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ADSORPTION CHROMATOGRAPHY OF POLYMERS

B.G.Belenkii

Institute of Macromolecular Compounds, Academy of Sciences of the USSR, Leningrad 199004, USSR

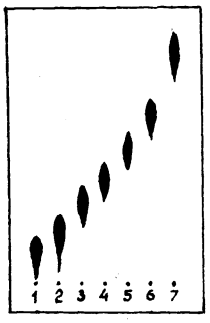
Abstract - Adsorption chromatography is a universal method for the investigation of various types of polymer polydispersity.
The behaviour of the macromolecule during adsorption in pores is determined by the energy of interaction of a polymer unit with the adsorption surface $-\varepsilon$ and its ratio to the critical energy $-\varepsilon_c$.
In the range of $-\varepsilon < -\varepsilon_c$ exclusion chromatography occurs ($-\Delta F<0$) whereas $-\varepsilon > -\varepsilon_c$ is the range of adsorption chromatography ($-\Delta F > 0$).
Both of them together form a single chromatographic process of the penetration of macromolecules into pores. The chromatographic behaviour of copolymers and oligomers with functional groups was considered.
New methods of quantitative adsorption chromatography are described: TLC with plate calibration by polydisperse polymers for the determination of MMD of homopolymers and micro-column chromatography for the analysis of composition heterogeneity of block copolymers with the determination of their composition by photometric detection at two wavelengths.

INTRODUCTION

Synthetic polymers and partially also natural polymers are polydisperse systems with components differing in molecular mass, chemical composition, micro-structure, functional groups etc. The character of polydispersity reflects the mechanism and kinetic features of polymerization and is related to the physico-chemical and physico-mechanical properties of polymers which determine the conditions of the manufacture of plastics and the service properties of the articles manufactured from them.
The following types of the polydispersity of polymers and oligomers can be distinguished. The polydispersity of:
- the molecular mass M (the molecular-mass distribution, MMD);
- the chemical composition (the composition heterogeneity, CH);
- the microstructure (distribution of geometrical and stereo-isomers);
- the quantity and type of the functional groups of oligomers (distribution of the types of functionality (DTF);
- the chain structure (branched, block, graft and ladder polymers and copolymers);
- the presence of defective structure an d
- the contents of low molecular products and the contents and MMD of polymers of other types (polymer purity).

Naturally, the liquid chromatography of polymers being a highly effective and universal fractionation method occupies the leading part in the analysis of these types of polydispersity.
However, at present only the investigation of the first type of polydispersity of polymers, that of their MMD, is carried out by a reliable high-speed automatic method of chromatographic analysis, by exclusion chromatography (gel permeation chromatography, GPC).
The method of GPC makes it also possible to analyse the MMD of block copolymers on the basis of the Benoit universal calibration technique (Ref.1) with the determination of the chemical composition of the GPC fractions by using two detectors (Ref.2). It is also possible to determine the MMD and branching indices of branched polymers by combining GPC with other methods (viscometry (Ref.3) and sedimentation (Ref.4).
Some achievements in the analysis of other types of polydispersity were possible as a result of the successful use of the thinlayer chromatography (TLC) of polymers (Refs.5 & 6) proposed in 1968 for the analysis of CH of

random copolymers by Inagaki (Ref.7) and Belenkii and Gankina (Ref.8). The use of TLC for investigating various types of polydispersity shows that adsorption chromatography is the most effective method for their analysis. Many examples of its successful use have been described (Refs.5 & 6). Adsorption TLC is particularly effective in the fractionation of random copolymers according to composition. In this case chromatographic systems with low resolution can be used for the separation of copolymers widely differing in composition (Fig.1) and systems with high resolution can be used for



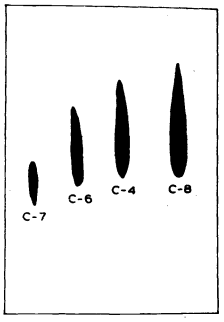
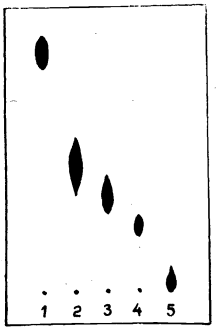


Fig.1. TLC of random copolymers of styrene (St) and acrylonitrile (AN) containing (1) 41%, (2) 34.1%, (3) 27.6%, (4) 19.3%, (5) 14.7%, (6) 8.7% and (7) 0 AN. A system with gradient from a mixture of tetrachloromethane and acetonitrile (6.5:0.5) to acetonitrile.

Fig.2. TLC of azeotropic copolymers of St and methylmetacrylate (MMA) with 54% of St and various conversions: 0.5% (C-7); 11.7% (SC-6); 33.8% (C-4 and 70.6% (C-8) on KSK silica gel in a chloroform-diethyl ether system (12:4.2).

the separation of the copolymers of similar compositions such as azeotropic copolymers with different conversions (Ref.6) (Fig.2). Adsorption TLC permits the separation of the copolymers of the same composition differing in the type of the alternation of units (block, random and alternating copolymers) (Ref.9) (Fig.3),the separation of some polymers, such as polymethylme-



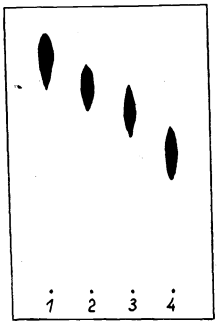


Fig.3. TLC of St-MMA copolymers. (1) Random copolymer with 71.2% St; (2) random copolymer with 56% St; (3) random copolymer with 49.1% St; (4) alternating copolymer with 49.5% St and (5) block copolymer with 49.6% St. Silica gel; solvent gradient: chloroform-acetic acid.

Fig.4. TLC of PMMA with various contents of syndiotactic units (T_s) on KSK silica gel in a system: ethyl acetate-isopropyl acetate (25:7). (1) M_w=1.86·10^5, M_n=0.80; (2) M_w=2.85·10^5, T_s=0.71; (3) M_w=2.79·10^5, T_s=0.66; (4) M_w=2·10^5, T_s=0.53.

thacrylates, PMMA, according to the type of stereoisomerism (atactic and syndiotactic PMMA) (Ref.10) (Fig.4), and such as polybutadienes according to their geometrical structure (1,4-trans and 1,4 cis) (Ref.11) (Fig.5). Adsorption TLC is also very effective in the separation of polymers according to M up to the separation of oligomers into separate polymer homologues (Ref.6) (Fig.6). It should be noted that adsorption TLC is very sensitive even to very small changes in the chemical structure of the polymer. Thus, it is possible to separate completely the molecules of polystyrene (PS) with M $5\cdot10^4$ containing one or two carboxylic groups from those that do not contain them (Ref.12). This peculiarity of adsorption TLC is used to se-

parate oligomers according to the types of functionality irrespective of their M (Ref.13) (Fig.7).

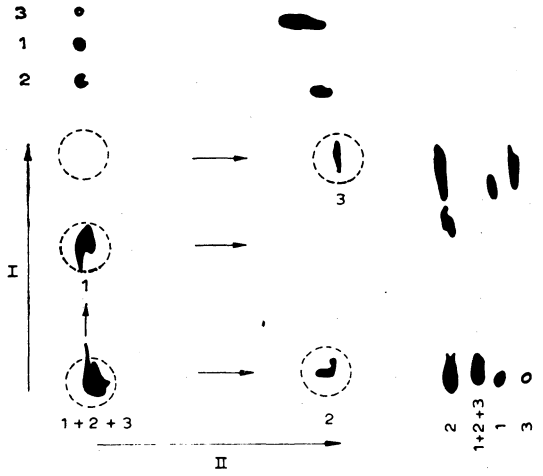


Fig.5. Two-dimensional TLC of trans - 1,4 (1), cis - 1,4 (2) and 1,2 - vinyl (3) polybutadienes in tetrachromomethane (adsorption TLC) - direction I and in amyl chroride (precipitation TLC) - direction II.

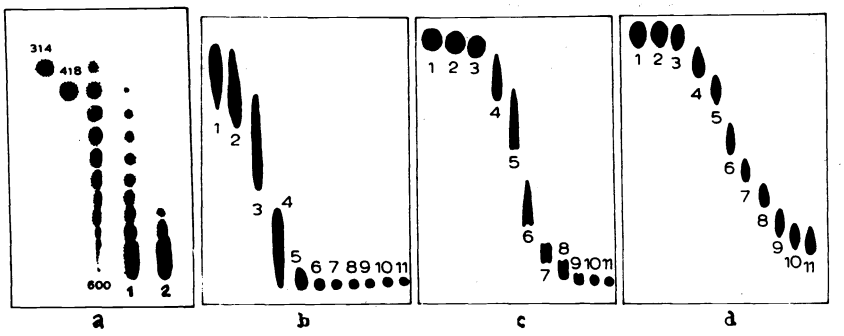


Fig.6. TLC of PS samples with narrow dispersity (M_w/M_n 1.2) in systems cyclohexane-benzene-acetone (a) 14:3:0; b) 13:3:0.1; (c) 12:4:0.4; (d) 12:4:0.7.
PS samples: 314 - PS-trimer and 418-tetramer, 600-PS with M_n=600, 1(M_n=900), 2(M_n=2,3·10^3); 3(M_w=5·10^3; M_n=4.5·10^3), 4(M_w=10.3·10^3; M_n=9.7·10^3), 5(M_w=1.985·10^4; M_n=1.9 65·10^4); 6(M_w=5.1·10^4; M_n=4.9·10^4), 7(M_w=9.82·10^3), M_n=9.62·10^4), 8(M_w=1.73·10^5; M_n=1.64·10^5), 9(M_w=4.11·10^5; M_n=3.92·10^5), 10(M_w=8.67·10^5; M_n=7.73·10^5), 11(M_w=2.145·10^6, M_n=1.78·10^6).

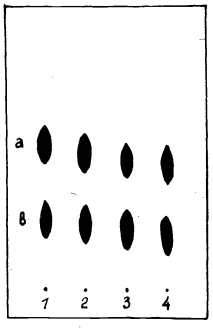


Fig.7. TLC of polypropylene diols (a) and polypropylene triols (b) with different M: (1) -250 (diol); 300 (triol); (2) -1000; (3) -2000; (4) -3000. KSK silica gel in ethyl acetate saturated with water containing 2% of methyl ethyl ketone.

However, up to the present there were some difficulties preventing the wide use of adsorption TLC for the mass analysis of polymers. First, the selection of the separating systems was empirical because the theory of the adsorption chromatography of polymers on porous adsorbents was not available. Secondly, the thin-layer variation of adsorption chromatography used so far is a very good qualitative method but is very cumbersome and tedious when used for quantitative analysis, which is not very accurate owing to the optical inhomogeneity of the adsorbent layer on the plate.
Hence, it was possible to formulate a definite program of investigations in the field of the adsorption chromatography of polymers in order to transform it into a widely used automatic method of analysis. This program was as follows:

a) the development of the theory of adsorption chromatography of polymers on porous adsorbents;

b) the use of polydisperse polymer samples for calibrating thin-layer plates in the quantitative TLC of polymers;

c) the use of the analytical procedures developed for TLC in the column chromatography without any loss in the sensitivity and resolution attained in TLC but with the advantages inherent in column chromatography: precision, the sensitivity of analysis, high reproducibility and the possibility of the "on line" automation.

MODERN THEORY OF ADSORPTION CHROMATOGRAPHY OF POLYMERS ON POROUS ADSORBENTS

a) Adsorption chromatography of homopolymers. Comparison of the behaviour of the Gaussian chain and the actually existing polymer during adsorption in pores. Critical adsorption energy.

Extensive experimental material on the adsorption of polymers on porous adsorbents from solutions of high and average concentrations has been available (see e.g. Ref.14). The adsorption of single macromolecules on a plane surface (non-porous adsorbents) was investigated theoretically and experimentally (Ref.15).
However, before our publications in the field of polymer adsorption on porous adsorbents only one theoretical work by Di Marzio and Rubin has been published concerning the adsorption of a single macromolecule in a slit-like pore (Ref.16) dealing with polymer adsorption in the absence of concentration effects. The authors dealt with the behaviour of the Gaussian polymer chain in a slit-like pore with parallel smooth homogeneous surfaces. The polymer-adsorbent interaction was shown by the fact that any polymer segment arriving at the upper or lower plane of the slit acquired the energy $-\varepsilon$ *). The change in $-\varepsilon$ determines the probability w of the penetration of the macromolecule into the pores. It is expressed by the change in the free energy of the macromolecule in adsorption $-\Delta F$: $w = \exp(-\Delta F)$. Depending on the value of $-\varepsilon$ two ranges of changes in $-\Delta F$ exist: $-\Delta F < 0$ and $-\Delta F > 0$. They coincide at the point of the critical energy of interaction $-\varepsilon = -\varepsilon_c$ where $-\Delta F = 0$. The validity of the relationships of Di Marzio and Rubin for the adsorption and exclusion chromatography of polymers has been shown experimentally by TLC of PS (Refs.17 & 18). In particular, chromatographic effects were found related to the critical energy of interaction of the polymer with the adsorbent. It was important to elucidate in greatest detail the correlation between these models and the phenomena virtually observed in the adsorption of polymers on common porous adsorbents. We have investigated (Ref.19) correlation between the virtual behaviour of the macromolecule and that of the Gaussian chain during adsorption in pores. The behaviour of a model macromolecule which was represented as a series of random walks on a simple cubic lattice inside the space of a slit with ϕ of 3÷10 limited by two parallel planes has been investigated (Ref.19).
The results were compared to those of the TLC of narrow disperse PS samples ($M_w/M_n < 1.1$) on silicate adsorbents: silicagel KSK (pore diameter $D \simeq 100$ Å) and silochrome S-80($D \simeq 500$ Å). A mixed solvent was used: cyclohexane-benzene-acetone in the volume ratio of 40:16:γ (γ is the number of acetone volume fractions). The segment of the model chain corresponded to the Kuhn statistical segment of the PS molecule and the pore size ϕ corresponded to D of the adsorbent. A decrease in the volume fraction $x = \gamma/(56+\gamma)$ of acetone, the adsorption-active component, increased $-\varepsilon$, the energy of interaction of a polymer segment with the pore surface. The results of the chromatographic experiment served to determine directly the change in the free energy $-\Delta F$ in adsorption by measuring the ratio of the time t_p of the existence of the polymer chain in the adsorbed state (time of its residen-

*) Here and below the energy units are expressed in kT values.

ce in the pore) to the time t_o of its residence in the solution volume (in the mobile phase) since according to Boltzmann's principle

$$t_p/t_o=\exp(-\Delta F) \quad (1)$$

The value of $-\Delta F$ is the sum of the change in the conformational free energy of the macromolecule $-\Delta F$ and a term determining the change in the configurational space when the macromolecule enters the pore $\ln(v_p/v_o)$

$$-\Delta\tilde{F} = -\Delta F + \ln(v_p/v_o) \quad (2)$$

where v_p and v_o are volumes of the inter-particle space (the mobile phase) and of the adsorbent pores, respectively.
The value of $-\Delta F$ is obtained from the chromatographic mobility which is the ratio of the flow rates of the polymer and the solvent in the chromatographic layer (on the plate):

$$R_f = 1/[1 + \exp(-\Delta\tilde{F})] = 1/[1 + (v_p/v_o)K_d] \quad (3)$$

The distribution coefficient K_d allows the determination of changes in $-F$ when the macromolecule enters the pores: $-\Delta F = \ln K_d$.
Fig.8 shows the dependences of the changes in $-\Delta F$ on M for model Gaussian

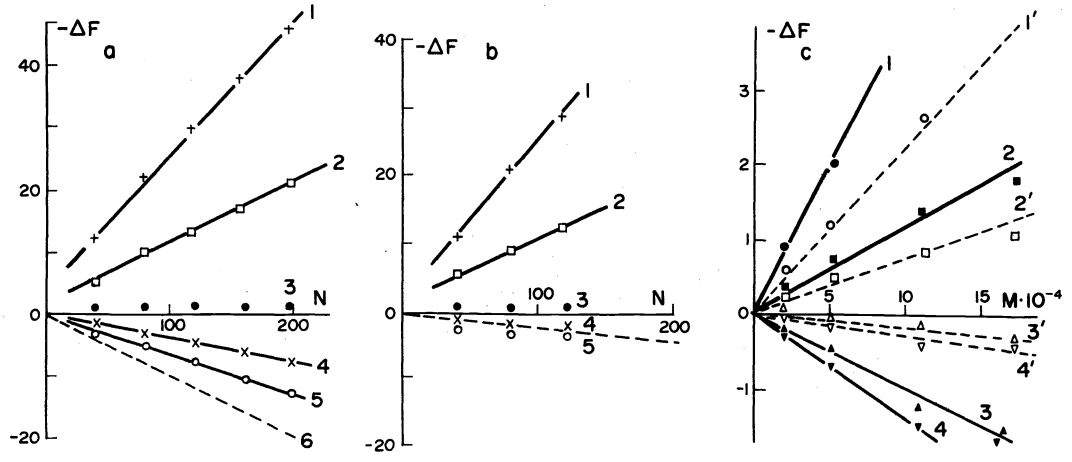


Fig.8. Molecular mass dependence of $-\Delta F$ when the model chain passes from the free volume into a slit-like pore with a width δ of (a) 5 and (b) 10. $-\varepsilon$ =0.6 (1); 0.4 (3); 0.2 (3); 0 (4); -0.3 (5); $-\infty$(6). (c) the same when PS passes into the pores of KSK silica gel (1-4) and silochrome S-80 (1'-4'); x=2.1 (1.1'); 2.8 (2.2'); 4.1 (3.3') and 5.1% (4.4').

chains of various sizes and for PS on silica gel and silichrome. It is clear that the features of the behaviour of model chains established by computer simulation are qualitatively similar to those of real macromolecules. Fig.8a and b shows that when the value of $-\varepsilon$ changes, two ranges of the dependence of $-\Delta F$ on M are observed. They are separated by the point of the critical energy of interaction $-\varepsilon = -\varepsilon_c$ and have different slopes. The lower range ($-\infty < -\varepsilon < -\varepsilon_c$) where the slope of $-\Delta F$ is negative corresponds to an increase in the free energy of the chain in adsorption with increasing M. Hence, the penetration of the macromolecule into the adsorbent pores is not advantageous. This range is the range of the molecular-sieve effect and corresponds to exclusion chromatography (GPC).
At the energies higher than the critical energy $-\varepsilon > -\varepsilon_c$ (the upper part of Fig.8) the slope of $-\Delta F$ proportional to $-\varepsilon$ increases infinitely with the increasing value of $-\varepsilon$. This is the range of the adsorption chromatography of macromolecules. As has already been shown (Refs.16 & 20), at these energies a part of the units of the macromolecule proportional to M becomes adsorbed on the surface.
At the boundary between the molecular-sieve and the adsorption ranges at the point of the critical energy $-\varepsilon = -\varepsilon_c$ the molecular-mass dependence of $-\Delta F$ disappears and $-\Delta F$ becomes zero. What is the critical energy? This is the energy of interaction at which the energetic gain due to the contact of the polymer with the surface, $-\Delta H$, completely compensates for the entropy losses of the macromolecule $T\Delta S$.

$$-\Delta F|_{-\varepsilon=-\varepsilon_c} = -\Delta H + T\Delta S = 0 \qquad (4)$$

In the molecular-sieve range $-\Delta H$ does not compensate or incompletely compensates for $T\Delta S$ and, hence: $-\Delta F < 0$ and $K_d < 1$. In the adsorption range the energetic gain exceeds the entropy losses: $-\Delta F > 0$ and $K_d > 1$. In the critical range at $-\varepsilon = -\varepsilon_c$ we have $-\Delta F = 0$ and $K_d = 1$. In this range (Fig.9) the macromolecules of PS with different M are not separated. They are not influenced by the pore structure and are distributed in the whole pore space of

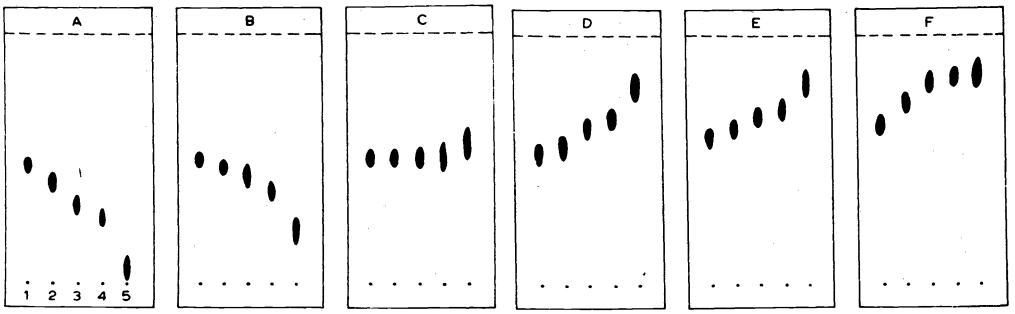


Fig.9. TLC of PS 5-9 (left to right) (see Fig.6) on KSK silica gel in a cyclohexane-benzene-acetone system (40:16:γ) where γ is 1.5 (a); 1.8 (b); 2 (c); 2.2 (d); 2.5 (e); 2.8(f) with preliminary plate saturation for 2 hr.

the adsorbent as if it consisted of one large cavity. For the model chains considered, $-\varepsilon_c = \ln(6/5) \simeq 0.182$ and does not depend on the slit width (Ref. 16). In chromatography (Refs.17 & 18) on silica gel with $D \simeq 100$ Å and silochrome S-80($D \simeq 500$ Å) the critical conditions were observed at the volume fraction of acetone $x_c = 0.03$ (Fig.8c). For attaining the critical conditions for the KSM silica gel with narrow pores, $D \simeq 30$ Å, a smaller amount of acetone was necessary (Fig.10), i.e., in this case the critical energy increased. Probably, this is associated with the effect of the chain volume pro-

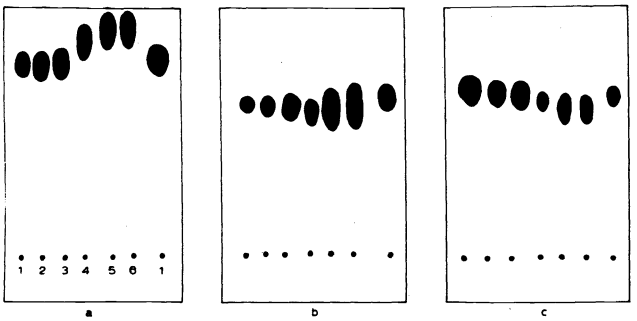


Fig.10. TLC of PS with M_n=600(1) $2\cdot10^3$(2); $4\cdot10^3$(3); $1.96\cdot10^4$(4); $9.82\cdot10^4$(5) and $1.64\cdot10^5$(6) on (a) KSM silica gels, ($D \simeq 30$ Å); (b) KSK silica gels ($D \simeq 100$ Å) and (c) silochrome S-80 ($D \simeq 500$ Å) in cyclohexane-benzene-acetone (40:16:2) with preliminary saturation for 2 hr.

per. In these experiments special measures were taken to maintain the chemical identity of the inner pore surface of the KSM, KSK and C-80 adsorbents (Ref.18).

If we mean by the molecular-sieve effect the influence of the pore size on the probability of the penetration of macromolecules into the pores and by adsorption the interaction of macromolecules with the adsorbent surface, this mutual effect (Fig.8a, b and c) may be formulated as follows: in the molecular-sieve range adsorption increases the accessibility of pores whereas in the adsorption range the molecular-sieve effect increases the adsorption of macromolecules in pores of smaller size. This observation contradicts the existing concepts on the decrease in the adsorption of macromolecules in small pores based on the experiments of polymer adsorption from the solutions of comparatively high (non-chromatographic) concentrations (Ref.21).

This phenomenon of the adsorption of large macromolecules in small pores (corresponding to the results obtained by computer simulation (Ref.20) and

the analytical theory (Ref.16) conclusively supports the following facts:

1) the character of the dependence of $-\Delta F$ on M in the adsorption of PS on the KSK silica gel (Fig.8b) is linear. This shows that the conditions of adsorption are identical for PS with $M=2.10^3$ which is known to penetrate into the adsorbent pores and for PS with $M=1.8\cdot10^5$ the size of whose macromolecule, $2\langle R^2\rangle^{1/2} \simeq 300$ Å, greatly exceeds that of the adsorbent pores $D \simeq 100$ Å.

2) The value of $-\Delta F$ does not depend on the size of the particles and, hence, on the value of the external surface of the adsorbent grains. This proves that the macromolecules are adsorbed inside the pores rather than outside the particles because the pore surface remains virtually unchanged when the adsorbent grains are ground more finely.

We will consider the dependence of $-\Delta F$ on $-\varepsilon$ or, correspondingly, on the volume fraction of acetone x. Fig.11 clearly shows the critical point at

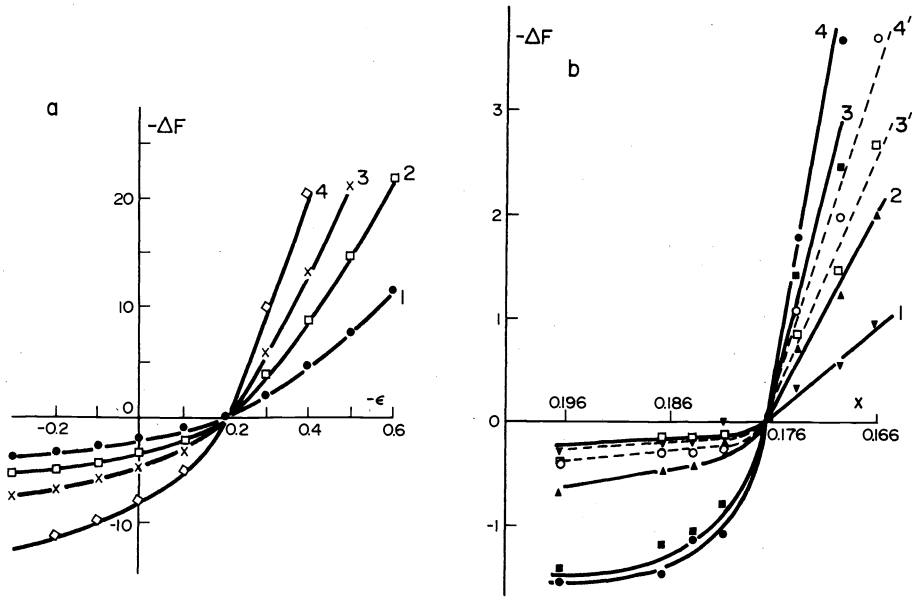


Fig.11. Value of $-\Delta F$ of the macromolecule when it enters the pore (a) vs. $-\varepsilon$ for model chains in a slit with a width ϕ of 5 with N=40 (1); 80(2); 120(3); 200(4) and (b) vs. volume fraction of acetone (x) in pores of KSK silica gel with $D \simeq 100$ Å (1-4) and silochrome S-80 with $D \simeq 500$ Å (3', 4') for PS with $M_w\cdot10^{-4}$=1.98(1); 5.1(2); 11.1(3,3'); 17.3 (4,4').

x_c=0.03 at which all the curves intersect the abscissa. To the left of this point, in the molecular-sieve range, the loss in $-\Delta F$ increases as the forces of the repulsion of the segments from the adsorbent surface increase, $-\varepsilon \to -\infty$. However, they tend to a certain limiting value. The adsorption range is to the right of $-\varepsilon_c$. In this range, when the macromolecule penetrates the pores, a gain in the free energy ($-\Delta F > 0$) occurs and increases infinitely with increasing value of $-\varepsilon$. However, only the range of relatively low values of $-\varepsilon \geqslant -\varepsilon_c$ is accessible for chromatography since with increasing $-\varepsilon$ adsorption becomes irreversible. All these considerations suggest a single type of the process of polymer adsorption which includes both the molecular-sieve range (negative adsorption) and the adsorption range proper (positive adsorption).

b) Chromatographic determination of the size of the pore space of the adsorbent and v_p/v_0.

Since the size of the pore space of the adsorbent is related to the accessibility of the monomolecular layer of the solvent for the segments of the macromolecule, it follows that this volume differs depending on the value of $-\varepsilon$. At $-\varepsilon = -\infty$ the probability of the penetration of the segments into the monomolecular layer of the solvent is equal to zero and the pore volume v_p. It is equal to the geometrical pore volume $v_{p,g}$ which can be determined for example, by mercury porosimetry with the substraction of the volume of the monomolecular layer with the thickness of one segment. At

$-\varepsilon = 0$*) the probability of the penetration of the segment into the monomolecular layer corresponds to the probability of its residence in the pore volume. Hence, $v_p = v_{p,g}$. At $-\varepsilon = -\varepsilon_c$ the residence of the segment in the monomolecular layer becomes more probable than that in the pore volume and, hence, the apparent pore volume determined from the chromatographic experiment will be greater than the geometrical volume $v_{p,g}$.

$$v_{p\,-\varepsilon=-\infty} < v_{p\,-\varepsilon=0} \simeq v_{p,g} < v_{p\,-\varepsilon=-\varepsilon_c} \qquad (5)$$

In thermodynamic calculations based on chromatographic data $v_{p\,-\varepsilon=-\varepsilon_c}$ should be used since only in this case the calculated value of $-\Delta F$ corresponds to the change in the conformational free energy. This value of v_p can be determined chromatographically at $-\varepsilon = -\varepsilon_c$ when the polymers of all M exhibit equal R_f (Fig.9): $v_p/v_o = (1-R_f)/R_f$. Eq.(5) explains the discrepancies between the pore volume of the adsorbent determined by mercury porosimetry and by chromatography observed in same papers (Ref.22).

c) Calibration dependences in the adsorption chromatography of polymers. In the entire molecular-sieve range the probability of the penetration of the macromolecule into the pore depends on the characteristic parameter: the ratio of the chain length to the pore size. For example, for long chains in slit-like pores at $-\varepsilon = 0$ (Ref.16) we have

$$-\Delta F = T\Delta S = N\ln[2/3 + (1/3)\cos(\pi/\phi)] \simeq \pi^2 N/6\phi^2 \qquad (6)$$

Since the mean-square radius of gyration $\langle R^2 \rangle$ is proportional to the number of units N, it is also possible to write:

$$-\Delta F \sim \langle R^2 \rangle/\phi^2 \sim N/\phi^2 \qquad (7)$$

Eqs (6) and (7) can be used in GPC as universal dependences relating $-\Delta F$ (retention volume, R_f) with N and $\langle R^2 \rangle$ for adsorbents of any porosity. The above considerations of the interaction of macromolecules with a porous adsorbent lead to the following conclusions:

1) Irrespective of the type of chromatography (exclusion or adsorption chromatography), i.e., at any fixed value of $-\varepsilon$, a linear dependence exists between $-\Delta F$ and M

$$-\Delta F = \alpha(-\varepsilon, D)M \qquad (8)$$

The slope of this dependence $\alpha(-\varepsilon, D)$ is determined by $-\varepsilon$ and the pore size D. This dependence may be recommended as the calibration dependence;

2) In the molecular-sieve range the following dependence holds: Fig.12 shows the relationship of $-\Delta F$ to N/ϕ^2 and $6\langle R^2 \rangle/\phi^2$ for model chains with various degrees of polymerization adsorbed in slits of various width at $-\varepsilon = 0$ and $-\varepsilon = 0.1$. The Figure shows that this dependence is universal, i.e., it describes in a unique manner the behaviour of macromolecules of different sizes on adsorbents of different porosities. Similar linear dependences are also observed in the chromatography of PS on microporous glasses (Fig.12 band c). Experimental calibration dependences should be obtained at fixed values of $-\varepsilon$ if these dependences are to be considered universal. It is possible that the experimental points in Fig.12b and c are spread because this condition was not observed. The most suitable energy is $-\varepsilon = -\infty$, i.e. the most suitable solvent is the solvent exhibiting the strongest interaction with the adsorbent, such as tetrahydrofuran.
It should be noted that when this condition is not observed (difference in the values of $-\varepsilon$ for the calibrating and the investigated polymers), the Benoit universal calibration is not valid.

3) In the adsorption range at high energies of interaction between the polymer and the adsorbent ($-\varepsilon \gg -\varepsilon_c$) the calibration dependence of $-\Delta F$ on N is only slightly affected by the pore size and its slope is virtually determined only by $-\varepsilon$: $-\Delta F \simeq \alpha(-\varepsilon)M$. Since in this range of energies adsorption is virtually irreversible, this range of the values of $-\varepsilon$ is of no interest for chromatography.

4) The range of $-\varepsilon \geqslant -\varepsilon_c$ is the range of the practical use of adsorption chromatography. Here $-\Delta F$ increases when the pore diameter decreases. At the critical point $\alpha(-\varepsilon, D) = 0$ and the chromatographic separation of polymers according to M is impossible.

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* This pore volume can be measured in the chromatography of the labelled solvent ($-\varepsilon = 0$).

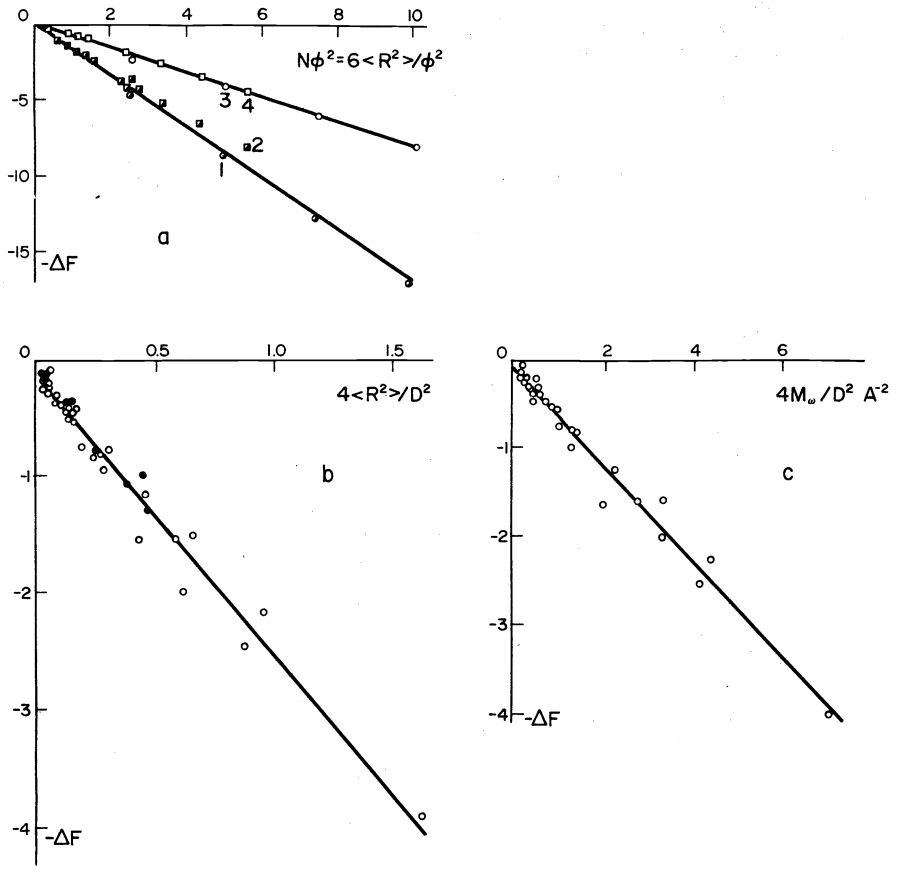


Fig.12. Value of $-\Delta F$ of the macromolecule when it enters the pore vs. the ratio of M (or $<R^2>$) to the square of the slit width ϕ^2 or the pore size D^2(a) model chains with $-\varepsilon=0$ (1,2) and $-\varepsilon=0.1$ (3,4); (b and c) experimental data for PS on macroporous glasses (● - from Refs.23 and 24, ○ - from Ref.25).

d) The behaviour of the macromolecule when the interaction energy changes from $-\varepsilon \lesssim -\varepsilon_c$ to $-\varepsilon \gtrsim -\varepsilon_c$ is the first-order phase transition.

The behaviour of the macromolecule on passing from the volume phase into the pore space of the adsorbent should be considered. In the molecular-sieve range ($-\Delta F<0$) the state of the polymer in the volume phase of the solution is the most advantageous. Consequently, the residence of the polymer in pores at $-\Delta F>0$ and in the volume phase at $-\Delta F>0$ is fluctuation. The greater is M, and the more narrow is the pore, the lower is the probability of this fluctuation.

In the adsorption range ($-\Delta F>0$) the penetration into pores is advantageous. For an infinitely long macromolecule the thermodynamic probability of its penetration into the adsorbent pores $w=\exp(-\Delta F)$ is equal to zero in the whole molecular-sieve range and to unity in the adsorption range. This abrupt transition between the states of the system is characteristic of phase transitions. It has been rigorously proved (Ref.20) that in the adsorption of the Gaussian chain in a slit-like pore the first-order phase transition occurs. The agreement in the behaviour of model and actually existing chains. (Figs.8 and 11) suggests that the first-order phase transition also occurs when PS is adsorbed on porous silicate adsorbents. These experiments show the reversible character of polymer adsorption in pores the size of which is much smaller than that of the polymer chain (adsorption of PS with $M=1.86\cdot10^5$, $2<R^2>^{1/2}=300$Å on KSK silica gel with D=100A). As can be seen from Fig.11c, this is accompanied by a very slight increase in the free energy $-\Delta F$ per unit ($\sim10^{-2}$ kT units). However, the reversibility of adsorption is related not only to the value of $-\varepsilon$ but also to the eluent composition - the presence of an adsorption-active component, in our case of acetone. If it is removed from the eluent and the

ratio of the remaining components, cyclohexane and benzene, is changed in such a way as to make the eluent equieluotropic (ensuring identical Rf) to the three-component eluent, then, as is shown in Fig.13, the chromatographic

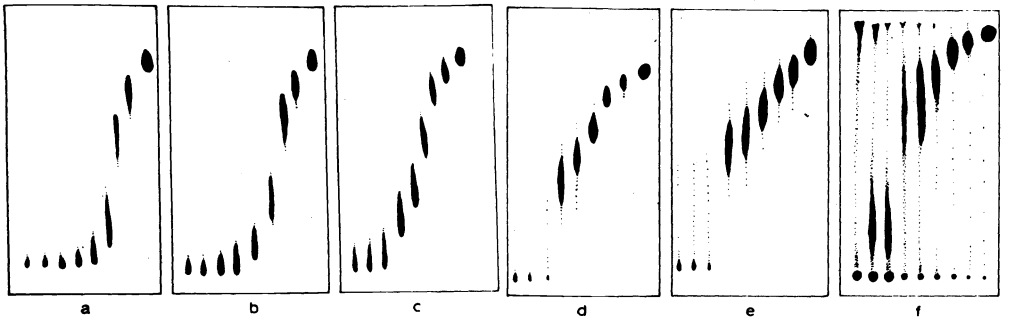


Fig.13. TLC of PS 3-11 (right to left) (see Fig.6) on KSK silica gel in benzene-cyclohexane: (a) 15:7, (b) 15:6.5) (c) 15:6); (d) 15:5.5); (e) 1.5:5.3; (f) 15:5.

behaviour of PS is changed. The spots on the chromatogram become elongated, the polymer partly moves with the solvent front and partly remains at the start. Evidently, under these conditions the equilibrium between the mobile and the stationary phases cannot be established.

e) Use of multicomponent eluents in the adsorption chromatography of polymers.

In the literature (Ref.26) indications are available on the impossibility of using adsorption chromatography in a single solvent for the separation of polymers according to molecular mass. It is recommended to use for this purpose binary solvents made up of components with different dielectric permittivities. The authors (Ref.26) are of the opinion that this is of primary importance for the separation of homopolymers according to M. Actually, the situation is simpler. An indispensable condition exists for the adsorption - chromatographic separation of polymers according to M: $-\varepsilon \geqslant -\varepsilon_c$. Sometimes it is difficult to find a single solvent that would ensure the required value of $-\varepsilon$ at the predetermined adsorption activity of the adsorbent and the polymer. Naturally, this can be achieved easier by using a binary solvent one of the components of which ensures Rf=1 and the other component Rf=0, in all the range of M of the polymer. A combination of these solvents makes it possible to select optimum values of $-\varepsilon$ for effective separation of polymers in the required range of M as is shown in Fig.6.

f) Adsorption chromatography of heteropolymers.

Heteropolymers contain units of different types with different adsorption activity and this determines the peculiarities of their chromatographic behaviour on porous adsorbents. Since the energetic gain of the adsorption interaction of the macromolecule is proportional to the number of adsorbed units with $-\varepsilon > 0$ and the entropy losses of the macromolecule are proportional to the number of all chain units ($-\varepsilon \gtrless 0$), it follows that in the adsorption of copolymers on adsorbents with $D \ll \langle R^2 \rangle^{1/2}$ the influence of M on $-\Delta F$ decreases and that of the chemical composition of the polymer acquises the greatest importance. Hence, for copolymers adsorption chromatography is mainly used to study their chemical heterogeneity.

Fig.14 shows the suppression of the molecular-mass dependence of $-\Delta F$ for random copolymers when an adsorbent with narrow pores is used. It is clear that on passing from KSK silica gel with $D \simeq 100$Å to the KSM silica gel with narrow pores, $D \simeq 30$Å, the molecular-mass dependence of Rf is substantially suppressed and Rf depends only on the chemical composition of the copolymer. The adsorption chromatography of oligomers with active functional groups on an adsorbent with large pores is a particular case (Ref.27). Here the molecular-sieve effect is not observed and $-\Delta F$ of the oligomer is related only to the adsorption of central units and end groups. In this connection it is possible to write the following dependences of $-\Delta F$ on N - the number of units and n - the number of the end groups of oligomers in adsorption at different values of the energies of interaction between the in-chain units ($-\varepsilon_{in}$) and the end groups ($-\varepsilon_e$).

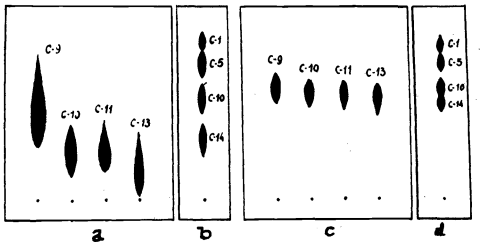


Fig.14. TLC of random copolymers of St-MMA. a) copolymers with 31% of St and $M_w.10^4$=26(C-13); 16(C-11); 18.8 (C-10) and 5 (C-9), KSK silica gel (D ≃ 100 Å) in chloroform$_4$- acetone (12:2.2); (b) copolymers with 80 (C-1, M_w=12.10^4), 54 (C-5, M_w=8.10^4), 31 (C-10, M_w=8,8.10^4) and 22 (C-14, M_w= =23.10^4) St %, KSK silica gel in chloroform-acetone (12:2.4); (c) copolymers with 31% St and M.10^{-4}=26(C-13), 16(C-11), 8.8(C-10) and 5 (C-9), KSM-5 silica gel (D ≃ 30 Å) in chloroform-acetone (12:3.2); (d) copolymers with 80(C-1, M_w=12.10^4), 54(C-5, M_w=8.10^4); 31(C-10, M_w=8,8.10^4) and 22(C-14, M_w= =23.10^4) St %, KSM-5 silica gel in chloroform-acetone (12: :3.4).

$$
\begin{aligned}
&a)\ -\varepsilon_e > 0\\
&1)\ -\varepsilon_{in} > 0; \qquad -\Delta F = (-\varepsilon_e)n + (-\varepsilon_{in})N\\
&2)\ -\varepsilon_{in} < 0; \qquad -\Delta F = (-\varepsilon_e)n - (-\varepsilon_{in})N\\
&3)\ -\varepsilon_{in} = 0; \qquad -\Delta F = (-\varepsilon_e)n\\
&b)\ -\varepsilon_e < 0\\
&1)\ -\varepsilon_{in} > 0; \quad -\Delta F = -(-\varepsilon_e)n + (-\varepsilon_{in})N\\
&c)\ -\varepsilon_e = 0\\
&1)\ -\varepsilon_{in} > 0; \quad -\Delta F = (-\varepsilon_{in})N
\end{aligned}
\qquad (10)
$$

Dependences of type a) correspond to the negative (a_1) and positive (a_2) dependences and to absence (a_3) of the dependence of Rf on the molecular mass of the oligomer N. In the latter case (a_3), $-\Delta F$ and, hence, Rf depend only on the number of end groups n and their chemical nature ($-\varepsilon_e$). Fig.15a shows that all three dependences of Rf on N and n for oligomers of

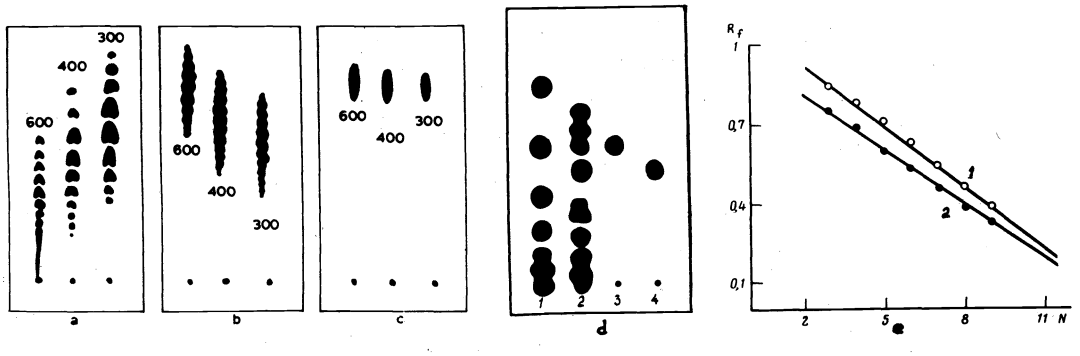
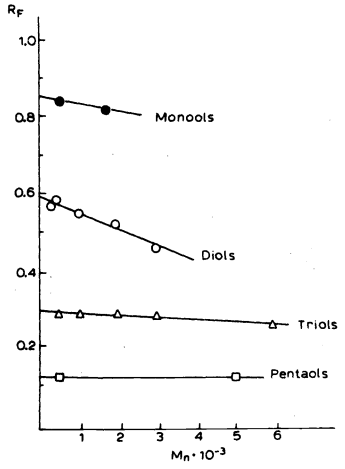


Fig.15. TLC of oligomers. a) TLC of polyoxyethylene with M_n= =300, 400 and 600 on KSK silica gel in pyridine-water (0.1: :10); b) the same on aluminium oxide in chloroform-ethanol (10:1); (c) the same on KSK silica gel in chloroform-pyridine (5:7); d) TLC of oligostyrenes with (1) secondary butyl end group, (2) without end groups and (3,4) corresponding tetramers; (e) Rf of oligostyrenes (1) and (2) vs N.

type (a) are possible in chromatography.
Cases (b) and (c) are possible only in one variation ($-\varepsilon_{in} > 0$) since at $-\varepsilon_{in} \leq 0$ the oligomers move with the solvent front. The separation of oligostyrene and butyloligostyrene in which all the polymer homologues of the

latter display high Rf is an example of the dependence of type (b) (Fig.15 d and e).
Of particular interest is the use of adsorption chromatography for the analysis of the functionality of oligomers (case a3). An example of this important analysis (Ref.13) is shown in Fig.16.



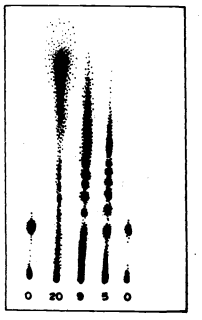


Fig.16. Value of Rf for polyoxypropylene polyols vs their M and functionality obtained on KSK silica gel in ethyl acetate saturated with water containing 2% of methyl ethyl ketone.

Fig.17. TLC of 3,5-dinitrobenzoates of poly(dimethylsiloxane) diols with the number of dimethyl siloxane groups n=0,5, 9 and 20 on KSK silica gel with 0.7% of fluorescein in benzeneethyl acetate (10:0.1), repeated twice. Luminescent photography.

It is clear that Rf of polyoxypropylenepolyols becomes virtually independent of M and is determined only by the number of OH end groups.
At $-\varepsilon_e \geq 0$ and $-\varepsilon_{in} \leq 0$ it is possible to prepare chromatographic systems with high resolution fractionating oligomers only according to M, i.e. separating polymer homologues. For this purpose the value of $-\varepsilon_e$ should be made similar to that of $-\varepsilon_{in}$. For example, end groups, such as OH group, should be blocked by less adsorption-active radicals, such as the residue of meta-di-nitrobenzoic acid. Fig.17 shows that under these conditions it is possible to achieve effective separation according to M even for polysiloxane diol (Ref.27) with units exhibiting very low adsorption activity.

g) Temperature effects in the adsorption chromatography of polymers. An increase in temperature decreases the viscosity of the solvent and the polymer solution and increases the diffusion coefficient of macromolecules. This leads to the following useful effects in the chromatography of polymers:

1) Decrease in pressure at the column inlet at the predetermined elution rate;

2) Suppression of concentration effects observed in the mobile phase which deform the polymer zone;

3) Decrease in the spread of the chromatographic zone owing to increasing inner- and outer-diffusion mass transfer and the resulting increase in the resolution and sensitivity of the analysis.

All this forms the basis of well known recommendations to carry out the chromatography of polymers at high temperature. These features refer both to exclusion chromatography and to adsorption chromatography. However, in the latter case a new factor appears: the effect of temperature on $-\Delta F$ in the adsorption of macromolecules. This temperature effect (T) becomes apparent in the change in $-\varepsilon(T)$. Moreover, since $-\varepsilon$ is the difference between the energies of interaction of the polymer segment $-\varepsilon_{pa}$ and of the solvent $-\varepsilon_{sa}$ with the surface of the adsorbent:

$$-\varepsilon(T) \simeq [-\varepsilon_{pa}(T)] - [-\varepsilon_{sa}(T)]$$

the temperature dependence $-\varepsilon(T)$ can be either positive or negative (owing to the difference in the temperature coefficients $-\varepsilon_{pa}$ and $-\varepsilon_{sa}$). As a result, when the temperature changes, $-\varepsilon(T)$ can pass through the point of the critical energy $-\varepsilon_c$ and the exclusion chromatography of polymers can

be transformed into the adsorption chromatography and vice versa. The effect of temperature on the chromatographic behaviour of PS on KSK silica gel has been studied (Ref.28). It was shown that as the temperature increases, the exclusion chromatography of PS becomes the adsorption chromatography passing through a series of states with various values of $-\varepsilon$ including that close to $-\varepsilon_c$. The latter should also depend on temperature, if only owing to the temperature change in the length of the PS segment. This temperature transition from adsorption chromatography to exclusion chromatography can be used for the continuous chromatography of polymers on one column with the simultaneous changes in the temperature and in the flow direction. As a result, in one direction the macromolecules are separated under the conditions of exclusion chromatography (macromolecules of higher M move faster) and in the opposite direction under the conditions of adsorption chromatography (large macromolecules move more slowly) (Ref.29). This exclusion-adsorption chromatography can be effective in the fractionation of polymers with similar values of M.

NEW METHODS OF QUANTITATIVE ADSORPTION CHROMATOGRAPHY

Among all types of the polydispersity of polymers the molecular-mass distributions, MMD, the composition heterogeneity, CH, of copolymers and the distribution of the types of functionality, DTF, of oligomers are of the greatest practical interest. MMD is determined by the standard GPC method and great advances have been made in this field. Adsorption chromatography is used in the analysis of CH of copolymers and DTF of oligomers. In the latter case owing to great differences in the adsorption characteristics of oligomers of various functionalities and, hence, their easy separation, a simple method has been used: adsorption TLC in combination with a scanning flame-ionization detector FID (Ref.30). Probably, the TLC-FID method with the use of chromatographic systems separating oligomers only according to functionality (Fig.7) solves the problem of DTF of oligomers.
The analysis of continuous distributions (MMD of homopolymer) and CH of copolymers) by adsorption chromatography is complicated by the absence of a universal calibration dependence of the type of the Benoit calibration in GPC. Hence, it is necessary to use for calibration polymers with narrow dispersity according to composition or M but their preparation is very difficult. Probably, this is one of the reasons hindering the use of adsorption chromatography in polymer analysis. Two methods of solving this problem can be used:

1) to use for calibration polydisperse samples with a known distribution and 2) to use a detecting system directly characterizing the polymer fraction according to the property in which we are interested (M or chemical composition).

a) Determination of MMD of homopolymers by TLC with the calibration of the plate by a polydisperse polymer with a known MMD.

Polydisperse samples of any polymer used for calibration can readily be characterized by GPC. This permits the use of adsorption TLC for mass analyses of MMD of new homopolymers in scientific laboratories and in industry. However, quantitative TLC is difficult because it is a two-stage process. Fig.18 shows the stages in the determinations of the MMD of polymers by TLC with plate calibration by using a polydisperse polymer. When the spot undergoes densitometry in the direction transverse to the eluent flow at present intervals Δx (Fig.18a), it is possible to obtain the distribution of the substance along the spot axis. If this normalized integral distribution $F(x)=\int_a^x P(x')dx' / \int_a^b P(x')dx'$ is compared to the normalized integral MMD of this polymer obtained from GPC: $f(\log M)=\int_c^d w(\log M)dM/M / \int_c^d w(\log M)dM/M$ (where a, b, c and d are the integration limits) at $F(x)=f(\log M)$ (Fig.18b), we obtain the calibration dependence $x(\log M)$ (Fig.18c). This dependence is in good agreement with the calibration dependence obtained by using polymer standards (points*) in Fig.18c). This ensured good agreement of the MMD values for PS obtained from TLC by using this calibration and from GPC (Fig. 18d).
In fact, the values of $M_w \cdot 10^{-5}$ (GPC-1.15, TLC-1.19), $M_n \cdot 10^{-4}$ (GPC-4.1, TLC-5.2) and M_w/M_n (GPC-2.8, TLC-2.3) are in good agreement. It should be noted that in the case of TLC the more narrow MMD at low M and the resulting high value of M_w depend on the final sensitivity of detection on a thin layer plate which does not permit the determination of polymer fractions at low concentrations.

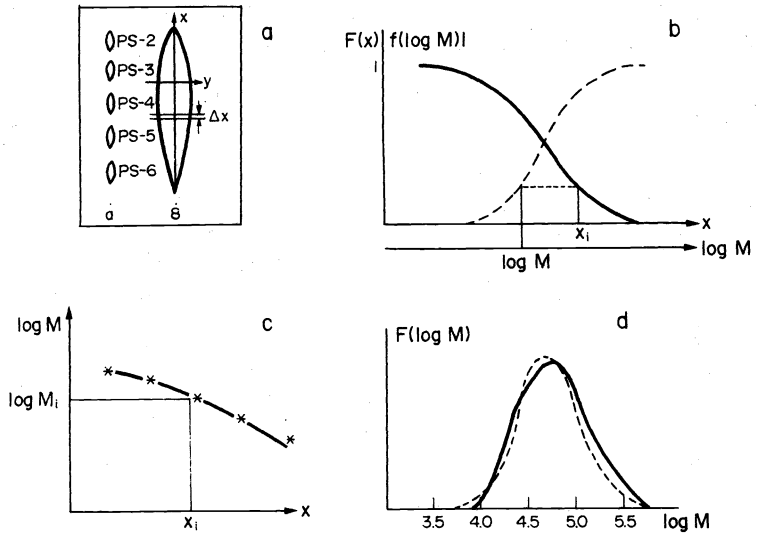


Fig.18. Determination of MMD of PS by TLC. a-thin-layer chromatogram of PS (a) with narrow disperse standards and (b) polydisperse samples; b-integral PS distribution of PS on the plate (——) and integral MMD of PS according to GPC (------); c - calibration dependence log M(x) obtained for polydisperse PS, * - PS standards; d - MMD of PS according to GPC (----) and TLC (——).

b) Micro-column adsorption chromatography with photometric detection at two wave-lengths - an absolute method for the determination of the composition heterogeneity of block copolymers.

As has been shown in section 1a, in adsorption chromatography on an adsorbent with the pore size smaller than the size of macromolecules in the free state, the separation of the block copolymer occurs predominantly according to composition and exhibits little dependence on M. If a detecting system is used permitting the determination of the copolymer composition in the eluent, it is possible to determine the CH of the copolymer by the absolute method, i.e., without calibrating the chromatograph by using samples with narrow dispersity according to composition. Unfortunately a spectrophotometric detector with photometry at two wave-lengths makes it possible to analyse by this method only the CH of block copolymers because in the case of random copolymers the extinction of its components varies depending on the type of the neighbouring units. This idea was carried out in the studies of CH of a block copolymer of styrene and methyl metacrylate by using a micro-column liquid chromatograph KhZh-1305 (the special Design Bureau of analytical Instruments, Academy of sciences of the USSR).

The separation of the copolymer was made on a column 0.6x220 mm packed with KSK silica gel (D ≃ 100 Å, grain diameter, d_p=9±1 μ). The value of HETP of this column 40 μ (for biphenyl in exclusion chromatography, K_d=1) was attained, it is ~4 dp. Fig.19 shows the separation of PS-standards and diphenyl on this column.

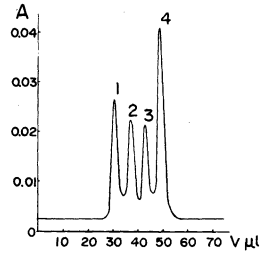


Fig.19. Exclusion chromatography of PS with M_n=3.3·10^4 (1) 10^4(2), 2.1·10^3(3) and diphenyl (4) on a microcolumn liquid chromatograph KhZh-1305 (the Special Design Bureau of analytical Instruments, Academy of Sciences of the USSR). Column 0.6x220 mm with KSK silica gel (d_p= 9±1μ), eluent-dichloromethane, elution rate 2.8 μl/min. Sample: 0.6 μg of PS and 0.01 μg of diphenyl.

Fig.20 shows the chromatography of an AB block copolymer (St-MMA) containing 52% of MMA with a bimodal distribution according to M (block copolymer exhibits two maxima with $M=10^5$ and $3\cdot10^5$). This polymer sample also contains a PS precursor with $M_w=6\cdot10^4$ and a low molecular component of unknown nature.

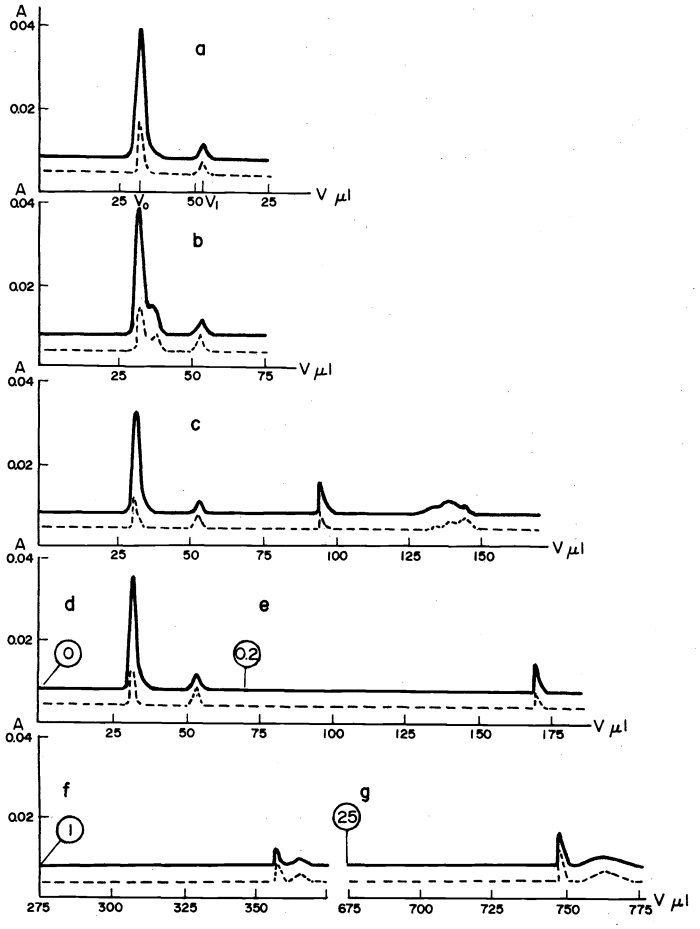


Fig.20. Micro-column chromatography of S-MMA block copolymer containing an admixture of PS ($M_w = 6\cdot10^4$) on a KhZh-1305 chromatograph; column 0.6x220 mm with KSK silica gel ($d_p = 9\pm1$ μ). Eluent-dichloromethane with methanol, elution rate 2.8 μl/min. a) in pure dichloromethane, b) in 2.7% methanol, c) with a methanol gradient from 2.3 to 2.5%, d)-g) stepwise elution. The arrow denotes the moment of eluent change (the percentage of methanol in the eluent is shown in the circle). Photometry at $\lambda =$ = 260 nm (—) and $\lambda = 236$ nm (---).

It is clear that as the methanol contents in dichloromethane decreases, exclusion chromatography (Fig.20a and b) passes into adsorption chromatography (Fig.20c). The block copolymer fraction with the highest content of MMA begins to interact with the adsorbent surface and is separated from PS (Fig.20b) which continues to be eluted with the free column volume v_o. The retention volume v_R of block copolymer fractions gradually changes approaching the total volume of the column v_T (this is still exclusion chromatography. Fig.20b) and finally its v_R becomes higher than v_T (this is already adsorption chromatography - Fig.20c).

To determine the composition inhomogeneity of the block copolymer it was introduced into the column in pure dichloromethane. In this case only the PS-precursor and the low molecular component were eluted from the column under conditions of exclusion chromatography at $v_R=v_o$ and $v_R=v_T$, respectively (Fig.19d). After this the column was successively eluted with mixtures of dichloromethane and methanol with a gradually increasing content of the latter. Some chromatograms are shown in Figs 20d-g. These chromatograms are characterized by a narrow zone of the block copolymer which is eluted at the front of the methanol zone moving down the column. This zone includes the fractions of the block copolymer the composition of which corresponds to $-\varepsilon \leqslant -\varepsilon_c$. This zone moves according to the laws of displacing chromatography in front of the methanol zone (from the standpoint of the mechanism of interaction of the block copolymer with the adsorbent these are the conditions of exclusion chromatography). The second zone spread and containing the fractions of the block copolymer with $-\varepsilon > -\varepsilon_c$ moves at a lower rate under the conditions of adsorption chromatography.

The photometry of the eluate at two wavelengths $\lambda=260$ nm (PS absorption) and $\lambda=236$ nm (PS and PMMA absorption) makes it possible to determine con-

tinuously the copolymer composition and to calculate the distribution of the block copolymer according to composition from the chromatogram (Table 1). The calculated mean composition of the block copolymer (54% MMA) is in good agreement with that determined by spectrophotometry (52% MMA)

TABLE 1. Fractions of the St-MMA block copolymer obtained by micro-column chromatography

Fraction number	1	2	3	4	5	6	7	8	9	10
Methanol % in the eluent	0	0.2	0.6	1.0	1.0	1.3	1.8	2.2	2.5	2.5
MMA content,	0	49	62	72	84	21	30	43	82	92
Quantity of the polymer (n mole)	10.7	3	10.5	1.9	1.3	1.2	2.9	4.2	6.9	10

Table 1 shows that macromolecules of two types are present in the copolymer (in fractions 2-5 and 6-10, respectively); the content of MMA in them is the same but they are eluted from the column at different v_R. Since M of the block copolymer increases with the increasing content of MMA, these results may be attributed to an increase in the adsorbability with increasing M. (It should be borne in mind that the copolymer investigated is bimodal according to M.)

The structural features of the MMA block (such as different stereoregularities) can drastically affect the adsorbability of the block copolymer. The adsorption chromatography of block copolymers with detection at two wavelengths described here is an absolute method for the determination of the composition heterogeneity. It should be noted that in principle the microcolumn chromatography of block copolymers is similar to the TLC of block copolymers with the scanning of the chromatogram at two wavelengths (Ref.31). However, it has no drawbacks of quantitative TLC related to light scattering on the adsorbent layer and two-stage quantitative analysis. Evidently the procedure of the investigation of CH of the block copolymer shown in Fig.20 requires much time but it can be greatly reduced by using a continuous methanol gradient. Further development of this method for the analysis of CH of copolymers should involve the use of other more universal detecting systems, in particular, the use of infrared spectrophotometry.

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