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

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### SUMMARY

A method based on adsorption thin-layer chromatography has been developed for diagnosing linear and branched polystyrenes according to the character of the dependence of the  $R_F$  values on the eluent composition.

It has been shown that micro-fractionation of narrow-disperse mixtures of linear and branched polystyrenes by means of gel permeation chromatography, with subsequent thin-layer chromatographic analysis of the fractions, permits the quantitative determination of the percentage of linear and branched components, the molecular weight of linear polystyrenes and the hydrodynamic radii of linear and branched components.

The hydrodynamic radii permit the determination of the values of molecular parameters for branched polystyrenes (molecular weight, length of branches) within the limits of the selected model concepts.

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### INTRODUCTION

The synthesis of macromolecular compounds yields, as a rule, polydisperse products. In the case of homopolymers, the synthesized macromolecules differ in molecular weight (MW), molecular unit arrangement ("head-to-tail" and "head-to-head" stereoregularity) and degree of branching. In random copolymers, the polydispersity is manifested in differences of MW and composition (compositional inhomogeneity) of macromolecules. In complex polymer systems, such as block copolymers, graft copolymers and branched homopolymers, the polymer contains, apart from the main product (which is also characterized by polydispersity of MW and of composition and type of branching), the corresponding linear homopolymers. Up to the present, the investigation of these polydisperse systems has been a very complex and laborious task and often cannot be carried out at all by classical methods of polymer analysis. Important progress in this field was attained after gel permeation chromatography (GPC) of polymers had been developed<sup>1</sup>, which permits the easy determination of their molecular-weight distribution (MWD) and of their average molecular weights (AMW). The thin-layer chromatography (TLC) of polymers<sup>2,3</sup> permits the determination of the MWD and AMW of homopolymers<sup>4-6</sup>, of composition

homogeneity of random copolymers<sup>7-9</sup>, and the diagnosis of stereoregular polymers<sup>10</sup> and block and graft copolymers<sup>2</sup>. The TLC of polymers provides great analytical possibilities owing to the high sensitivity of this method (several micrograms of the polymer are sufficient for analysis) and the speed of the analysis (10-15 min). Nevertheless, the TLC of polymers is not an absolute method because reference polymer samples should be used and their method of preparation is difficult.

This defect can be overcome and the possibility of obtaining information on the polymer by TLC can be greatly increased if TLC is combined with other methods, such as GPC and pyrolytic gas chromatography (PGC). GPC is essentially an absolute method for determining the size of macromolecules<sup>11</sup>. When viscometry or osmometry are used in combination with GPC for the analysis of polydisperse samples, their MWD can also be determined, and consequently in this case GPC provides an absolute method for determining MWD<sup>12,13</sup>. Hence polymer fractions (even the fractions of an unknown polymer) obtained by means of GPC can be easily characterized in terms of the MW and the size of the macromolecules. PGC is a precise, reliable and very sensitive method for the determination of the copolymer composition<sup>14</sup>. GPC permits the determination of the copolymer composition even with a component ratio of less than 1:50 (ref. 15). Also, PGC can be used for estimating the AMW of some homopolymers (such as polymethylmethacrylate<sup>16</sup>) and for investigating the stereoregularity of polymers (polypropylene<sup>17</sup>) and short-chain branching (polyethylene<sup>18</sup>).

It is also advisable to combine these three chromatographic methods because analytical instruments for GPC permit the very effective fractionation of milligrams of polymers, while TLC and PGC require microgram amounts. Hence the analytical instrument for GPC may be used for the micro-preparative separation of polymers into fractions, which are subsequently analyzed by TLC and PGC.

This paper describes the application of combined chromatographic methods, including TLC and GPC, for the analysis of mixtures of polystyrenes containing low-molecular linear and branched components.

## EXPERIMENTAL

### *Materials and methods*

*Gel permeation chromatography.* Experiments on GPC were carried out with a Soviet ChZh 1302 liquid chromatograph for polymer analysis (Special Design Office of Analytical Instruments of the Academy of Sciences of the U.S.S.R.) using five Waters Associates chromatographic columns:  $10^5 + 3 \cdot 10^4 + 10^4 + 10^3 + 5 \cdot 10^2$  Å. Toluene was used as eluent. The sensitivity of the refractometer was  $2 \cdot 10^{-4}$  refractive index units for the whole scale.

*Thin-layer chromatography.* Silica Gel KSK was used with a mean pore diameter of 80 Å, a specific pore volume of 0.9 ml/g and a particle diameter of 20-40 μm. The plates, 6 × 10 cm with a sorbent layer 200 μm thick, were prepared with an automatic applicator (K1Ch-01 equipment for thin-layer chromatography manufactured by the Special Design Office of Analytical Instruments of the Academy of Sciences of the U.S.S.R.).

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

For developing the spots, the plates were sprayed with a 1% solution of  $\text{KMnO}_4$  in concentrated  $\text{H}_2\text{SO}_4$  and heated at  $160^\circ$  for 10–15 min. The polymer zones were developed as black spots.

Densitometric analysis of the chromatograms was carried out with an MFTCh-1 microabsorptiometer-fluorimeter<sup>10</sup>.

*Reference polymers.* Standard polystyrenes samples with narrow fractionation (Waters) with  $M_w/M_n < 1.05 - 1.2$  were used.

*Polymer samples.* Samples of linear and branched polymer systems were prepared by polymerization of styrene with butyllithium and polystyryllithium as initiators.

## RESULTS AND DISCUSSION

Linear and branched macromolecules of the same MW differ in hydrodynamic size. Nevertheless, neither classical methods of fractionation nor GPC permit the adequate separation of linear and branched macromolecules of similar size. This makes it impossible to analyse mixtures of linear and branched macromolecules by these methods.

### *Thin-layer chromatography of linear and branched polymer systems*

Using TLC, we have established that the character of the dependence of the  $R_F$  values on the content of the adsorption-active component (acetone) in the eluent is different in linear and branched polystyrenes: in linear polystyrenes this dependence is stronger than in the branched ones. Furthermore, linear and branched polymer systems with similar hydrodynamic dimensions are readily separated on the chromatographic plate (Fig. 2).

These principles were used as a basis for the analysis of polymer samples with narrow dispersity with  $M_w/M_n < 1.1$  (according to GPC) containing linear and branched polystyrenes.

Using the dependence of the  $R_F$  value of the polymer component on the acetone content in the system cyclohexane-benzene-acetone (Fig. 2), it is possible to identify

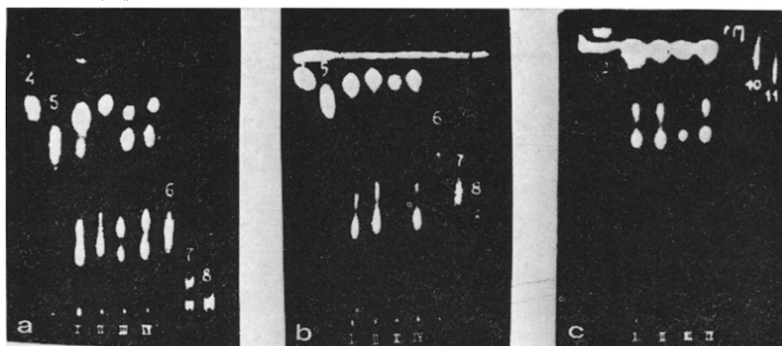


Fig. 1. TLC of four samples (I, II, III, IV) containing linear and branched components and of standard polystyrenes with  $M_w$ :  $4800$  (3),  $10 \cdot 10^3$  (4),  $19.75 \cdot 10^3$  (5),  $50 \cdot 10^3$  (6),  $100 \cdot 10^3$  (7),  $171 \cdot 10^3$  (8),  $830 \cdot 10^3$  (10) and  $2 \cdot 10^6$  (11) in the system cyclohexane-benzene-acetone (12:4:2) where  $\gamma$  is (a) 0.4, (b) 0.8, and (c) 1.5.

linear and branched components in the investigated mixture by comparing their chromatographic behaviour with that of the reference sample of linear polystyrenes.

Although the theory of linear polymer adsorption is well developed<sup>20-23</sup>, the adsorption of branched macromolecules has not been considered theoretically. It may be suggested, however, that differences in the adsorption capacity of linear and branched polymer systems are associated with the following peculiarities of their adsorption behaviour. At high interaction energies (low content of acetone in the eluent), linear polymers are flattened to a much greater extent than branched polymers, and consequently a larger proportion of segments comes into contact with the adsorbent. As a result, under these conditions, their adsorption capacity is higher than that of branched polymers. In contrast, at low interactions (high content of acetone in the eluent), branched macromolecules in which the segment density per unit of surface area is higher than in the linear ones, are adsorbed more strongly than the latter. It is clear that differences in the adsorption capacity of linear and branched macromolecules should increase with the degree of their branching. Evaluating the experimental results (Fig. 2) from this standpoint, it can be concluded that components 1 and 2 of the sample I are branched (component 1 to a greater extent), while components 3 and 4 are linear. Although component 3 is close to the corresponding linear polymer system with  $M_w$  of 19,750 by its chromatographic

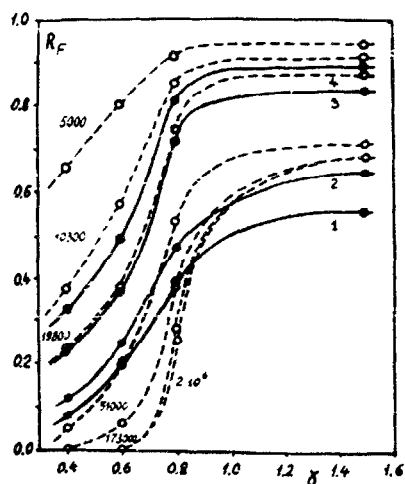


Fig. 2. The dependence of the  $R_F$  values on acetone content ( $\gamma$ ) in the system cyclohexane-benzene-acetone (12:4: $\gamma$ ) for linear and branched components of sample I (solid lines) and linear reference polystyrenes (broken lines).

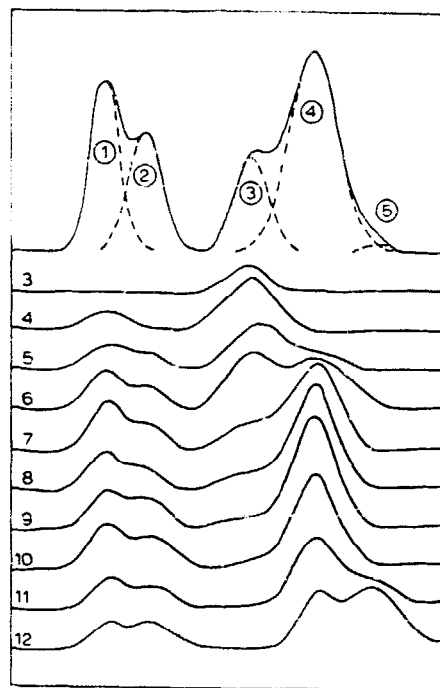


Fig. 3. Densitograms of thin-layer chromatograms of the total polymer sample No. 1 and its fractions, obtained by means of GPC.

behaviour, nevertheless there are slight differences that may be due to a low degree of branching in component 3.

*Microfractionating polymer samples by means of GPC and TLC of the fractions obtained*

Further analysis of the polymer samples was carried out by their separation into 12 fractions by GPC on a ChZh-1302 chromatograph with a system of styrogel columns, by the TLC of each fraction and by densitometry of the chromatograms.

Densitograms of sample I (upper part) and of its fractions (3-12) are shown in Fig. 3. The upper part shows the method for separating densitometric peaks into components. These results enabled us to represent the chromatogram of the polymer sample obtained by TLC as a superimposition of the elution curves of linear and branched polystyrenes constituting this sample (Fig. 4). In this case we detected a fifth, linear, component of low molecular weight. This procedure permitted (according to the GPC data) the determination of the percentage of the components, the estimation of molecular weights of linear components and the  $M_w$  of branched polystyrenes (components 1 and 2) using definite model concepts concerning the structure of branched polymers (as will be shown below).

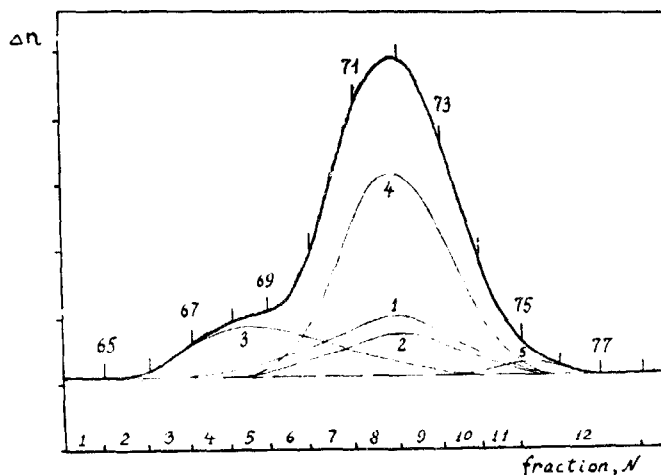


Fig. 4. Elution curve obtained for sample No. 1 by means of GPC and the component distribution in this sample (according to TLC data). The figures on the upper curve refer to elution volumes (counts).

Table I shows the contents of the polymer components in the four samples under analysis as well as the AMW of linear polymers (according to the TLC data of the unfractionated sample and to the combination of GPC and TLC) and the AMW of branched polystyrene (according to the combination of GPC and TLC).

As can be seen from Table I, the results obtained by GPC and TLC are in good agreement. Moreover, the combination of GPC and TLC enabled us to detect and characterize a minor component of the linear polymer system (component 5) present in the polymer samples to the extent of 1-4%.

*Determination of the molecular weights of branched polymer systems*

According to the recommendation of COLL<sup>24</sup>, we calibrated the chromatographic columns in hydrodynamic radii ( $R_h$ ):

TABLE I  
RESULTS OF ANALYSIS OF MULTICOMPONENT SAMPLES OF POLYMER SYSTEMS CARRIED OUT BY MEANS OF A COMBINATION OF GPC AND TLC

Sample	Method of analysis	Components		Linear polymer system							
		Branched polymer system									
		1	2	3	4	5					
			$M_{\text{MPP}} \times 10^{-3} \%$	$M_{\text{MPP}} \times 10^{-3} \%$	$M_{\text{MPP}} \times 10^{-3} \%$	$M_{\text{MPP}} \times 10^{-3} \%$	$M_{\text{MPP}} \times 10^{-3} \%$	$M_{\text{MPP}} \times 10^{-3} \%$	$M_{\text{MPP}} \times 10^{-3} \%$		
1	GPC	17	12.5	14	11.7	16	21.5	57	11.5	1	5.5
	TLC	22		16		17	20.5	45	12.6	—	5.0
2	GPC	23	10.5	15	10.6	16	19.5	42	10.5	4	5.0
	TLC	20		15		14	18.0	45	10.0	—	5.0
3	GPC	25	13.8	17	13.3	13	23.3	44	11.0	1	5.5
	TLC	22		15		15	21.0	48	12.0	—	5.0
4	GPC	26	12.1	20	11.8	18	22.0	32	10.0	4	5.0
	TLC	25		21		18	20.0	31	11.0	—	5.0

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

and on the basis of Fig. 4 we obtained the elution curves of polymer samples in the form of functions of  $C$  against  $\log R_s$  (Fig. 5). Here  $[\eta]$  is the intrinsic viscosity of the standard polymer system and  $N_A$  is Avogadro's number.

Fig. 5 permits the determination of the  $R_s$  values corresponding to the maximum of each component, and even for the component representing a very narrow polymer fraction ( $M_W/M_N < 1.1$ ) these values correspond to their mean hydrodynamic radii.

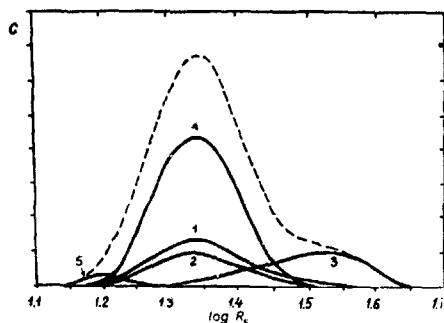


Fig. 5. Concentration curves of the component distribution in sample No. 1 as a function of the logarithm of the hydrodynamic radii ( $\log R_s$ ).

According to TSVETKOV *et al.*<sup>25</sup>, the hydrodynamic radius  $R_s$  is related to the number of random segments  $N$ , segment length,  $b$ , and the branching factor,  $h$ , which represents the ratio between  $R_s$  for branched and linear macromolecules with  $N$  segments by the following equation:

$$R_s = 0.78 \cdot \frac{h}{\sqrt{6}} \cdot b \cdot N^{\frac{1}{2}} \quad (2)$$

For the given polymer system it is easy to relate its  $R_s$  to the MW:

$$R_s = 0.225 \cdot h \cdot MW^{\frac{1}{2}} \quad (3)$$

Hence, if we know  $R_s$  and  $h$ , we can find the MW of the component of the branched polymer system.

Using the kinetic data obtained in the synthesis of polymer system samples and the results of TLC, we have suggested the structures of the branched polymer system components and have selected for them the  $h$  values in accordance with data of GRECHANOVSKII<sup>26</sup>.

For instance, for sample 2 obtained in the polystyrenes synthesis by using polystyryllithium as the initiator, the comb-like structure of the polymer chain with different degrees of branching is the most probable one; the sample may also contain the unreacted initiator (component 5). Consequently, the models of component branching are as follows (Table II).

The data in Table II permit the determination of the MW of the branched

TABLE II

MODELS OF COMB-LIKE BRANCHING FOR POLYMER SYSTEM COMPONENTS IN SAMPLE 2 AND THEIR CHARACTERIZATION (FACTOR  $h$ )

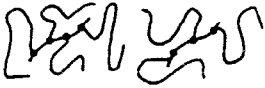
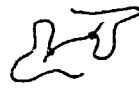



Property	Component				
	1	2	3	4	5
Type of branching according to TLC	Branched	Branched	Slightly branched	Linear	Linear
Models of branching					
$h$ for random distribution of the branch length	0.916	0.931	0.950	0.972	1.0
$h$ for fixed branch length	0.888	0.903	0.922	0.947	1.0

TABLE III

RESULTS OF ANALYSIS OF POLYMER SYSTEM SAMPLE 2

Parameter	Component					
	Branched polymer system		Linear polymer system			
	1	2	3	4	5	
$R_g$ (Å)		20.5	21.5	32.5	22.5	16.5
MW of the polymer	10,500	10,600	19,500	10,500	5500	
MW of the comb-like structure	5,000	5,000				
MW of the branch	1,400	1,900				
Contents of the component (%)	23	15	16	42	4	

component and the length of the branches by using eqn. 2 with the assumption that component 5 represents the backbone of the macromolecule. The MW of the polymer depends only slightly on the selection of the branching model, while the lengths of the branches depend on it to a greater extent. Table III lists as an example the complete results of analysis of polystyrene sample 2.

## CONCLUSIONS

These studies have shown the possibility of characterizing in detail the complex narrow-disperse ( $M_w/M_n < 1.1$ ) polymer system containing linear and branched polymer systems by means of the GPC-TLC combination. For a sample of 5 mg, it was possible to determine the following characteristics: percentage of the components, type of branching, MW and MWD of linear components, and, within the limits of the model used, the parameters of branched macromolecules (their MW, MW of the backbone and of the branches). A component present in an amount of less than 4% (in samples 1 and 3, less than 1%) has been detected and characterized.

This example of a complex multicomponent polymer system that cannot be



characterized by classical methods shows very clearly the great analytical possibilities of combined chromatographic methods for investigating polymers.

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