THIN-LAYER CHROMATOGRAPHY OF POLYMERS

INTRODUCTORY LECTURE

B. G. BELENKII AND E. S. GANKINA

Institute of High Molecular Compounds, Academy of Sciences of the U.S.S.R., Leningrad (U.S.S.R.)

SUMMARY

1. Principal peculiarities of thin-layer chromatography (TLC) of polymers on porous adsorbents have been considered on the basis of the concept that macromolecules are adsorbed as a flexible polymer chain. A dependence relating R_F of the polymer to its molecular weight has been suggested.

2. A method for TLC of homopolymers has been used with separation according to the molecular weight and using systems with low and high resolution on silica gels of various porosity. A method for determining the molecular weight distribution of polymers has been worked out. It takes into account chromatographic spreading of polymer fractions by comparison of one- and two-dimensional TLC in one solvent system.

3. A method of TLC of copolymers according to their composition has been suggested. It may be used for determining their homogeneity. The effect of the molecular weight on the chromatographic distribution of copolymers on plates has been investigated. This effect was found to decrease when silica gel with small pores was used.

4. The concentration dependences in TLC of homopolymers and copolymers have been studied. They were shown to be of the nature of adsorption in the lower part of the plate. In its upper part these dependences are characteristic for gel chromatography when the rate of the movement of macromolecules decreases with the increase in concentration.

5. A method has been worked out for determining homopolymer admixtures in the block and graft copolymers by two-dimensional TLC. Block and graft copolymers were diagnosed by comparing their chromatographic mobility with that of the corresponding homopolymers of equal molecular weight.

INTRODUCTION

At the present time, chromatographic methods are widely used for the investigation of macromolecules. Gel permeation chromatography (GPC) is used for determining molecular weight distribution (MWD) and for fractionating polymers[1,2]. Precipitation chromatography[3] has been adopted as a method for fractionating large

amounts of polymer. Adsorption chromatography is much less developed, nevertheles: this method is worth consideration as a method in connection with the variou: specific peculiarities of macromolecules which become apparent in their adsorption

Despite the fact that there are many reports dealing with the TLC of oligo. mers[4–8] and investigations on gel TLC of polymers have also been carried out[9,10] the study of adsorption TLC for polymers began comparatively recently. At presen1 work is being developed in two laboratories: Prof. INAGAKI's laboratory in Kyot(University[11–15] and in our laboratory in the Institute of High Molecular Compound: of the Academy of Sciences of the U.S.S.R. in Leningrad[16–19].

INAGAKI's publications deal with the possibilities of using adsorption TLC fo1 the study of the compositional homogeneity of copolymers[11], their structural proper. ties[12] and stereoregularity and stereocomplexes of poly(methyl methacrylate)[13,14].

The possibility of applying TLC to the molecular-weight study of homopolymer: is also mentioned[15]. Our work on the TLC of polymers also commenced with the in. vestigation of statistical copolymers[16–18]. Later we studied the use of TLC for in. vestigating homopolymers and their MWD determination[19].

In addition we have examined the possibilities of TLC for determining the purit) and structural peculiarities of block and graft copolymers. Our work deals with thes€ questions.

EXPERIMENTAL

Characteristics of the sorbents

For the chromatography of polymers we used silica gels with the propertie: described in Table I and with the pore size distribution shown in Fig. 1.

TABLE I

PROPERTIES OF SILICA GELS

Silica Gel	Apparent density (g/cm^3)	True density (g/cm^3)	Specific surface area (m^2/g)	The total pore volume (cm^3/g)	Porometric pore volume (cm^3/g)	Pore volume with radii $2.9–31 A$
Microporous Silica Gel KSM-5	1.050	2.195	715 .	0.497	0.079	0.41
Silica Gel KSK with large pores	0.727	2.176	350	0.916	0.870	0.046
Macroporous Silica Gel MSA-1	0.997	2.186	25	0.646	0.521	0.025

Fig. 1 also shows the distribution coefficients of polystyrenes (K_d) obtained from TLC data as functions of their unperturbed size, $(h_0^2)^{1/2}$, size in θ-solvent, corresponding to MW of polystyrene samples. It is noteworthy that strong adsorption of polystyrenes with a MW $> 4 \times 10^5$ takes place despite the fact that Silica Gel KSK pores are practically inaccessible to them.
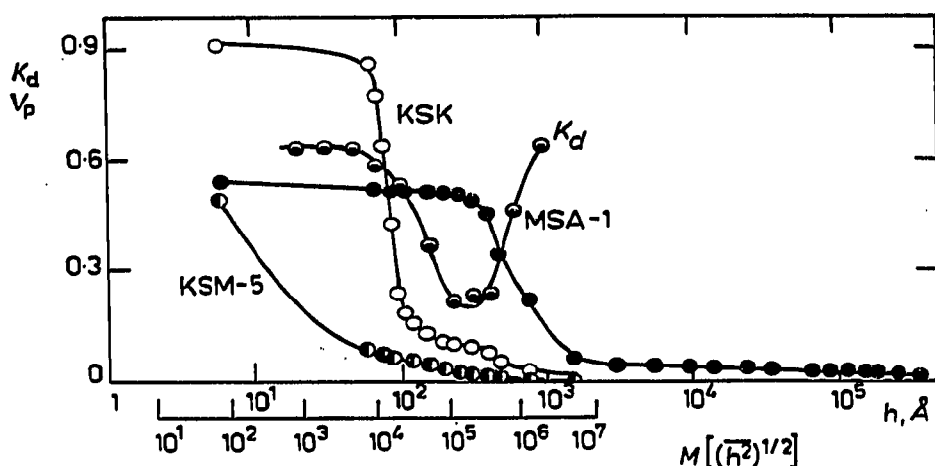
Fig. 1. Pore size distribution of Silica Gels KSM-5, KSK and MSA-1 determined by means of mercury porosimetry. K_d distribution coefficient of PS in Silica Gel KSK.

Chromatographic procedure

Glass plates, measuring 6 × 6, 6 × 9 and 6 × 12 cm were used for the TLC of the polymers. They were prepared by pouring a suspension of silica gel with the particle size 20–30 μ.

Before applying the samples the thin-layer plates were heated for 30 min at 120°. Chromatographic solvent systems were used only once and were prepared from freshly rectified solvents. Homopolymers: polystyrene (PS); poly(methyl methacrylate) (PMMA) and polyethylene oxide (PEO) as well as graft and block copolymers were subjected to chromatography in the usual way. Sandwich chambers (S-chambers) were used for chromatographing statistical copolymers; they were obtained by covering a chromatographic plate from above with glass at 0.8–1 mm distance from the silica gel layer. By placing the S-chambers in a vessel with a solvent it is possible to create the conditions for gradient chromatography owing to the gradual evaporation of the solvent into the air space in the S-chamber when the solvent moves along the sorbent layer. The presence of gradient conditions in S-chambers may be easily detected if the starting points of styrene (St) and methyl methacrylate (MMA) copolymers are placed diagonally on the plate. Fig. 2 shows that under these conditions the finishing points are arranged in a straight line which is parallel to the immersion line of the plate irrespective of the position of the starting points. This fact indicates the presence of a gradient on the plate. After the chromatography had been completed, the plates were placed in a thermostat for 10–30 min at 20° in order to remove traces of solvents. For solvent systems see Table III.

Detection and photographic registration of thin-layer chromatograms

For detection of the polymers the plates were sprayed with a 3 % solution of $KMnO_4$ in concentrated H_2SO_4 and heated in an oven for 15–30 min at 150°.

The spots of polymers acquire a black colour which stands out against the light background of a plate.

The sensitivity of detection for PS was 0.5–1 μg. Chromatographic plates were photographed by means of a contact-print method on reflex photo-paper or film. After developing in the usual manner the negative prints of thin-layer chromatograms
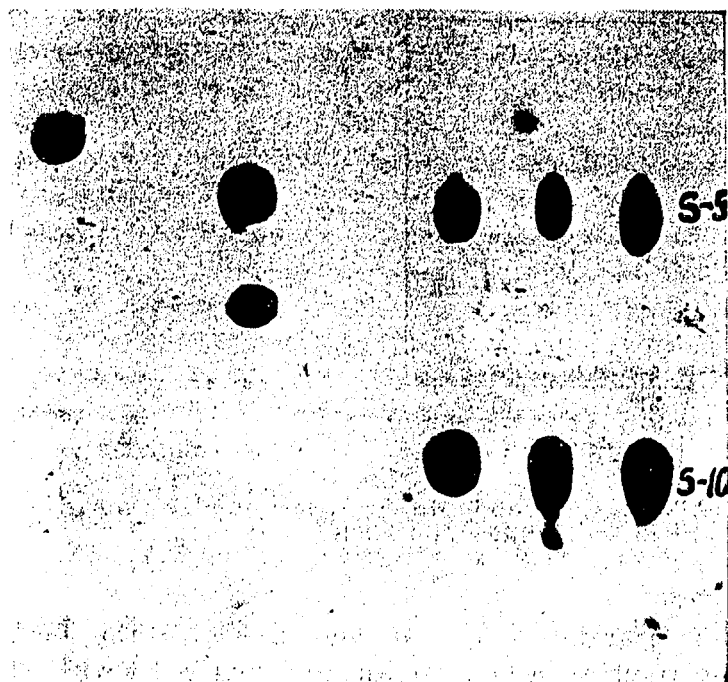
Fig. 2. TLC of the copolymers St-MMA, S-5 and S-10 in an S-chamber with Silica Gel KSK and an acetone–CHCl$_3$ system (1.2:12) with the points of sample application placed diagonally on the plate. Positive print.

were obtained as white spots against black background*. For the detection of block copolymers of styrene (ST) and ethylene oxide (EO) a modified Dragendorff reagent[4] was used.

This reagent visualised the PEO in the form of reddish-orange spots against the yellow background of the chromatographic plate.

Subsequent spraying of the plate with a 3% solution of KMnO$_4$ in concentrated H$_2$SO$_4$ led to the disappearance of the yellow colour and development became more contrasting. Sensitivity of detection was 0.1–0.5 μg PEO. If the plate was heated at 140–150°, black spots appeared instead of reddish PEO spots, but sensitivity of detection diminished to 1–2 μg.

RESULTS AND DISCUSSION

Chromatography of polystyrenes

Narrow fractions of polystyrene (PS) were used, their properties are presented in Table II. PS samples were applied to the plate from benzene solution at a concentration of 5 mg/ml.

Chromatography of polystyrene on silica gels with different porosity. Three types of silica gels (macroporous, microporous and with large pores) were examined in order to study the influence of the pore size distribution on the TLC of polystyrenes. The chromatographic behaviour of PS with molecular weights from 50 × 10^3 to 2 × 10^6 was investigated. In Fig. 3 chromatograms obtained under conditions of maximum resolution according to molecular weight (MW) are presented; chromatography was carried out in the system cyclohexane–benzene–acetone (C–B–A). Fig. 3 shows an

----

* The photographs are negatives unless otherwise indicated.

TABLE II

MOLECULAR WEIGHT AND POLYDISPERSION INDEX FOR POLYSTYRENES INVESTIGATED BY MEANS OF TLC

PS-1 + PS-2 — Pressure Chemical Co. (Japan); PS-3 to PS-11 — Waters Associates (U.S.A.).

Samples	PS-1	PS-2	PS-3	PS-4	PS-5	PS-6	PS-7	PS-8	PS-9	PS-10	PS-11
$M_w \times 10^{-3}$	0.9	2.03	5	10.3	19.85	51	98.2	173	411	867	2145
$M_n \times 10^{-3}$			4.6	9.7	19.65	49	96.2	164	392	773	1730
M_w/M_n			1.10	1.09	1.01	1.04	1.02	1.055	1.05	1.12	1.2

TABLE III

R_F VALUES FOR CHROMATOGRAPHY OF POLYSTYRENES 1–11 ON SILICA GEL KSK WITH LARGE PORES IN VARIOUS SOLVENT SYSTEMS

| No.	Composition of the solvent system (with saturation for 30 min) C–B–A	PS-1	PS-2	PS-3	PS-4	PS-5	PS-6	PS-7	PS-8	PS-9	PS-10	PS-11
1	13:3:0.1	0.90	0.80	0.61	0.10	0	0	0	0	0	0	0
2	12:4:0.4	0.96	0.96	0.94	0.85	0.76	0.33	0.14	0.05	0	0	0
3	12:4:0.7	0.97	0.97	0.97	0.87	0.78	0.58	0.46	0.37	0.27	0.22	0.20
4	12:4:1	0.98	0.98	0.98	0.91	0.86	0.74	0.66	0.62	0.58	0.58	0.58
5	12:4:2	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98
6	12:4:0.2	0.63	0.63	0.63	0.65	0.67	0.74	0.83	0.82	0.82	0.70	0.63
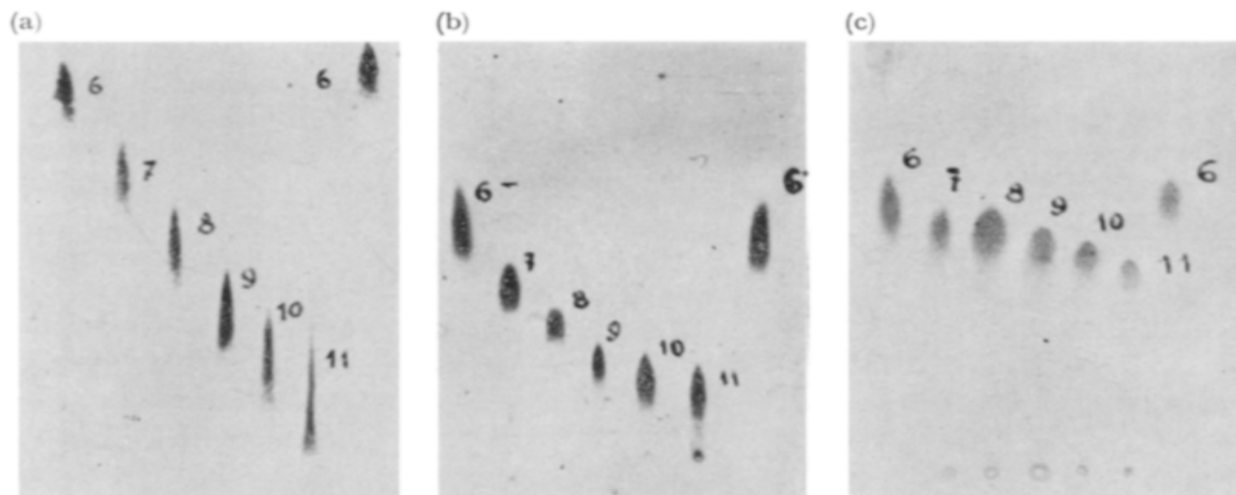
Fig. 3. TLC of polystyrenes 6 to 11 on silica gels. (a) MSA-1 in the system C–B–A (13:3:1.1);
(b) KSK in the C–B–A system (12:4:0.6); (c) KSM-5 in the C–B–A system (12:4:0.8). Positive
prints.

almost linear dependence of R_F on MW for the MSA-1 silica gel, whereas for the
Silica Gel KSK and an MW close to 4×10^5, as well as for the Silica Gel KSM-5 and
an MW close to 5×10^4, this dependence becomes less marked. This is due to the molec-
ular-sieve (gel) effect on PS adsorption.

*Chromatography of polystyrenes on Silica Gel KSK with large pores in different
solvent systems.* The 9×12 cm plates were used for studying the chromatographic
behaviour of PS 1-11 in various solvent systems on Silica Gel KSK with large pores.
The experimental results are summarised in Table III and illustrated in Fig. 4. In
system I containing a minimum of acetone — 0.66% (Fig. 4a) — only the lowest
molecular weight PS (MW up to 5×10^3) were observed to move.

When the acetone content is increased to 2.5% (Fig. 4b) PS with an MW not
exceeding 5×10^3 moved with the front, PS with MW's between 5×10^3 and 9.7×10^4
are distributed along the plate and those with MW 1.73×10^5 remain on start. When
the acetone content increases to 4.2% (Fig. 4c), PS with MW lower than 5×10^3
move with the front whereas PS with MW between 10^4 and 2×10^6 are distributed
along the plate. A still greater increase in the acetone content to 5.9% (Fig. 4d)
produces an increase in the R_F of high molecular weight PS to 0.6, the dependence
of R_F on MW being weakened. If the acetone content is increased to 11%, the poly-
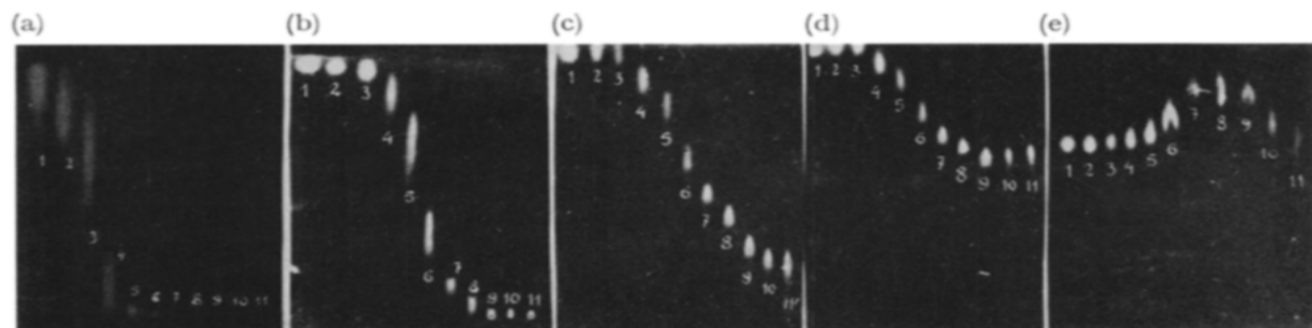mers move with the front of the solvent. Under these conditions when the adsorption

Fig. 4. TLC of polystyrenes 1 to 11 on Silica Gel KSK in the C–B–A systems: (a) 13:3:0.1;
(b) 12:4:0.4; (c) 12:4:0.7; (d) 12:4:1.0; (e) 12:4:2 (with saturation).

of PS is completely suppressed, the gel effect should take place and large macromolecules move faster than small ones. However, to have it noticeably displayed, the TLC must be conducted with the plates saturated with the solvent vapour. The fact is that chromatography on dry (unsaturated) plates involves the consumption of solvent for filling not only canals between the particles of adsorbent but the pores as well. Under these conditions velocity of the solvent front movement is lower than the flow rate and corresponds to the velocity of movement for any non-adsorbing macromolecules for which all pores of adsorbent are entirely accessible.

When the plate is saturated by the solvent vapour, the silica gel pores are filled with the solvent and the velocity of movement of the solvent front is in accordance with the flow rate of the mobile phase. It makes the macromolecules, for which the adsorbent pores are accessible, move slower than the solvent front.

Under these conditions (Fig. 4e) the gel effect becomes apparent. PS with MW of not over 10^4 move to a certain distance from the solvent front. When the MW is higher than 2×10^4, the PS velocity increases owing to partial exclusion of macromolecules from the silica gel pores.

In the range of MW $> 4 \times 10^6$ the velocity of the macromolecules decreases again owing to their adsorption in large pores and on the surface of the silica gel grains. Fig. 4 shows a continuous transition from strong adsorption of macromolecules to weak adsorption and finally to the gel effect. These peculiarities of TLC permit one to choose special conditions of chromatography for the PS samples of every MW range to obtain maximum resolution according to MW. Similar results of chromatographic separation according to MW have been obtained with the TLC of polyethylene oxide and poly(methyl methacrylate).

Concentration dependence of R_F for polystyrenes with different molecular weight on Silica Gel KSK with large pores. For studying dependence of R_F values on the concentration of the PS, samples with 5, 10, 15, 20 and 40 μg of PS were applied to the plate and the solvent systems permitting the observation of PS spots in the lower, middle and upper parts of the plate were used. Results for PS-5 and PS-9 are shown in Fig. 5.

It can be seen that with increased concentrations the PS spots in the lower part of a plate are stretched upwards, this effect is characteristic of the Langmuir (convex) adsorption isotherm.

In the upper part of the plate, the centre of a spot is displaced downwards with increasing concentration. This effect is associated with a concave adsorption isotherm which is the result of the gel effect from the adsorbent pores owing to reduction of their size. In the middle part of the plate where the gel and the adsorption effects oppose each other, a linear adsorption isotherm occurs producing the minimum concentration dependence. Furthermore we find that the gel effects of concentration become stronger with increasing MW of PS, because in this case the increase in the accessibility of the silica gel pores for PS with concentration is much higher. When the PS concentration is small (*i.e.* in the absence of the concentration effects), there is maximum stretching of the chromatographic spots and hence the best chromatographic resolution according to MW occurs in the middle part of the plate.

Determination of the molecular weight distribution of polystyrene. In order to determine the MWD of polymers by means of TLC it is necessary to eliminate chromatographic spreading due to the polymer distribution on the plate. For this purpose
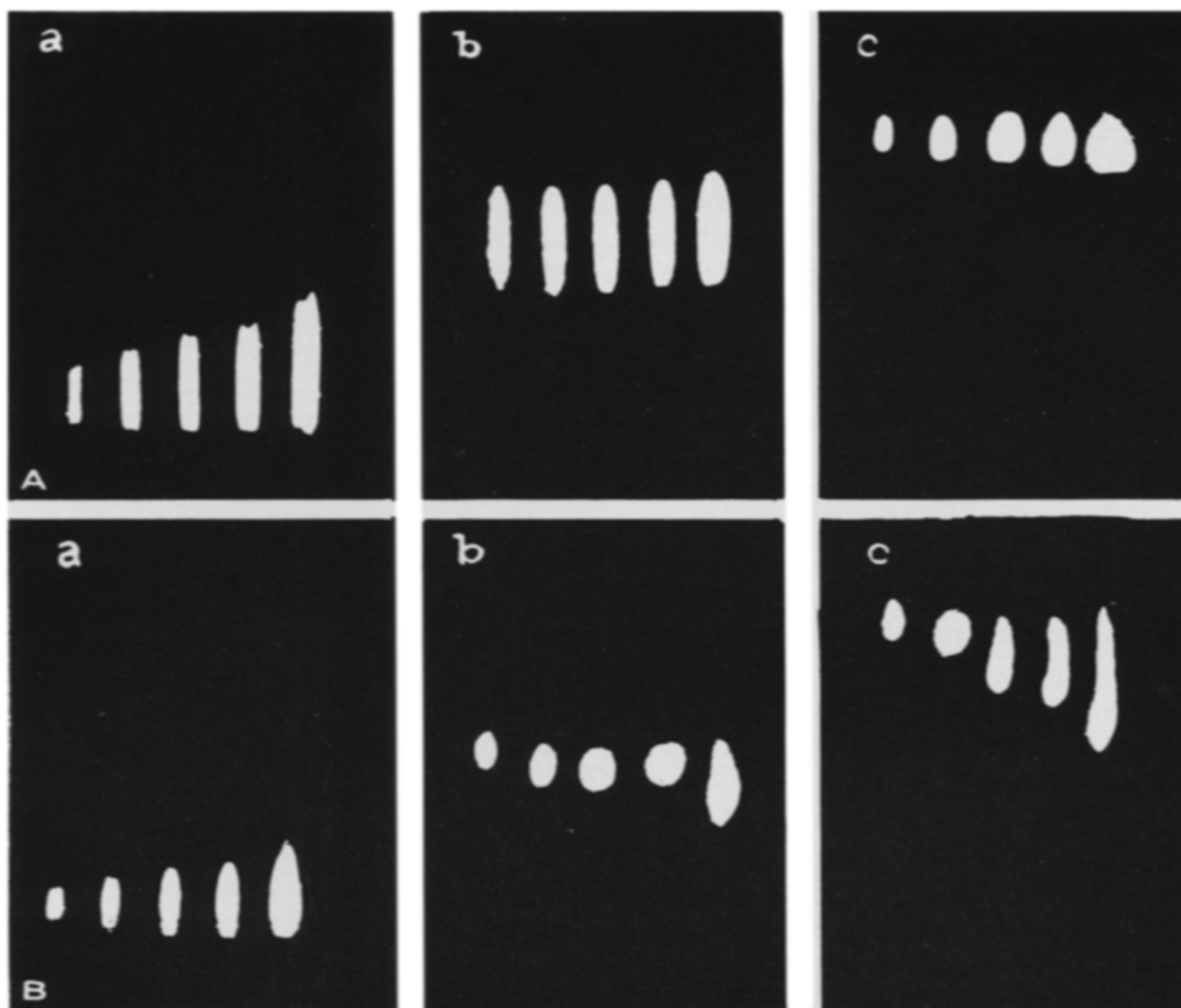
Fig. 5. Concentration effects in TLC of PS on Silica Gel KSK. (A) for PS-5 in the C–B–A system
(a) 12:4:0.25; (b) 12:4:0.5; (c) 12:4:1; (B) for PS-9 in the C–B–A systems: (a) 12:4:0.5; (l
12:4:1; (c) 12:4:1.3; 5, 10, 15, 20 and 40 μg of PS were applied.

a method is proposed (Fig. 6) which is based on two-dimensional chromatograph
of a polymer in the directions A and B, and a comparison of the width of the chroma
tographic spots arranged diagonally on the plate with the width of a spot obtaine
for a single chromatographic run in direction B in the same solvent system. If th
starting spots of two samples both have the same size, and are applied at equal di:
tances from the immersion line and the solvent run is the same for both direction
then under these conditions a spot of sample 1 can be treated as the starting zone fc
sample 2 when it is subjected to chromatography in the B direction.

If we carry out densitometry of both spots along the line B'B'' which is parall
to B, we can obtain the dispersion of a chromatographic sample (1) in the form c
difference between the dispersions of concentration distributions in the spots (1) an
(2) along the line B'B'',

$$\sigma^2 = \sigma_1{}^2 - \sigma_2{}^2.$$

(:

It is noteworthy that this method for determining chromatographic dispersion of a polymer does not distort the shape of the distribution curve for polymer homologues which is characteristic for example of the reverse elution method of TUNG et al.[20]. For determining the MWD of PS-5 with a MW 19870 two samples of this polymer (1, 2) were applied to the plate 6 × 9 cm at the points shown in Fig. 6.
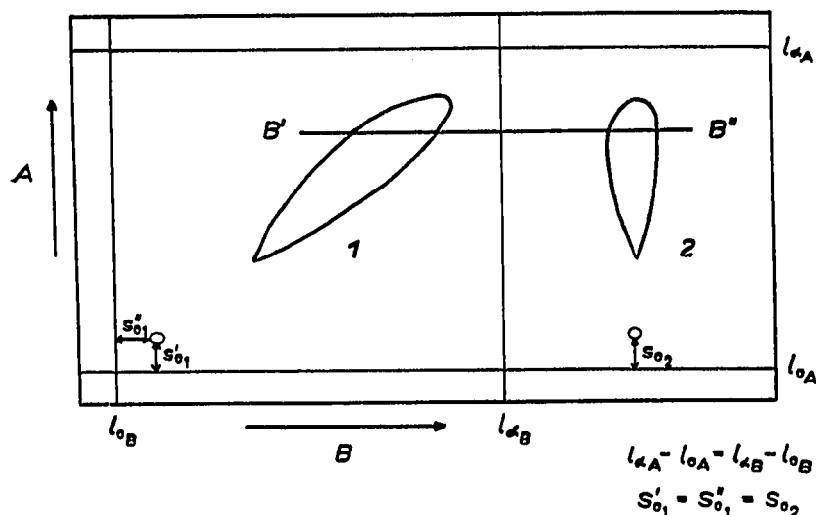

Fig. 6. Determination of chromatographic spreading in TLC of polymers by means of two-dimensional chromatography.

For studying concentration effects some samples of this PS-5 in increasing quantities (3–5) were also applied together with PS of MW 500, 10000 and 50000 (6–8) in order to graduate the chromatographic plate according to MW. After two-dimensional chromatography in the C–B–A system (12:4:4.5) a chromatogram was obtained (Fig. 7a). By means of a densitometer with a slit width of 0.1 mm, densitograms of samples 2–8 in the A direction and of the samples 1, 2 in the B direction were obtained (Fig. 7b). These results permitted one to ascertain the absence of concentration effects upon the densitogram shape and to obtain the graduation curve MW–R_F value shown in Fig. 7b.

These data together with the data on chromatographic spreading calculated by means of formula (1) or with the help of TUNG's method[21] make elimination of spreading possible by means of the MWD curve for PS-5 which is shown in Fig. 7b. The value of polydispersity for PS, $Mw/Mn = 1.02$, is in good agreement with data in the table for this PS sample ($Mw/Mn < 1.06$) and its MWD coincides well with TUNG's results obtained with the help of GPC[22]. As a PS sample with narrow MWD was examined in these experiments, detection of increments of it was assumed to be constant. For the samples with a broader MWD the changes in the optical density increment with increasing MW should be taken into account. It is worth noting that not only PS samples with narrow MW distribution can be used for graduating the plate but also a polymer with broader MWD as was done in GPC[23]. Fig. 8 illustrates the comparative efficiency of GPC[24] and TLC for the same PS samples.

The separation of these samples on a thin-layer plate (6 cm in length) is mucl more efficient than the separation by means of 4 columns of a GPC. The HETP o TLC is 300 times smaller than in the case of GPC. The above data show that deter mination of the MWD of polymers by means of TLC requires a 1000–10000 time smaller quantity of the substance with a considerably better separation than a de termination by means of GPC and it is carried out 5–10 times faster. Another ad vantage of TLC is the possibility of simultaneous chromatography of several sample on a single plate.
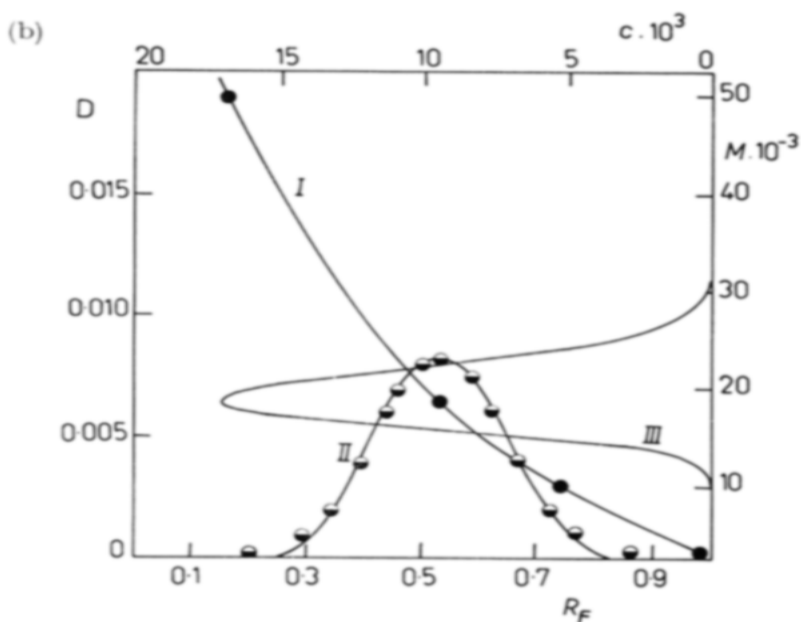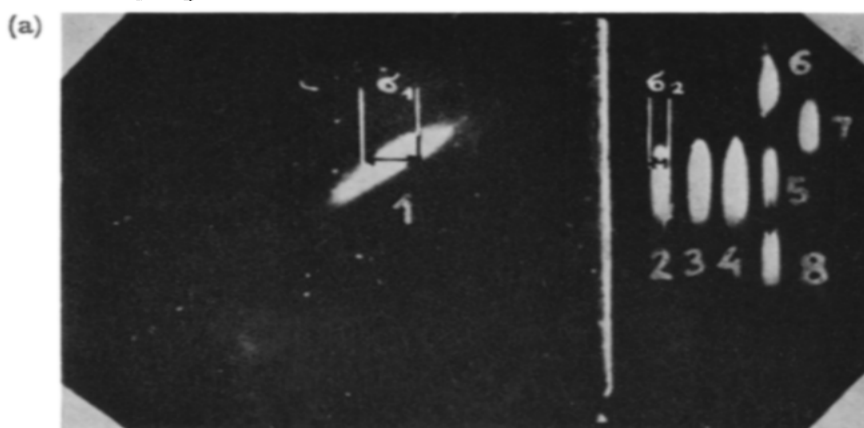

Fig. 7. Determination of the MWD for PS-5 by means of TLC on Silica Gel KSK: (a) Two-di mensional chromatogram of sample (1) and one-dimensional chromatogram of samples (2) and (3 in the C–B–A system (12:4:4.5); (b) graduating curve R_F–MW (I), densitogram of sample (2 in direction A (II) and MWD of PS-5 (III).

Chromatography of statistical copolymers of styrene and methyl methacrylate

TLC of statistical copolymers synthesised by LITMANOVITCH and coworkers[2] and characterised in Table IV was investigated. The composition of the copolymers was determined by elementary analysis with the help of pyrolytic gas chromatography[1] and by means of the refraction index increment in 3–4 solvents. Molecular weight
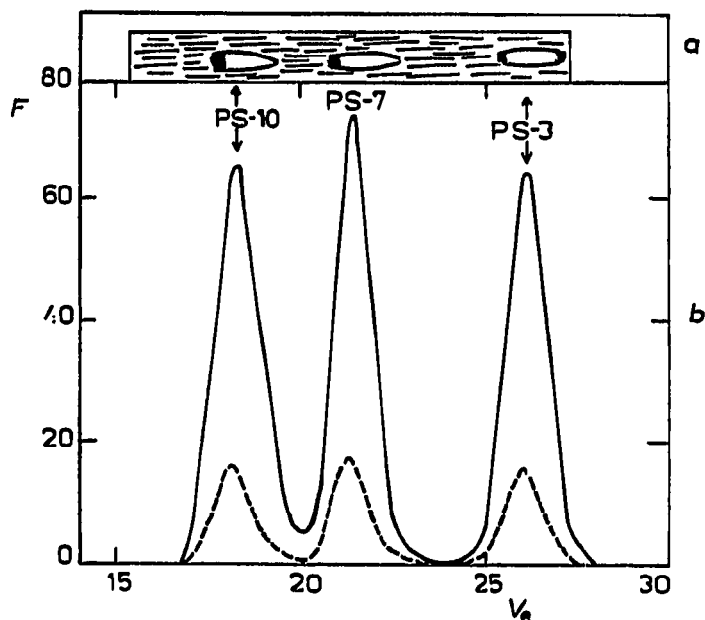
Fig. 8. TLC and GPC of polystyrenes 3, 7, and 10. (a) TLC on Silica Gel KSK in the C–B–A system (12:4:0.7); (b) GPC[24] with the concentration of the sample: (————) 0.1 g/100 ml; (– – – –) 0.025 g/100 ml.

was examined by means of the light scattering method[25]. TLC of copolymers was carried out on chromatographic plates 6 × 6 cm with layers of Silica Gel KSK with large pores.

The copolymer samples, in amounts of 1–5 g, were applied to the plate from a dichloroethane solution with a concentration of 5 mg/ml and subjected to chromatography in the solvents listed in Table V. These solvents can be divided into two classes: (a) solvents containing oxygen which forms hydrogen bonds with the silanol hydroxyl groups of the silica gel[26] ("displacers") and (b) true solvents (chlorinated hydrocarbons).

The above solvents may be arranged in the following eluotropic series according to the R_F values of the copolymers containing 31 and 54 % of styrene:

A: diethyl ether < methyl ethyl ketone < acetone < tetrahydrofuran < dioxane

B: dichlorobenzene < dichloroethane < chloroform.

It is obvious that these series depend both on the displacement power of the solvents and on their solvation ability with respect to the copolymers. Thus separation systems of low or high resolution for separating copolymers according to their composition, can be obtained with different mixtures of A and B type solvents.

Chromatography with low resolution. Strong "displacers" in small quantities (THF, dioxan acetone) or weak "displacers" (diethyl ether, MEK) in large quantities allow chromatographic systems to be devised for the separation of copolymers which differ greatly in their composition. Fig. 9 illustrates TLC of copolymers with 22, 31, 53 and 80% of styrene, respectively, and shows that the R_F value of a copolymer increases with the St content. As in the case of homopolymers, there is also a concentration dependence of R_F values for the copolymers (Fig. 10), in the lower part of the plate it is characteristic of the Langmuir's adsorption isotherm and in the upper part it corresponds to the concave isotherm characteristic of GPC. Owing to high

TABLE IV

PROPERTIES OF STYRENE–METHYLMETHACRYLATE COPOLYMERS SAMPLES EXAMINED BY MEANS OF TLC

Samples	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10	S-11	S-12	S-13	S-14
Composition (mol % of styrene)	80	80	80	54	54	54	54	54	31	31	31	31	32	22
$M_w \times 10^{-3}$	120	—	—	73	80	130	160	260	50	88	160	180	260	230

TABLE V

R_F VALUES FOR COPOLYMERS OF STYRENE AND METHYLMETHACRYLATE WITH 31 % (S-10) AND 54 % (S-5) OF STYRENE IN SYSTEMS CONTAINING 10 % OF THE "DISPLACER"

Solvents	Displacer									
	Ether		Methyl ethyl ketone (MEK)		Acetone		Tetrahydrofuran (THF)		Dioxan	
	S-10	S-5	S-10	S-5	S-10	S-5	S-10	S-5	S-10	S-5
Dichlorobenzene (DCB)	0	0	0	0	0	0.52	0	0.71	0	0.83
Dichloroethane (DCE)	0	0	0	0	0	0.70	0.69	0.92	0.77	0.92
Chloroform (CHCl₃)	0	0.17	0	0.32	0.49	0.85	0.70	0.90	0.83	0.95

sensitivity of detection, however, the experiments can be carried out in the range where the R_F-concentration dependence is absent.
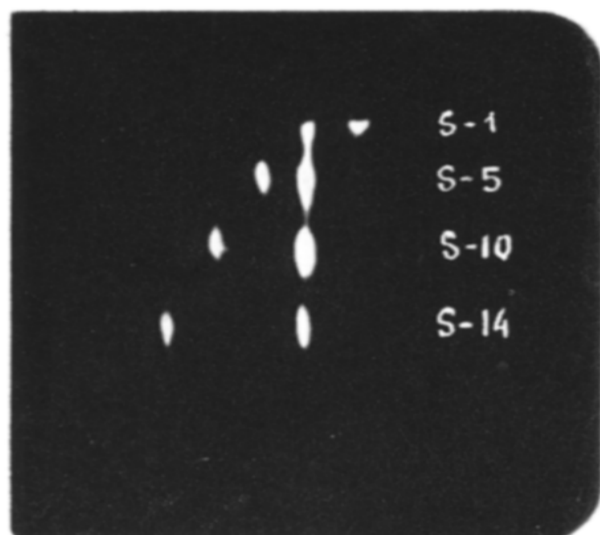

Fig. 9. Low resolution TLC on KSK Silica Gel of statistical copolymers St–MMA with 80, 54, 31 and 22% of St (S-1, S-5, S-10 and S-14) in the $CHCl_3$–acetone system (12:2.4).
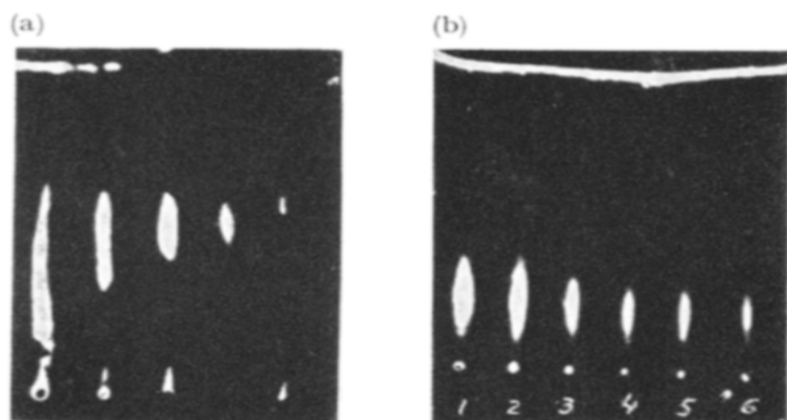

Fig. 10. Concentration effects for the copolymer S-5 with 54% of St on Silica Gel KSK in the $CHCl_3$–MEK systems: (a) (12:2.4); (b) (12:1.2); 1, 2, 4, 8, 16, and 32 μg of sample was applied.

The effect of the MW of a copolymer on its behaviour during TLC. Fig. 11 shows TLC of copolymers with different MW containing 3% and 54% of styrene. Comparatively strong dependence of the R_F value on MW is noticeable when the MW does not exceed 10^5. In the range of MW higher than $1.0-1.5 \times 10^5$ this dependence weakens and the chromatographic distribution of the copolymers on the plate becomes governed mainly by their composition. It would also be possible to reduce the dependence of the R_F of the copolymer on MW, in the range of MW > 10^5, if the microporous Silica Gel KSM-S, with pores inaccessible for macromolecules with a MW > 40×10^5, is used instead of Silica Gel KSK with large pores. Chromatograms of copolymers on Silica Gel KSK and KSM-5 are presented for comparison in Fig. 12. These silica gels differ little in their sensitivity to the composition of the copolymers.

However, the dependence of the R_F value on MW for Silica Gel KSM is considerably less pronounced than for Silica Gel KSK. It is evident that the use of the micro-

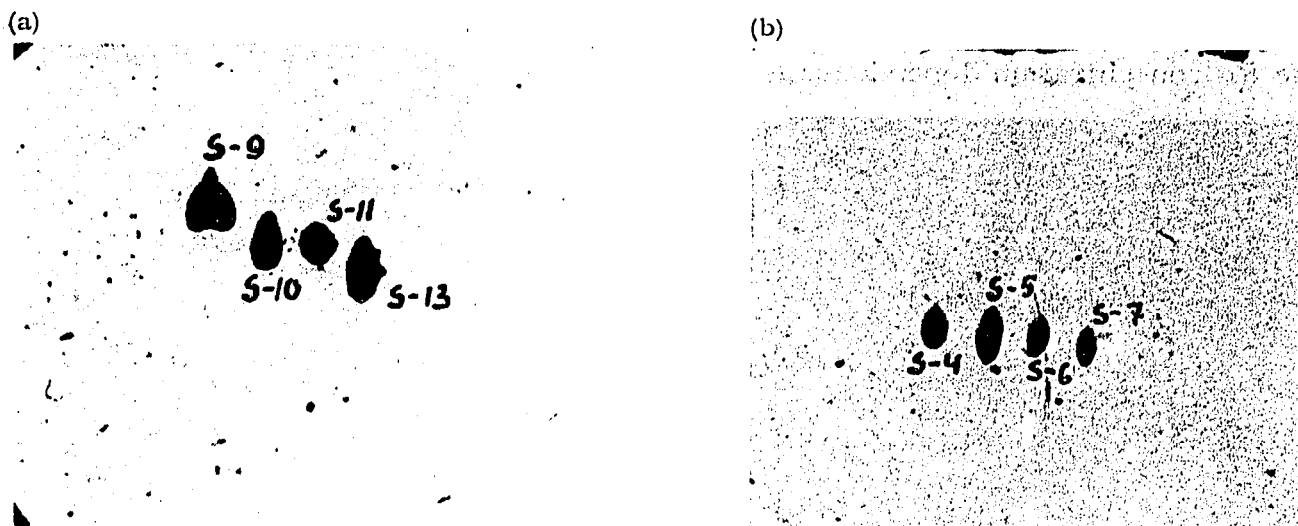(a)   (b)

Fig. 11. Effect of the MW on the chromatographic behaviour of statistical copolymers St–MM on Silica-Gel KSK. (a) Copolymers with 31% of St and MW 2.6 × 10⁵, 8.8 × 10⁴ and 5 × 1 (S-13, S-11, S-10, S-9) in a $CHCl_3$–acetone system (12:2.2); (b) copolymers with 54% of St at MW 1.6 × 10⁵, 1.3 × 10⁵, 8 × 10⁴, 7.3 × 10⁴ (S-7, S-6, S-5, S-4) in the $CHCl_3$–MEK syste (12:1.6). Positive prints.

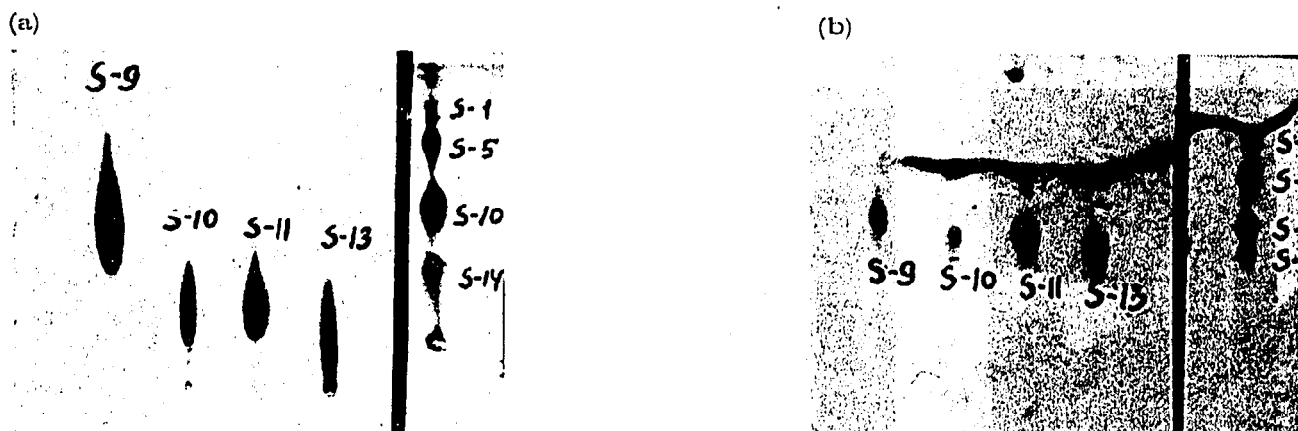(a)   (b)

Fig. 12. TLC of statistical copolymers St–MMA on various silica gels. (a) Copolymers with 31 of St and MW 2.6 × 10⁵, 1.6 × 10⁵, 8.8 × 10⁴, 5 × 10⁴ (S-13, S-11, S-10, S-9) on KSK in t $CHCl_3$–acetone system (12:2.2); (b) copolymers with 80, 54, 31 and 22% of St (S-1, S-5, S-1 S-14) on KSK in the $CHCl_3$– acetone system (12:2.4); (c) copolymers with 31% of St and M 2.6 × 105, 1.6 × 10⁵, 3.8 × 10⁴ (S-13, S-11, S-10, S-9) on KSM-5 in the $CHCl_3$–acetone syste (12:3.2); (d) copolymers with 30, 54, 31 and 22% of St (S-1, S-5, S-10, S-14) on KSM-5 in t $CHCl_3$–acetone system (12:3.4). Positive prints.

porous Silica Gel KSM-5 is advisable for TLC of copolymers with a MW not over 1(whereas for copolymers of higher MW Silica Gel KSK with large pores should be use

TLC of copolymers with high resolution. Using weak "displacers" (diethyl ethe MEK), one can obtain chromatographic systems of high resolution for the separatic of copolymers slightly differing in composition. Fig. 13a illustrates the TLC separatic of copolymers having similar composition — 80 % St according to elementary analys and refraction index increment data. In this case, despite the gradient conditions chromatography, the chromatographic spots may be found to be connected by narrow path of bi-modal distribution.

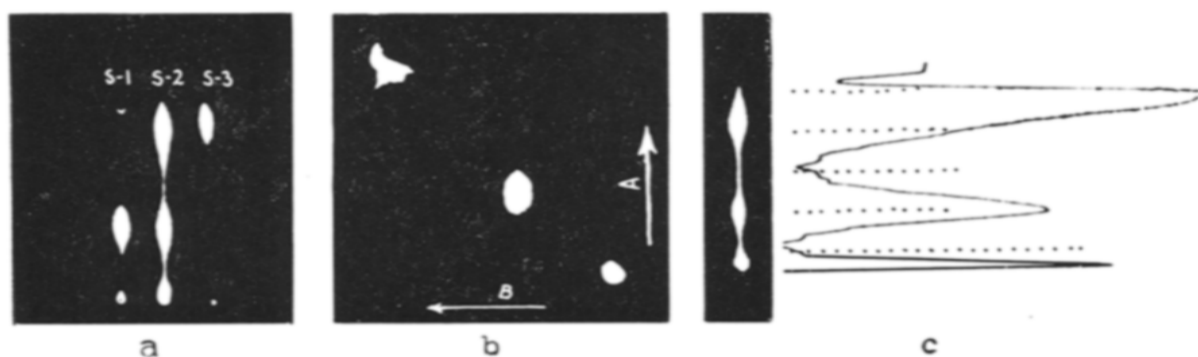In order to distinguish this phenomena from tailing, two-dimensional chrom

Fig. 13. TLC with high resolution. (a) The copolymers St–MMA with 80% of St (S-1, S-2, S-3) in the CHCl₃–MEK system (12:0.6); (b) two-dimensional chromatogram S-2; (c) one-dimensional chromatogram and densitogram of S-2.

tography in a single system of solvents was used. Fig. 13b represents a two-dimensional chromatogram of the copolymer S-2 which is separated into three isolated spots positioned diagonally on the plate. This fact indicates that they are individual components. A densitogram of this copolymer is shown in Figure 14b. The resolution of this method of TLC is so high that it permits the detection of inhomogeneity of copolymers of azeotropic composition with the increase in the conversion. As shown in Fig. 14a, the extent of the stretching of the spots of 54 % St copolymers becomes higher with increasing conversion. A two-dimensional chromatogram of S-5 confirms that these results are not due to the formation of chromatographic artifacts. When the S-chamber is used, it must be taken into account that the "displacer" gradient only extends for a short distance on the plate near the front. The chromatographic spots are compact and occur near each other in this zone.

The other copolymers (with a lower St content), for which the concentration of the "displacer" is not sufficient, are found either on the start or move in the non-gradient zone of solvent and form wide bands as shown in Fig. 9. Apparently, the gradient zone corresponds to conditions of low resolution whereas the non-gradient zone moving next gives high resolution.
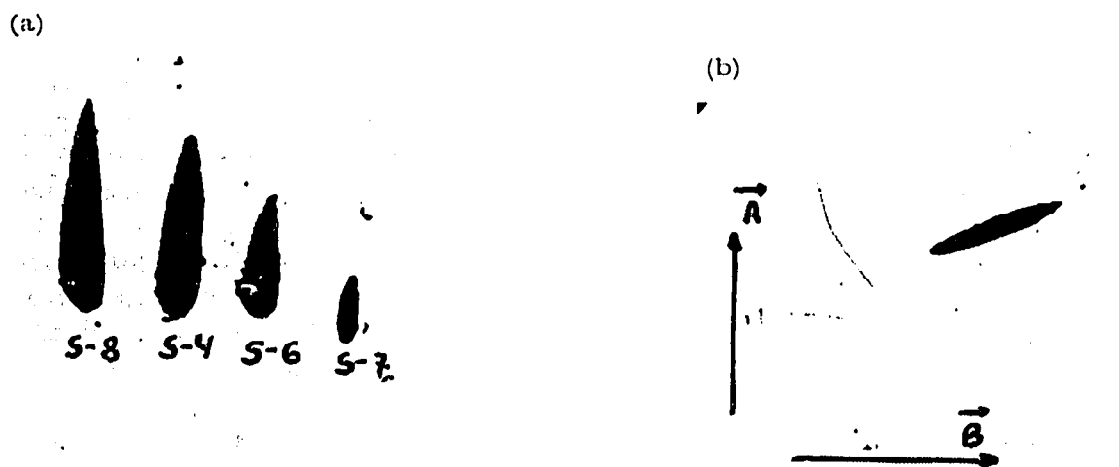

Fig. 14. TLC of azeotropic copolymers St–MMA with 54% of St. (a) Copolymers with different conversion: S-7 (0.5%), S-6 (11.7%), S-4 (3.3%), S-8 (70.6%) on Silica Gel KSK in the CHCl₃–diethyl ether system (12:4.2); (b) two-dimensional chromatogram of S-4. Positive prints.

Thin-layer chromatography of block and graft copolymers

The two main tasks for TLC of block and graft copolymers are to determin
homopolymer admixtures in the copolymer and to diagnose block and graft copoly
mers. The first problem is solved by means of two-dimensional TLC in two solven
systems where the two homopolymers are moved in different directions, while th
block (graft) copolymer remains on start. In the case when the copolymer moves ii
one of the solvent systems, one of the homopolymers moves with it in the same solven
system. Then after two-dimensional chromatography with a suitable second solven
system the copolymer and the homopolymers mixed with it will be moved so that the
are positioned in different corners of the plate.

The problem of diagnostics of block and graft copolymers may be solved in tw
ways. The first is to compare the mobilities of the copolymer and the homopolymer
which are known to be of much higher MW. A second approach (which is more reliable
is possible if we succeed in finding two solvent systems, the first of which keeps on
of the homopolymers at the start making the copolymer move, while in the secon
system the copolymers move with the front as before but the homopolymers exchang
their places. For differentiating graft copolymers and in general branched linea
macromolecules, a highly specific method can be used; it is based on the differenc
in their thermodynamic rigidity which determines the number of adsorbed segment
and hence the stability of the adsorption bond. As a result, the R_F value of a graf
copolymer corresponds to the R_F value of the linear homopolymer with the same com
position as that of the side branches of the graft copolymer but with a considerabl
lower MW.

Investigation of graft copolymers of styrene and methyl methacrylate. TLC wa:
used for graft copolymers whose backbone consisted of poly(methyl methacrylate
(PMMA) with a MW of 5×10^3, and have side branches of St with a MW of 2×10^3
The ratio St/MMA was 1/10, hence the MW of the graft copolymer obtained wa:
1.5×10^6. Fig. 15a presents the two-dimensional chromatogram of a graft copolyme
on a Silica Gel KSK plate with dimensions of 6×6 cm. The graft copolymer wa
applied in the amounts of 50–100 μg from a chloroform solution. Chromatograph
in the first direction was carried out with a solvent system in which PMMA of an
MW and low molecular weight PS move with the front and the graft copolymer re
mains at the start. When chromatography was carried out in the other direction, w
used a solvent system in which PMMA did not move whereas PS of any MW (an
hence the graft copolymer, as well) moved with the front. As a result all the compo
nents of the graft copolymer were found in different corners of the plate. Moreove:
a substance of unascertained nature was found at the start (apparently it was :
product of further cross-linking of the graft copolymer).

When another pair of solvents was used (Fig. 15b), graft copolymer and P:
moved in the first direction while PS and PMMA moved in the second one. In thi:
case PS and PMMA was found in the upper and lower left hand corners of the plate
respectively, whereas the graft copolymer was placed above the starting spot (se
Fig. 15b).

Fig. 15c also shows that the graft copolymer with a MW of 1.5×10^6, bein
more rigid than linear PS, moves on the level of PS with a MW of 1.7×10^5.

Thin-layer chromatography of block copolymers. Block copolymers of ethylene
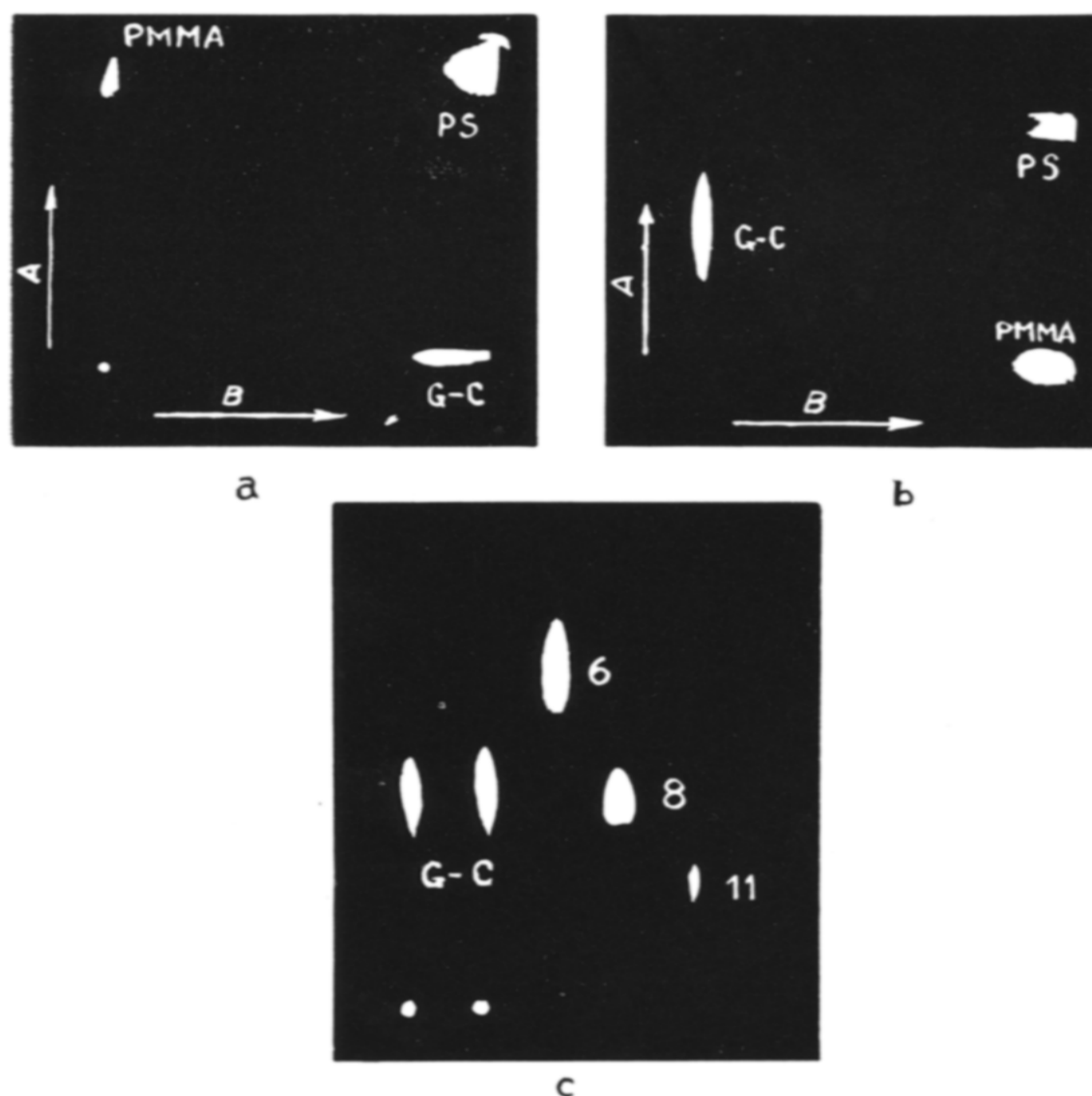oxide (EO) and styrene in the ratio 1:1 were investigated. TLC was carried out or

Fig. 15. TLC of graft-copolymer PMMA–PS (G–C). (a) Chromatogram in the acetone–acetic acid system (12:2) in direction A and in the CHCl$_3$–MEK system (12:2) in direction B; (b) two-dimensional chromatogram in the C–B–A system (12:4:0.7) in direction A and in the acetone–acetic acid system (12:2) in direction B; (c) one-dimensional chromatogram of the graft-copolymer PMMA–PS and of polystyrenes 6, 8, and 11 in the C–B–A system (12 + 4 + 0.7) on KSK Silica Gel.

the plates 6 × 6 cm with the Silica Gel KSK. Block copolymer samples were applied in the amount of 50–100 μg from a chloroform solution. After the chromatographic process the polymer spots were detected with the help of a 3 % KMnO$_4$ solution or Dragendorff's reagent. Fig. 16 illustrates a two-dimensional chromatogram of the block copolymer ST–EO. The chromatographic systems used were selected so that PS (MW 3 × 10^6) and PEO (MW > 10^6) moved with the front. The block copolymer was found at the start and the colour of its spot was developed with both reagents. The chromatogram shows that free PS moving in the C–B–A system was present in the block copolymer sample together with a small quantity of PEO moving in the pyridine–water system. Unfortunately, owing to a great difference in polarity between PEO and PS, we failed to find a solvent system which would force the block copolymer

under investigation to move, as well. Such a system was, however, successfull
selected for the block copolymer of St with the less polar monomer MMA (50:50)
In the system containing acetone the block copolymer ST–MMA moved on the sam
level as the PS while the PMMA remained on start and the statistical copolymer c
the same composition was in the middle of the plate. In another system containin
methanol the block copolymer also moved with the front together with PMM.
whereas PS remained on start. As in the first case, the statistical copolymer wa
placed in the centre of the plate. These results show that in these solvent system
one of the copolymer blocks, either PMMA (in the first case) or PS (in the secon
case), collapses and the chromatographic behaviour of these copolymers resemble
that of PS or PMMA, respectively. Similar changes in the conformation of bloc
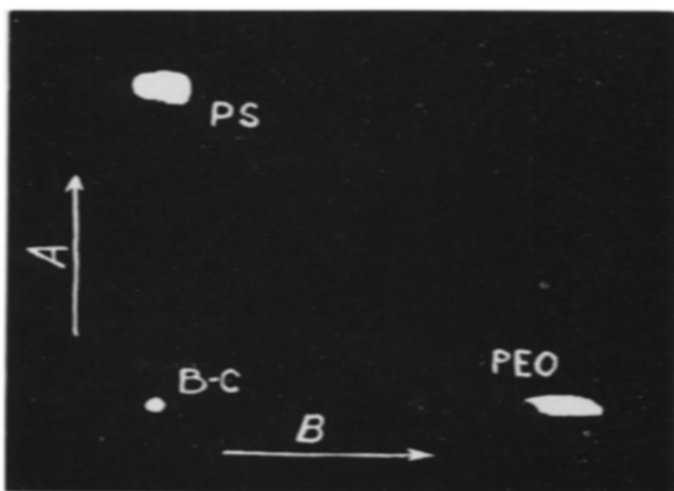copolymers in different solvents are described in literature[27].

Fig. 16. Two-dimensional TLC of block-copolymer (B–C) St–EO (50:50) in the systems: C–B–,
(12:4:2) in direction A and pyridine–water (3:7) in direction B.

CONCLUSIONS

The results of the TLC of polymers (copolymers) reported above show thi
method to be effective for the investigation, with high resolution, of such propertie
of macromolecules as MW and MWD, and the composition of homopolymers an
structural properties of copolymers. This method also permits diagnosis of block an
graft copolymers and the determination of the homopolymer admixtures in them
Using the microporous adsorbent KSM-5, it is possible to eliminate, to a considerabl
extent, the influence of MW on TLC of copolymers. Two-dimensional TLC permit
one to distinguish between the chromatographic phenomena on the plate, viz. which
causes the formation of a stretched spot and which causes tailing. This method als
enables us to determine the homopolymer admixtures in graft and block copolymers
Finally, two-dimensional TLC permits one to take into account chromatographi
spreading when MWD of homopolymers is to be determined by means of TLC. Th
concentration dependences were established for the TLC of polymers; the adsorptio
isotherms were of the gel type in the upper part of the plate and of the adsorption typ
in the lower one. It should be noted that INAGAKI paid no attention in his work[11] t
the dependence of the R_F values of polymers on the concentration and the MW o

copolymers. This dependence does not follow from the diad model he used[12,15] for interpreting the peculiarities of TLC of polymers.

We shall examine the mechanism of the polymer movement along the thin-layer plate. During the elution movement in the adsorbent layer, the polymers are distributed between the mobile and the stationary phases. The mobile phase is homogeneous in structure and has a section β, while the stationary phase is subdivided into two zones: firstly a film with a section α' accessible for macromolecules of all sizes which covers the surface of the adsorbent grains and fills the spaces between these particles, and secondly the space of adsorbent pores which is accessible only for macromolecules smaller than the pore entrance diameter. The section of such pores (we shall designate it as α_N^{acc}) according to MOORE's relation[28] can be expressed as $\alpha_N^{acc} = \alpha(1 - \log N/\log N_m)$, where α is the overall section of the porous part of adsorbent, N is the number of macromolecular units (the degree of polymerisation), N_m represents the maximum size of macromolecules for which the largest of the adsorbent pores
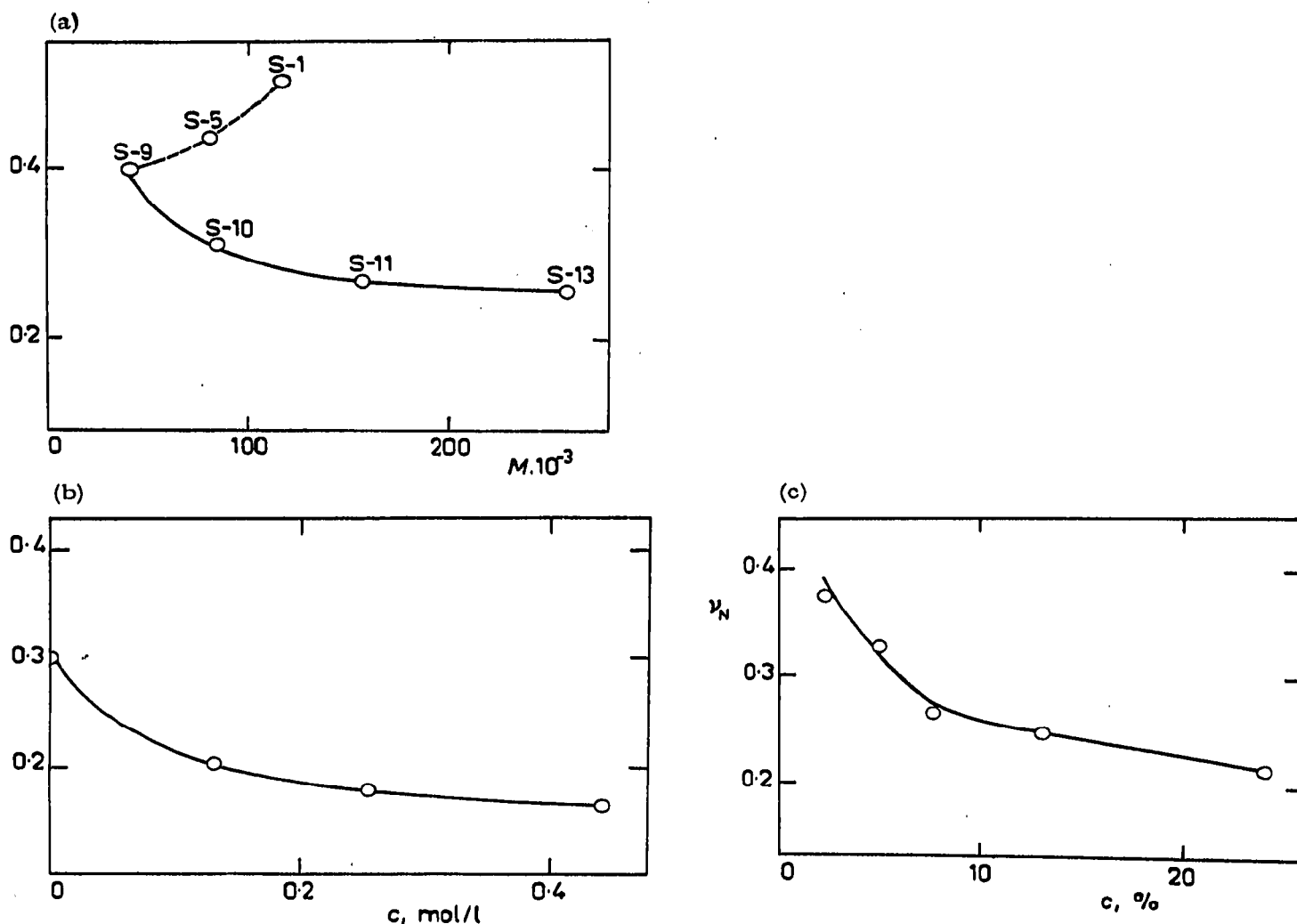

Fig. 17. Dependence of ν_N for statistical copolymers St–MMA during the adsorption on aerosil with the specific surface 150 m²/g on: (a) MW of copolymers with 31% of St (S-9, S-10, S-11, S-13) and the content of St in copolymers (S-1, S-5, S-9); (b) the concentration of displacer (dioxan in moles/l) for copolymers with 24% of St; (c) concentration (%) of the solution of copolymer with 24% of St.

are accessible. As shown in reference 29, when the energies of interaction with the ad
sorbent are not very high, the macromolecules represent slightly deformed randor
coils and come into contact with the adsorbent only by some fraction, ν_N, of the:
units, and on the whole are located above the adsorbent surface having the shap
of loops. The number of the adsorbed units ν_N can be determined experimentally b
means of infrared spectroscopy, for example, for the MMA units it is calculated fror
the shift of the carbonyl adsorption band from $\nu = 1732$ cm^{-1} to $\nu = 1710$ cm$^-$
Fig. 17a shows the percentage of the adsorbed units (ν_N) determined by this metho
for a copolymer St–MMA as a function of its composition, MW, the composition c
the solvent and the concentration of the solution. This figure shows that ν_N decrease
with increasing MW and with decreasing percentage of the St units. The latter fac
is probably due to a decreasing probability of contact between the adsorbent and th
MMA units when these units are arranged sufficiently close to each other in the cc
polymer loops (Fig. 17a) and when the displacing power of the solvent (per cent c
dioxan) is increased (Fig. 17b). The increase in the polymer concentration (Fig. 17(
leads to a decrease in ν_N produced by a deformation of the coils in the direction tar
gential to the adsorbent surface. This fact explains why an adsorption isother
having the LANGMUIR characteristics for macromolecules is distinctly seen in th
TLC of polymers (see Figs. 5 and 10).

With adsorption of the macromolecules, its entropy diminishes owing to
deformation of the coil. The loss of entropy is compensated by the energy of inter
action of macromolecular units with the active centres of adsorbent, $\theta = \varepsilon/KT$. Her
ε is the mean energy of mutual exchange in the adsorption of a single unit from th
solution, $\varepsilon = \omega(\varphi_{23} + \varphi_{11} - \varphi_{12} - \varphi_{13})$, where ω is the coordination number, φ is th
energy of intermolecular interaction (indices 1, 2 and 3 refer to the solvent, the poly
mer and the adsorbent, respectively). During the adsorption the configuration
entropy ΔS_c in the solution also changes owing to the formation of a macromolecula
adsorption layer in the large pores and to the separation of the solvent from the macrc
molecular solution in the small pores. Since the stratification of the polymer solutio
takes place in the whole pore volume, ΔS_c must only slightly depend on the porot
structure of the adsorbent and the MW of the polymer. If we examine the free energ
change in the macromolecular solution during adsorption according to the conceptior
of FLORY–HUGGINS[30], we can write for the adsorption coefficient of macromolecule:

$$K = P \exp (N\nu_N\theta)$$ (

where $P = \exp (\Delta S_c/K)$. Since ν_N decreases with increasing N and increases wit
increasing θ (Figs. 18a and 18b) ($\nu_N = \xi N^{-a}\theta^b$), where ξ, a and b are dimensionle:
parameters, the distribution coefficient for macromolecules can be expressed as fo
lows:

$$K_d = P \exp [\xi N^{1-a}\theta^{1+b}]$$ (

From this equation the expression for the R_F value can be derived:

$$R_F = \left(1 + \frac{\alpha'}{\beta} + \frac{\alpha_N^{acc}}{\beta} K_d\right)^{-1} = \left[1 + \frac{\alpha'}{\beta} + \frac{\alpha_N^{acc}}{\beta} P \exp (N\nu_N\theta)\right]^{-1} =$$

$$= \left[1 + \frac{\alpha'}{\beta} + \frac{\alpha}{\beta} (1 - \log N/\log N_m) P \exp (\xi N^{1-a}\theta^{1+b})\right]^{-1}$$ (
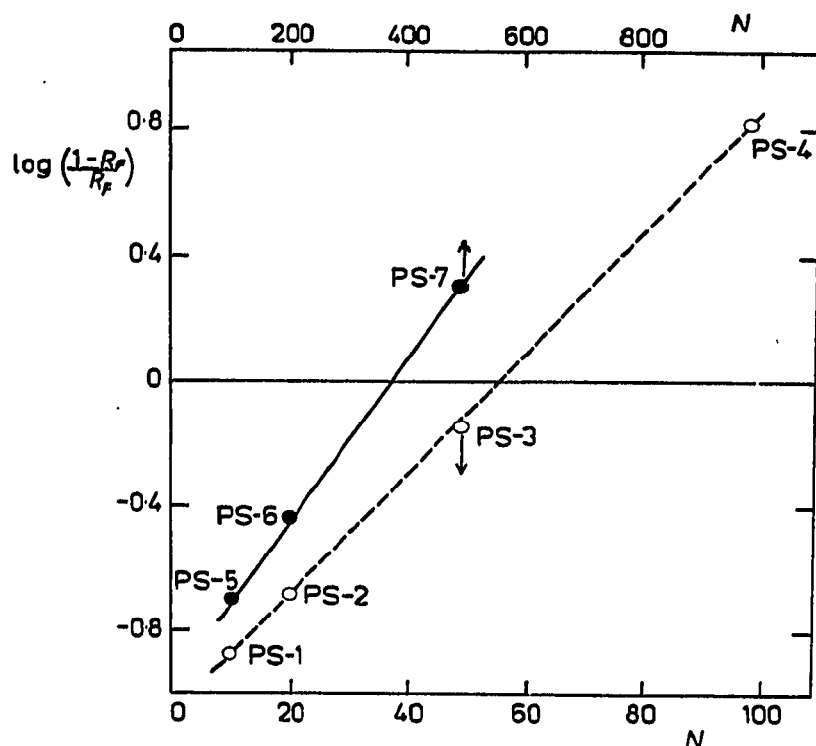
Fig. 18. Dependence of log(1 — R_F)/R_F on MW(N): for PS 1, 2, 3, 4 in the C–B–A-system (13:3:0.1); for PS 5, 6, 7 in the C–B–A system (12:4:0.4) on the Silica Gel KSK.

We shall examine this expression for the case when $\alpha_N^{acc} = \alpha$. Then eqn. 4 can be written:

$$R_F = \left(1 + \frac{\alpha'}{\beta} + \frac{\alpha}{\beta} P \exp [Nv_N\theta]\right)^{-1} = \left[1 + \frac{\alpha'}{\beta} + \frac{\alpha}{\beta} P \exp (\xi N^{1-a_\theta 1+b})\right]^{-1} \qquad (5)$$

The term α'/β in eqn. 5 can be omitted (which is permissible for plates with a well prepared adsorption layer) and the resulting equation then becomes linear:

$$\log [(1 — R_F)/R_F] = — \log (\beta/\alpha P) + v_N\theta N \qquad (6)$$

Fig. 18 shows that this equation is correct. In fact, we find a linear dependence of log [(1 — R_F)/R_F] on MW (N) for PS 1–4 and PS 5–7 on the Silica Gel KSK; this shows that it is correct to describe TLC of polymers by means of eqn. 4. It must be noted that the slope of the lines in Fig. 18 is equal to $v_N\theta$, *i.e.*, it is connected with the energy of interaction between the polymer unit and the adsorbent.

It is interesting that for low molecular weight PS this slope is steeper and, hence, for TLC of such polymers the interaction energy between the polymer and the adsorbent must be increased (for example, by decreasing the displacer content in the eluent). We shall determine the sensitivity of TLC to MW (N) and to the composition (θ); differentiating eqn. 5 we obtain

$$\frac{\partial R_F}{\partial N} = \frac{\dfrac{\alpha'}{\beta} P \exp (\xi N^{1-a_\theta 1+b})}{\left[1 + \dfrac{\alpha'}{\beta} + \dfrac{\alpha}{\beta} P \exp (\xi N^{1-a_\theta 1+b})\right]^2} \times (1 — a)N^{-a_\theta 1+b} \qquad (7)$$

and

$$\frac{\partial R_F}{\partial \theta} = \frac{\frac{\alpha'}{\beta} P \exp (\xi N^{1-a_0 1+b})}{\left[1 + \frac{\alpha'}{\beta} + \frac{\alpha}{\beta} P \exp (\xi N^{1-a_0 1+b})\right]^2} \times (1 + b)N^{1-a_0 b} \qquad (8$$

Examination of eqns. 7 and 8 permits the following conclusions to be drawn.

(1) Since the maximum value of $x/(a + x)^2$ is attained when $x = a$, it follow that $\partial R_F/\partial N$ and $\partial R_F/\partial \theta$ have maximum values when

$$\frac{\alpha'}{\beta} P \exp (\xi N^{1-a_0 1+b}) \approx 1 + \frac{\alpha'}{\beta'}$$

i.e. with $R_F \leqslant 0.5$; this is clear from Fig. 5.

(2) The sensitivity of the analysis to MW (*i.e.*, the quotient $\partial R_F/\partial N$) increase and its sensitivity to composition ($\partial R_F/\partial \theta$) decreases with MW; this is also in goo agreement with experimental results (Fig. 4).

(3) The presence of the term v_N in the exponential of eqn. 4 permits one t connect R_F with the thermodynamic rigidity of macromolecules. It follows from ou studies that the R_F of graft-copolymers and other branched macromolecules wit increased rigidity must be higher than R_F for linear polymers of the same MW

In conclusion, the advisability of combining the TLC and GPC methods mus be noted. GPC can be used for obtaining standard samples of known MW which ar necessary for the calibration of TLC plates. In addition, the relation between th volumes of macromolecules determined by GPC and their adsorption determined b TLC can be used for studying the structural peculiarities of the polymer sample including the diagnostics of graft-copolymers.

REFERENCES

1 B. G. BELENKII, L. S. VILENCHIK AND D. D. NOVIKOV, in *Novoe v metodach issledovaniy polimerov*, Mir, Moscow, 1968, p. 81.
2 *Analytical Gel Permeation Chromatography*, *J. Polymer Sci.*, C-21 (1968).
3 R. M. SCREATON, in *Noveishie metody issledovaniya polimerov*, Mir, Moscow 1966, p. 361.
4 K. BURGER, *Z. Anal. Chem.*, 224 (1967) 421.
5 L. FAVRETTO, G. PERTOLDI MARIETTA AND L. FAVRETTO GABRIELLI, *J. Chromatog.*, 46 (197c 255.
6 M. T. BRIK, A. S. SHEVLYAKOV AND O. B. KRESUB, *Vysokomol. Soedin.*, 10B (1968) 893.
7 M. S. Y. DALLAS AND M. F. STEWART, *Analyst*, 92 (1967) 634.
8 V. A. DORMAN-SMITH, *J. Chromatog.*, 29 (1967) 265.
9 H. HALPAAP AND K. KLATYK, *J. Chromatog.*, 33 (1968) 80.
10 N. HEITZ, K. KLATYK, F. KRAFFCZYK, K. PFITZNER, D. RANDAU AND E. MERK, in *Sevent Intern. Gel Permeation Chromatog. Seminar*, Monte Carlo, 1969, p. 217.
11 H. INAGKI, H. MATSUDA AND F. KAMIYAMA, *Macromolecules*, 1 (1968) 520.
12 F. KAMIYAMA, H. MATSUDA AND H. INAGAKI, *Makromol. Chem.*, 125 (1969) 286.
13 H. INAGAKI, T. MIYAMOTO AND F. KAMIYAMA, *Polymer Letters*, 7 (1969) 329.
14 H. INAGAKI AND T. MIYAMOTO, *Macromolecules*, in press.
15 H. INAGAKI, *Bull. Inst. Chem. Res. Kyoto Univ.*, 47 (1969) 196.
16 B. G. BELENKII, E. S. GANKINA AND L. D. TURKOVA, in *Lektsii 2-oj shkoly po metodam ochistl i ozenki chistoty monomerov i polimerov*, Chernogolovka, 1968, p. 216.
17 I. A. BARANOVSKAYA, B. G. BELENKII, E. S. GANKINA AND V. E. ESKIN, in *Sintez, structur i svoistva polimerov.*, Trudy XV nauchn. konfer. Instituta Vysokomolekularnykh Soedinen Acad. Nauk S.S.S.R. (April 1967), Nauka, Leningrad, 1970, p. 77.

18 B. G. BELENKII AND E. S. GANKINA, *Dokl. Akad. Nauk S.S.S.R.*, 186 (1969) 857.
19 B. G. BELENKII AND E. S. GANKINA, *Dokl. Akad. Nauk S.S.S.R.*, in press.
20 L. H. TUNG, J. C. MOORE AND G. W. KNIGHT, *J. Appl. Polymer Sci.*, 10 (1966) 1261.
21 L. H. TUNG, *J. Appl. Polymer Sci.*, 10 (1966) 375.
22 L. H. TUNG AND J. R. RUNYON, *J. Appl. Polymer Sci.*, 13 (1969) 2397.
23 M. CANTOW, R. S. PORTER AND J. F. JOHNSON, *J. Polymer Sci.*, A-1 5 (1967) 1391.
24 J. E. HAZELL, L. A. PRINCE AND H. E. STAPELFELDT, *J. Polymer Sci.*, C-21 (1968) 43.
25 I. A. BARANOVSKAYA, A. D. LITMANOVICH, M. S. PROTASOVA AND V. E. ESKIN, *Vysokomol. Soedin.*, 7 (1965) 509.
26 A. B. KISELEV AND YA. I. YASHIN, *Gaso-adsorbtsionnaya chromatografiya*, Nauka, Moscow, 1967.
27 E. G. ERENBURG, G. G. KAZTASHEVA, M. A. EREMINA AND I. YA. PODDUBNYI, *Vysokomol. Soedin.*, A-9 (1967) 2709.
28 I. E. MOORE, *J. Polymer Sci.*, A-2 (1964) 835.
29 R. R. STROMBERG, in P. WEISS AND G. D. CHEEVER (Editors), *Interface conversion for polymer coating*, Elsevier, New York, 1968, p. 321.
30 P. J. FLORY, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, 1953.