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# *Analysis*

## Applications of the Critical Phenomena Concept in Liquid Chromatography for Functionally Type Separation of Macromolecules

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SUMMARY

Functional type separation of hydroxyl-containing poly(butylen terephtalates) by liquid chromatography of molecules in "critical conditions" was investigated. Under such conditions the change in the free energy, $\Delta F$, of a homogeneous macromolecule equals zero when entering a pore, irrespective of its length; in this case the chromatogram obtained is not complicated by the separation of the molecules in terms of sizes, and contains information only on the types of functionality. The critical conditions of investigation have been determined on silica in a heptane-tetrahydrofuran (THF) mixture.

INTRODUCTION

An essential quantitative characteristic feature of reactive oligomers along with the molecular mass distribution (MMD) is the functionality type distribution (FTD) determining the content of zero-, mono- and bifunctional macromolecules in a sample (ENTELIS et al. 1973). "Defect" functionality molecules together with definite efficient functionality molecules are formed in the process of oligomer synthesis, as a result of different side reactions. Depending on the synthesis conditions, the share of these defect functionality molecules may be very substantial. Such defect functionality macromolecules will have a notable influence on the properties of oligomer based polymers, converting them, for example, from linear to branched. Therefore, it is important to determine the quantity and type of defect molecules or, in a general case, the FTD function.

One such method which proved to be sensitive to macromolecule functionality is liquid chromatography. By using the difference in the interaction of the end functional group and macromolecule chain groups with a stationary phase and choosing the necessary mobile phase, it is possible to develop, in a number of cases, a technique which allows one to analyse the FTD. However, to develop such a technique requires significant time, because it is, as a rule, carried out by the trial-and-error method. These specific techniques are not versatile and the chromatograms produced with their help often complicate their interpretation in view of the fact

that the molecular mass separation superpose the functionality types separation.

The purpose of this paper is to describe a principally new approach to determine the FTD oligomers using hydroxyl-containing poly(butylen terephtalate) (PBT) as an example. This approach is based on the general regularities of macromolecular chromatography, and was applied earlier for the analysis of poly(diethylenglycoladipates) FTD (GORSHKOV et al. 1983a).

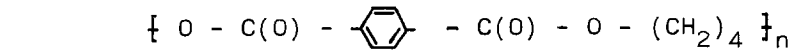
A fundamental feature distinguishing chromatography of macromolecules from that of low molecular substances is the existence of two chromatographic regimes: exclusion and adsorption. In the former case when the entropy contribution of $T\Delta S$ to the change in the free energy, $\Delta F$, of the molecules which enter the stationary phase pore exceed the change in the energy E at the expense of the contacting of the links with the pore walls; and in the latter case when $\Delta E > T\Delta S$. These modes are characterized by the elution sequence of molecules with different molecular masses leaving the chromatographic column. Under exclusion regime, the higher the molecular mass of the molecules, the sooner it elutes from the column, whereas under adsorption regime, it is quite the reverse.These two regimes are separated by a point referred to "critical conditions" whereat the entropy losses are compensated by the energy gain. In so doing, the free energy of the homogeneous macromolecule that has entered the pore equals zero, $\Delta F = 0$, while the distribution coefficient between the mobile and stationary phases, $K_d$, equals unity. According to the theory developed for the lattice model in slit-like pores (SKVORTSOV and GORBUNOV 1980; GORBUNOV and SKVORTSOV 1980; GORSHKOV et al. 1982 ) and the equality $\Delta F = 0$ in critical conditions is reached, irrespective of the chain length and pore size. Hence, it follows that the distribution coefficient for the functional macromolecules, $K_d^{(i)}$, in critical conditions depends on the functionality types (the number of functional groups in the macromolecule).

The theory was used for sufficiently long flexible macromolecules which can be simulated by the lattice model therefore the application of this theory to oligomers, strictly speaking, is inadequate. However, the main conclusion that the molecular mass separation vanishes in critical conditions, remains also valid for oligomers, as will be shown in this paper as well as in works GORSHKOV et al. (1983a,b).

Thus, the chromatogram of the oligomer sample obtained in critical conditions contains information only on FTD which is not complicated by the molecular mass separation. The molecules having a different number of functional groups elute at varied times. The elution time for macromolecules having a similar number of functional groups but differing in their molecular mass is one and the same.

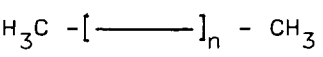
## EXPERIMENTAL

PBT oligomer samples at polymerisation degree, n , ranging from n = 0 to n = 10 were investigated. The oligomer residue assumes the form:

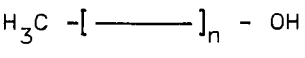


The PBT samples along with bifunctional macromolecules having the structure

contained zero functional molecules



and monofunctional molecules



The experiment was carried out on a high precision liquid chromatograph (HPLC) "SP8700", the sorbent being "Lichrosorb Si 60", the pore sizes being 60 A, the particle size being 7um. Detecting was carried out with a UV detector "SP8400" operating on a 264 nm wavelength (the sample absorption maximum), the volume of the introduced specimen being 10 ul, the sample concentration in the specimen being 0.1% vol. A "SP4100" integrator was used for quantitative processing of the chromatogram.

## RESULTS AND DISCUSSION

It is very simple to find the critical conditions for any polymer. For this purpose it is necessary to select two solvents in one of which the exclusion regime is realized on the chosen adsorbent (in our case on silica) while in the other - the adsorption regime (GORSHKOV et al. 1983b). For PBT, such solvents are THF and heptane. By smoothly changing the heptane content in mixed eluent, it is possible to pass over from adsorption to exclusion (or on the contrary) through the critical conditions, Fig. 1.

In the adsorption mode the small molecules are the first to eluate, in the exclusion mode - the large molecules, which is in agreement with the theoretical conceptions. The presence of functional groups, without changing the elution sequence, corresponding to the adsorption or exclusion regimes shift all the peaks to the region of large retention volumes $V_R$. In critical conditions there is practically no molecular mass separation; molecules of different degrees of polymerisation with one and the same functionality have one and the same retention volume.

The retention volume of zero functional molecules, $V_R^{(o)}$, in critical conditions is $V_R^{(o)} = V_O + V_P$, according to the main chromatographic equation. For the distribution coeffi-

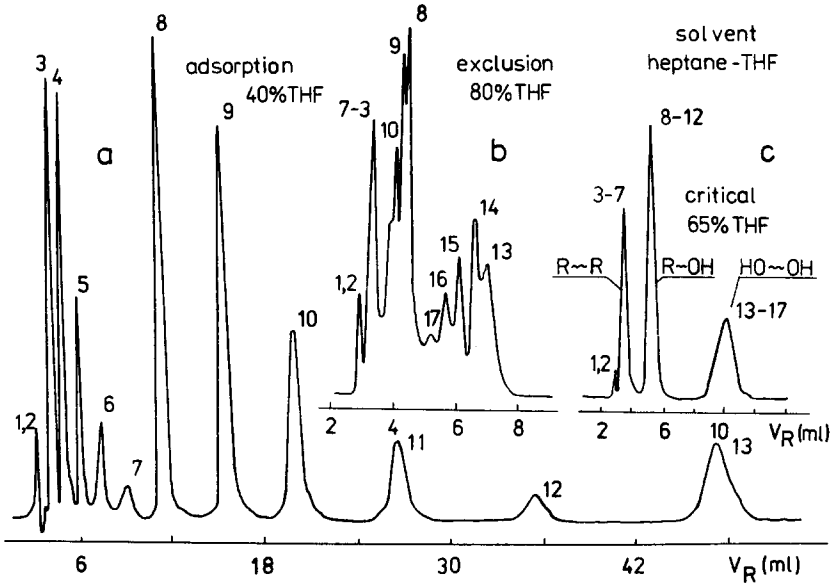



Fig. 1. Chromatograms of a PBT oligomer sample in different regimes of separation upon changing the composition of the THF-heptane eluent. Peaks 1,2 represent the solvent, peaks 3 to 7 - the zero functional (i=0) homologs with polymerisation degree n=0-4; peaks 8-12 monofunctional (i=1,n=0-4) ; peaks 13-17 bifunctional (i=2, n=0-4).

cients of mono- and bifunctional molecules, $K_d^{(1)}$ and $K_d^{(2)}$, we have a simple approximate relation, $K_d^{(2)} \approx [K_d^{(1)}]^2$ (SKVORTSOV and GORBUNOV 1980). For the system under investigation $K_d^{(1)} \approx 2.2$; $K_d^{(2)} \approx 5.2$, i.e. factually $K_d^{(2)} \sim [K_d^{(1)}]^2$.

Since $\ln K_d = \Delta F$, the change in the free energy is additive in respect of the number of functional groups. This may be accounted for by the fact that in such narrow pores,60 A, at least for a high-molecular tail of the MMD, the size of the macromolecules become comparable with that of the pores, which leads to statistical independence and additive contribution of the chain terminals to the change in the free energy.

Chromatograms of several PBT oligomer samples in critical conditions are illustrated in Fig.2. The same figure shows their gel-chromatograms for comparison. It is seen that the chromatograms of the samples having different (total) MMD are identical in critical conditions and distinguish only by different contents of molecules of different functionalities.

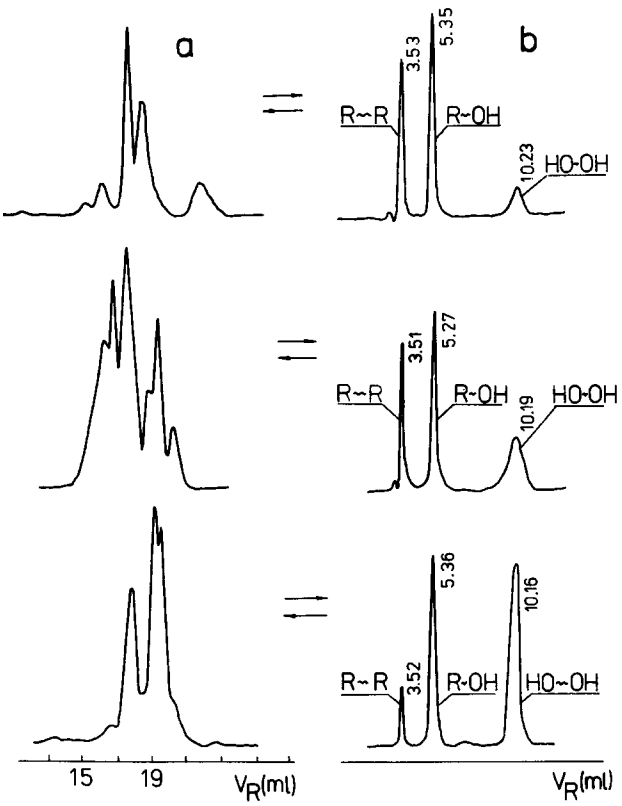



Fig.2. Gel-chromatograms (a) and chromatograms in critical conditions (b) of three PBT samples. a-microstyrogel 50,100,500 A, chloroform, 1 ml/min. b- Lichrosorb Si-60, THF-heptane (65%-35% vol), 1 ml/min. Sample volume - 10 ul.

## CONCLUSION

In conclusion, we wish to note the following. In those cases when the difference in energies between the interaction of the end-functional groups and the chain groups is small, because of the broadening, the peaks of different functionalities may not resolve in critical conditions. In this case it is necessary to choose other stationary phase of more selectivity. When the functional group is strongly adsorbed in critical conditions this is also not a desirable situation, since the retention volumes of monofunctional and particulary bifunctional molecules may become very large(this is noticeable in the case of rubber containing -OH groups on silica). In this case one should make the pore size larger, choose some other stationary phase or make use of the gradient. In the latter case one should bear in mind that peaks attributed to different functionality types may overlap and that there may take place a change in the separation regime. Finding the critical point is also very useful in this case.

The above-indicated consideration along with the theory was referred to a case of linear macromolecules. In practice however, we often encounter cases with branched molecules of

the star- or comb-like types. In order to separate such molecules it is necessary to comprehensively study first of all the chromatographic behaviour of the branched molecules near critical conditions. In this case only the adjacent branch nodes will make a contribution to the change in the free energy, since $\Delta F=0$ both for tails and linear sections in critical conditions.

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