositional heterogeneity and molecular weight distribution were determined quantitatively. In the graft copolymers the main chain is formed by the second monomer.

Polymer	*Type of polydispersity*	*Adsorbent*	*Eluent*	*Visualization**	*Reference*
I. Homopolymers					
PMMA	MW ($2 \cdot 10^{-3}$–$1.5 \cdot 10^6$)	SiO_2	$CHCl_3$–Ac (12:3.7)	1	115
PMMA	Stereoregularity (separation of a- and s-PMMA from i-PMMA)	SiO_2	EtOAC	2	17
PMMA	Separation of stereocomplex of i- and s-PMMA (1:1) from i- and s-PMMA	SiO_2	Ac	2	18
PMMA	Separation of PMMA stereoblock into i- and s-PMMA	SiO_2	EtOAC	2	18
PMMA	MW ($2.0 \cdot 10^5$–$1.2 \cdot 10^6$) and separation of s- and a-PMMA	SiO_2	iPrOAC–EtOAC (8:25)	2	16
PBD	Separation of 1,4-*trans*- and 1,2-vinyl-PBD from 1,4-*cis*-PBD	SiO_2	CCl_4	3	19
PI	Separation of 1,4-*trans*- and 3,4-vinyl-PI from 1,4-*cis*- and 1,4-*trans*-PI	SiO_2	Ch–*p*-xylene (20:80)	3	116
PI	Separation of 3,4-vinyl-PI from 1,4-*cis*- and 1,4-*trans*-PI	SiO_2	CCl_4–*p*-xylene	3	116
PS	MW (314–$2 \cdot 10^6$)	SiO_2	Ch–Bz–Ac (40:16:0.4–2)	1	3, 10
PS	Separation of four-branched star from the linear polymer	SiO_2	Ch–Bz–Ac (40:16:0.4:1.5)	1	23
PS	Separation of four-branched star from the linear polymer	SiO_2	Ch–Bz (50:50) → (25:75)	4	116
PEO	MW (300–$2.0 \cdot 10^4$)	SiO_2	H_2O–pyridine (9:1)	5	115
PS	Separation according to functionality (end –COOH and glucoside groups)	SiO_2	THF	4	24, 113
II. Random copolymers					
Co (St–MA)	Composition (heterogeneity) (9.98–76% St)	SiO_2	CCl_4–MeOH (5:1) → MeOAC	2	2

Co (St–MA)	Composition (9.98–76% St)	SiO_2	$CHCl_3 \rightarrow$ EtOAc	2	2
Co (St–MMA)	Composition (22–80% St)	SiO_2	($CHCl_3$, $C_2H_4Cl_2$, Cl-Bz)-(diethyl ether, MEK, Ac, dioxan, THF)	1	1, 36
Co (St–MMA) azeotropic	Composition (54% St)	SiO_2	$CHCl_3$–diethyl ether (12:4.2)	1	3, 6
Co (St–MMA)	Separation of random, alternating and block copolymers	SiO_2	CCl_4–MeOAc (5:1) $\rightarrow$ MeOAc	2	25
Co (St–MMA)	Separation of random, alternating and block copolymers	SiO_2	$CHCl_3 \rightarrow$ EtOAc or $CHCl_3$–EtOAc $\rightarrow$ EtOAc	2	25
Co (St–AN)	Composition (15–31.2% AN)	SiO_2	$CHCl_3$–MeOAc	2	117, 118
Co (St–AN)	Composition (heterogeneity) (up to 60% AN)	SiO_2	$C_2H_2Cl_2 \rightarrow$ EtOAc	2	116
Co (St–AN)	Composition (18.7–50.7% AN)	SiO_2	(Bz, toluene) $\rightarrow$ Ac	2	9
Co (St–BD)	Composition (5–60% St)	SiO_2	Ch–Bz	4	119
Co (St–BD)	Composition (heterogeneity) (14.6–62.4% St)	SiO_2	$CCl_4 \rightarrow CHCl_3$–CCl_4 (20:50)	4	32
Co (St–BD)	Separation of random, alternating and block copolymers	SiO_2	Ch–$CHCl_3$ (9:1) $\rightarrow CHCl_3$ Ch–$CHCl_3$ (140:75)	4	28
Cellulose acetate	Composition (heterogeneity) (52.5–60.5% CA)	SiO_2	CH_2Cl_2–MeOH (85:15)	6	120
Cellulose nitrate	Composition (heterogeneity)	SiO_2	Ac–EtOAc (20:30) $\rightarrow CHCl_3$–EtOAc (1:2)		121
Co (ω-amino-capron, λ-amino-lauryl)	Composition	SiO_2	HCOOH or HCOOH–phenol		121
III. Block copolymers					
Co (St–b-MMA)	Composition (heterogeneity) (5–80.5% St)	SiO_2	$CCl_4 \rightarrow$ MEK	2	27
Co (St–b-MMA)	MW ($68 \cdot 10^3$–$276 \cdot 10^3$) and composition (9.1–53.7% St)	SiO_2	nitroethane $\rightarrow$ Ac; $CCl_4 \rightarrow$ MeOAc; Bz $\rightarrow$ MEK	2	20
Co (St–b-MMA)	Sequence of AB and ABA blocks	SiO_2	CCl_4–MEK (the ratio of components depends on the block copolymer composition)	2	27
Co (St–b-MMA)	Separation of homopolymers	SiO_2	$CHCl_3$ (separation of PS); Bz–MEK (separation of block copolymer from PMMA)	4	28, 122

(Continued on p. 86)

TABLE A1 (*continued*)

Polymer	*Type of polydispersity*	*Adsorbent*	*Eluent*	*Visualization**	*Reference*
Co (St–b-BD)	Sequence of AB and ABA blocks	SiO_2	Ch–$CHCl_3$ (9:1) → $CHCl_3$	2	28, 122
Co (St–b-BD)	Separation of random, "tapered", two- and three-block copolymers	SiO_2	Ch–$CHCl_3$ (140:75)	4	28, 122
Co (St–b-BD)	Separation of "tapered" and two-block from three-block copolymers	Al_2O_3	CCl_4	4	28, 122
Co (St–b-BD)	Separation of "tapered", two-block and three-block copolymers	Al_2O_3	CCl_4–*n*-hexane (9:1)	4	28, 122
Co (St–b-EO)	Separation of PS and PEO from the block copolymer	microcryst. cellulose	Ch–Bz–Ac (12:4:2) separation of PS pyridine–H_2O (3:7) separation of PEO	1, 5	3, 6
IV. Graft copolymers					
Co (St–g-EO)	Separation of homopolymers	SiO_2	Ac–acetic acid (12:2) separation of PMMA and PS; $CHCl_3$–MEK (12:2) separation of PMMA and PS Ch–Bz–Ac (12:4:0.7) separation of graft copolymer and PS from PMMA Ac–acetic acid (12:2) separation of PS and PMMA from graft copolymer	1	3
Co (St–g-cellulose)	Separation of PS	SiO_2	THF, Bz	4	122
Co (St–g-TAcC)	Separation of homopolymers	SiO_2	CH_2Cl_2–MeOH (1:1) or $CHCl_3$–dioxan (3:1) separation of TAcC; $CHCl_3$ separation of PS	7	123
Co (St–g-VAc)	Separation of homopolymers	SiO_2	MeOH–H_2O (9:1) separation of PVAc; $CHCl_3$ separation of PS	7	123
Co (St–g-VAc)	Separation of homopolymers	SiO_2	MeOH–H_2O (9:1) separation of PVAc; MEK–CCl_4 (8:2) separation of PMMA	8	123
Co (St–g-nylon)	Separation of homopolymers	SiO_2	HCOOH separation of nylon; $CHCl_3$ separation of PS	8	123
Co (St–g-ETPh)	Separation of homopolymers	SiO_2	phenol–H_2O (75:25) separation of PETPh; $CHCl_3$ separation of PS	9	123
Co (St–g-cellulose)	Separation of PS and grafted PS	SiO_2	THF	4	113, 122
Co (St–g-BD)	Separation of PS and Co (PS–g-BD), the main chain of the graft copolymers	SiO_2	CCl_4–$CHCl_3$	4	116

* 1, 3% $KMnO_4$–conc. H_2SO_4 solution followed by charring at 180°; 2, 1% I_2–methanol solution; 3, 14.7% H_2SO_4–water solution followed by charring at 100°; 4, saturated solution of Thymol Blue in ethanol–water (1:1, v/v) followed by spraying with a 3 *N* H_2SO_4 solution; 5, Dragendorff reagent; 6, 10% H_2SO_4–water solution followed by charring at 110°; 7, 10% $HClO_4$–water solution; 8, 0.05 *N* I_2–water solution; 9, Kayalon Fast Brown R solution in a mixture of methanol–water; 10, $ZnSiO_3$ as indicator; 11, I_2 vapour.

TABLE A2

USES OF PTLC IN POLYMER ANALYSIS

For symbols and methods of visualization, see Table A1.

Polymer	*Type of polydispersity*	*Adsorbent*	*Eluent*	*Visualization*	*Reference*
I. Homopolymers					
PS	MW ($1.98\cdot10^4$–$5.1\cdot10^4$)	SiO_2	$CHCl_3$–Ac (10:1) → $CHCl_3$	4	116
PS	MW (10^4–$2\cdot10^4$)	SiO_2	Ac	10	12
PS	MW (10^4–$1.6\cdot10^5$)	SiO_2	Ac–$CHCl_3$	10	12
PS	MW (10^4–10^6)	SiO_2	Ac → Ac–$CHCl_3$ (95:5–70:30) Ac → Ac–THF (95:5–70:30) Ac → Ac–toluene (95:5–70:30)	10	12
PS	MW (10^4–10^6)	SiO_2	Bz–iPrOH (64.2:35.8)	10	13
PS	MW (10^4–10^6), MWD	SiO_2	dioxan–MeOH (71.4:28.6)	7	13
PS	MW (10^4–10^6), MWD	SiO_2	Ac–iPrOH (96:4) → Ac–$CHCl_3$–iPrOH (66:30:4)	7	13
PS	MW ($2\cdot10^4$–$8.6\cdot10^5$)	SiO_2	dioxan–iPrOH (55:45)	10	30
PS	MW, MWD	SiO_2	Ac–Bz–EtOH (3:1:2); Bz–MEK (1:1)	4	113
PS	MW ($2\cdot10^3$–$5\cdot10^4$)	SiO_2	Bz–MEK–Ac–EtOH (5:3:6:4)	4	113
PS	separation of *i*-PS from a-PS	SiO_2	Ch–Bz–Ac (40:16:2)	1	115
PS	Separation of four-branched star from PS with MW 10^5–10^6	SiO_2	$CHCl_3$–Ac (10:1) → $CHCl_3$	4	116
PS	Separation according to MW of polymers with –COOH end groups ($1.1\cdot10^4$–$5\cdot10^4$) and $2.3\cdot10^4$–$1.2\cdot10^5$)	SiO_2	THF–Ac (1:10) → THF	4	24
PMMA	MW ($4\cdot10^4$–$4\cdot10^5$)	SiO_2	$CHCl_3$–MeOH (29:71)	2	15
PMMA	MW ($1.6\cdot10^5$–$4.12\cdot10^5$)	SiO_2	Bz–Ac (2:8), i-PrOH–MeOOCH (100:62), EtOAC–MeOAc (100:23)	2	4, 54
PMMA	MW and separation of s- and a-PMMA	SiO_2	acetonitrile–MeOH (20:40), (46:54)	2	16
PEO	MW ($1.5\cdot10^3$–$6\cdot10^3$)	SiO_2	ethylene glycol–MeOH (80:20)	11	12
PEO	Separation of 1,4-*cis*- and 1,2-vinyl-PBD from 1,4-*trans*-PBD	SiO_2	amyl chloride	3	19
PEO	MW ($1.5\cdot10^3$–$2.8\cdot10^4$)	Al_2O_3	MeOH → MeOH–DMF (80:20)	11	12
II. Copolymers					
Co (St–BD)	MW ($6.1\cdot10^4$–$1.46\cdot10^5$)	SiO_2	THF → MeOH	4	122
Co (St–b-MMA)	Separation of PMMA from Co (St–b-MMA)	SiO_2	$CHCl_3$–MeOH (6:16–4:16)	1	22
Co (St–b-BD)	MW and separation of low-molecular-weight PS	SiO_2	$CHCl_3$–MeOH (3:2) → MeOH	3	122
Co (St–g-BD)	Separation of PS from Co (St–g-BD)	SiO_2	MEK	3	116

XI. SUMMARY

The thin-layer chromatography (TLC) of polymers is based on the use of virtually all kinds of polymer distribution: adsorption (adsorption TLC), molecular-sieve effect (thin-layer gel-permeation chromatography) and dissolution–precipitation (precipitation and extraction TLC). The method permits the investigation of all types of polymers polydispersity: polydispersity according to molecular weight, chemical composition, geometrical and stereo-isomerization and the number and nature of functional groups. TLC is particularly effective for determining the molecular weight distribution of homopolymers, the composition heterogeneity of copolymers, the degree of blocking of block copolymers, the functionality of oligomers and the admixtures of homopolymers in block and graft copolymers. By combining various TLC methods, such as precipitation and adsorption TLC, it is possible to determine the composition and the molecular weight of random copolymers.

The use of TLC in combination with other chromatographic methods (gel-permeation and pyrolysis gas chromatography) provides great possibilities for the investigations of complex polymer systems.

Quantitative TLC methods based on double-wave densitometry, the determination of the size of chromatographic zones and the use of flame-ionization detectors make it possible to obtain numerical characteristics of polymer polydispersity.

The TLC of polymers presents all the advantages of this type of chromatography: simple instruments, high sensitivity and speed of analysis and a relatively easy choice of separating systems. The method has the following disadvantage: in each experiment it is necessary to carry out simultaneous chromatography of reference samples of the investigated polymers due to a relatively low reproducibility of this method.

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