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Thin-layer Chromatography of Polymers

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A new method for the investigation of the polydispersity of polymers in terms of molecular weight, composition, regularity, and stereoregularity—the thin-layer chromatography of polymers—is described. The theoretical principles of the method, quantitative analysis, and its application to the study of various classes of polymers and oligomers are considered. The bibliography includes 102 references.

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I. INTRODUCTION

A major advance in the development of thin-layer chromatography (TLC) has been its application to the analysis of high polymers. The first studies on the TLC of statistical copolymers were carried out in 1968 simultaneously at the Analytical Laboratory of the Institute of Macromolecular Compounds of the USSR Academy of Sciences [1] and in Inagaki's laboratory at Kyoto University[2]. Since then the following principal trends have been established in this new field of chromatography [3-6]: the study of the heterogeneity of polymers [molecular weight distribution (MWD) and inhomogeneity with respect to composition]; identification (diagnosis) of polymers differing in microstructure; analysis of MWD and the functionality of oligomers.

Depending on the nature of the interactions in chromatographic systems, the following types of TLC of polymers are possible: (a) adsorption TLC of polymers (ATLC) in which differences in the adsorption activity of polymers are used, the differences increasing with increase of the molecular weight (MW) and the fraction of adsorption-active polar groups in the copolymer or oligomer; (b) thin-layer gel-permeation chromatography (TLGPC) based on the use of the molecular sieve effect, in which the separation of polymers is associated with the differences between the relative dimensions of the macromolecule and the dimensions of the pores in the adsorbent; (c) precipitation TLC of polymers (PTLC) based on differences between the solubilities of polymers having different molecular weights and different chemical structures; (d) extraction TLC (ETLC), in which polymers of different types are selectively dissolved in the initial spot on the "all or nothing" principle. These versions of the TLC of polymers can be usefully combined into two groups, differing in the mechanism of the fractionation of macromolecules: (1) adsorption methods (ATLC) with positive adsorption and TLGPC with negative adsorption; (2) methods based on differences between the solubilities of polymers (PTLC and ETLC).

At the present time TLC is used widely in the study of high-molecular-weight substances. Here one may point out that TLC is used successfully in the quantitative analysis of polymers: for the analysis of the molecular weight distribution (MWD) of homopolymers (ATLC, PTLC), statistical copolymers (PTLC), and oligomers (ATLC), the inhomogeneity of block and statistical copolymers with respect to composition (ATLC), the functionality of oligomers (ATLC), and the functionality of polymers (with $M < 5 \times 10^4$) having terminal adsorption-active groups (ATLC, ETLC). TLC is also employed for the quantitative analysis (diagnosis) of the branching of homopolymers and oligomers (ATLC) and the microstructure of polymers: the regularity of polybutadiene and polyisoprene (ATLC, ETLC), the stereoregularity of poly(methyl methacrylate) and polystyrene (ATLC, PTLC, ETLC), statistical, alternating, and block copolymers (ATLC) and two- and three-block copolymers (ATLC), and the analysis of the purity and homogeneity of polymer fractions, the admixture of homopolymers in block and graft copolymers (ATLC, PTLC, ETLC), and the side chains split off from graft copolymers and the corresponding homopolymers (ATLC). TLC is also used in combination with other chromatographic techniques [gel permeation (GPC) and pyrolytic gas chromatography (PGC)] in the analysis of complex polymer systems where the problems enumerated above are solved with the aid of TLC.

II. THIN-LAYER CHROMATOGRAPHY OF POLYMERS BASED ON ADSORPTION

1. Adsorption TLC (ATLC) of Copolymers

ATLC was the first version of the TLC of polymers developed by ourselves [1,7-9] and Inagaki [2] for the fractionation of statistical ST–MMA and ST–MA copolymers† with respect to composition. Eluent systems consisting of chlorinated hydrocarbons and solvents and adsorption-active oxygen compounds as displacing agents were used for the TLC of ST–MMA copolymers; they can be arranged in the following eluotropic series: ethyl ether < EMK < acetone < THF < dioxan; chlorobenzene < dichloroethane < chloroform. The copolymers were chromatographed in sandwich chambers (S-chambers), where a concentration gradient of the displacing agent was set up by its gradual evaporation into the air space within the chamber while flowing along the plate. High gradients were used to separate copolymers with large differences in composition (Fig. 1‡). ST and MMA copolymers, the elemental compositions of which are virtually indistinguishable, can be fractionated by high-resolution TLC with a weak displacing agent concentration gradient; for example, it is possible to observe differences in the polydispersity of copolymers having an azeotropic composition (with 54 mole % ST), obtained for different conversions. It was observed [3,7] that the R_f (relative migration) of the copolymer depends not only on the composition, but also on its molecular weight (for MW < 10^5). Similar results for the TLC of ST–MA statistical polymers were obtained in a study [2] where gradient TLX was used with addition of methyl and ethyl acetates to chloroform.

The distribution and inhomogeneity with respect to composition of many other statistical copolymers (styrene–butadiene, styrene–acrylonitrile, incompletely substituted cellulose nitrates and acetates, and ω-amino-acid copolymers) were investigated with the aid of ATLC—see Appendix (Table 1).

Inagaki established [10] that the chromatographic mobility of ST–MMA copolymers is related to their structure. Thus the R_f for these copolymers in the chloroform–ethyl acetate system increase in the following sequence: block copolymers < alternating copolymers < statistical copolymers; the values of R_f for block copolymers vary as a function of the number of blocks incorporated in them [11,12].

2. ATLC of Homopolymers

The considerable possibilities of ATLC for the separation of homopolymers on the basis of their molecular weights have been demonstrated [13]. Fig. 2 illustrates chromatograms for narrowly disperse polystyrenes ($M_w/M_n \leq 1.2$) on KSK silica gel plates in the cyclohexane–benzene–acetone system.

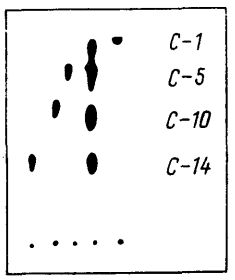


Figure 1. TLC of statistical ST–MMA copolymers on KSK silica gel in the 12 : 2.2 chloroform + acetone system in an S-chamber: C-14 (22% ST, $M_w = 2.3 \times 10^5$); C-10 (31% ST, $M_w = 8.8 \times 10^4$); C-5 (54% ST, $M_w = 8 \times 10^4$); C-1 (80% ST, $M_w = 1.2 \times 10^5$).

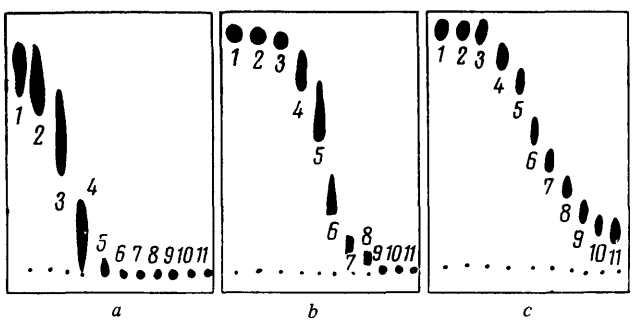


Figure 2. TLC of polystyrenes ($M_w/M_n \leq 1.2$) on KSK silica gel in the cyclohexane + benzene + acetone system: *a*) 13 : 3 : 1; *b*) 12 : 4 : 0.4; *c*) 12 : 4 : 0.7; 1) $M_n = 10^3 \times 0.9$; 2) $M_n = 10^3 \times 2.03$; M_w/M_n; 3) 5/4.5; *4*) 10.3/9; 5) 19.85/19.65; 6) 51/49; 7) 98.2/96.2; 8) 173/164; 9) 411/392; 10) 867/773; 11) 2145/1780.

If solvents with relatively low adsorption activity, for example, a mixture of cyclohexane and benzene, are used for the ATLC of polystyrene, then polystyrenes with MW > 10^5 do not form compact spots and are smeared over the plate, which is due to the low rate of the adsorption-desorption processes involving high-molecular-weight polymers in such systems.

It has also been possible to resolve PMMA by adsorption TLC in the 5 : 95 methanol–chloroform system [14,15] and PEO in the ethylene glycol–methanol system on silica gel and the methanol–DMF system on alumina on the basis of their molecular weights [16].

†The following abbreviations have been adopted in this review: ST = styrene, PS = polystyrene, MMA = methyl methacrylate, MA = methyl acrylate, PMMA = poly(methyl methacrylate), EO = ethylene oxide (epoxyethane], PEO = poly(ethylene oxide), PB = polybutadiene, BD = butadiene, P-α-methylstyrene, AN = acrylonitrile, PI = polyisoprene, CTA = cellulose triacetate, PVA = poly(vinyl acetate), ETP = ethylene terephthalate, PETP = poly(ethylene terephthalate), PPG = poly(propylene glycol), EMK = ethyl methyl ketone, THF = tetrahydrofuran, and DMF = dimethylformamide.

‡Fig. 1 and other figures represent contact photographs of thin-layer chromatograms.

3. Thin-Layer Gel-Permeation Chromatography of Polymers (TLGPC)

The possibility of separating polymers with the aid of TLC on the basis of the molecular sieve mechanism was first established by Halpaap and Klatyk[17], and the feasibility of its application to the analysis of TLGPC was first studied by Belenkii et al.[3] This form of TLC of polymers has also been studied in other investigations[18,19]. In order to reveal the molecular-sieve effect in TLC, it is necessary to suppress the adsorption activity of silica gel and to fill the adsorbent pores with the solvent before the start of elution. This can be achieved in two ways: with the aid of so-called pre-elution, i.e, by passing the solvent along the plate before depositing the sample[18], or by capillary condensation involving the preliminary saturation of the chromatographic layer on the plate with solvent vapour[3,13]. It has been shown[18] that the effectiveness of TLGPC in the separation of polymers on the basis of their molecular weights depends on the degree of saturation with the solvent of the adsorbent pores and of the space between the particles of the chromatographic layer. This is the reason for the differences in the effectiveness of TLGPC as a function of the thickness of the adsorbent layer and the direction of motion of the eluent (upwards or downwards) along the plate. For this reason, column GPC is more effective than TLGPC, where the packing density of the adsorbent is lower.

4. Fundamental Characteristics of Adsorption TLC Methods for Polymers (ATLC and TLGPC)

The adsorption of polymers has been studied in many theoretical and experimental investigations[20]. The most notable achievement in this field has been the prediction[21-24] of the phase transition occurring after the attainment of a critical value ϵ_{cr} in the energy of the interaction of the polymer unit with the adsorption surface (ϵ). In this transition all the properties of the adsorbed macromolecule change: its size, the fraction of adsorbed segments, and the sign of the free energy change (there is a transition from negative to positive adsorption), i.e. $-\Delta F = 0$ when $-\epsilon = -\epsilon_{cr}$. It has been shown theoretically[24] that these features are characteristic of the adsorption of isolated macromolecules both on a planar surface and within pores.

The chromatographic experiments made it possible to investigate the adsorption behaviour of macromolecules in the absence of concentration effects, i.e. one can study experimentally the behaviour of isolated macromolecules. These features of the adsorption behaviour of macromolecules have been tested experimentally[25] by TLC on silica gels in the hydrogen-form ensuring the energetic equivalence of the surfaces of silica gel adsorbents of different porosities[26]. Narrowly disperse PS were chromatographed in the $40:16:x$ cyclohexane–benzene–acetone system, where changes in the acetone content (x) regulated the energy of the interaction ($-\epsilon$) of the macromolecular segment with the adsorbent surface. The quantity $-\epsilon$ (in units of kT) can be expressed in the form $-\epsilon = \epsilon_{pa} - \epsilon_{sa}$, i.e. as the difference between the energies of the adsorption interactions of the polymer segment (ϵ_p) and the solvent (ϵ_{sa}). Since ϵ_p remains constant when the solvent composition is altered, ϵ is determined in terms of the quantity ϵ_s, which may be calculated by Snyder's method[27].

Fig. 3 presents PS chromatograms on KSK silica gel (pore diameter 100 Å).[25] Evidently, with increase of the acetone content and hence with decrease of $-\epsilon$, there is a gradual transition from adsorption to molecular sieve chromatography. The chromatograms illustrated in Fig. 3 have the following features: (1) with increase of $-\epsilon$ (i.e. with increase of x) in the region of the preferential operation of the molecular sieve effect (MSE), where negative adsorption is observed (Figs. 3*d*–3*f*), the R_f for the large PS macromolecules diminish; the macromolecules are, as it were, "drawn into" previously inaccessible pores, i.e. the limit corresponding to the exclusion of macromolecules from the pore space is determined not only by the MSE (the ratio of the dimensions of the macromolecules and pores) but also by the adsorption in the pores; (2) there exists a composition of the eluent for which the energy of the interaction of the molecular segments with silica gel is close to the critical value $-\epsilon_{cr}$ (Fig. 3*c*); PS molecules with different molecular weights then exhibit identical values of K_d and R_f and the macromolecules are, as it were, insensitive to the pore dimensions (zero adsorption); (3) on further decrease of x (on increase of $-\epsilon$), there is a transition to the region of positive adsorption (ATLC—Figs. 3*c* and 3*a*), where an increase of the molecular weight of the polymer entails a decrease of its R_f.

The free energies of the adsorption ($-\Delta F$) of the macromolecules can be readily evaluated from the thin-layer chromatograms. For this purpose, one may use the equation

$$R_f = \left(1 + \frac{V_p}{V_0} K_d\right)^{-1}, \qquad (1)$$

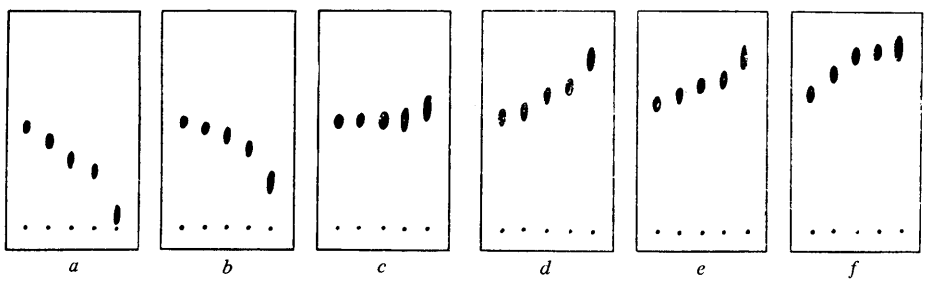


Figure 3. TLC of polystyrenes *5–9* (see Fig. 2) from left to right on KSK silica gel in the $40:16:x$ cyclohexane + benzene + acetone system; x: *a*) 1.5; *b*) 1.8; *c*) 2.0; *d*) 2.2; *e*) 2.5; *f*) 2.8; with preliminary saturation of the plate in solvent vapour for 2 h.

where V_p/V_0 is the ratio of the volumes of the pore and interparticle spaces in the adsorbent, as well as the expression

$$K_d = \exp\left(-\frac{\Delta F}{kT}\right). \quad (2)$$

Eqns.(1) and (2) make it possible to determine the ratio V_p/V_0, since we have $-\Delta F = 0$, $K_d = 1$, and

$$\frac{V_p}{V_0} = \left(\frac{1-R_f}{R_f}\right)_{-\varepsilon=-\varepsilon_{cr}} \quad (3)$$

when $-\epsilon = -\epsilon_{cr}$.

Fig. 4[25] illustrates the experimental relation between $-\Delta F/kT$ and $-\epsilon$, calculated by Eqns. (1) and (2) for silica gels of different porosity. The observed relation is similar to the theoretical relation[23]. Fig. 4 shows clearly the presence of two energy regions corresponding to the adsorption of macromolecules with energies smaller and greater than $-\epsilon_{cr}$ (the regions of negative and positive adsorption). The experimental relations for PS with different molecular weights then make an intercept on the abscissa axis at the same point, corresponding to $-\epsilon_{cr}$. At this point the entropy losses ΔS by the macromolecule on adsorption are fully compensated by the increase of the enthalpy ΔH:

$$\Delta F(-\varepsilon) = \Delta F(-\varepsilon_{cr}) = \Delta H - T\Delta S = 0 .$$

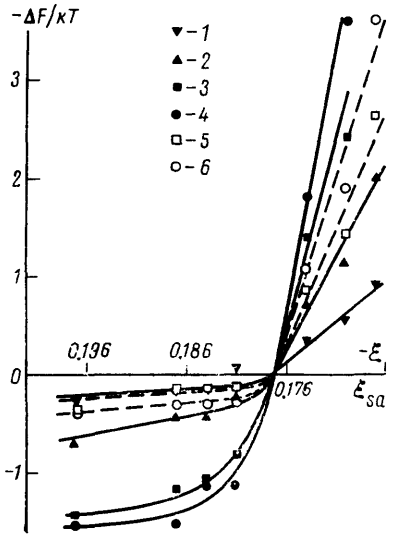


Figure 4. Dependence of the change in the free energy of PS macromolecules ($-\Delta F/kT$) on entering pores on the energies of the interaction of the macromolecular segment ($-\epsilon$) and solvent molecules (ϵ_{sa}) with the surface of the pores. Curves *1–4* represent data for KSK silica gel (pore diameter 100 Å) and curves *5* and *6* represent data for silochrome K-80 (pore diameter 500 Å); molecular weight of polystyrenes M_w: 1) 1.98×10^4; 2) 5.1×10^4; 3) and 5) 1.11×10^5; 4) and 6) 1.73×10^5.

It is possible to show with the aid of TLC on silica gels of different porosity using eluents of the same composition for the same values of $-\epsilon$) that, as the pore size increases, the TLGPC of polystyrene is transformed into ATLC at high acetone concentrations, i.e. with increase of pore size $-\epsilon_{cr}$ diminishes. The observation that, for high values of $-\epsilon$, the macromolecules enter small KSM silica gel pores and are adsorbed in the latter more strongly than in the large KSK and K-80 silica gel pores is of considerable interest[25]. This fundamentally new result conflicts with the results of a number of investigations[20] carried out in non-chromatographic concentration ranges, but is fully consistent with the theory[24].

Experiments[3] on the TLC of PS yielded a linear relation between $-\Delta F/kT$ and the number of segments (i.e. M_w) of the polymer (Fig. 5), which is consistent with the relation predicted by the theory[25]:

$$K_d = \exp(-\lambda_\epsilon N), \quad (4)$$

where λ_ϵ is the change in the free energy of the macromolecule per unit and N the number of polymer units. Using Eqn. (4), we can formulate an expression for R_f in the case of adsorption TLC of polymers:

$$R_f = \left(1 + \frac{V_p}{V_0}\exp(-\lambda_\epsilon N)\right)^{-1}. \quad (5)$$

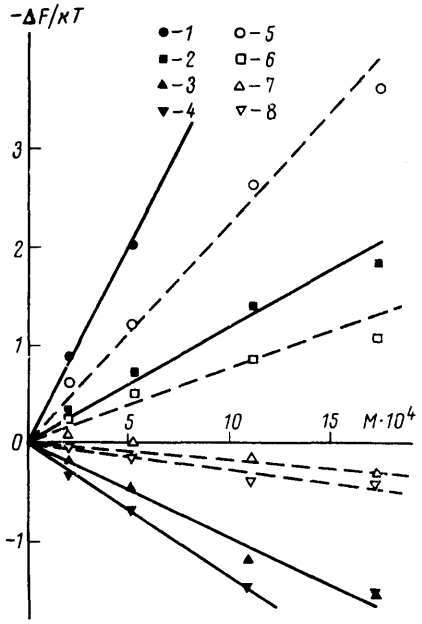


Figure 5. Dependence of the change in the free energy ($-\Delta F/kT$) of PS macromolecules on entering KSK silica gel (curves *1–4*) and silica gel K-80 (curves *5–8*) pores on the molecular weight. ϵ_{sa}: 1) and 5) 0.167; 2) and 6) 0.173; 3) and 7) 0.181; 4) and 8) 0.197.

Having differentiated Eqn. (5) with respect to N and λ_ϵ, we find that the sensitivity of R_f to the molecular weight of the polymer ($\partial R_f/\partial N$) decreases with increase of N and the dependence of $\partial R_f/\partial N$ on $-\lambda_\epsilon$ passes through an extremum near ϵ_{cr}. For each molecular weight there is a characteristic extremum in λ_ϵ, i.e. near the eluent composition;

consequently the region of the maximum sensitivity of TLC to the molecular weight of the polymer in each range of M_W values is characterised by the particular eluent composition, as can be seen in Fig. 2. The variation of the influence on R_f of the chemical composition of the polymer, characterised by $\lambda\epsilon$, i.e. of $\partial R_f/\partial\lambda\epsilon$, also passes through a maximum. It follows from studies of ATLC that the sensitivity of R_f to the copolymer composition persists at least up to $M_W \simeq 5 \times 10^5$.

It has been suggested in the literature [18,28-30] that in ATLC polymers are fractionated on the basis of their chemical compositions and not their molecular weights. In reality, when a binary or ternary mixture of solvents, preferably containing an adsorption-active component, is used instead of a pure solvent, it is always possible to obtain the value of $-\epsilon$ necessary for the separation of polymers over a fairly broad range of molecular weights, with R_f in the range 0.1–0.8. The upper limit to the molecular weights in the separation of polymers by the ATLC method is set by the low rates of adsorption and desorption processes involving high-molecular-weight polymers. However, by introducing an adsorption-active component into the eluent, for example acetone, it is possible to increase this limit significantly (Fig. 2*c*).

III. THIN-LAYER CHROMATOGRAPHY BASED ON DIFFERENCES BETWEEN THE SOLUBILITIES OF POLYMERS

Inagaki and coworkers [14,28] proposed precipitation TLC as the main method for the separation of polymers on the basis of their molecular weights. Precipitation TLC has been used successfully by these and other investigations in the fractionation of homopolymers [14,28,31,32] and statistical copolymers [30] in terms of their molecular weights, for the separation of atactic and syndiotactic PMMA [15], for the fractionation of ST–MMA block copolymers [32], and for the separation of block copolymers of this type and PMMA.[33]

1. Characteristics of the Precipitation and Extraction TLC of Polymers

The elementary step in precipitation TLC involves the separation of the polymer solution into a dilute phase and a concentrated gel phase, which is precipitated on the surface of the adsorbent particles; the dilute phase is removed with the solvent stream and the chromatographic process is thus achieved. In order to carry out precipitation TLC (PTLC), it is necessary to suppress the adsorption of the polymer. Hence arise two requirements which must be met by eluents: they must be adsorption-active and must at the same time be poor solvents for the polymer (the latter may be assessed with the aid of the Flory–Huggins solubility parameter [34] χ, which is defined as the change in free energy, in units of kT, on transferring a solvent molecule from the pure solvent to the polymer solution). When $\chi > 0.5$, the solubility of the polymer falls and the formation of the gel phase begins.

According to the Flory-Huggins theory [34], the phase separation of the polymer solution (at a constant temperature) can occur under the influence of two factors: (1) with increase of χ, i.e. when $\chi > 0.5$ or (2) with increase of the polymer concentration in solution φ_p (for $\chi \simeq 0.5$). χ may be increased by raising the content of the precipitant in the eluent composition, while the bulk-phase concentration of the polymer may be increased by altering the phase ratio r (the ratio of the volume of the eluent to the weight of the adsorbent). Since the removal of the dilute polymer phase with the stream of eluent is accompanied by the formation of a gel phase in equilibrium with it only when χ and φ_p are varied, an essential condition for PTLC is the creation of a solvent concentration gradient (i.e. χ) and (or) the establishment of the given phase ratio r on the plate. Two procedures are used for this purpose: (1) by the reduction of the solubility of the polymer, as the eluent rises along the plate, owing to the evaporation of the solvent in the unsaturated chromatographic chamber and by its frontal separation on the adsorbent layer (intrinsic PTLC); (2) by applying to the chromatographic plate an eluent in which the content of the solvent is increased (the extraction version of PTLC).

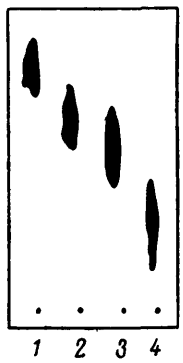


Figure 6. TLC of PMMA on silica gel in the 29 : 71 chloroform + methanol system. Molecular weight of PMMA M_W: 1) 4.3×10^4; 2) 1.14×10^5; 3) 1.65×10^5; 4) 4.12×10^5.

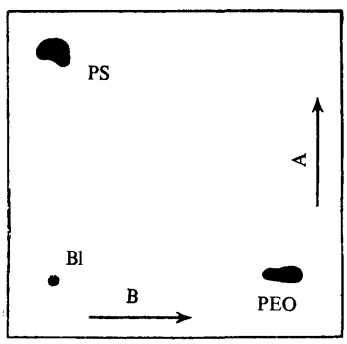


Figure 7. Two-dimensional TLC of a 50 : 50 ST-OE [EO?] block copolymer (Bl) on KSK silica gel in the 12 : 4 : 2 cyclohexane + benzene + acetone system in the *A* direction and in the 3 : 9 pyridine + water system in the *B* direction.

TLC based on the solubilities of polymers includes ETLC, where polymers with appreciably different solubilities are separated with the aid of a gradient-free eluent at the starting point on the "all or nothing" principle.

Examples of the extraction version of PTLC are provided by the separation of PS on the basis of their molecular weights following the addition to acetone of acetone–chloroform and acetone–toluene mixtures[31] and the separation of PMMA in the chloroform (solvent)–methanol (precipitant) system[14] (Fig. 6). An example of PTLC proper is the separation of PS in the 5 : 3 : 6 : 4 benzene–EMK–acetone–ethanol system, where the first two components are solvents and the last two are precipitants. Examples of ETLC are provided by the separation of isotactic and atactic PS and of the ST–EO block copolymer and the PS and PEO present in it[3] (Fig. 7). It has been stated in the literature that the effectiveness of fractionation on the basis of molecular weights is greater in ATLC and PTLC respectively in the regions where $M_W < 10^5$ and $M_W > 10^5$.[18,28-30] A combination of these methods is used in the study of the distribution in the polymer on the basis of its composition (ATLC) and its molecular weight (PTLC). For example, it has been used to separate statistical ST–BD copolymers in ethyl acetate and in the THF–methanol system[30]. The dependence of R_f on M_W and the mole fraction of ST is then determined by the equation $R_f = A + B[ST] - C_2 \lg M_W$, where A, B, and C_2 are constants. Similarly PS with terminal COOH groups are separated on the basis of their functionalities following successive elution with benzene and chlorobenzene (ATLC) and on the basis of the molecular weights in the 1 : 10 THF–acetone system to which THF has been added (PTLC).[36] Other examples of the employment of precipitation TLC in the analysis of polymers are given in the Appendix (Table II).

It is noteworthy that the main application of the PTLC of polymers involves fractionation on the basis of the molecular weights and determination of the molecular weight distribution. The molecular weight distributions of polystyrene found with the aid of PTLC and by the GPC method in columns have been compared[16,37]. The results agreed satisfactorily, but there is no doubt that the TLC method is inferior to GPC as regards the speed and accuracy of analysis. In the fractionation of polymers on the basis of their molecular weights, it is desirable to employ two-dimensional PTLC with the simultaneous analysis of the inhomogeneity of the polymers with respect to composition by means of ATLC.

The decrease of the solubility of the polymer in the presence of the support[19], while the chemical nature of the adsorbent and its porosity have no effect on the separation of polymers with the aid of PTLC (i.e. the precipitation of the polymer takes place on the outer surface of the adsorbent grain[35]) is important for the understanding of the PTLC mechanism.

2. The Formation of False Chromatographic Bands in Precipitation TLC of Polymers

In TLC in a solvent–precipitate system where the solvent does not exhibit adsorption activity while the precipitant does possess it (for example, in the chloroform–methanol system for PMMA[14]) there are two methanol concentration ranges where its content is less than 5% (ATLC) and more than 70% (PTLC) and R_f for the polymer changes from 0 to 1 (Fig. 8). This finding explains the formation of double chromatographic spots on plates in the PTLC of polymers (Fig. 9).[33] A PMMA chromatogram has been obtained (Fig. 9) with the starting spots applied to the plate along the diagonal. Evidently, with increase of the distance of the starting zones from the line along which the plate is immersed in the solvent, the substance is, as it were, pumped from the starting spot to the upper spot, moving with the eluent surface. The essential feature of this phenomenon consists in the frontal separation of the eluent into the chloroform and chloroform–methanol zones. On reaching the starting point, the diffuse front of the second zone dissolves PMMA until the methanol concentration rises above 80%. Naturally, the lower the flow rate of the eluent, i.e. the higher the position of the polymer starting zone on the plate, the greater the proportion of the polymer which is able to dissolve and pass to the upper chromatographic spot and the lower the residual amount of the polymer at the starting point.

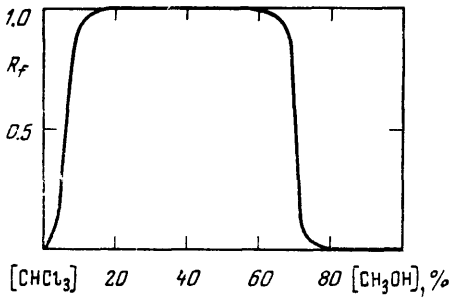


Figure 8. Dependence of R_f for PMMA with $M_W = 4.1 \times 10^5$ on the composition of the chloroform + methanol mixture in TLC on silica gel.

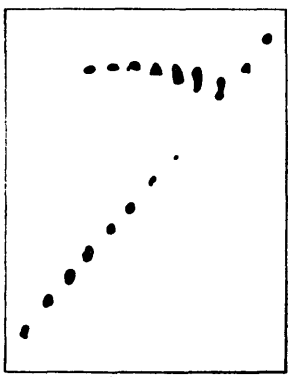


Figure 9. TLC for PMMA with $M_W = 10^5$ in the 6 : 16 chloroform + methanol system on KSK silica gel in an S-chamber (samples deposited along the diagonal of the plate).

IV. CONCENTRATION DEPENDENCE OF THE SHAPE OF THE CHROMATOGRAPHIC SPOT IN THE THIN-LAYER CHROMATOGRAPHY OF POLYMERS

The shape of the chromatographic spot is determined by the type of the adsorption isotherm (Fig. 10).[3] A concave isotherm is characteristic of weak adsorbability ($R_f \to 1$) and with increase of the concentration of the substance the chromatographic spot is extended towards

the rear (Fig. 10*c*). A convex isotherm is characteristic of strong adsorbability ($R_f \to 0$) and with increase of concentration the chromatographic spot is extended forward (Fig. 10*a*). When $R_f \simeq 0.5$, the adsorption isotherm is close to linearity and the shape of the chromatographic spot depends little on the concentration of the substances (Fig. 10*b*). Two-dimensional spreading in TLC leads to additional concentration effects. Along the sides of the chromatographic zone, the concentration of the substance diminishes and hence the velocity of the zone is determined by a partition coefficient different from that in the central zone. As a result, the spot assumes a sharper shape: in the front and in the rear it is characteristic of convex and concave adsorption isotherms respectively. In precipitation TLC the higher the polymer concentration in the chromatographic spot, the lower the precipitant concentration corresponding to the polymer solubility threshold and the spot is more extended in the direction opposite to that of the motion of the polymer on the plate.

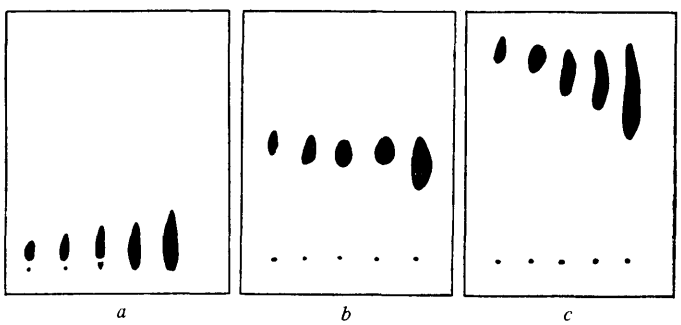


Figure 10. Concentration dependence of the shape of the chromatographic spot in TLC of PS with $M_W = 4 \times 10^5$ in cyclohexane + benzene + acetone systems: *a*) 12 : 4 : 0.25; *b*) 12 : 4 : 0.5; *c*) 12 : 4 : 1. 2, 5, 10, 20 and 40 μg of PS deposited from left to right.

The shape of the chromatographic spot in the TLC of polymers depends also on the characteristics of the viscous flow of the polymer solution along the plate. In the centre of the spot, where the polymer concentration is high, the velocity of the solvent is a minimum. In the peripheral regions it increases and reaches a maximum in the gaps between the chromatographic spots. As a result, the spot assumes a drop-like shape (Fig. 11) [4] characteristic of the streams formed when a viscous liquid flows past obstacles[38]. Under these conditions, the rear boundary of the spot undergoes additional sharpening by the incoming flow of liquid, which prevents the diffusional spreading of the spot, while in the front section of the zone the velocity of the diffusing molecules and the flow rate of the stream are added together[39]. These processes lead to instability of the chromatographic zone. It can assume an irregular shape and can actually be split into several spots moving separately.

V. TLC STUDY OF THE MICROSTRUCTURES OF POLYMERS

1. The Study of the Stereoregularity of Polymers

Inagaki and coworkers[15] showed that the separation of stereoregular polymers may be based on the differences between their solubilities. Using ethyl acetate as the eluent, Inagaki and coworkers succeeded in separating by ETLC [40] isotactic (*i*) PMMA, which remained in the starting spot, from syndiotactic (*s*) and atactic (*a*) PMMA, which moved with the solvent front. When the elution is carried out with acetone[41], *i*-PMMA is also desorbed, but the 1 : 1 stereocomplex of *i*-PMMA and *s*-PMMA remains at the starting point; thus 2 : 1 and 1 : 2 mixtures of these polymers appear on the chromatogram as two spots—at the starting point and near the solvent front. The lower spot represents the 1 : 1 stereocomplex and the upper spot corresponds to *i*-PMMA or *s*-PMMA respectively. Stereoblock PMMA with a high content of iso- and syndio-tactic triads can also be separated with the aid of TLC.[40]

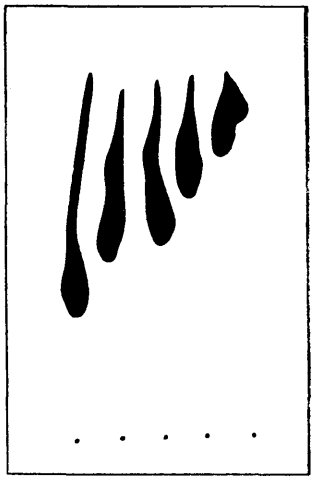


Figure 11. The "viscous" form of the chromatographic spot of PS with $M_W = 8.7 \times 10^5$ in TLC on KSK silica gel in benzene; 100, 40, 30, 20 and 10 μg of PS deposited from left to right.

We obtained analogous results[4] in the TLC of polystyrene (Fig. 9). It was shown that *a*-PMMA and *s*-PMMA may be separated[41] with the aid of ATLC in the ethyl acetate–isopropyl acetate system and with the aid of PTLC in the acetonitrile–methanol system. Under these conditions, R_f is found to depend not only on the content of syndiotactic triads (Ts) but also on M_W: $R'_f = 1.73\,[Ts] - 0.51 \lg M_W - 2.2$ in the acetonitrile–methanol system and $R''_f = -1.74\,[Ts] - 0.08 \lg M_W + 6.0$ in the ethyl acetate–isopropyl acetate system. [Ts] and M_W for PMMA may be determined to within approximately 10% with the aid of the above equations.

The conditions found for the isolation of *i*- and *s*-PMMA by ATLC were used for preparative isolation of *i*-PMMA from their mixture by adsorbing *i*-PMMA on silica gel

from solution in chloroform. The *i*-PMMA obtained in this way was 80–90% pure[42].

2. The Study of the Regularity and Isomerism of Polybutadienes and Polyisoprenes

1,4-*trans*-, 1,4-*cis*-, and 1,2-Polybutadienes can be separated by ATLC in tetrachloroethane and by ETLC in pentyl chloride on silica gel and alumina plates[43]. This method may be used to test the homogeneity of the so-called equibinary PB in which 1,4-*cis*- and 1,2-vinylbutadiene units are present. In TLC in tetrachloroethane these polymers move with the solvent front; on the other hand, when the specimen is a mixture of 1,4-*cis*- and 1,2-PB, they are separated into the corresponding zones on the plate.

It has been shown[44] that 3,4-vinyl-PI can be separated from 1,4-*cis*- and 1,4-*trans*-PI with the aid of ATLC in tetrachloroethane, while in the 20 : 80 cyclohexane–*p*-xylene system 3,4-vinyl- and 1,4-*trans*-PI can be separated from 1,4-*cis*-PI.

3. TLC of Block Copolymers

The possibility of separating two-block and three-block ST–MMA copolymers with the aid of ATLC in gradient-free tetrachloroethane–EMK systems to which EMK is added has been demonstrated[32]. Under these conditions, R_f is independent of the molecular weight of the copolymer. Fig.12 shows[32] that R_f for ST–MMA copolymers having the same composition increases in the sequence statistical < three-block < two-block copolymers. ST–BD block copolymers can be separated by ATLC in the 9 : 1 cyclohexane–chloroform system with gradual addition of chloroform[11]. R_f for ST–BD copolymers increases in the following sequence: two-block (ST–BD) < three-block (ST–BD–ST) copolymers (i.e. two- and three-block ST–BD copolymers move on the plate in a sequence different to that of the analogous ST–MMA copolymers). In this chromatographic system R_f for the ST–BD copolymers is independent of their molecular weight. When PTLC is used in the 3 : 2 chloroform–methanol system with addition of methanol, the ST–BD block copolymers can be separated on the basis of their molecular weights.

The application of these chromatographic systems made it possible to establish with the aid of two-dimensional TLC that the Kraton 1101 industrial block copolymer consists of three components: two three-block copolymers having the same composition but different molecular weights and PS with $M_W = 10^4$. These data agreed with the results of GPC analysis using two detectors (refractometric and spectrophotometric), which permitted a direct determination of the compositions of the copolymers chromatographed.

The conditions found for the ATLC of ST–MMA copolymers, where R_f depends only on the copolymer composition, enabled Inagaki and coworkers[45] to suggest a method for the determination of the inhomogeneity of these copolymers with respect to composition (Section VII, 3), based on the densitometry of thin-layer chromatograms at two wavelengths: $\lambda_1 = 225$ nm (where the ST and MMA units absorb) and $\lambda_2 = 265$ nm, where only the ST units absorb. The distribution of two- and three-block ST–MMA copolymers with respect to composition, investigated by this method, showed that it corresponds fully to the distribution obtained by cross-fractionation and calculated on the assumption of a random mechanism of the coupling of the blocks in anionic polymerisation.

In the TLC of block copolymers one can use the precipitation mechanism instead of the adsorption mechanism. In a solvent which is ineffective in relation to one of the blocks the block copolymer enriched in this particular block then frequently undergoes selective precipitation. Thus, in order to separate PMMA from the ST–MMA block copolymer, a chloroform–methanol gradient system may be employed. Since PS is initially precipitated in this system and then PMMA, as the chloroform content is reduced, in the PTLC of PMMA and the ST–MMA block copolymer in an S-chamber, one can employ a system having a composition (with 72–80% of methanol depending on the molecular weight of PMMA) such that the copolymer remains at the start. $R_f < 1$ for PMMA under these conditions, since the concentration of methanol in the eluent becomes sufficient for the precipitation of PMMA at a certain height as a result of the gradual evaporation from the plate.

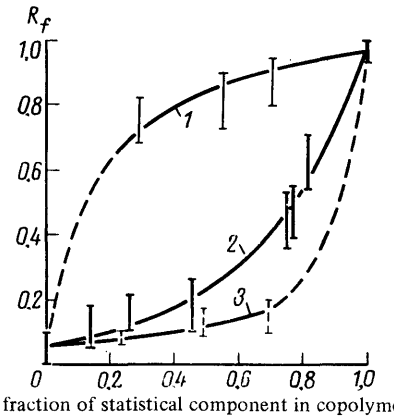


Figure 12. Separation of statistical (curve *1*), three-block (MMA–ST–MMA) (curve *2*), and two-block (curve *3*) ST–MMA copolymers using EMK gradients ranging from 0 to 2.5 in the EMK + carbon tetrachloride system.

In the study of block copolymers the determination of the admixture of homopolymers plays an important role. In this type of analysis of the EO–ST block copolymer use was made of two-dimensional ETLC [3] (Fig.7), which makes it possible to separate the corresponding homopolymers from the EO–ST block copolymer. This copolymer may be subjected to analogous analysis by one-dimensional TLC on microcrystalline cellulose in the 9 : 1 ethyl acetate–methanol system[46]. Under these conditions, PS moves with the solvent front, the block copolymer passes to the centre of the plate, and PEO remains at the start. Wesslen and Nansson[46] developed a preparative method for the isolation of the block copolymer by column chromatography: PS was separated by elution with ethyl acetate, the block copolymer was then eluted with a 4 : 1 mixture of ethyl acetate and methanol, and finally PEO was eluted with methanol; the column chromatography was checked by TLC.

4. TLC of Graft Copolymers

In the analysis of graft copolymers TLC is used to determine their purity, to detect the presence of homopolymers corresponding to the main and side chains, and to separate the polymers forming their grafted side chains (after the cleavage of the main chain of the graft copolymer) and the homopolymers present in the graft copolymer (Section VIII, 3).

The use of TLC for the solution of the first problem was first demonstrated[3] in the separation of the ST–MMA graft copolymer, PS, and PMMA. Methods have been proposed[47] for the separation of copolymers of PS grafted on CTA, PVA, PETP, and polyamide, and of PMMA grafted on PVA from the corresponding homopolymers with the aid of flow ATLC. The separation conditions discovered made it possible to proceed to preparative adsorption chromatography on columns, whereupon a PS–CTA graft copolymer contains less than 0.5–1% of impurities was obtained in quantitative yield.

It is of interest to use TLC in the study of impact-resistant PS. Here ETLC in EMK on silica gel[44] was employed to separate PS from the PS–PBD graft copolymer (see Appendix, Table III).

VI. THIN-LAYER CHROMATOGRAPHY OF OLIGOMERS

1. Principal Characteristics of the TLC of Oligomers

The TLC of many classes of oligomers has been described: polyols[48–58], polyethers[59–63], polyolefins[64], and polyamides[65]. Most of the studies demonstrated the possibility of separating oligomers differing in the number and structure of terminal groups. Many investigators[48–50,58,61] demonstrated the independence of the chromatographic behaviour of oligomers of their molecular weights, while the differences in the R_f values are determined solely by the number of functional groups present in the oligomers. This makes it possible to achieve an extremely important form of the analysis of oligomers—the determination of their functionality[66], which is responsible for the quality of the high polymers obtained from oligomers, for example, polyurethane. On the other hand, substituted polyoxyethylenes can be separated on the basis of their molecular weights, with isolation of the individual polymer homologues in terms of the degree of polymerisation[12–15]. It has been shown[57] that the efficiency of the separation of polyols on the basis of their molecular weights is related to the type of substituent blocking the hydroxyl in the terminal units. The more hydrophobic the substituent (i.e. apparently the greater the bulk of the hydrocarbon group of the substituent and hence the lower the adsorbability of the terminal units), the greater the efficiency of the separation of the oligomers into individual homologues.

The characteristics of the adsorption of oligomers are associated with the presence of terminal functional groups. These terminal units as a rule show a greater adsorption activity than the central units of the oligomer and the change in the free energy of the latter on adsorption is determined mainly by the adsorption of the terminal groups. The free energy of adsorption ($-\Delta F$) of oligomers is associated with the decrease of the entropy ΔS, owing to the decrease of the number of possible conformations of the oligomer on adsorption, and with the increase of the enthalpy of the system $-\Delta H$ on formation of contacts between the units of one mole of the oligomer and the adsorbent surface:

$$-\frac{\Delta H}{RT} = N_A[(-\varepsilon_t)N_t + (-\varepsilon_c)(N - N_t)], \qquad (6)$$

where $-\epsilon_t$ and $-\epsilon_c$ are the energies of the interaction of the terminal and central units with the adsorbent surface in units of kT, N and N_t are the total number of units and the number of terminal units in the oligomer molecule, and N_A is the Avogadro number. The partition coefficient in adsorption is expressed as follows:

$$K_d = \exp\left(-\frac{\Delta F}{RT}\right) = \exp\left(-\frac{N_A \Delta F_M}{RT}\right) = \exp\left(-\frac{\Delta F_M}{kT}\right), \qquad (7)$$

where $-\Delta F_M$ is the free energy of adsorption of one molecule of the oligomer. One can specify an energy $-\epsilon_0$ such that the enthalpy of adsorption fully compensates the decrease of entropy and $-\Delta F_M = 0$. Then $-\Delta F/kT$ for the oligomer undergoing adsorption is

$$-\frac{\Delta F}{kT} = [(-\varepsilon_t) - (-\varepsilon_0)]N_t + [(-\varepsilon_c) - (\varepsilon_0)](N - N_t). \qquad (8)$$

We shall consider the influence of the relative values of $-\epsilon_c$ and $-\epsilon_0$ (in TLC, we always have $-\epsilon_c > -\epsilon_0$) on the R_f of oligomers in ATLC: $R_f = 1/[1 + (V_p/V_0)\exp(-\Delta F_M/kT)]$. There can be three instances of the dependence of R_f on N (i.e. on the molecular weight of the oligomer):

(1) $(-\epsilon_c) > (-\epsilon_0)$; $-\Delta F/kT = [(-\epsilon_t) - (-\epsilon_0)]N_t + [(-\epsilon_c) - (-\epsilon_0)](N - N_t)$, where R_f decreases with increase of N;

(2) $(-\epsilon_c) < (-\epsilon_0)$; $-\Delta F/kT = [(-\epsilon_t) - (-\epsilon_0)]N_t - [(-\epsilon_c) - (-\epsilon_0)](N - N_t)$, where R_f increases with increase N;

(3) $(-\epsilon_c) = (-\epsilon_0)$; $-\Delta F/kT = [(-\epsilon_t) - (-\epsilon_0)]N_t$, where R_f is independent of N and is determined by the number of terminal groups N_t.

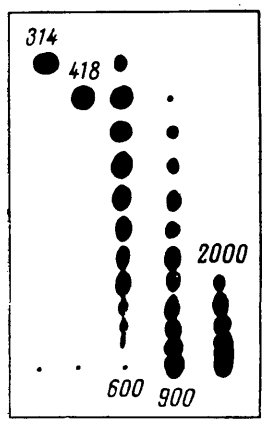


Figure 13. TLC of oligomers: PS with M_n = 314, 418, 600, 900, and 2000 in the 14 : 3 cyclohexane + benzene system on KSK silica gel.

It is noteworthy that in the absence of functional groups ($N_t = 0$) only the dependence of the first type can be observed. Fig. 13 illustrates chromatograms of PS oligomers of this type[67,68]. Clearly the dependence of R_f on the molecular weight of oligomers with $N_t = 0$ will be manifested to the greatest extent. On the other hand, when

the oligomer contains functional groups, the dependence of R_f on the molecular weight becomes less marked with increase of the differences between $-\epsilon_t$ and $-\epsilon_c$.

Fig. 14 illustrates the TLC of poly(ethylene oxide) with M_n = 300, 400, and 600 in chromatographic systems where the dependence of R_f on the molecular weight is of the first, second, and third type[67]. Attention should be drawn to the correspondence of the polymer homologues in poly(ethylene oxides) with different molecular weights. The dependence of R_f on the molecular weight of poly(ethylene oxide) shown in Fig. 14*b* is characteristic of the molecular sieve effect, but the mechanism of TLC is in this case different since the oligomers investigated begin to be excluded from the pore space of these adsorbents when the molecular weight exceeds 10^4. The moon shape of the chromatographic spot is associated (see above) with the convex adsorption isotherms for polyols. It is noteworthy that an effective separation on the basis of molecular weights of oligomers with weakly adsorption-active central units (for example, polydimethylsiloxanediols) is impossible without blocking the terminal groups. However, even when the terminal hydroxyls are blocked, (for example, by the dinitrobenzoic acid residue) only the second type of dependence of R_f on the molecular weight can be obtained.

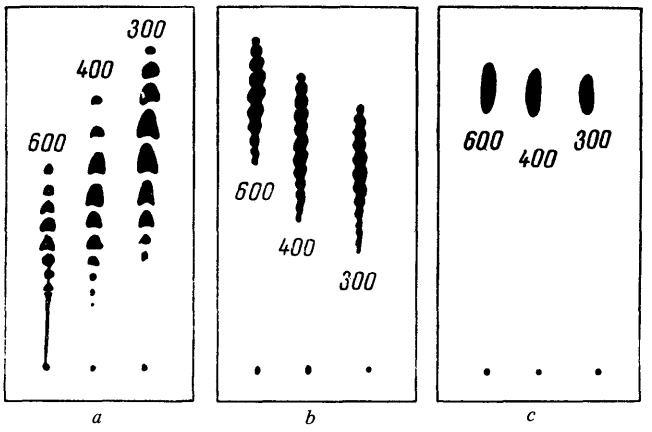


Figure 14. TLC of poly(ethylene oxides) with M_n = 300, 400, and 600: *a*) on KSK silica gel in the 0.1 : 10 pyridine + water system; *b*) on alumina in the 10 : 1 chloroform + ethanol system; *c*) on KSK silica gel in the 5 : 1 chloroform + pyridine system.

2. Separation of Oligomers on the Basis of Their Functionality

The separation of oligomers on the basis of their functionality in the absence of a dependence of R_f on the molecular weight (third type of dependence of R_f for the oligomer on the molecular weight) is of great practical interest. The possibility of separating mono-ols, diols, and triols over a wide range of molecular weights is illustrated in Fig. 15 in relation to polyoxypropylenepolyols (POPP).[68] This method for the determination of the functionality of oligomers makes it possible to separate linear and branched oligomers differing in the number of terminal functional groups. The separation of linear and branched oligomers with the same molecular weight is of great analytical interest, because it has been established[69] that in GPC they emerge with the same retention volumes. Thus the molecular weight distribution of oligoethers obtained with the aid of GPC may be significantly supplemented by information about the distribution of branched polyfunctional oligoethers in the specimen analysed.

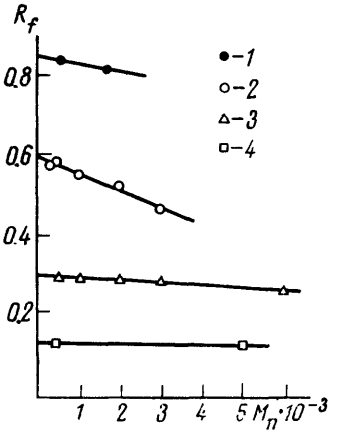


Figure 15. Dependence of R_f for polyoxypropylenepolyols (POPP) on their molecular weight and functionality on KSK silica gel in ethyl acetate saturated with water and containing 2% EMK: 1) mono-ols; 2) diols; 3) triols; 4) pentols.

VII. DETERMINATION OF POLYMER MOLECULAR WEIGHT AND COMPOSITION DISTRIBUTIONS FROM THIN-LAYER CHROMATOGRAPHIC DATA

1. Quantitative Interpretation of Thin-Layer Chromatograms of Polymers

Two fundamentally different methods for the quantitative analysis of thin-layer chromatograms are known[70]. The first is based on the extraction of the substance from the layer of adsorbent on the chromatographic plate with its subsequent determination, and the second involves the analysis of the substance directly in the chromatographic spot *in situ* from the distribution of the concentrations of the compounds in the spot[71,72] or from its size[73,74], the second method being more accurate and sensitive. For quantitative calculations on chromatograms of polymers from the distribution of concentrations or from the size of the spot, it is necessary to be able to view the chromatogram in visible light (i.e. it must be made visible), photographed, and then scanned to determine the distribution of the polymer concentrations in the chromatographic spot, or or to obtain with the aid of high-contrast photography the image of the polymer zone with distinct boundaries and, having measured the distance between the latter, to find the distribution of the spots with respect to size. Having

at one's disposal more sophisticated methods and equipment, for example, luminescence and ultraviolet photographic techniques and scanning ultraviolet densitometers and fluorimeters, it is possible to reduce the number of stages required for quantitative analysis. Each stage introduces its own error into the result, but in certain cases the more complex procedure has advantages over the simpler method. For example, the linear relation between the blackening occurring when the spot is made visible by means of a corroding reagent and the polymer concentration in the spot is retained up to a concentration of 200 $\mu g\ cm^{-2}$ in photodensitometry in the visible part of the spectrum, which is much higher than in the direct densitometry in the ultraviolet [2,3,7,16,40]. Furthermore, direct densitometry is possible only when the polymer contains chromophores strongly absorbing ultraviolet light, for example, styrene units. In this case the linear dependence of the signal on the amount of substance is maintained up to 100 $\mu g\ cm^{-2}$. Direct densitometry (particularly in reflected light) suffers also from other disadvantages, associated with the mutual influence of the monomer units of the polymer on their extinction and the preferential accumulation of the polymer in the lower layer of adsorbent adjoining the glass support. On the other hand, direct densitometry in the ultraviolet made it possible to suggest an absolute method for the determination of the inhomogeneity of copolymers with respect to composition by scanning their chromatographic zones on the plate at two wavelengths.

An interesting and promising version of quantitative TLC of polymers when the latter are separated into discrete zones involves the use for this purpose of a flame-ionisation detector (FID), the quartz plate with the deposited layer of silica gel being drawn directly through the flame [72].

In the analysis of radioactive polymers by TLC the method of lumoautoradiography [73], which makes it possible to determine up to 10^{-9} c of tritium without using complex apparatus, may prove to be very useful.

It is possible to distinguish the following varieties of quantitative TLC: (a) in terms of the method used to detect the chromatographic spots (by making them visible, by direct photography, and by direct detection on scanning); (b) in terms of the photographic process (photography in the visible or ultraviolet regions, lumoautoradiography, luminescence photography, equidense photography and ultrahigh-contrast photocopying); (c) in terms of the type of scanning (direct scanning of the chromatogram or of its photographic image); (d) in terms of the type of detecting system (detection using photometry, fluorimetry, radiometry, or a flame-ionisation detector); (e) in terms of the method used to carry out calculations on the chromatograms (based on the distribution of the concentrations of the given substance and the dimensions of the spot).

Evidently different combinations of these processes make it possible to obtain a multiplicity of different versions of quantitative TLC, about which the following comments may be made: methods based on procedures for rendering the chromatograph visible and direct photography consist of many stages and are therefore very time consuming. However, these methods, particularly those involving calculations on chromatograms based on the size of the spot, do not require expensive equipment. On the other hand, such equipment (scanning ultraviolet densitometers, fluorimeters, radiometers, FID) makes it possible to employ high-speed methods for the direct scanning of thin-layer chromatograms with an improved accuracy of the analysis. Methods involving ultraviolet and luminescence photography of chromatograms and lumoautoradiography occupy an intermediate place (as regards the speed of analysis and the complexity of equipment). Less expensive photometers, scanning in the visible region of the spectrum, are used in this case.

Methods for calculations on chromatograms, based on scanning and the determination of the size of the chromatographic zone, are considered below in relation to the analysis of the polydispersity of polymers.

As can be seen from the foregoing considerations, in order to determine the distribution of the molecular weights or compositions from TLC data, it is necessary (a) to make the polymer zone visible on the chromatogram (by dyeing it)§, (b) to determine the dependence of R_f for the polymer on the fractionating **X** (the molecular weight of the polymer) or on the composition of the copolymer, i.e. $R_f(X)$ must be found, (c) to measure the dependence of the sensitivity of the detection (the ratio of the surface concentration of the given substance c to the colour intensity i) on R_f, i.e. to determine $(dc/R_f)di$, (d) to measure the distribution of the colour intensity in the section of the chromatographic spot along the y axis, in the direction of motion of the spot, as a function of R_f, i.e. $I = I(R_f)$, where $I(R_f) = \int_{-\infty}^{+\infty} i(R_f, y)dy$, (e) to determine the distribution of the polymer in the chromatographic spot along the x axis, i.e. $Q(R_f) = I(R_f)$: $(dc/R_f)di$, where $Q\int_{-\infty}^{+\infty} c(y)dy$, and finally (f), knowing $R_f(x)$, to obtain the normalised differential distribution of the molecular weights of the polymer or the compositions of the copolymer:

$$P(X) = \tilde{Q}(R_f) \cdot \left|\frac{dR_f}{dX}\right|, \qquad (10)$$

where $\tilde{Q}(R_f)$ is the normalised distribution $Q(R_f)$:

$$\tilde{Q}(R_f) = Q(R_f) \Big/ \int_0^1 Q(R_f)\,dR_f,$$

$$\int_0^1 \tilde{Q}(R_f)\,dR_f = 1.$$

In the study of narrowly disperse polymers it is necessary, in addition, to correct $Q(R_f)$ for chromatographic spreading—for example by means of two-dimensional chromatography (Fig. 16). The chromatogram of the polymer along the first direction, which is homogeneous with respect to the molecular weight (composition) along the spot diameter, may be regarded as the starting zone for chromatography in the second direction.

The difference between the dispersions of the zones at the finish and at the start in the direction of the second chromatographic process constitutes the dispersion of the chromatographic spreading. The correction may be applied in the simplest way by substracting the dispersion

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§A 1% solution of iodine in methanol [2], a saturated solution of Thymol Blue in 50% aqueous ethanol with subsequent treatment with 3 N H_2SO_4, [37] a 5% solution of $KMnO_4$ in concentrated H_2SO_4, [3] and, for oxygen-containing polymers, Dragendorff reagents [3] and iodine vapour [46] are most frequently used for this purpose. It is possible to detect PS on plates from the extinction of the luminescence due to a phosphor introduced into the chromatographic layer and excited with ultraviolet radiation at 254 μm.

of the chromatographic spreading from the dispersion of the distribution, or by a more complex and rigorous procedure, as in the analysis of the molecular weight distribution of polymers by the GPC method [75].

The normalised integral distribution $P(X) = \int_0^X F(X')dX'$ and the weight-average quantity $\bar{X} = \int_0^\infty XF(X)dX$ may be obtained from the weight distribution of the polymer $P(X)$ [Eqn. (10)].

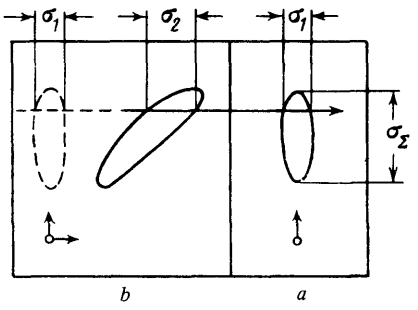


Figure 16. Determination of the chromatographic spreading in TLC: *a*) chromatogram along the first direction; *b*) two-dimensional chromatogram.

2. Photometric Method for Quantitative TLC of Polymers

In the photometric scanning of the polymer zone along the chromatographic axis (x), multistep scanning with an accurate light probe and integration of the signal with respect to the y axis, perpendicular to the chromatographic axis, is necessary in order to obtain accurate results. These integral properties represent the distribution $I(R_f)$ with an accuracy which is inversely proportional to the size of the step Δx. In order to determine the distribution of the compositions of the copolymers (provided that R_f for the copolymer is independent of its molecular weight), the method based on the scanning of the chromatographic plate at two wavelengths (265 and 225 nm), at which the molar extinction coefficients of the copolymer components differ markedly, has been proposed [45]. The absorption I at point x, corresponding to the fraction X of ST in the copolymer is then given by $I'(x) = X\epsilon'_{ST}W(x)$ for $\lambda' = 265$ nm and $I''(x) = [X\epsilon''_{ST} + (1 + X)\epsilon''_{MMA}]W(x)$ for $\lambda'' = 225$ nm, where $W(x)$ is the amount of polymer in the region $(x \pm \Delta x)/2$ and ϵ is the molar extinction coefficient.

Having determined the areas A' and A'' under the densitograms of the polymer, using $I'(x)$ and $I''(x)$, and knowing $(\epsilon''_{ST}/\epsilon''_{MMA})$ and $(\epsilon'_{ST}/\epsilon''_{MMA})$, it is then possible to calculate the following characteristics of the copolymer:

(a) the normalised weight distribution of the copolymer $\tilde{P}(X)$:

$$\tilde{P}(X) = \frac{W(x)}{\sum_i W_i(x)} = \frac{[1 - (\epsilon''_{ST}/\epsilon''_{MMA})]I'(x) + (\epsilon'_{ST}/\epsilon''_{MMA})I''(x)}{[1 - (\epsilon''_{ST}/\epsilon''_{MMA})]A' + (\epsilon'_{ST}/\epsilon''_{MMA})A''}; \quad (11)$$

(b) the calibration relation $X(x)$:

$$X(x) = \frac{I'(x)}{[1 - (\epsilon''_{ST}/\epsilon''_{MMA})]I'(x) + (\epsilon'_{ST}/\epsilon''_{MMA})I''(x)}; \quad (12)$$

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

$$\bar{X} = \frac{A'}{[1 - (\epsilon''_{ST}/\epsilon''_{MMA})]A' + (\epsilon'_{ST}/\epsilon''_{MMA})A''} \quad (13)$$

without using reference copolymer specimens for the calibration of $X(x)$. The parameters $\epsilon'_{ST}/\epsilon''_{MMA}$ may be determined by Eqn. (12) from the known values of $\epsilon'_{ST}/\epsilon''_{MMA}$ and the average composition of the copolymer $\bar{X}$ determined independently.

3. Analysis of the Distribution of a Polydisperse Polymer Along the Width of the Chromatographic Zone

Since the distribution of the substance along the y axis in TLC is always described by a Gaussian curve, it is possible to determine the amount of substance in the given section (ith along the x axis) of the polymer zone on the chromatographic plate, having measured the width of the zone at a specific boundary (limiting detectable) concentration C_b. For a Gaussian distribution of the substance, we have

$$C_b = C_{m,i}\exp\left(-\frac{y_i^2}{8\sigma_{y,i}^2}\right), \quad (14)$$

where $C_{m,i}$ and $\sigma^2_{y,i}$ are the concentration of the polymer at the maximum and the variance of the distribution in the ith (along the x axis) section of the zone and y_i is the distance along the y axis between the points C_b (the width of the zone in the ith section). The amount of substance in the ith section with the width Δx is then expressed as follows:

$$W_i = \sqrt{2\pi}\bar{C}_{m,i}\bar{\sigma}_{y,i}\,\Delta x = \sqrt{2\pi}k_i D_b\,\sigma_{yi}\Delta x\exp\left\{\frac{\bar{y}_i^2}{8\bar{\sigma}_{y,i}^2}\right\}; \quad (15)$$

where the width of the zone $\bar{y}_i$ and the variance $\bar{\sigma}^2_{y,i}$ are averaged with respect to Δx and C_b is replaced by the corresponding optical density D_b ($C_b = k_i D_b$, where k is a coefficient, which is constant for a homopolymer and which depends on the composition for a copolymer). In order to be able to use Eqn. (15), it is necessary to determine $\bar{\sigma}_{y,i}$ having expressed it in terms of the experimental width of the chromatographic zone $\bar{y}_i$. For this purpose, one can employ two procedures: (a) two chromatograms of the polymer containing different amounts of the substance, Q_1 and Q_2, are obtained, whereupon in each ith section in the two chromatographic zones the ratio of the amounts of the substance $W'_i/W''_i = Q_1/Q_2$, or (b) the polymer chromatogram is photographed with two different exposures, so that the contour of the spot corresponds to different values of C_b (i.e. D_b) and the ratio D'_b/D''_b is determined.

The corresponding formulae for the calculation of the distribution $\tilde{P}_i = W_i/\sum_i W_i$ by methods (a) and (b) are as follows:

$$\text{(a)}\ \tilde{P}_i = \frac{[ka^{1/2}b^{y_1^2/a}]_i}{\sum_i [ka^{1/2}b^{y_1^2/a}]_i\big|_{b=e}} = \frac{[ka^{1/2}\exp(y_2^2/a)]_i}{\sum_i [ka^{1/2}\exp(y_1^2/a)]_i}, \quad (16)$$

$$a = y_1^2 - y_2^2,\quad b = Q_1/Q_2;$$

$$\text{(b)}\ \tilde{P}_i = \frac{[k(a')^{1/2}c^{(y')^2/a'}]_i}{\sum_i [k(a')^{1/2}c^{(y')^2/a'}]_i},$$

$$a' = (y')^2 - (y'')^2,\quad c = D'_b/D''_b. \quad (17)$$

If method (a) is used to determine $\bar{P}_i$, it is convenient to employ chromatograms on which polymers have been deposited in proportions $Q_1/Q_2 = e$, whereupon Eqn. (16) for $\bar{P}_i$ simplifies.

As already stated, k = const. in the TLC of homopolymers or copolymers with narrowly disperse compositions and may be omitted from Eqns. (16) and (17). In the analysis of copolymers with polydisperse compositions, it is necessary to take into account the dependence of k on the composition of the copolymer (or R_f) and P_i must be calculated from Eqns. (16) and (17).

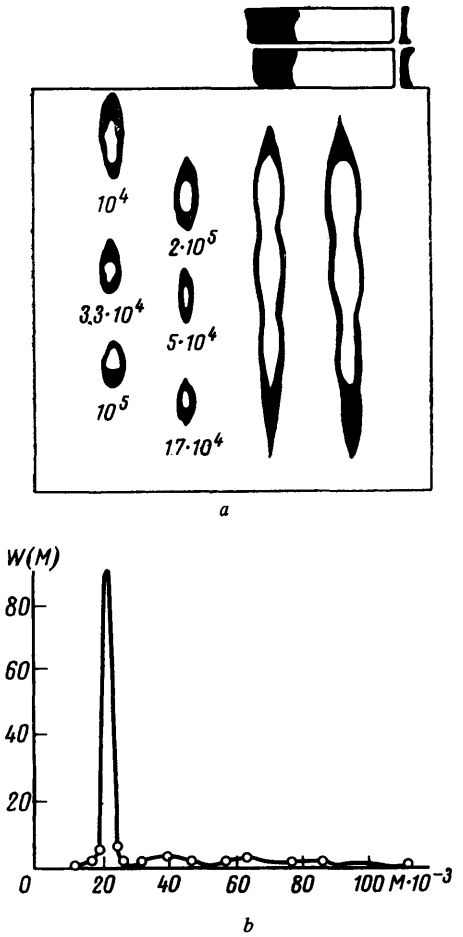


Figure 17. Determination of the molecular weight distribution in polystyrene by the equidense method: *a*) equidense representation of the chromatograms of PS specimens at two concentrations in the 12 : 4 : 0.9 cyclohexane + benzene + acetone system (on the left—chromatograms of reference PS specimens; above—image of optical wedge); *b*) molecular weight distribution in polystyrene.

Among the equations presented for the calculation of P_i, Eqn. (17) is of great interest, since its application requires only one chromatogram and there are no errors associated with the inaccuracy in the deposition onto the plate of calculated amounts of the polymers, Q_1 and Q_2, and with concentration effects distorting the shape of the chromatographic spot. In order to employ Eqn. (17), it is necessary to know D_b. An equidense method of obtaining the images of the chromatographic spot, based on the Sabatier phenomenon, which is well known in photography[76] (consisting in the complete or partial reversal of a briefly developed image under the influence of secondary illumination), was devised for this purpose[4]. An equidense image is achieved if a print is obtained, with a certain exposure, from the object for which photometric measurements are being made (the negative, in our case the thin-layer chromatographic plate), on a high-contrast photographic material, is developed for a short time, and, without fixation, is re-exposed to uniform secondary illumination. After redevelopment, the images of the chromatographic spots (equidense images) consist of pale contours of the spots against a dark background. The optical density D of the given equidense image of the object is determined by the duration of the first exposure. By varying this duration, it is possible to obtain equidense images corresponding to different optical densities $D_b^{(i)}$, which can be readily determined by photographing a calibrated optical wedge together with the object for which photometric measurements are made. In order to increase the contrast of the image, it is useful to photocopy the equidense image on an ultrahigh-contrast photographic material, which yields black equidense images against a light background.

The accuracy of the equidensitometric method of quantitative analysis discussed above was tested[4] by determining on the chromatograms the ratios of two polymers whose mixture had been deposited on the plate in proportions Q'/Q''. The ratios of 2.48 and 0.592 obtained agree satisfactorily with the ratios Q'/Q'' of the polymers in the samples (2.5 and 0.6). Fig. 17 illustrates an example of the analysis of the molecular weight distribution of PS by the equidensitometric method[4]. It is noteworthy that, owing to the relatively low sensitivity of the width of the chromatographic spot to the amount of substance it contains, the method described is inferior as regards accuracy to densitometric scanning methods in quantitative analysis. On the other hand, by virtue of the enhanced dependence of y on q on the wings of the curve, which is characteristic of a Gaussian distribution, the proposed method is particularly sensitive to the determination of microimpurities.

4. Determination of the Distribution of the Molecular Weights of Oligomers Using Equidense Images of Thin-Layer Chromatograms

A characteristic feature of the TLC of oligomers is the discrete nature of the chromatographic zones of individual polymer homologues up to $N \leq N'$, where $N' = 10$–12. Polymer homologues with higher molecular weights ($N > N'$) are chromatographed in the form of a continuous zone, which may be analysed in the same way as the chromatograms of high-molecular-weight polymers. If the limiting detectable concentration of the substance on the chromatograms is denoted by C_b, then the equation of the ellipse surrounding the chromatographic spot (x_b, y_b) is[77]:

$$C_b = \frac{q}{2\pi\sigma_x\sigma_y}\exp\left[-\frac{1}{2}\left(\frac{x_b^2}{\sigma_x^2}+\frac{y_b^2}{\sigma_y^2}\right)\right], \qquad (18)$$

where q is the amount of substance in the chromatographic spot and σ_x^2 and σ_y^2 are the variances of the distribution of the substance along the x and y axes. By denoting the half-axes of the ellipse by x_0 and y_0 (for $y = 0$ and $x = 0$ respectively), we obtain from Eqn. (18)

$$\frac{x_0^2}{\sigma_x^2} = \frac{y_0^2}{\sigma_y^2}. \qquad (19)$$

Using Eqn. (18) with $x_b = x_0$ and $y = 0$, and replacing σ_y with the aid of Eqn. (19), we have

$$q = 2\pi C_b \sigma_x^2 \frac{y_0}{x_0} \exp\left[\frac{1}{2}\frac{x_0^2}{\sigma_x^2}\right] = 2\pi k D_b \sigma_x^2 \frac{y_0}{x_0} \exp\left[\frac{1}{2}\frac{x_0^2}{\sigma_x^2}\right]. \qquad (20)$$

If two equidense images of the chromatogram with optical densities D'_b and D''_b are used, it is possible to obtain with the aid of two corresponding equations of type (20) an expression for q which includes only the experimentally determined quantities D_b, x_0, and y_0, obtained for two exposures:

$$q = 2\pi k D'_b \frac{(x''_0)^2 - (x'_0)^2}{2 \ln\left[\frac{D'_b}{D''_b} \cdot \frac{y'_0/x'_0}{y''_0/x''_0}\right]} \cdot \frac{y''_0}{x''_0} \left(\frac{D'_b}{D''_b} \cdot \frac{y'_0/x'_0}{y''_0/x''_0}\right)^{\frac{x'_0}{(x''_0)^2-(x'_0)^2}}. \qquad (21)$$

It is also possible to find the amount of substance in the unresolved spots on the chromatograms (where $i > N'$). Using the $R_f(i)$ calibration relation in the form of a second-degree polynomial $R_f(i) = a + bi + ci^2$, where the coefficients a, b, and c are obtained by the method of least squares, we find the values of R_f for $i > N'$. Next, linear extrapolation (valid for $R_f < 1/3$) yields the values of x'_i, x''_i, y'_i, and y''_i for $i > N'$, using the values of the above quantities for $i = N'$ and $i = N' - 1$.

5. Quantitative Determination of Low-Functional Impurities in Polyoxypropylenepolyols with the Aid of TLC

A method based on the dependence of the mobility of the chromatographic spot on its oligomer content is used for the quantitative determination of low-functional components in polyoxypropylenepolyols[69]. The chromatographic spots of polyoxypropylenepolyols have a sharpened forward "tip" with a sharply defined leading boundary, while the rear front is diffuse. As stated above, this shape of the chromatographic zone is due to the concentration effects associated with a convex adsorption isotherm. It is natural to employ the chromatographic mobility of the "tip" of the chromatographic spot, which is related to the polymer concentration; R_f for the tip may be measured accurately in order to determine the amount of oligomer which it contains (under conditions such that R_f is independent of the molecular weight). An experimental test showed that this type of relation does exist (Fig. 18).[69] It is linear and retains a constant slope in a concentration range corresponding to two orders of magnitude, the slope of the straight line being related to the molecular weight of polyoxypropylenepolyol and the distance traversed by the substance on the chromatographic plate. A similar relation may be obtained theoretically on the basis of a simplified model of the ATLC of oligomers, where the adsorption is characterised by the Freundlich equation.

The proposed method for the quantitative analysis of thin-layer chromatograms is distinguished by its extreme simplicitiy; its error does not exceed 2–3%. Admixtures ($\leq$ 1–2%) of the mono-ol and diol in the specimens of polyoxypropylenepolyols can be determined by the above procedure[69].

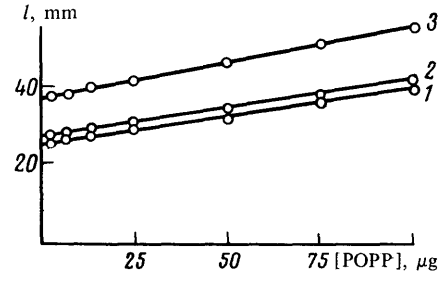


Figure 18. Dependence of the length of the chromatographic spot l on the amount of POPP with different M_n 1) 10^3; 2) 425; 3) 10^3 (40% EMK was added to the system) in TLC on silica gel in ethyl acetate saturated with water and containing 2% EMK.

6. The Use of a Scanning Flame-Ionisation Detector for the Quantitative TLC of Polymers with Separation of the Components into Individual Zones

The employment of a TLC–FID combination for the quantitative analysis of polymers, separated into individual zones, i.e. for the investigation of mixtures of fairly heterogeneous polymers has been described. The system described by Padley[72], where TLC is carried out on a quartz rod 0.45 mm in diameter coated by a layer of silica gel 75 μm thick, is used for this purpose; the polymer is deposited in an amount of several μg. After the completion of chromatographic process, the quartz rod is drawn through an FID during several tens of seconds.

The TLC–FID combination[44] has been used to determine the PS impurity in a copolymer obtained by grafting PS on to CTA, PS being separated by flow ETLC in EMK, and for the analysis of the functionality (the content of COOH and OH groups) of low-molecular-weight rubbers using the 100 : 1 carbon tetrachloride–THF system, in which PB molecules were separated into bifunctional molecules ($R_f = 0$), monofunctional molecules ($R_f = 0.3$), and molecules without functional groups ($R_f = 1.0$).

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

In the synthesis of complex polymer systems, such as block copolymers, graft copolymers, and branched homopolymers the corresponding linear homopolymers are obtained together with the main product, which is characterised by its polydispersity with respect to molecular weight and composition (type of branching). The study of such polydisperse systems has constituted hitherto an extremely complex and laborious task and frequently could not be achieved at all by the classical methods for the analysis of polymers. Important results in this field may be obtained by using a combination of chromatographic

methods for the analysis of polymers, GPC for the micropreparative fractionation of polymers involving the determination of the hydrodynamic radii R_S of the fractions obtained, TLC for the qualitative and quantitative analysis of the structural and chemical heterogeneity of the fractions, and pyrolytic gas chromatography (PGC) for the determination of their overall composition. The PGC method is unequalled under these conditions as regards the sensitivity of the analysis (it requires an amount of substance of the order of several μg) and as regards the accuracy of the determination of the composition of copolymers with a component ratio less than 1/20–1/50.[78]

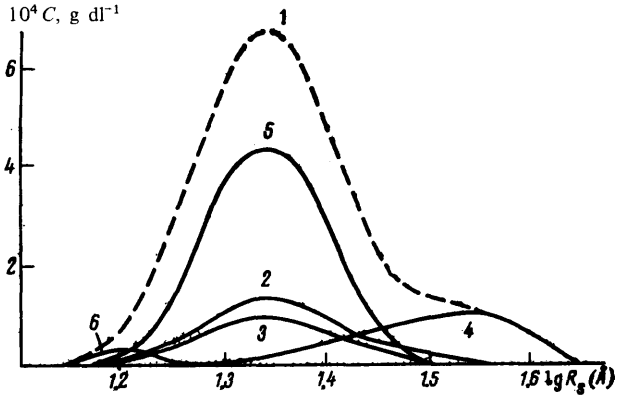


Figure 19. Concentration distribution curves for a PS specimen (curve *1*) and its components (curves *2–6*) as a function of the logarithm of the hydrodynamic radius lgR_S.

1. The Study of Mixtures of Linear and Branched Polymers by Gel-Permeation and Thin-Layer Chromatographic Methods

The possibility of studying a mixture of linear and branched PS using GPC and TLC has been demonstrated[79]. The micropreparative fractionation of the PS investigated has been achieved by means of GPC with determination of the hydrodynamic radius R_S of each fraction. For this purpose, use was made of the calibration relation obtained for linear PS specimens. Next, the GPC fractions were studied by ATLC methods in the 12 : 4 : γ cyclohexane–benzene–acetone system on KSK silica gel plates. In each fraction several components were detected with different dependences of R_f on the acetone content in the system (γ).[78] Some of these components behave similarly to the linear PS standards; they were identified as linear PS. Others show a weaker dependence of R_f on γ; these components were identified as branched PS and it was suggested that the differences between the adsorbabilities of linear and branched PS must increase with increase of the degree of branching. The GPC fractions were analysed quantitatively with the aid of a densitometer[79], which made it possible to obtain the distribution of the linear and branched components in the PS specimen, illustrated in Fig. 19.[78] In conformity with the $R_f(\gamma)$ relation, these PS components were identified as branched (components 1 and 2), weakly branched (component 3), and linear (components 4 and 5). Assuming that the PS components form a continuous series ranging from linear to strongly branched, it was possible to conclude that the fifth component is true linear PS, while the fourth, third, second, and first components are respectively branched PS with one, two, three, and four units. It is now possible to employ the familiar relation[80] between R_S and the molecular weights of branched polymers, which is of the following form for PS: $R_S = 0.255\ hM^{1/2}$, where h is the branching factor and M the molecular weight. Since the PS investigated were synthesised with polystyryl-lithium as the initiator, they should have a comb-like structure. The corresponding values of h were selected for this model[81], which made it possible to obtain the molecular weights of the main and side chains of this branched polymer. Table 1[79] presents the results of a similar analysis of one of the PS specimens. It is noteworthy that 2 mg of the polymer was sufficient for such detailed analysis of the narrowly disperse PS specimen (with $M_W/M_n < 1.1$). The molecular weights of linear (found with the aid of TLC and PGC) and branched specimens and their branching parameters were determined, and component 5, whose content in the specimen analysed was 1–4%, was characterised.

Table 1. Results of the analysis of a polystyrene specimen (comb-like model).

Parameters	Component				
	branched			linear	
	1	2	3	4	5
R_S, Å	20.5	21.5	32.5	22.5	16.5
MW of polymer	10 500	10 600	19 500	10 500	5500
MW of backbone	5 000	5 000	—	—	—
MW of branch	1 400	1 900	—	—	—
Content of component, %	23	15	16	42	4

2. Determination of the Polydispersity of Styrene–Methyl Methacrylate Block Copolymers with the Aid of Gel-Permeation, Thin-Layer, and Pyrolytic Gas Chromatography

The determination of the polydispersity of block copolymers includes the analysis of the distribution of their molecular weights, compositions, and admixtures of the corresponding homopolymers. It has been shown[33] that the polydispersity of block copolymers can be effectively studied with the aid of a combination of chromatographic methods with the following sequence of chromatographic operations. After the preliminary fractionation of the macromolecules in terms of size (by the GPC method), the fractions obtained are again chromatographed (this time by TLC), with respect to composition, and the block copolymer is separated from the admixture of homopolymers; finally, using PGC,[78] the compositions of the fractions obtained by the GPC and TLC methods are determined. The above procedure was used to investigate a block copolymer of the ABA type (where A = PMMA and B = PS).

The PGC method makes it possible to determine to within 1–2% the overall compositions of fractions containing the ST and MMA polymers, regardless of their molecular weight and chemical structure. The amount of specimens sufficient for analysis is 0.1–5 μg, and the

method can therefore be used both for the analysis of the GPC fractions and the fractions separated with the aid of TLC. Interesting possibilities arise from a comparison of the compositions of the complete fraction and its separated components. It is easily shown that, when the compositions of two fractions, obtained with the aid of TLC, namely $x = m_1'/m_2'$ and $y = m_1''/m_2''$, and of the initial fraction (obtained by GPC), namely $z = m_1'''/m_2'''$, are known, then the ratio of the components separated by TLC ($\omega = q_1/q_2$) may be determined by the equation

$$\omega = \frac{(z-x)(1+y)}{(1+x)(y-z)}. \qquad (22)$$

The block copolymer analysed was fractionated with the aid of GPC[33] in DMF on styrogel columns calibrated with respect to the R_S, and PMMA was fractionated simultaneously on similar columns. The fractions were analysed by PTLC in the chloroform-methanol system containing 80–72% of methanol as a function of R_S of the GPC fraction analysed (the molecular weight of PMMA). In this system PMMA moved along the plate, while the block copolymer remained at the start. Analysis of the GPC and TLC fractions by PGC made it possible to calculate by Eqn.(22) the content of the block copolymer in each fraction and, knowing the composition of the fraction and the increments in the refractive indices for PS and PMMA, to obtain (taking into account the additivity of the refractive indices in the copolymer solution[82]) the distribution in the block copolymer specimen analysed of the PS and PMMA components and the composition of the block copolymer as a function of R_S, as shown in Fig. 20.[33]

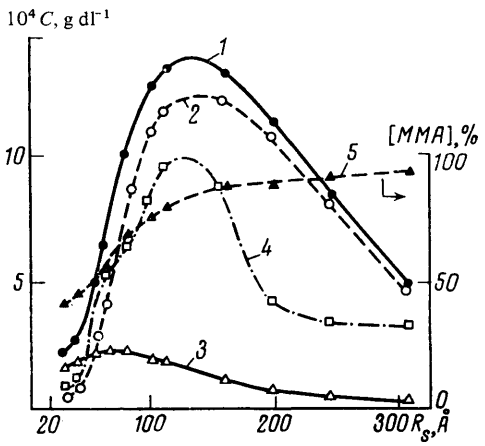


Figure 20. Distribution of PMMA–PS–PMMA block copolymers and PS and PMMA homopolymers as a function of R_S according to GPC, TLC, and PGC data: 1) initial polymer; 2) PMMA; 3) PS; 4) block copolymer; 5) PMMA content in block copolymer.

An interesting application of the combination of the two-detector (refractometer, spectrophotometer) GPC of an ST–BD block copolymer (with the simultaneous determination of its molecular weight distribution and compositions) and TLC for the investigation of the sequence of blocks in the copolymer has been demonstrated[83]. Since TLC established that the entire copolymer is of the three-block type, it was concluded that its bimodal distribution in GPC is associated with the presence of two types of three-block copolymers having different molecular weights.

3. Investigations of Graft Cellulose Copolymers with the Aid of Gel-Permeation and Thin-Layer Chromatography

In the study of gel copolymers it is usually necessary to establish whether the corresponding free homopolymers are present. TLC may be used for this purpose, as shown in relation to a PS–PMMA graft copolymer[3]. Another type of study of graft cellulose copolymers is based on the disruption of the cellulose base by acid hydrolysis or acetolysis and the determination of the molecular characteristics of the liberated graft homopolymer. However, difficulties are encountered here in the separation of the graft homopolymer and the homopolymer present as an admixture in the copolymer. A version of this method, proposed[84] for the study of a cellulose–styrene graft copolymer, consists in the acid hydrolysis of the copolymer, the separation of the free and grafted PS by adsorption TLC, and the determination of the molecular weight distribution of its PS by GPC. The polystyrene chains split off in the acid hydrolysis of the graft copolymer contain polysaccharide units at their ends, which exhibit a high adsorption activity. This, at first sight striking, high sensitivity of ATLC to the terminal glucosidic group of PS with $M = 10^5$ is co-related with the observed[36] sensitivity of ATLC in the separation of PS with $M = 5 \times 10^4 - 10^5$ and different numbers of terminal carboxy-groups.

Table 2. Results of the GPC analysis of polystyrene in the copolymer obtained by grafting PS on cellulose.

Specimen	$10^{-5}M_n$	$10^{-5}M_w$	M_w/M_n
PS after hydrolysis—PS_{tot}	2.8	13.0	4.65
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

Thus the free and grafted PS may be separated with the aid of ATLC on silica gel plates using THF as the eluent. The lower (starting) spot consists of grafted PS and the zone moving with the solvent front is free PS. If the chromatogram is developed by gradual spraying with a saturated solution of Thymol Blue in 50% aqueous ethanol and 3 N H_2SO_4, then the intensity of the blackening of the upper and lower spots makes it possible to determine the fraction of grafted PS (P_g) in the total amount of PS. Polystyrene was extracted from the plate with the aid of THF and its molecular weight distribution was determined by GPC on styrogel columns in THF. The observed values of M_w and M_n are listed in Table 2.[71] These data make it possible to determine the frequency index of the graft (F_g)—the ratio of the average number of polystyrene chains to the average number of cellulose chains in the graft

copolymer: $F_g = [AP_g/M_n.(PS_{tot})][100/M_n\ (\text{cellulose})]$, where A is the increase in the weight of cellulose after PS has been grafted (expressed as a percentage) [71].

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The thin-layer chromatography of polymers is a universal method for the study of the polydispersity of polymers and the diagnosis of different types of regularity and stereoregularity. This method combines all the useful features of TLC: simple apparatus, high sensitivity and speed of analysis, and comparative ease of selection of separating systems. At the same time the TLC of polymers also suffers from limitations: a relatively low reproducibility and the necessity to use in many instances reference polymer specimens (which may be obtained and characterised with the aid of GPC): however, the high sensitivity of TLC results in an economical use of such reference specimens.

Further progress in the TLC of polymers will involve the standardisation of analytical methods, in the first place quantitative methods, and the extension of the applications of this method to new classes of polymers and types of polydispersity. There is no doubt that the present development of the TLC method permits its effective employment both in the study of new polymers and in the industrial control of manufactured polymeric materials.

IX. APPENDIX

Table I. The use of adsorption chromatography in the study of polymers (on silica gel as the adsorbent). The following notation has been adopted: (MWD) = quantitative determination of MWD; (IC) = quantitative determination of inhomogeneity with respect to composition; an arrow represents the eluent gradient.

Polymer	Polydispersity investigated	Eluent	Method of development*	Refs.
	Homopolymers			
PMMA	w.r.t. MW (2×10^3 – 1.5×10^6)	chloroform + acetone (12:3.7)	1	101
PMMA	w.r.t. stereoregularity (separation of *a*- and *s*-PMMA from *i*-PMMA)	ethyl acetate	2	40
PMMA	Separation of the stereocomplex of *i*- and *s*-PMMA from *i*- and *s*-PMMA	acetone	2	41, 85
PMMA	Separation of *s*- and *a*-PMMA and w.r.t. MW (2×10^5–1.2×10^6)	isopropyl acetate + ethyl acetate (8:25)	2	15
PB	Separation of *trans*-1,4- and 1,2-vinyl-PB from *cis*-1,4-PB	carbon tetrachloride	3	43
PI	Separation of *trans*-1,4- and 3,4-vinyl-PI from *cis*-1,4-PI	cyclohexane + *p*-xylene (20:80)	3	44
PI	Separation of 3,4-vinyl-PI from *cis*-1,4-PI and *trans*-1,4-PI	carbon tetrachloride–*p*-xylene	3	44
PS	w.r.t. MW (from 314 to 2×10^6)	cyclohexane + benzene + acetone (40:16:0.4–2)	1	3, 13
PS	Separation of linear and branched polymers	cyclohexane + benzene + + acetone (40:16:0.4–1.5)	1	78
PS	Separation of 4-pointed star from linear polymer	cyclohexane + benzene (50:50) (25:75)	4	44, 86
PEO	w.r.t. MW (3×10^2–2×10^4)	water + pyridine (9:1), THF	5	101
	Statistical copolymers (co)			
Poly(ST-co-MA)	w.r.t. composition (IC) (9.98–76% ST)	carbon tetrachloride + methylacetate (5:1) → methyl acetate	2	2

Table I (cont'd.)

Polymer	Polydispersity investigated	Eluent	Method of development*	Refs.
Poly(ST-co-MA)	w.r.t. composition (9.98–76% ST)	chloroform → ethyl acetate	2	2
Poly(ST-co-MMA)	w.r.t. composition (22–80% ST)	chloroform, dichloroethane, chlorobenzene + ethyl ether, EMK, acetone, dioxan, THF	1	1,3,7
Poly(ST-co-MMA) (azeotropic)	w.r.t. composition (54% ST)	chloroform + ethyl ether (12:4.2)	1	3,7
Poly(ST-co-MA)	Separation of statistical, alternating, and block copolymers	carbon tetrachloride + methyl acetate (5:1) → methyl acetate	2	12
Poly(ST-co-MMA)	Separation of statistical, alternating, and block copolymers	chloroform + ethyl acetate (25:5) → ethyl acetate, chloroform → ethyl acetate	2	12
Poly(ST-co-AN)	w.r.t. composition (15–31.2% AN)	chloroform + methyl acetate	2	87,88
Poly(ST-co-AN)	w.r.t. composition (IC) (up to 60% AN)	dichloroethylene → ethyl acetate	2	44
Poly(ST-co-AN)	w.r.t. composition (18.7–50.7% AN)	benzene, toluene → acetone	2	89,90
Poly(ST-co-BD)	w.r.t. composition (5–60% ST)	cyclohexane + benzene	4	91
Poly(ST-co-BD)	w.r.t. composition (IC) (14.6–62.4% ST)	carbon tetrachloride → chloroform + carbon tetrachloride (20:50)	4	30
Poly(ST-co-Bd)	Separation of statistical, alternating, and block copolymers	cyclohexane + chloroform (9:1) → chloroform, cyclohexane + chloroform (140:75)	4	11
Cellulose acetate	w.r.t. composition (IC) (52.5–60.5% CA)	dichloromethane + methanol (85:15)	6	92
Cellulose nitrate	w.r.t. composition (IC)	acetone + ethyl acetate (20:3) → chloroform + ethyl acetate (1:2)	6	93
Poly(ω-aminocapron. λ-co-aminolauryls)	w.r.t. composition	formic acid, formic acid + phenol	8	93
	Block copolymers			
Poly(ST-block-MMA)	w.r.t. composition (IC) (13.5–80.5% ST)	carbon tetrachloride → EMK	2	45
Poly(ST-block-MMA)	w.r.t. MW (68×10^3) and w.r.t. composition (9.1–53.7% ST)	nitroethane → acetone, carbon tetrachloride → methyl acetate, benzene → EMK	2	32
Poly(ST-block-MMA)	Block sequence (AB and ABA)	carbon tetrachloride + EMK**	2	45
Poly(ST-block-MMA)	Separation of PS, separation of block copolymer from PMMA	chloroform, benzene + EMK	4	84
Poly(ST-block-BD)	Block sequence (AB and ABA)	cyclohexane + chloroform (9:1) → chloroform	2	11
Poly(ST-block-BD)	Separation of statistical, two-block, and three-block copolymers	cyclohexane + chloroform (140:75)	4	84
Poly(ST-block-BD)	Separation of two-block copolymers from three-block copolymers	carbon tetrachloride***	4	84
Poly(ST-block-BD)	Separation of two-block and three-block copolymers	carbon tetrachloride + n-hexane*** (9:1)	4	84
Poly(ST-block-EO)	Separation of PS	cyclohexane + benzene + acetone (12:4:2)	1,5	3,7
" "	Separation of PEO	pyridine + water (3:7)	1,5	3,7
	Graft copolymers (gr)			
Poly(MMA-gr-ST)	Separation of PMMA and PS	acetone + acetic acid (12:2)	1	3,7
" "	Separation of PMMA and PS	chloroform + EMK (12:2)	1	3,7
" "	Separation of graft copolymer and PS from PMMA	cyclohexane + benzene + acetone (12:4:0.7)	1	3,7
" "	Separation of PS and PMMA from graft copolymer	acetone + acetic acid (12:2)	1	3,7
Poly(cellulose-gr-ST)	Separation of PS	THF, benzene	4	84
Poly(CTA-gr-ST)	Separation of CTA	dichloromethane + methanol (1:1), chloroform + dioxan (3:1)	7	47
" "	Separation of PS	chloroform	7	47
Poly(PVA-gr-ST)	Separation of PVA	methanol + water (9:1)	7	47
" "	Separation of PS	chloroform	7	47
Poly(PVA-gr-MMA)	Separation of PVA	methanol + water (9:1)	8	47
" "	Separation of PMMA	EMK + carbon tetrachloride (8:2)	8	47
Poly(nylon-gr-ST)	Separation of nylon	formic acid	8	47
" "	Separation of PS	chloroform	8	47
Poly(ETP-gr-ST)	Separation of PETP	phenol + water (75:25)	9	47
" "	Separation of PS	chloroform	9	47

Table I (cont'd.).

Polymer	Polydispersity investigated	Eluent	Method of development	Refs.
Poly(cellulose-gr-ST)	Separation of PS and graft PS	THF	4	71,84
Poly(BD-gr-ST)	Separation of PS and (PS-block-BD) copolymer	carbon tetrachloride + chloroform	4	44

*Methods of development: 1) 3% $KMnO_4$ in concentrated H_2SO_4, with subsequent heating to 180°C; 2) 1% I_2 in methanol; 3) 14.7% H_2SO_4, with subsequent heating to 100°C; 4) saturated solution of Thymol Blue in 1:1 ethanol-water mixture, with subsequent spraying with 3 N H_2SO_4; 5) Dragendorff reagent; 6) 10% H_2SO_4, with subsequent heating to 110°C; 7) 10% $HClO_4$; 8) 0.05 N I_2; 9) Kayalon Fast Brown R solution in water-methanol mixture.

**The ratio depends on the composition of the block copolymer.

***Adsorbent — Al_2O_3.

Table II. The use of precipitation TLC in the study of polymers* (adsorbent-silica gel).

Polymer	Polydispersity investigated	Eluent	Method of development	Refs.
	Homopolymers			
PS	w.r.t. MW (1.98×10^4–5.1×10^4)	chloroform + acetone (10:1) → chloroform	4	44,86
PS	w.r.t MW (10^4–2×10^4)	acetone	10***	31
PS	w.r.t. MW (10^4–1.6×10^5)	acetone + chloroform	10	31
PS	w.r.t. MW (10^4–10^6)	acetone → acetone + chloroform (95:5–70:30)	10	31
PS	Ditto	acetone → acetone + THF (95:5–70:30)	10	31
PS	"	acetone → acetone + toluene (95:5–70:30)	10	31
PS	w.r.t. MW (10^4–10^6)	benzene + isopropyl alcohol (64.2–35.8)	10	16
PS	w.r.t. MW (10^4–10^6), (MWD)	dioxan + methanol (71.4:28.6) (θ)	7	16
PS	w.r.t. MW (10^4–10^6) (MWD)	acetone + isopropyl alcohol (96:4) → acetone + chloroform + isopropyl alcohol (66:30:4)	7	16
PS	w.r.t. MW (2×10^4–8.6×10^5)	dioxan + isopropyl alcohol (55:45)	10	19
PS	w.r.t. MW (MWD)	acetone + benzene + ethanol (3:1:2), benzene + EMK (1:1)	4	71
PS	w.r.t. MW (2×10^3–5×10^5)	benzene + EMK + acetone + ethanol (5:3:6:4)	4	71
PS	Separation of *i*-PST from *a*-PST	cyclohexane + benzene + acetone (40:16:2)	1	101
PS	Separation of 4-pointed star from PS with MW = 10^5–10^6	chloroform + acetone (10:1), chloroform	4	44,86
PS	Separation w.r.t. MW of polymers with terminal COOH groups (1.1×10^4–5×10^4 and 2.3×10^4–1.2×10^5)	THF + acetone (10:1) → THF	4	
PMMA	w.r.t. MW (4×10^4–4×10^5)	chloroform + methanol (29:71)	2	
PMMA	w.r.t MW (1.6×10^5–4.12×10^5)	benzene + acetone (2:8), isopropyl alcohol + methyl acetate (100:62), ethyl acetate + methyl acetate (100:23)	2	
PMMA	Separation of *s*- and *a*-PMMA and w.r.t. MW	acetonitrile + methanol (20:40, 46:54)	2	
PEO	w.r.t. MW (1.5×10^3–6×10^3)	ethylene glycol + methanol (80:20)	2	15
PEO	w.r.t. MW (1.5×10^3–2.8×10^4)	methanol → methanol + DMF (80:20)	2	31
PB	Separation of *cis*-1,4- and 1,2-PB from *trans*-1,4-PB	pentyl chloride	3	43

Table II (cont'd.).

Polymer	Polydispersity investigated	Eluent	Method of development	Refs.
	Copolymers (co)			
Poly(ST-co-BD)	w.r.t. MW (6.1×10^4–1.4×10^5)	THF → methanol	4	84
Poly(ST-block-MMA)	Separation of PMMA	chloroform + methanol (6:16–4:16)	1	33
Poly(ST-block-BD)	Separation w.r.t. MW, separation of low-molecular-weight PS	chloroform + methanol (3:2) → methanol	3	84
Poly(BD-gr-ST)	Separation of PS	EMK	3	44

*For the methods of development and the significance of abbreviations, see Table I of the Appendix.

**Adsorbent — Al_2O_3.

***Method of development — $ZnSiO_3$.

Table III. The use of TLC in the study of oligomers* (adsorbent – silica gel).

Oligomer	Polydispersity investigated	Eluent	Method of development	Refs.
Polyisoprene	w.r.t. MW (700–2100), M_n = 1780	benzene + acetone (17.43:28.57)**	1	64
Polybutene	w.r.t. MW, M_n = 300	hexane	2	102
Poly-1,2-butadiene	w.r.t. functionality (COOH and OH groups)	*p*-xylene, carbon tetrachloride + THF (100:1)	3	44
	Non-functional, mono- and bi-functional	cyclohexane + benzene (14:3)	4	67
PS	w.r.t. MW (n = 3–9), M_n = 900	carbon tetrachloride + heptane (2:1)	4	67
Poly-α-methylstyrene	w.r.t. MW (n = 3–10)	ethyl acetate + isopropyl alcohol + acetone + methanol + water (50:15:15:4:16), isopropyl alcohol + ethyl acetate + water*** (30.5:55:14.5)	5	56
Polyglycerols	(1) w.r.t. MW (n = 1–4) (2) separation of linear and branched oligomers			
PEG	w.r.t. MW (n = 1–3) (M_n = 200–2000)	chloroform + ethanol (92:8)***	1	50
PEG (3,5-dinitrobenzoates)	w.r.t. MW (M_n = 200–2800)	EMK sat. with water	6	51
PEG (dichloro-derivatives)	w.r.t. MW (up to n = 21)	EMK sat. with water	1	94
PEG (dichloro-derivatives, triphenylmethyl derivatives)	w.r.t. MW (n = 13.2) (n = 17.2)	EMK sat. with water	1	95
PEG (3,5-dinitrobenzoates	w.r.t. MW (M_n = 200–4000) (MWD)	EMK sat. with water	7	53
PEG	w.r.t. MW (M_n = 600)	pyridine + water (0.1:10), chloroform + ethanol (10:1)*****	6	67
PPG	w.r.t. functionality	hexane + di-isopropyl ether + ethanol + water (5:10:5:3)	8	61
PPG	w.r.t. MW (M_n = 150–2000)	ethyl acetate + acetic acid (97.5:2.5)	1,9, 10	53
PPG	w.r.t. functionality (monools, diols, triols, and pentols) M_n = 500–5000)	ethyl acetate sat. with water	6	48
Mixture of PPG and PEG	Separation	chloroform + white spirit (85:15)	7	53
Mixture of PPG, PEG, and poly-THF	Separation (M_n = 2000)	chloroform + ethanol (92:8)	1	50
PEG–nonyl ether	w.r.t. MW (n = 9)	EMK sat. with water	11	59
PEG and its derivatives (–O–CH_2CH_2SR, where R = phenyl, n-hexyl, n-octyl, or n-decyl; –O–CH_2CH_2Cl and –OR, where R = phenyl or triphenylmethyl)	w.r.t. MW (up to n = 13)	EMK and EMK sat. with water	1	57

Table III (cont'd.)

Oligomer	Polydispersity investigated	Eluent	Method of development	Refs.
PEG and its derivatives $R-O(CH_2CH_2O)_nR'$, where R = R′ = H, R = R′ = phenyl, or R = *p*-t-nonylphenyl and R′ = H	w.r.t. MW (up to $n = 17$) $n = 6.5$ $n = 7.3$ $n = 5.4$	EMK, EMK + water (9:1); EMK + water (95:5); EMK sat. with water	1	2
PEG-*p*-t-nonyl phenyl ether	w.r.t. MW ($n = 6.5$-12.9)	EMK sat. with water	1	60
Surfactants based on PEG	w.r.t. MW (up to $n = 8.6$)	EMK sat. with water	1	96
Surfactants based on PEG of the type $RO(CH_2CH_2.O)_n$, where R = alkylphenyl or alkyl	w.r.t. MW	EMK sat. with water	1	97
Products of condensation of PEG with aliphatic acids, alcohols, amines, phenols, and amides	w.r.t. MW and degree of hydroxyethylation (up to 1:20)	EMK + water (1:1)—upper phase, EMK + 2.5% aqueous ammonia (1:1)—upper phase, butanol + acetic acid + water (4:1:5)	6	49
Esters of PEG and adipic acid	Separation of linear and branched oligomers ($M_n = 1000$-3000)	benzene + ethanol (3:1)		
Poly(methylene-2-hydroxybenzoate)	w.r.t. MW (138-1100)	benzene + acetic acid + water (2:2:1)	12	98
ε-Caprolactam and its cyclic oligomers	w.r.t. MW ($n = 1$-8)	THF + petroleum ether (100-120°C) + water (80:14:10); 1-butanol + acetic acid + water (10:2:5); 2-butanol + formic acid + water (7.5:1.5:1); 1-butanol sat. with water; isopropyl alcohol + methanol + water (1:1:1); 1-butanol + conc. HCl + water (10.2:3.8)	6	65
Poly(ethylene terephthalates)	Separation w.r.t. functionality	benzene + ethyl acetate (85:15, 55:45) → ethyl acetate	13	63
Diethylene glycol in poly(ethylene terephthalate)		Dichloromethane + 25% aqueous ammonia + methanol (8:3:17)	14	100
Polydimethylsiloxane-diols	w.r.t. MW ($n = 1$-20)	benzene + ethyl acetate (10:0.1)	15	67

Methods of development: 1) I_2 vapour; 2) 1% vanillin and 10% $HClO_4$ with subsequent heating at 110°C for 1 h; 3) 14.7% H_2SO_4 with subsequent heating to 100°C; 4) 3% $KMnO_4$ in concentrated H_2SO_4 with subsequent heating to 180°C; 5) 0.5% Thymol Blue in 95:5 ethanol–H_2SO_4 mixture with subsequent heating at 120°C for 1 h; 6) Dragendorff reagent; 7) acetic acid solution of $KMnO_4$; 8) cobalt thiocyanate; 9) 0.05% ethanol solution of rhodamine B; 10) 2% $KMnO_4$ in 2 *N* H_2SO_4; 11) 1% I_2 in methanol; 12) u.v. irradiation at 366 nm; 13) Methyl Red, Bromothymol Blue, and formaldehyde in 95% ethanol; 14) 0.5% $KMnO_4$ and $K_2S_2O_8$; 15) luminescence of background at 365 nm.

*For the notation employed, see Table I.

**Al_2O_3 (17% of water), neutral unfixed layer.

***Mixture of kieselguhr and silica gel.

****Al_2O_3 with first degree of activity, unfixed layer.

*****Adsorbent—Al_2O_3.

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