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Functional Type Separation of Oligocarbonates by Liquid Chromatography Under Critical Conditions
Effects of Pore Size

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SUMMARY

The separation of linear oligocarbonates has been carried out by the type of functionality, namely the number and nature of terminal chloroanhydride and hydroxyl groups. The analysis was performed with the aid of a novel variant of HPLC - "separation in a critical region" (SCR), on the boundary of the exclusion and adsorption separation modes. The SCR method is characterised by practically complete disappearance of separation by molecular masses (sizes) while chromatograms obtained in the critical region give information only on the types of functionality of oligomers under study. The critical point for the oligocarbonates has been found on silicas "Silasorb 600" and "Lichrosphere Si 500" in a binary solvent carbon tetrachloride-chloroform. An effect of pore size on the retention volumes of macromolecules of different functionality under critical conditions is discussed.

INTRODUCTION

In the behaviour of reactive oligomers the important role is played both by the nature and number of their functional groups which are characterized by the functionality type distribution (FTD) (ENTELIS et al. 1973).

Liquid chromatography methods are usually used for the experimental determination of FTD (relative contents of the macromolecules with various number and types of functional groups). However, almost in all cases the separation by the functionality is accompanied by separation according to molecular masses which complicates the processing of the obtained chromatograms.

We have recently proposed and substantiated experimentally (GORSHKOV et al. 1983, 1985a,b) a new method for chromatography of macromolecules - a separation in the critical region (SCR), which permits one to solve the problem of FTD determination for telechelic polymers. The essence of the method consists in that in the critical point of coil - adsorbed coil transition, the dependence of the retention volumes on macromolecule sizes vanishes and separation is determined by other factors, e.g. by the number and types of terminal functional groups.

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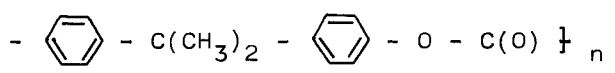
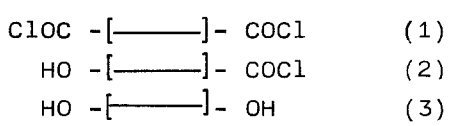
In the present work the SCR method has been applied to the determining FTD for oligocarbonates. A possibility of optimization of chromatographic separation with respect to functionality types due to a change in the size of adsorbent pores is discussed.

EXPERIMENTAL

Oligocarbonates with the following repeated units have been studied:



The samples studied contained bifunctional macromolecules ($n \sim 10$) with different functionality:



ClOC -[———]- COCl (1)

HO -[———]- COCl (2)

HO -[———]- OH (3)

Silasorb 600 (pores diameter D < 100 A) and Lichrosphere Si 500 (D = 500 A) were used as adsorbents; binary solvent CCl_4-$CHCl_3$ served as a mobile phase. However, CCl_4 is a bad solvent for poly(carbonates) which causes certain difficulties in creating critical conditions since the "critical" composition of a binary solvent is near the solubility limits of the sample.

The experiment was carried out on a SP-8700 liquid chromatograph and the results were treated on a SP-4100 integrator.

RESULTS AND DISCUSSION

Several fractions of the sample containing only macromolecules of type 1 of different molecular masses were preliminary collected at the exclusion mode (100% of $CHCl_3$, Silasorb). An addition of CCl_4 to $CHCl_3$ made it possible to find the critical point (17% of $CHCl_3$ in CCl_4, Silasorb).

However, only macromolecules of type 1 are eluted within a detectable range of retention volumes upon separation in the critical region of the oligomers with all three types of functionality while molecules of types 2 and 3 are adsorbed "irreversibly" (Fig 1a). To overcome this obstacle, it is possible to increase the solvent polarity, i.e. to pass to the exclusive mode. But in this case the separation of molecules by their size leads to overlapping of zones with different functionalities which makes it impossible to determine FTD.

In such a situation the simpliest way to optimize the separation by functional types under the critical conditions is to change the size of stationary phase pores. As follows from the theory developed for lattice and Gauss chains, the distribution coefficients $K_d^{(i)}$ for non-, mono- and bifunctional molecu-

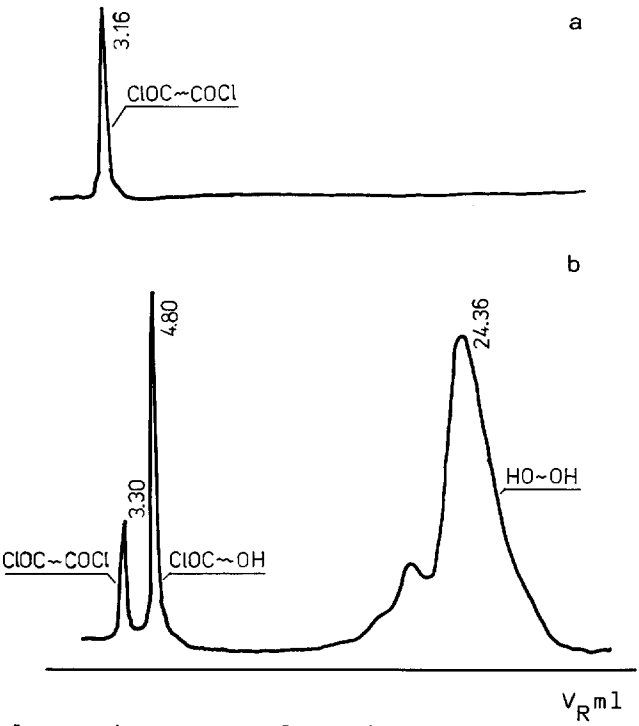


Fig.1. Effect of pore size of stationary phase on retention volume scale of oligocarbonate functional molecules. (eluent CCl_4-$CHCl_3$, u=1 ml/min, sample volume 10 ul, UV,column 250x4 mm) a-Silasorb 600, 17% $CHCl_3$; b-Lichrosphere Si500, 30% $CHCl_3$.

les under critical conditions have the form (GORSHKOV et al. 1982; GORBUNOV and SKVORTSOV 1984):

$$K_d^{(o)} = 1$$

$$K_d^{(1)} = 1 + \frac{2a\,(\exp(\vartheta_f - \vartheta_c) - 1)}{D}$$

$$K_d^{(2)} = [K_d^{(1)}]^2 \qquad R > D$$

$$K_d^{(2)} = 1 + \frac{4a}{D}(\exp(\vartheta_f - \vartheta_c) - 1) + \frac{2a^2}{\sqrt{\pi}RD}(\exp(\vartheta_f - \vartheta_c) - 1)^2 \qquad R < D$$

where $\vartheta_f - \vartheta_c$ is the difference between interaction energies of the terminal (functional) and middle units with the adsorbent surface, a- is the value of the order of segment size, D is the pore size, R is the macromolecule size.

As is seen from expressions, the greater the pore size, the smaller K_d and, hence, V_R. For molecules containing ClOC- groups, $\vartheta_f \approx \vartheta_c$, and in terms of equations they may be attributed to "nonfunctional" (type 1) and "mono-" and "bifunctional" molecules (type 2,3) with respect to -OH.

When R > D for the bifunctional molecules the terminal groups are ststistically independent. When R < D it is necessary to take into account a correlation in the disposal of chain

ends. It should be noted that, in wide pores $R < D$ contrary to narrow ones $R > D$, some dependence of $K_d^{(2)}$ on the macromolecules size R is observed.

Since the pore size affects the scale V_R of the functional molecules, the use of wide porous Lichrosphere Si 500 permitted us to separate oligocarbonates by functional types in critical region within an optimum range of V_R values, Fig. 1b.

Other possibilities for optimization of the separation of functional macromolecules under critical conditions consist in regulating the difference $\theta_f - \theta_c$ due to specific interactions of the functional groups with the mobile phase, modification of the adsorbent which changes its selectivity with respect to terminal and chain units, or modification of functional groups themselves in the analysed oligomer.

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