Journal of Chromatography, 523 (1990) 91–102
Elsevier Science Publishers B.V., Amsterdam

CHROM. 22 708

Chromatographic investigations of macromolecules in the "critical range" of liquid chromatography

I. Functionality type and composition distribution in polyethylene oxide and polypropylene oxide copolymers

A. V. GORSHKOV
Institute of Chemical Physics, U.S.S.R. Academy of Sciences, Kosygina 4, 117977 Moscow (U.S.S.R.)
H. MUCH*, H. BECKER and H. PASCH
Academy of Sciences of the G.D.R., Central Institute of Organic Chemistry, Division of Macromolecular Chemistry, Rudower Chaussee 5, 1199 Berlin (G.D.R.)
and
V. V. EVREINOV and S. G. ENTELIS
Institute of Chemical Physics, U.S.S.R. Academy of Sciences, Kosygina 4, 117977 Moscow (U.S.S.R.)
(First received February 1st, 1990; revised manuscript received July 16th, 1990)

ABSTRACT

Polyethers obtained from ethylene oxide (EO) and propylene oxide (PO) and corresponding copolyethers were analysed by liquid chromatography under critical conditions (near the critical point of polymer adsorption) to obtain information on the functionality type distribution and structural inhomogeneity of copolymers. Homopolyether species were separated according to the number and type of their end groups. Copolymers of EO and PO (random and block) were split into groups depending on chemical composition, block length and the character of order in the monomer distribution. The experimental results are explained by considering the theory of polymer adsorption.

INTRODUCTION

The problem of determining functionality type distribution (FTD) is a classical one in the chemistry of reactive oligomers (telechelics) [1]. We have recently developed a method for the chromatography of macromolecules in the critical region close to the critical point of adsorption of macromolecules [2]. In this region, located at the boundary of the exclusion and adsorption separation modes, the dependence of the retention volumes V_R of homopolymers on their size (molecular weight) disappears, and separation is accomplished by other criteria, *e.g.*, by the number and type of terminal groups. The theory of this method has been described [1,2,11]. The method has subsequently been successfully used to investigate the FTD of a wide class of polyethers and polyesters [3,4], polycondensation oligomers [5–8] and oligobutadienes [9].

0021-9673/90/$03.50

The problem of analysing the FTD of copolymers is much more complex than that of homopolymers. In the general case, the separation by functionality types will be superimposed by the separation according to copolymer composition and structure. Therefore, to solve the problem of the FTD of copolymers, it is first necessary to investigate their heterogeneity in composition and the nature of the disordering of different monomers in the chain. This work was devoted to the analysis of the FTD of polypropylene oxide (PPO) and polyethylene oxide (PEO) and the structure of copolymers based on them.

THEORY AND METHOD

Separation in chromatography is defined by the distribution coefficient K_d, associated with a change in free energy when the macromolecule passes from the mobile phase (interparticle space) into the stationary phase pores:

$$K_d = \exp(-\Delta G)$$

(all the energy values will be expressed in kJ K^{-1} units). The variation of ΔG depends on the macromolecule size, R, pore size, D, and the energy of the interaction of monomers with the surface, $\varepsilon(x)$. The $\varepsilon(x)$ value depends on the chemical structures of the monomer and solvent, solvent composition and temperature and constitutes the effective potential of monomer interaction with the pore surface. The laws governing chromatography in the critical region can only be understood on the basis of the theory of the adsorption of macromolecules. Despite the great complexity of the current theory of macromolecule adsorption [10], requiring the application of the concepts of statistical physics unknown to most chromatographers, the final conclusions of this theory are simple, and can be easily used for the chromatographic analysis of heterogeneous macromolecules.

A fundamental consequence of the adsorption theory is the existence of a finite, critical depth of potential, ε_c, starting with which the adsorption of macromolecules in the pores takes place. If $\varepsilon > \varepsilon_c$ the energy of the interaction of monomers with the surface exceeds the entropy losses, and the macromolecule is adsorbed. If $\varepsilon < \varepsilon_c$ we have the reverse relationship, and the macromolecule is almost unabsorbed and remains in the interparticle space all the time. At $\varepsilon = \varepsilon_c$ the energy of interaction exactly compensates the entropy losses.

Corresponding to these three cases are the three modes in the chromatography of macromolecules: adsorption, exclusion and critical, differing in the sequence in which macromolecules of different size elute. The existence of these modes has been confirmed experimentally and well studied [1,2].

In the adsorption mode, K_d is exponentially dependent on the degree of polymerization, N. The adsorption of macromolecules soon becomes irreversible, and so the adsorption mode is appreciably limited from above with respect to molecular weight.

In the exclusion mode, K_d values for a Gaussian model of the chain are given by

$$K_d \approx \exp(-R^2/D^2); \qquad R > D$$

$$K_d \approx 1 - (2R/D); \qquad R < D$$

At the critical point, ΔG is zero irrespective of the size of the macromolecule and the pore size. In this case $K_d = 1$. Such a "disappearance" of the effect of the size of the macromolecules and their molar mass distribution (MMD) in the critical region opens up new possibilities for investigating the structure of heteropolymers such as telechelics and copolymers.

Polymers with functional groups

The simplest type of a heteropolymer is a telechelic, *i.e.*, a macromolecule containing terminal groups. The presence of these groups causes a difference in the interaction with the pore surface. If a binary solvent is chosen, corresponding to the critical conditions of adsorption for the polymer chain, the polymer chain itself will not contribute to any variations of ΔG. For a monofunctional macromolecule, the contribution to the ΔG variations will only be made by the terminal unit. This contribution is easy to find and thereby the determination of $K_d^{(1)}$, which numerically coincides with the statistical sum for a monofunctional macromolecule:

$$K_d^{(1)} = 1 - \frac{2a}{D} + \frac{2a}{D} \cdot \exp(\varepsilon_f - \varepsilon_c) = 1 + \frac{2a}{D}[\exp(\varepsilon_f - \varepsilon_c) - 1] \tag{1}$$

where ε_f is the energy of interaction of the terminal unit with the pore surface and a is the unit size. Let us now consider a bifunctional macromolecule with two terminal units (joined by an "invisible" filament that makes no contribution to ΔG). For such a macromolecule one can obtain

$$K_d^{(2)} = \left\{1 + \frac{2a}{D}[\exp(\varepsilon_f - \varepsilon_c) - 1]\right\}^2 = [K_d^{(1)}]^2; \qquad R > D \tag{2}$$

and

$$K_d^{(2)} = 1 - \frac{2R}{D} + \frac{2R}{D}\left\{1 + \frac{a}{R}[\exp(\varepsilon_f - \varepsilon_c) - 1]\right\}^2; \qquad R < D \tag{3}$$

These equations reflect the fact that at $R > D$ the macromolecule does not undergo any interactions with the pore surface. At $R \approx D$ the interaction of the solvated macromolecule with the pore surface takes place with one terminal unit only (*cf.*, eqn. 2).

At $R < D$ (*cf.*, eqn. 3), the ends of the chain are assumed to be statistically independent and make an additive contribution to free energy variations. Within the accuracy of a numerical coefficient of the order of unity, the equations coincide with strict dependences obtained for a Gaussian model [12].

Note that even at the critical point, when the chain joining the terminal groups becomes "invisible", the dependence of $K_d^{(2)}$ $(R < D)$ on the size or molecular weight does not disappear. However, $K_d^{(2)} > [K_d^{(1)}]^2$ and the zones of different functionality under these conditions cannot overlap.

A macromolecule containing several functional units in the chain is "polyfunctional", turning in the critical region into a new one, a "chain of functional groups" joined by "invisible" Gaussian filaments of size l_i. As distinct from the usual model of a polymer chain, the length of these filaments is different and reflects the nature of the ordering of defects in the chain. The distribution coefficient $K_d^{(n)}$ for such macromolecules can be estimated similarly to the derivation of eqns. 2 and 3. For instance, when all $l_i > D$ the defects are statistically independent [2], and

$$K_d^{(n)} = [K_d^{(1)}]^n \tag{4}$$

Regularities of the chromatography of block copolymers

Let us consider block copolymers of the AB and ABA′ types in the critical region. This problem is similar to a mono- and a bifunctional telechelic, where the role of a functional group is played by the block A. Let us define $\varepsilon_A < \varepsilon_B$. It is obvious that at the critical solvent composition for the block A one should observe separation according to the size of block B, and *vice versa* [13]. The distribution coefficients K_d^{AB} in this instance will be

$$K_d^{AB} = K_d^B; \qquad \varepsilon = (\varepsilon_A)_c \tag{5}$$

$$K_d^{AB} = K_d^A; \qquad \varepsilon = (\varepsilon_B)_c \tag{6}$$

where K_d^B and K_d^A are the distribution coefficients of the corresponding homopolymers.

For a three-block copolymer ABA′ under the critical conditions, for the outer blocks A, irrespective of their MMD functions, only the inner block B is seen in the adsorption mode and

$$K_d^{ABA'} = K_d^B; \qquad \varepsilon = (\varepsilon_A)_c \tag{7}$$

When the critical conditions are assigned for the inner block B, similarly to a bifunctional molecule, $K_d^{ABA'}$ depends on the ratio between the sizes of block B and the pores, R_B and D. If $R_B > D$ blocks A and A′ are statistically independent, and

$$K_d^{ABA'} = K_d^A\, K_d^{A'}; \qquad \varepsilon = (\varepsilon_B)_c \tag{8}$$

When $R_B < D$ and $R_{ABA'} < D$, we can, similarly to eqn. 3, determine $K_d^{ABA'}$ as

$$K_d^{ABA'} = 1 + \frac{2\, R_{ABA'}}{D}\left[\left(1 - \frac{R_A}{R_{ABA'}}\right)\left(1 - \frac{R_{A'}}{R_{ABA'}}\right) - 1\right] \tag{9}$$

The $K_d^{ABA'}$ value is a minimum when $R_A = R_{A'}$ and a maximum when the size of one of the blocks tends to zero (however, $R_{ABA'}^2 = R_A^2 + R_B^2 + R_{A'}^2 =$ constant). In principle, this makes it possible to separate two- and three-block macromolecules of the same composition.

In the general case the relationship between K_d and the homopolymer structure is extremely complex and reflects the interrelation of such factors as its size and composition and the nature of the ordering of monomers in the chain. These aspects are beyond the scope of this work.

EXPERIMENTAL

Apparatus

A DuPont System 8800 high-performance liquid chromatograph consisting of a Model 8770 pump, a column oven and a manually operated Rheodyne Model 7125 injection valve with a 20-μl loop, together with an RIDK 101 differential refractive index detector from Laboratorní Přístroje (Prague, Czechoslovakia), was used. The separation was performed on a 250 × 4.6 mm I.D. Chrompak RP-18 C_{18} column at 298 K using acetonitrile–water or tetrahydrofuran–water as the mobile phase. A flow-rate of 1 ml min^{-1} was used in the isocratic mode.

Materials

PEO with number-average molecular weights of M_n = 150, 600, 2000, 6000 and 20 000 and PPO with M_n = 425, 1025 and 2000 were obtained from Merck (Darmstadt, F.R.G.). The following polymers were synthesized by anionic polymerization at 110°C using the corresponding potassium alcoholates and glycolates as initiators:

Monofunctional polyethers:

$HO(CH_2CH_2O)_{40}CH=CH_2$;
$HO(CH_2CH_2O)_{40}C_4H_9$;
$HO(CH_2CH_2O)_m[CH(CH_3)CH_2O]_nC_4H_9$ ($n = 10$; $m = 10$ or 30);

difunctional block copolyethers:

$HO(EO)_m(PO)_n(EO)_mOH$ ($n = 11$; $m = 5$, 10, 15 or 20);

difunctional random copolyether:

$HO(PEO)_{30}(PPO)_{11}OH$.

RESULTS AND DISCUSSION

Characteristic functions of the telechelic and block copolymer of the AB type are given in Fig. 1. For the telechelic it is a set of MMD functions for different functionalities (FTD), and for the block copolymer the surface in composition–molecular weight coordinates. These functions fully determine the properties of the given macromolecules.

The problem of determining the FTD for the telechelic is easily solved. In the critical mode, the separation is performed exclusively by the functionality types and the selected fractions are then defined by their molecular weights in the exclusion mode. The second part of this analysis is trivial and will not be dealt with here.

For PPO homopolymers with terminal OH groups the problem of separation by functionality types was previously solved using silica with ethyl acetate–methyl ethyl ketone [4]. The separation of PEO with terminal HO---OH, HO---OC_4H_9 and $CH_2=CH$---OH groups is considered in this work.

Corresponding to the critical conditions for PEO on the Chrompak RP-18 phase is the composition acetonitrile–water (42:58). In this instance the retention volume *versus* macromolecule size dependence disappears up to a molecular weight of 20 000 (Fig. 2). These conditions are optimum for the separation of PEO according to the

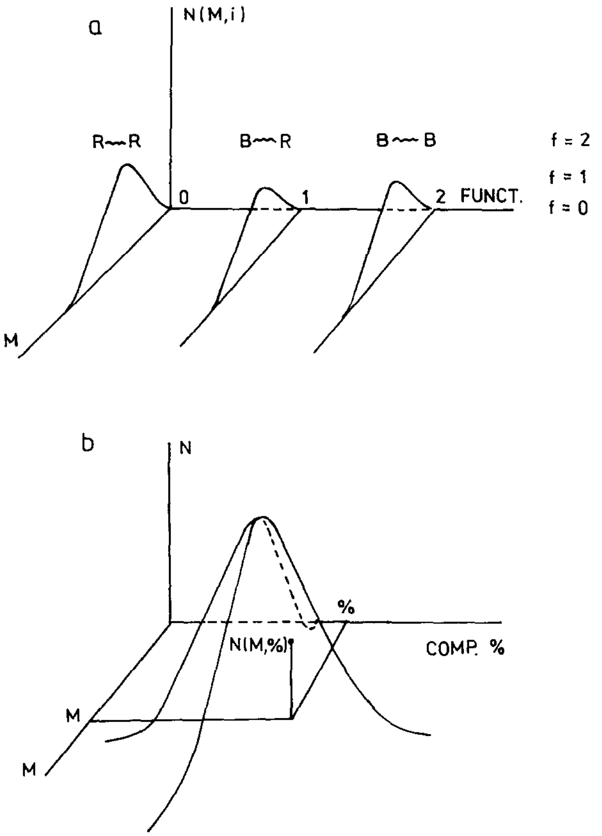


Fig. 1. Distribution functions (FTD, MMD) of (a) the telechelic and (b) the two-block copolymer.

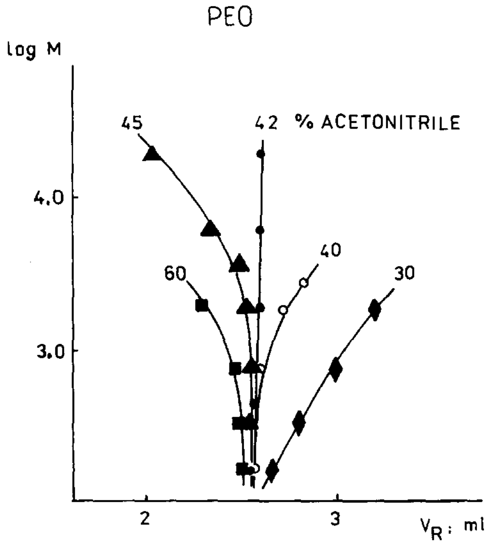


Fig. 2. Realization of the critical conditions for PEO. Column, RP-18; eluent, water–acetonitrile of different compositions. V_R = retention volume.

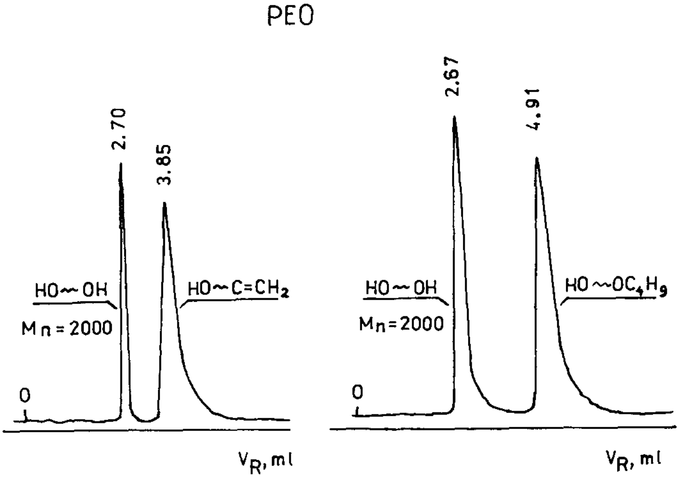


Fig. 3. PEO separation by functionality types under critical conditions. Column, RP-18; eluent, water–acetonitrile (58:42, v/v); flow-rate, 1 ml min^{-1}; loop volume, 20 μl; refractometric detection.

types of terminal groups (Fig. 3). As was to be expected, for the reversed phase the retention of macromolecules with the aliphatic end RO is stronger than that with a double bond. As follows from eqns. 2 and 3, the scale of retention volumes can be effectively changed by changing the pore size *D*. An increase in pore size leads to a decrease in retention volumes, as the fraction of conformations in which the end interacts with the surface decreases. Under the conditions established it is therefore very easy to determine the defectiveness of PEO in HO---OC_4H_9 or CH_2=CH---OH functionality over a wide range of molecular weights.

To solve a similar problem for PPO on a reversed phase it is necessary to choose a different mixture, *e.g.*, water–tetrahydrofuran (THF), as in 100% acetonitrile a weak adsorption regime occurs with PPO.

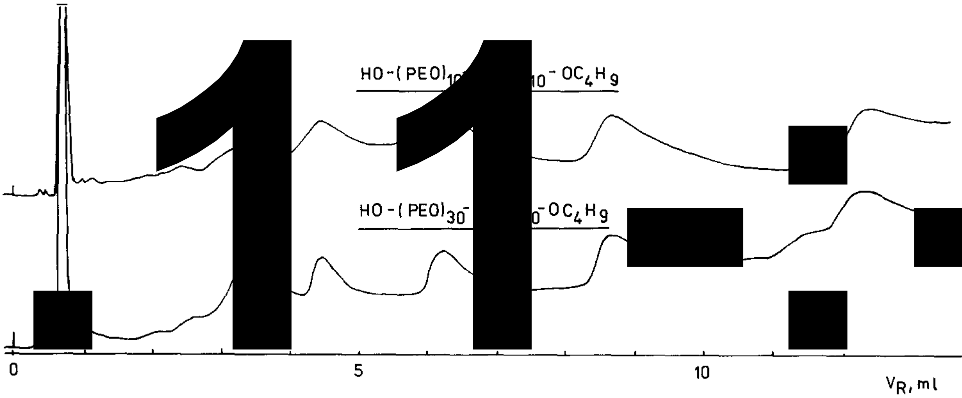
Let us consider the regularities characterizing the chromatography of PPO and PEO block copolymers. The copolymer composition and the nature of the ordering of different molecules in its chain (randon, block, regular, etc.) exert a decisive influence on its properties.

The simplest type of AB copolymer, $(PEO)_m(PPO)_n$, in our samples contained also a terminal aliphatic group, $-OC_4H_9$, which complicates the simple picture of the PPO block separation by size under the critical conditions for PEO (Fig. 4) by increasing the retention volumes. However, this example shows that the disappearance of the PEO tail does not depend on its length. In accordance with eqn. 6,

$$K_d^{AB}(-OC_4H_9) = K_d^B(-OC_4H_9)$$

Let us now consider a three-block copolymer, ABA′. At the critical point for PEO the outer blocks disappear, irrespective of their length, and therefore

$$K_d^{ABA'} = K_d^B$$



[redacted]

Fig. 4. Disappearance of PEO blocks and the MWD of PPO blocks for two-block PEO–PPO copolymers of different size and composition. Conditions as in Fig. 3.

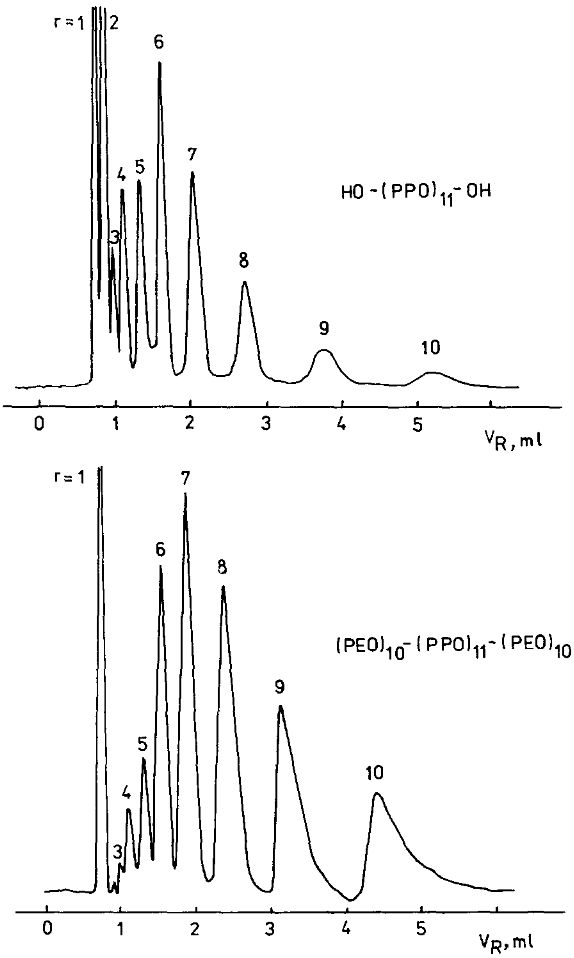


Fig. 5. Chromatograms of PPO and three-block PPO–PEO copolymer, obtained under the critical conditions for PEO. Conditions as in Fig. 3.

This phenomenon is illustrated in Figs. 5 and 6. Note the correspondence between the PPO homopolymer homologues and the macromolecules with a different degree of polymerization in the inner block B in the copolymer. As with functional molecules, one can decrease the scale of retention volumes of the copolymer by increasing the pore size.

It is now of interest to find the critical point for the inner PPO block in a three-block copolymer. For the outer blocks we would then have the exclusion mode and, depending on the ratio between the size of the PPO block and the pore size, the separation would be described by eqns. 8 and 9. Unfortunately, it proved impossible to do this on the chosen phase. The critical point occurs on PPO in a THF–water mixture with a small water content. Under these conditions the unmodified sites of the reversed phase, containing–SiOH groups, become significant. Because of the extremely strong interaction of PEO with these sites, the chromatograms, even for the PEO homopolymer, are strongly distorted by elongated tails. In other words, under the critical conditions for the inner PPO block, the exclusion mode for the outer PEO blocks cannot be realized on this phase.

In order to understand the differences in the chromatographic behaviour of a block copolymer and a random polymer of the same composition, let us consider

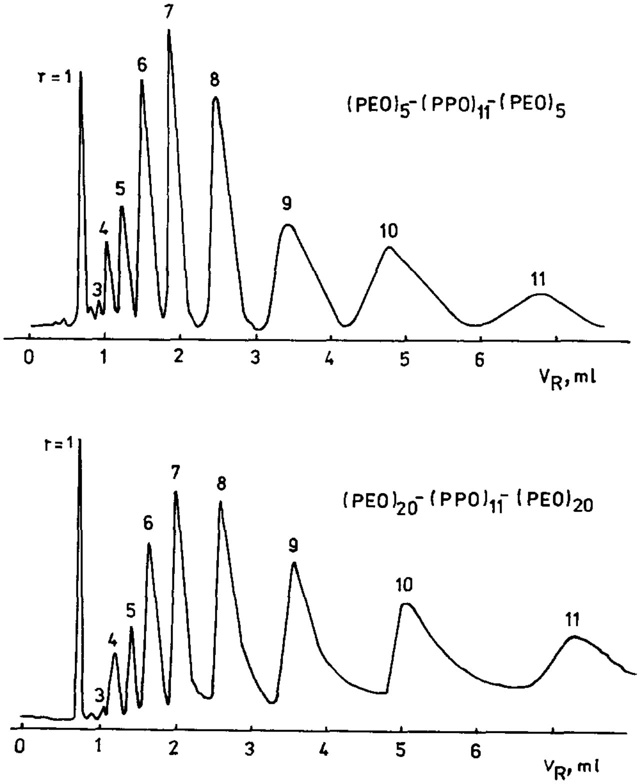


Fig. 6. Disappearance of PEO blocks and the MWD of visible PPO blocks of different size and compositions under the critical conditions for PEO. Conditions as in Fig. 3.

a simple example. Let us take two macromolecules of the same length and composition (number of PPO monomers). For the first chain we shall distribute the PPO monomers along the whole length of the chain at a scale l (Fig. 7). Under the critical conditions for PEO the parts of the chain joining the PPO monomers do not interact. To calculate $K_d^{(n)}$ it is only necessary to take into account the interaction of PPO monomers with the surface at a scale R in the first instance and at a scale $l \ll R$ in the second. Calculation according to eqn. 5 yields

$$
\begin{aligned}
K_d\ (\text{block}) &\approx 1 - \frac{2l}{D} + \frac{2l}{D}\left\{1 + \frac{a}{l}\left[\exp(\varepsilon_B) - 1\right]\right\}^n \\
K_d\ (\text{random}) &\approx 1 - \frac{2R}{D} + \frac{2R}{D}\left\{1 + \frac{a}{R}\left[\exp(\varepsilon_B) - 1\right]\right\}^n
\end{aligned}
\tag{10}
$$

As seen from eqn. 10, the "random" copolymer with PPO situated along the whole chain must be eluted earlier than the "block copolymer" of the corresponding composition. This conclusion is confirmed by the experimental chromatogram in Fig. 7. On average, a random polymer emerges sooner than a block copolymer of the corresponding composition.

The chromatogram of a random polymer contains information on the nature of the ordering of monomers in its chain, not taken into account in the calculation of the

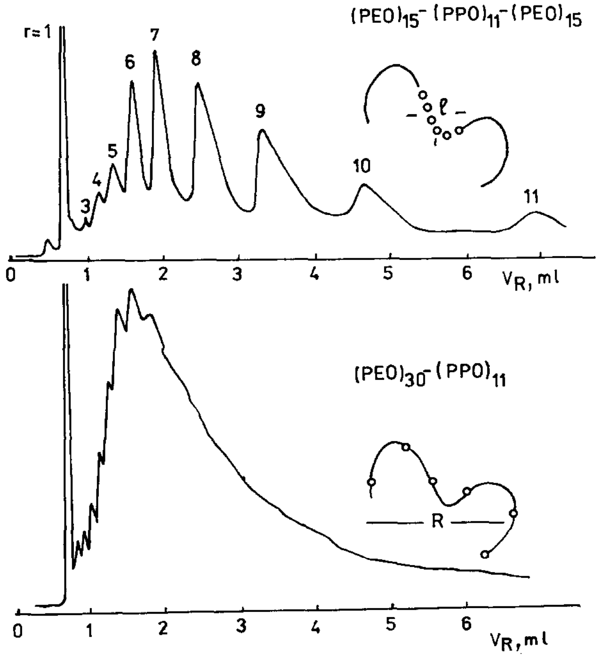


Fig. 7. Chromatograms of a block and a random copolymer of similar overall composition under the critical conditions for one of the PEO homopolymers. Separation conditions as in Fig. 3.

type in eqn. 10. Note that in the general case the chromatograms of heteropolymers close to the critical point should apparently reflect the fine differences from the truly random distribution, microblock parameters, etc. However, the qualitative difference in the form of the chromatogram of a random and a block copolymer of the same composition already allows the unambiguous attribution of the investigated polymer to one of these types of ordering.

When we return to the functionality of copolymers, it must now be obvious that separation according to functionality types in the critical region is superimposed by the polymer structure separation. To solve this problem it is necessary to choose a phase that gives a minimum difference in the interaction with the surface of PO and EO monomers. For the given system such a possibility seems to exist. On an RP-1 phase with a shorter aliphatic chain cross-linked to the surface, the sequence of emergence of PPO and PEO polymers is inverted in comparison with the C_{18} phase. Therefore, by changing the length of this tail one can choose a length for which the difference in PPO and PEO interactions is a minimum.

The heterogeneity of the reversed phase based on silica gel and the anomalously strong PEO interaction with the unmodified sites of this phase did not allow us to solve definitively the problem of determining the structure of the block copolymer and to construct the characteristic surface of the type shown in Fig. 4. Polymeric reversed phases have recently appeared that are free from the shortcomings of modified silica gels, in particular of residual –SiOH groups [14]. These phases, when critial conditions are realized on them, seem to be ideally suited for the analysis of the structure of PPO and PEO copolymers.

CONCLUSIONS

The questions of the chromatography of PPO and PEO macromolecules and their copolymers in the critical region have been considered theoretically and experimentally. The critical conditions for PEO have been established, making it possible to separate PEO according to the types of terminal groups, and copolymers according to the molecular weights of PPO blocks and the nature of their ordering in the chain. The method of chromatography in the critical region thus allows unique information to be obtained on the structure of macromolecules.

Some of the questions relating to the analysis of block copolymers have not been completely solved in this work. The same is true of questions regarding the functionality of block copolymers. However, we first wanted to demonstrate new opportunities in the analysis of the structures of heteropolymers offered by the method of chromatography near the critical point of adsorption.

REFERENCES

1 S. G. Entelis, V. V. Evreinov and A. I. Kuzaev, *Reactive Oligomers*, Khimiya, Moscow, 1985.
2 S. G. Entelis, V. V. Evreinov and A. V. Gorshkov, *Adv. Polym. Sci.*, 76 (1987) 129.
3 A. V. Gorshkov, V. V. Evreinov and S. G. Entelis, *Zh. Fiz. Khim.*, 59 (1985) 958.
4 A. V. Gorshkov, V. V. Evreinov, B. Lausecker, H. Pasch, H. Becker and G. Wagner, *Acta Polym. Berlin*, 37 (1986) 740.
5 V. V. Evreinov, A. V. Gorshkov, T. N. Prudskova, V. V. Gur'yaova, A. V. Pavlov, A. Ya. Malkin and S. G. Entelis, *Polym. Bull.*, 14 (1985) 131.

6 T. N. Prudskova, A. V. Gorshkov, V. V. Evreinov, V. V. Gur'yanova, A. V. Pavlov and C. G. Entelis, *Vysokomol. Soedin. Ser. B*, 28 (1986) 329.
7 A. V. Gorshkov, T. N. Prudskova, V. V. Gur'yanova and V. V. Evreinov, *Polym. Bull.*, 15 (1986) 465.
8 T. N. Prudskova, V. V. Gur'yanova, A. V. Gorshkov, V. V. Evreinov and A. V. Pavlov, *Vysokomol Soedin. Ser. B*, 28 (1986) 757.
9 A. V. Gorshkov, V. V. Evreinov and S. G. Entelis, *Zh. Fiz. Khim.*, 57 (1983) 2665.
10 E. Eisenrigler, K. Kremer and K. Binder, *J. Chem. Phys.*, 77 (1982) 6296.
11 P. G. De Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, 1979, p. 352.
12 A. A. Gorbunov and A. M. Skvortsov, *Vysokomol. Soedin. Ser. A*, 26 (1984) 946.
13 A. M. Skvortsov and A. A. Gorbunov, *Vysokomol Soedin. Ser. A*, 21 (1979) 339.
14 F. Nevejans and M. Verzele, *J. Chromatogr.*, 406 (1987) 325.