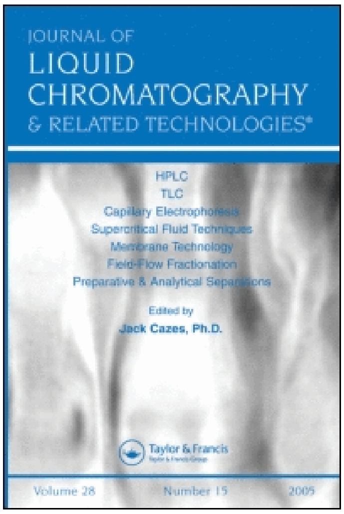

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ANALYSIS OF POLYDISPERSITY OF OLIGOMERS AND POLYMERS BY ADSORPTION THIN-LAYER CHROMATOGRAPHY

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Thin-layer chromatography /TLC/ has been widely used for the analysis of virtually all classes of low molecular weight organic substances.

In 1968 Inagaki /Japan/ /1/ and Belenkii and Gankina /2/ demonstrated that TLC could be successfully applied to the separation of high molecular weight compounds, such as synthetic polymers. This method has recently become a powerful analytical tool for the investigation of various types of polydispersity of polymers and oligomers. The principal mechanisms of the separation of polymers in TLC are the adsorption and

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the precipitation mechanisms. Precipitation TLS has been widely used by Inagaki for the separation of homopolymers and copolymers according to their molecular weight !MW/ /3,4/. The present authors dealt mainly with the development of the adsorption TLC /ATLC/ of polymers /5, 6/. The investigation of experimental possibilities of using ATLC of high polymers and oligomers was developed simultaneously with the theory of this method. This theory showed that the adsorption and the exclusion /gel-permeation/ chromatography of polymers and oligomers exhibit the same mechanism and also elucidated the mechanism of polymer distribution according to MW. composition and functionality /7, 8/. This theory made it possible to separate polymers and oligomers by ATLC according to one of these types of polydispersity.

Now one should consider some peculiarities of the TLC of macromolecular compounds and demonstrate wide possibilities of using it for the investigation of various kinds of polydispersity of oligomers and high polymers.

ATLC allows the separation of homopolymers over a wide range of MW from polymer homologues in oligomers /MW 300/ up to polymers with MW of $2 \cdot 10^6$. Fig. 1 shows the ATLC of oligomers. One can clearly see the high resolution of TLC permitting the separation of polystyrene /PS/ with MW of 600 into individual polymer

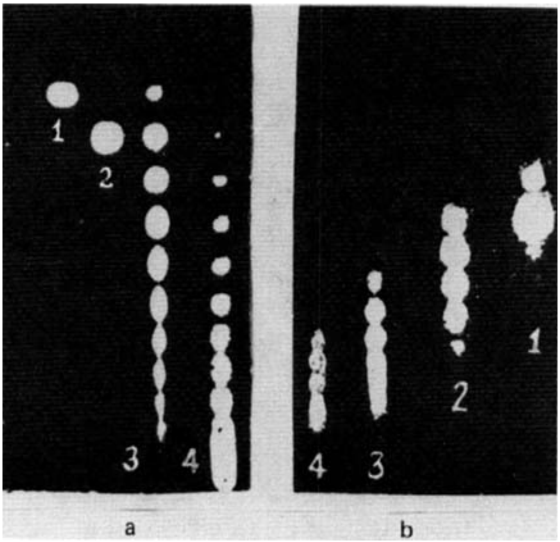

Fig.1.

ATLC of (a) polystyrenes with Mn: (1) 314, (2) 418, (3) 600, (4) 900 in cyclohexane - benzene (14:3) and (b) poly(- methylstyrene) fractions (1, tetramer, 2, hexamer, 3, octamer, 4, decamer) in carbon tetrachloride - heptane (2:1) on KSK silica gel.

homologues from 3 to 13-mers /9/. Fig. 1 also shoes the ATLC of oligo / -methylstyrene/. It can be seen that the 4-mer contains a small admixture of the 3-mer but 5-mer, 6-mer and 7-mer are a mixture of several polymer homologues. For example, 5-mer is a mixture of homologues from 4-mer to 8-mer.

When polymers are separated according to their MW by ATLC, the porosity of the adsorbent plays an important

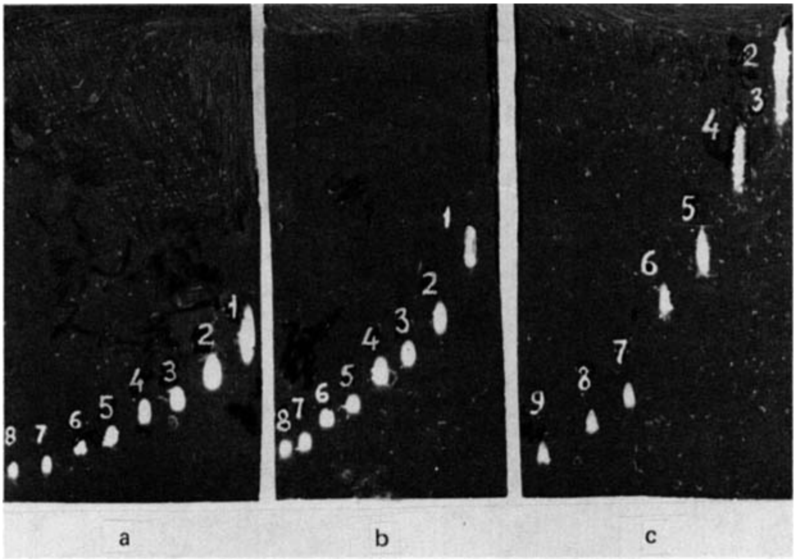

Fig.2.

Effect of pore size of silica gels / a) $\emptyset_p$ = 60 Å, b) $\emptyset_p$ = = 100 Å and c) $\emptyset_p$= 500 Å/ on the R_F of narrow-disperse PS (M_w /Mn 1.1) with M_n: (1) $9.6\cdot10^3$, (2) $20\cdot10^3$, (3) $36\cdot10^3$, (4) $49\cdot10^3$, (5) $111\cdot10^3$, (6) $193\cdot10^3$, (7) $404\cdot10^3$, (8) $773\cdot\cdot10^3$, (9) $1.99\cdot10^6$ in ATLC in cyclohexane - toluene - 2--butanone (17:2:1.6) (a,b) and (17:2:1.4) (c).

part /10/. The pore diameter of silica gels commonly used in TLC is 60 Å /"Merck"/ or 100 Å /"KSK", USSR/. Fig. 2 shows the separation of PS with MW ranging from 10.10^3 up to 10^6 on silica gels of different porosities. It is evident that a silica gel with the pore diameter of 60 Å permits the separation of PS only up to the MW of 50.10^3; when the pore diameter is 100 Å, effective separation up to the MW of 400.10^3 takes places; for the separation of polymers up to the MW of 10^6 it is necessary to use silica gels with the pore diameter of 500 Å.

It should be noted that the exclusion limits of ATLC correspond to much higher MW than those of gel-permeation chromatography /silica gels with the pore diameter of 60, 100 and 250 Å correspond to MW of 10^4, 5.10^4 and 2.10^5/. This fact can be explained by tje theory if ATLC showing that a macromolecule adsorbed in pores undergoes great conformational changes. When the pore size decreases /up to exclusion limit/, the adsorption energy of macromolecules increases. Precipitation TLC does not allow the separation of oligomers but is very effective for the separation of high polymers with MW up to 24.10^6 /11/.

Otoca has demonstrated for precipitation chromatography, macromolecules never penetrate the pores but interact only with the outer surface of adsorbent particles. The nature of the adsorbent does not play an important part in this process /12/.

ATLC not only permits the separation of polymers over a wide range of MW but is also very sensitive to adsorption active end groups in homopolymers. It is known that one sugar residue per PS molecule with MW 100.10^3 greatly increases its adsorption activity as compared to that ot common PS of the same MW /13/. On the basis of these data TLC allowed the estimation of the true percentage of grafting for PS grafted onto cellulose after the acid hydrolysis of the copolymer /11/. The possibility of the separation of PS of similar MW but with one or two carboxyl end groups or without any carboxyl groups was also shown my Min /14/.

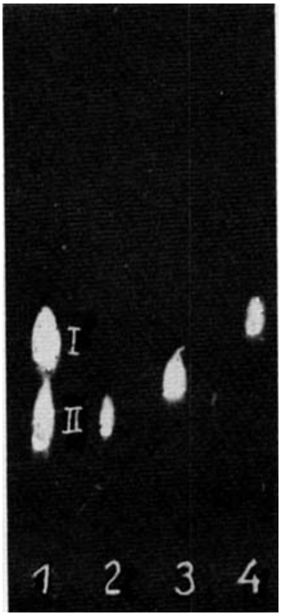

Fig.3.

ATLC of PS with M_n (1) $100\cdot10^3$ and narrow-disperse PS with M_n: (2) $404\cdot10^3$, (3) $193\cdot10^3$ and (4) $111\cdot10^3$ in cyclohexane - - benzene - acetone (12:4:0.7) on KSK silica gel.

ATLC was widely used to evaluate the homogeneity of homopolymers. Fig. 3 shows the ATLC of PS which according to the data of exclusion and precipitation chromatography, is narrow-disperse and unimodal. However, it can be seen that PS consists of two components one of which contains an adsorption active and group and is more strongly adsorbed /its R_F value is lower/.

The application of gradient ATLC to the separation of random polymers and block copolymers according to their composition reveals interesting possibilities. Fig. 4 illustrates the gradient ATLC of styrene-acrylonitrile /ST-AN/ random copolymers with an AN content ranging from 12 up to 44.7% /wt./ AN /15/ and that of vinylchloride - vinylacetate /VC-VA/ containing 6 to 28% /wt./ of VA /16/. It is clear that by using the chromatography of an unknown copolymer together with marked copolymers of known composition one can rapidly evaluate the compositional heterogeneity of random copolymers. Thus, the ST-AN copolymer investigated by us and located in the middle of the chromatogram contains about 25-31% of AN.

The most important factor here is that the adsorbability of copolymers with MW 50.10^3 is much more closely related to their heterogeneity of composition than to MW. This results from the theory and is proven experimentally. However, the more similar is the che-

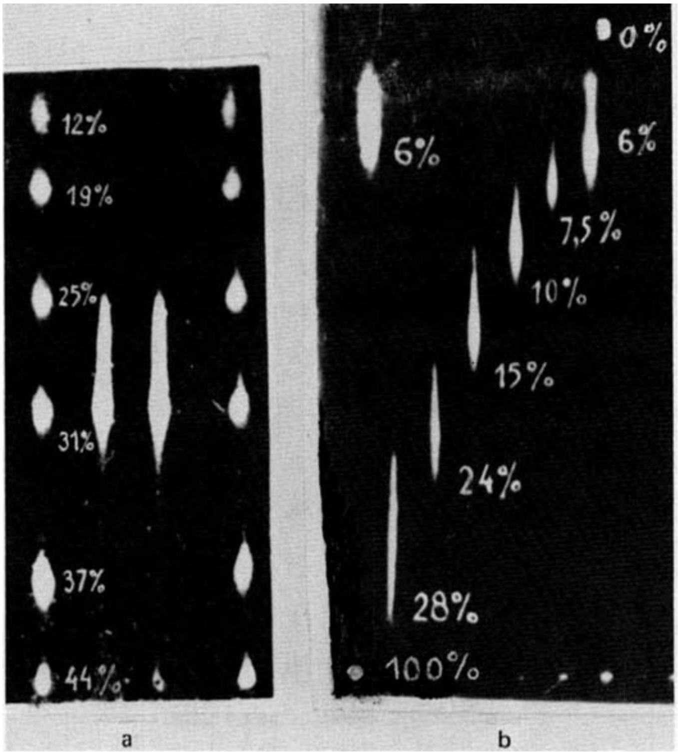

Fig. 4.

Gradient ATLC of (a) styrene-acrylonitrile (ST-AN) random copolymers (12-44% wt. AN) in carbon tetrachloride - methylene chloride (2:5) ——→ acetonitrile (3ml) (0.12 ml/min) and (b) vinyl chloride - vinyl acetate (VC-VA) random copolymers (6-28 % wt. VA) in 1.2 dichloroethane - carbon tetrachloride (1:1) (6 ml) ——→ 1.2 dichloroethane - 2-butanone (5:2) (6 ml) (0.24 ml/min) on KSK silica gel /15, 16/.

mical nature and, therefore, the adsorbability of copolymer units, the harder it is to carry out the fractionation of copolymers according to composition with the aid of ATLC regardless of their MW.

The important problem of the analytical chemistry of polymers has been the determination of the admixtures of homopolymers in block and graft copolymers. To solve this problem a number of TLC techniques was used. Fig.5

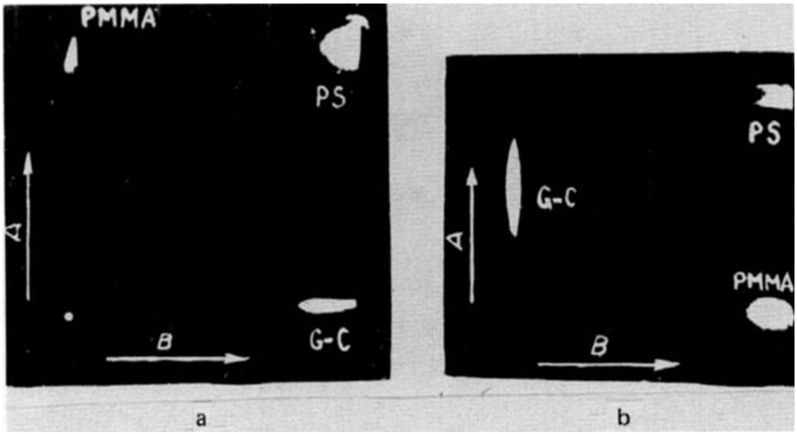

Fig. 5.

Two-dimensional ATLC of polymethylmethacrylate-polystyrene (PMMA-PS) graft copolymer. (a) chromatogram in acetone-acetic acid (12:2) in direction A and in chloroform - 2-butanone (12:2) in direction B, (b) chromatogram in cyclohexane - benzene - acetone (12:4:0.7) in direction A and in acetone - acetic acid (12:2) in direction B on KSK silica gel.

shows the use of two dimensional TLC for the determination of homopolymers in the polymethylmethacrylate- - polystyrene /PMMA.PS/ graft copolymer /5/. It is evident that by varying the eluent one can either displace both homopolymers and the graft copolymer arranging them on the chromatogram in different corners of the plate or displace only homopolymers into different plate corners, the graft copolymer remaining in the centre of the plate.

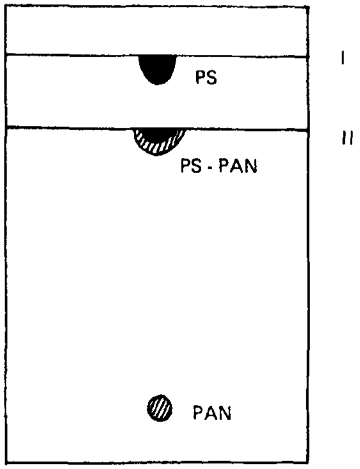

Fig. 6.

ATLC with multiple development of polystyrene-polyacrylonitrile (PS-PAN) block copolymer in toluene (I step) and toluene-dimethylformamide (1:1) (II step) on KSK silica gel. (● - black colour - 1.8 % $KMnO_4/H_2SO_4$, ◍ - yellow colour - 10 % NaOH).

For this purpose multiple development TLC can also be used. Fig. 6 shows the use of this technique for the investigation of a polystyrene - polyacrylonitrile /PS.OAN/ block copolymer /17/. It can be seen that the PS homopolymer moves at the toluene front. At the following elution step in the toluene - dimethylformamide system the PS-PAN block copolymer moves together with the front of the eluent, the PAN homopolymer remaining at the start.

Additional identification of these compounds was based on the colour test. The chromatogram was treated with a 1.8% $KMnO_4/H_2SO_4$ solution and a 10% NaOH solution with subsequent heating for 10 minutes at 140-150°C. /$KMnO_4$ detects only PS with the appearance of black colour whereas NaOH detects only PAN with yellow colour. The spot of the block copolymer turns black in the centre and yellow at the periphery.

If gradient ATLC is used, one can separate homopolymers from the block copolymer and simultaneously determine its composition and compositional homog

Fig. 7 shows the gradient ATLC[x] of the polystyrene

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[x] Here and below TLC was carried out on plates 6 x 9 cm with a silica gel layer with pore diameter of 10 ± 5 mm. The separated samples were detected my spraying the chromatograms with a 1.8% solution of $KMnO_4/H_2SO_4$ with subsequent heating at 140 to 150°C for 10 min. Polymer zones were developed as black spots on white background.

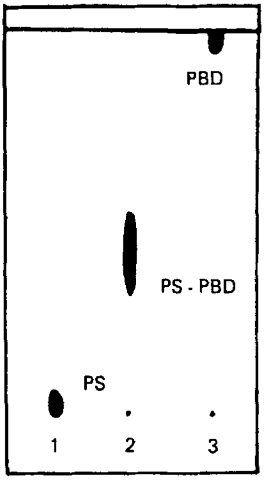

Fig. 7.

Gradient ATLC of (2)polystyrene-polybutadiene (PS-PBD) block copolymer and homopolymers: (1) PS and (3) PBD in cyclohexane - toluene (3.5:2.5) ⟶ toluene (6 ml) (0.12 ml/min) on KSK silica gel.

- polybutadiene /PS-PBD/ block copolymer. It is clear that under these conditions the block copolymer moves in the centre of the plate whereas the less adsorbed homopolymer /PBD/ moves together with the front of the eluent and the more adsorbed homopolymer PS remains at the start.

ATLC provides great possibilities for the separation of oligomers according to their MW and functionality. It was shown that the ATLC of oligomers with active end groups makes it possible to observe three types of R_F dependence on MW: when R_F increases with MW when it decreases and when R_F is independent of MW. The latter case provides the best conditions for the separation of oligomers according to their functionality /9/.

Fig. 8 illustrates the three above mentioned types of the R_F dependence upon MW for poly/ethylen oxides/ /PEO/. These dependences are related to different adsorbabilities of end and in-chain /or central/ units

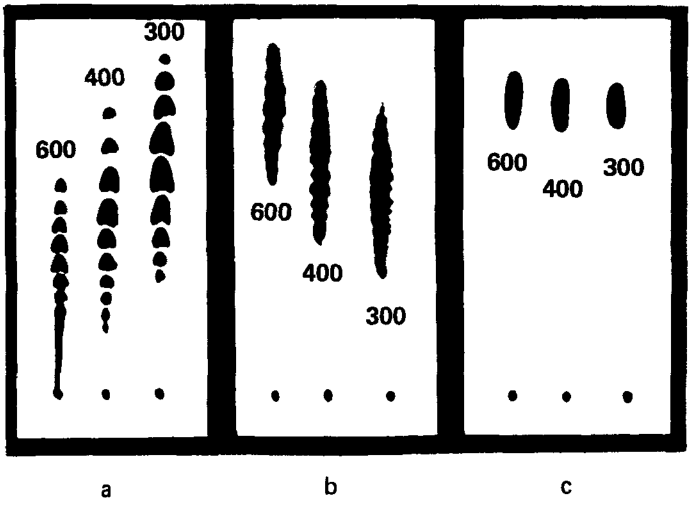

Fig.8'.

ATLC of poly(ethylene oxides) with M_n: 300, 400 and 600 on (a) KSK silica gel in pyridine - water (0.1:10), (b) Al_2O_3 in chloroform - ethanol (10:1) and (c) KSK silica gel in chloroform - pyridine (5:7).

of oligomers. When both types of units are adsorbed, adsorption increases with MW /negative R_F dependence/. When the adsorbability of the central units is zero /zero energy of adsorption/, the adsorbability of oligomers molecules does not depend on MW and they are separated only according to the number of adsorption-active end groups /according to functionality/.

We investigated non-functional, mono- and bifunctional oligoisoprenes /OI/ of different MW sent to us by Dr. Pokorny /Prague, CSSR Academy of Sciences/.

Fig. 9 shows the ATLC of these samples. It is clear that non-functional and monofunctional oligomers can be separated. Moreover, the mobility of non-functional oligomers decreases and that of bifunctional oligomers increases with increasing MW. Az eluent with a high displacing power is used to separate mono- and bifunctional oligomers. Non-functional OI move with the solvent front /i.e., according to the mechanism of exclusion chromatography/ and mono- and bifunctional OI are also separated according to MW. The R_F value increases with MW. It is evident that under these conditions the analysis of bifunctional and monofunctional oligomer admixtures can be carried out and the evaluation of the MW of functional OI can be made.

The possibility of the separation of 1.2-polybutadienes according to the type of functionality by

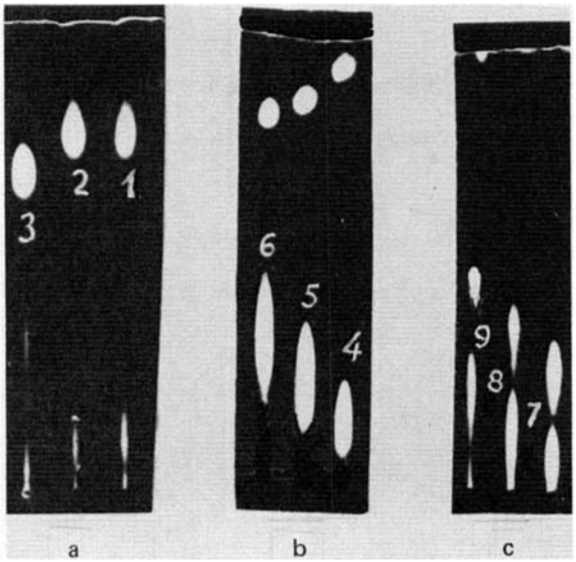

Fig. 9.

ATLC of oligoisoprenes (OI): (a) non-functional$^{x)}$OI with M_n: (1) 1600, (2) 3200 and (3) 9300 and (b) monofunctional OI with M_n: (4) 2600, (5) 5700 and (6) 9600 in heptane - chloroform (10:6) and (c) bifunctional OI with M_n: (7) 4300, (8) 8600 and (9) 9200 in cyclohexane - toluene - 2-butanone (10:1:0.5) on KSK silica gel. /^{x}) non-functional and monofunctional impurity components are located above samples 4-9/.

ATLC without their separation according to MW has been demonstrated /18/.

Using the effectiveness of ATLC for separating oligomers according to their functionality and MW we analyzed a complex oligomer compound. It was shown that the sample investigated was a mixture of two triols of poly /polypropylene oxide/ /PPO/ with different MW. One can see in Fig. 10 that in two-dimensional chromatography in water - pyridine the separation of PPO occurs

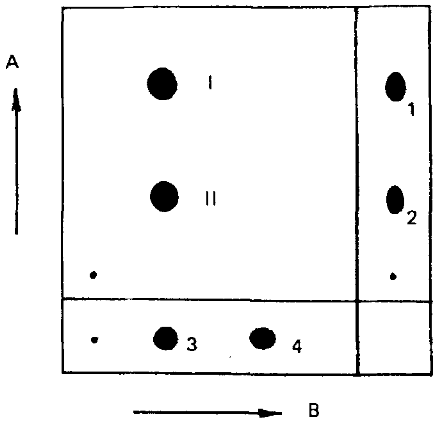

Fig. 10.

Two-dimensional TLC of an oligomer compound in water - pyridine (18:1.5) in direction A and in water-saturated ethylacetate in direction B on KSK silica gel. Poly(propylene oxides) (PPO) with M_n: (1) 425, (2) 1220, (3) 500 (PPO-triol) and (4) 425 (PPO-diol).

according to MW and the compound is separated into two components /I and II/ corresponding to PPO with MW 425 /1/ and 1220 /2/. When chromatography is carried out in water-saturated ethylacetate, PPO are separated according to their functionality /PPO - triol - 3 and PPO-diol - 4/, both components of compound moving on the triol level with MW of 500.

In the foregoing discussion various examples are given of the separation of oligomers with functional groups exhibiting a highes adsorption activity than the central units. It is interesting to study the behaviour of oligomers with end groups of lower adsorption activity than the central units.

<u>Fig. 11</u> shows the MW dependence of R_F for oligostyrenes with the secondary butil end group and non-alkyl oligostyrene. It is evident that when ATLC is carried out on silica gel, the secondary butil group has a lower adsorption activity than styrene units and therefore oligomers of this type have a greater R_F value than their non-alkyl analogues /19/.

Summarizing one should consider the main advantages introduced by the ATLC of polymers into the field of chromatography and analytical chemistry of polymers.

In the field of chromatography the method of the ATLC of polymers made it possible to increase the limits of using TLC for the analysis of macromolecular compounds

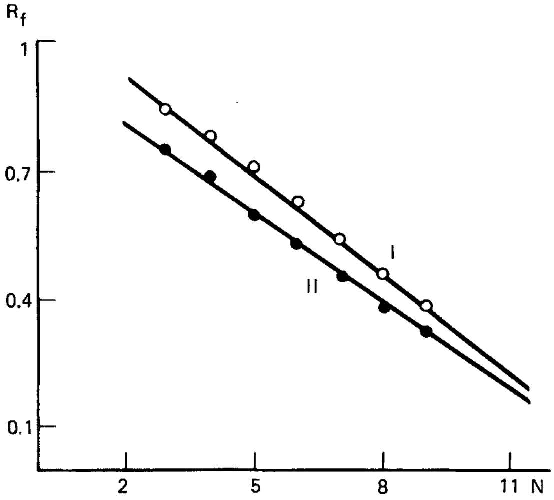

Fig. 11.

Dependence of R_F of oligostyrenes (I) with secondary butil group at the chain end and (II) non-alkyl species on MW (or degree of polymerization, N). ATLC in cyclohexane - benzene (20:0.5), twice on KSK silica gel /19/.

/with MW 10^6/. Moreover, taking as an example the analysis of functional oligomers it was possible to demonstrate the role of negative adsorption in adsorption chromatography. It manifests itself, for instance, in the positive MW-dependence of R_F for mono- and bifunctional OI.

Just as the highly effective GPC, ATLC demonstrated that polymers are a continuous series of polymer homologues with monotonously rising MW.

In the field of the analytical chemistry of macromolecular compounds the development of the ATLC of polymers provided a solution to a number of new problems that other physical and physico-chemical methods were unable to solve, such as to determine the functionally of oligomers apart from their polydispersity according to MW, separate macromolecules according to their geometry, stereoisomery, functionality and compositional heterogeneity regardless of their MW.

As to the fractionation of polymers and oligomers according to their MW, the advantage of GPC, this quantitative method of analysis of the molecular weight distribution of homopolymers, oligomers and block copolymers, are quite evident. However, one can successfully use ATLC for the express determination of the MW of homopolymers and oligomers. This method also permit the simultaneous determination of the homogeneity of polymers.

Hence, TLC is a highly effective and at the same time a simple, cheap and rapid method of investigation of various types of polydispersity of synthetic polymers and oligomers.

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