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STEP-BY-STEP ANALYSIS OF POLYCONDENSATION OLIGOMERS AND POLYMERS BY LIQUID CHROMATOGRAPHY

V. V. GUR'YANOVA* and A. V. PAVLOV

Research Institute of Plastics, Moscow (U.S.S.R.)

SUMMARY

The theoretical concept of polymer chromatography under "critical conditions" that allows the separation of oligomer samples by functional-type distribution is discussed. Calculation of the optimum conditions for the gradient separation of such mixtures for simultaneous determination of the molecular mass distribution and functional-type distribution is also considered.

To ensure a correct evaluation of the molecular mass distribution of the polymer products, a precise method of exclusion chromatography involving an internal standard and correction of the calibration equation according to a characterized sample is suggested.

Double detection, with a UV detector and a refractometer, makes it possible to estimate the role of low-molecular-weight fractions of polysulphone during heat-treatment, which influences the optical characteristics of polymers.

INTRODUCTION

Information about the molecular mass characteristics of polycondensation products at all process stages, as well as investigation of the kinetics of their formation, is of vital importance in the synthesis of tailor-made polymers. Of particular interest is the analysis of oligomeric compositions, molecular mass distribution (MMD) and functional-type distribution (FTD), during the first stage of synthesis, particularly the two-step polycondensation, *e.g.* polyalkyleneterephthalate and polycarbonate.

Until recently, kinetic parameters of the processes have been determined mainly from brutto kinetic data, but direct investigation of the initial stages of a reaction has remained unattainable. However, intensive developments in the application of liquid (particularly adsorption) chromatography have made it possible to penetrate into the very essence of polymer formation processes at different reaction stages.

It is known that by using the differences in the interaction energy of the functional end-groups and polymeric chain groups with the stationary phase and selecting an appropriate eluent, it is possible in a number of cases to develop satisfactory techniques for the analysis of oligomeric FTD and MMD^{1,2}. However the chromatograms thus obtained are often difficult to interpret because the separation by functional type is superposed on the separation by molecular mass.

Recently, a new approach has been successfully applied to determine the FTD of oligomers, based on chromatographing the oligomers under "critical conditions"^{3,4}. The technique allows the calculation of the MMD of every functional type and the optimization of the chromatographic separation⁵.

From macromolecular adsorption theory, it is known that the change ΔF in the free energy of a macromolecule as it enters a sorbent pore is determined by the changes in entropy $T\Delta S$ and in enthalpy ΔH ;

$$\Delta F = \Delta H - T\Delta S$$

In this case the entropy of the macromolecule always decreases, and the sign of ΔF depends on the nature of the polymer-sorbent interaction. When the enthalpy change due to this interaction exceeds the entropy loss, the adsorption mechanism of separation is realized. When $T\Delta S$ is greater than ΔH , an exclusion regime is observed. However, under the so-called "critical" conditions the entropy loss is exactly balanced by the energy gain so that $\Delta F = 0$, irrespective of the length of the macromolecule. Under such conditions, the distribution coefficient depends on the functional end-groups only, and is independent of the molecular mass. Hence one can determine the parameters of adsorption interaction of the chain and end segments for a given sorbent and eluent, and then calculate without using experimental chromatographing the chromatograms of the samples with simultaneous MMD and FTD determination with gradient elution. The optimum separation conditions can then be selected.

This paper describes the use of a number of representative polycondensation polymers to show the potential of exclusion and liquid chromatography for the detailed analysis of the molecular characteristics of oligomer and polymer products at all synthetic stages.

EXPERIMENTAL

Chromatograms were obtained on high-precision liquid chromatographs from Spectra-Physics (U.S.A.) and Knauer (F.R.G.). Detection was carried out with a UV detector and a refractometer. The sample volume was 10 μ l, the flow-rate 1 ml/min, and the sample concentration 0.1%. An SP 4100 integrator was used for quantitative processing of the chromatogram.

Chromatographic conditions

Polymers MMD. Sorbent, microgel; pore sizes, 10^3 , 10^4 and 10^5 Å; eluent, chloroform; UV detection wavelength, 254 nm.

Oligomers MMD. The same conditions as for polymers, except pore sizes 100 and 500 Å.

Oligocarbonate FTD. Sorbent, Si-500; eluent, chloroform-tetrachloromethane (30:70, v/v); UV detection wavelength, 275 nm.

Oligoterephthalate FTD. Sorbent, Si-60; eluent, chloroform-heptane, gradient elution; UV detection wavelength, 254 nm.

Oligosulphone. Sorbent Si-60, eluent chloroform-tetrachloromethane (53:47, v/v). UV detection wavelength, 275 nm.

Samples

Samples of aromatic polysulphone based on diphenylolpropane and dichlorodiphenylsulphone were obtained by high-temperature polycondensation at 150°C in dimethyl sulphoxide.

Samples of polycarbonate based on diphenylolpropane were synthesized by interfacial polycondensation at 20°C.

Polybutyleneterephthalate (PBT) oligomers based on dimethylterephthalate and 1,4-butanediol were obtained by *trans*-esterification at 180°C in a melt; the initial monomer ratio was 1:1.3% mol.

RESULTS AND DISCUSSION

Oligomer analysis

Fig. 1 shows chromatograms of PBT oligomer samples of three structural types, HO—OH, HO—OCH₃, H₃C—OCH₃, in three separation regimes (a) adsorption, (b) exclusion and (c) critical. The amount of tetrahydrofuran (polar component) in the binary mixture THF–heptane was varied as indicated. In the adsorption regime the small molecules are the first to elute, whereas in the exclusion regime it is the large molecules that appear first, which is in agreement with the theoretical predictions. The presence of one or two hydroxyl groups shifts all the peaks to higher retention volumes. Under critical conditions (Fig. 1c) there is practically no molecular mass separation; molecules of different degrees of polymerization with one and the

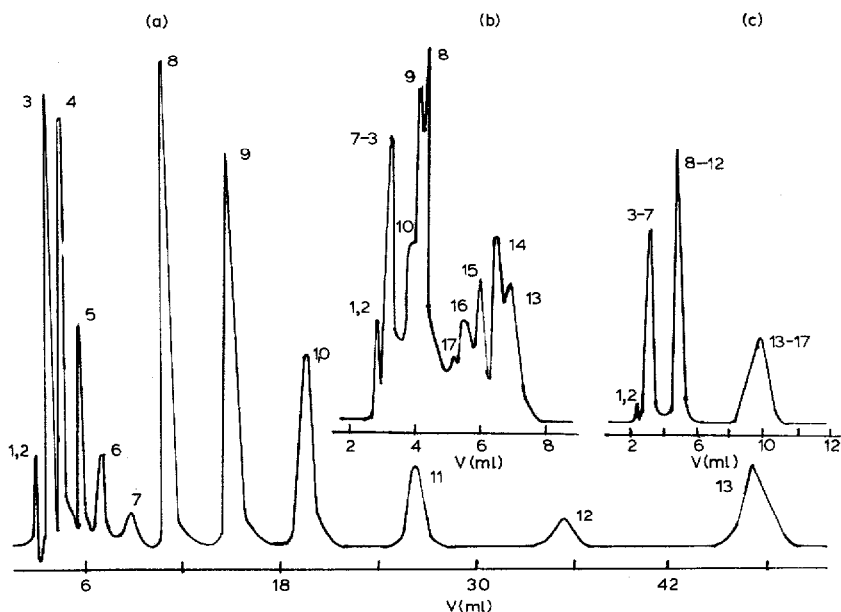


Fig. 1. Chromatograms of a PBT oligomer sample with different compositions of the THF–heptane eluent. Peaks 1 and 2 represent the solvent, peaks 3–7 the zero-functional ($f = 0$) homologues with polymerization degree $n = 0-6$, peaks 8–12 the monofunctional ($f = 1$) and peaks 13–17 the bifunctional ($f = 2$) homologues. (a) Adsorption regime in THF–heptane (40:60, v/v); (b) exclusion regime in THF–heptane (80:20, v/v); (c) critical conditions in THF–heptane (65:35, v/v).

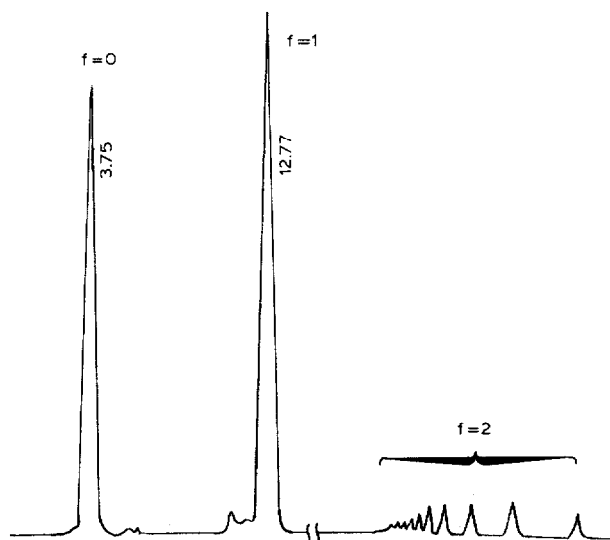


Fig. 2. Chromatograms of polysulphone oligomers under critical conditions: sorbent, Si-60; eluent, chloroform-tetrachloromethane (53:47, v/v); UV detection wavelength, 275 nm.

same functional group have one and the same retention volume. Similar chromatography of oligomers under critical conditions, allowing the total FTD to be determined, was carried out for oligocarbonates with $-\text{OH}$ and $-\text{C}(\text{O})\text{Cl}$ end-groups and for oligosulphones with $-\text{OH}$ and $-\text{Cl}$ end-groups (Figs. 2 and 3).

However, for a complete quantitative description of the synthesis, data on the molecular masses as well as on the functional groups are required. Such data can be

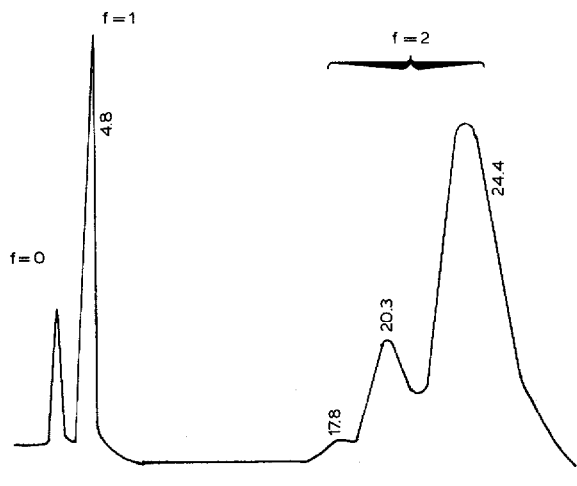


Fig. 3. Chromatograms of polycarbonate oligomers under critical conditions: sorbent, Si-60; eluent, chloroform-tetrachloromethane (30:70, v/v); UV detection wavelength, 275 nm.

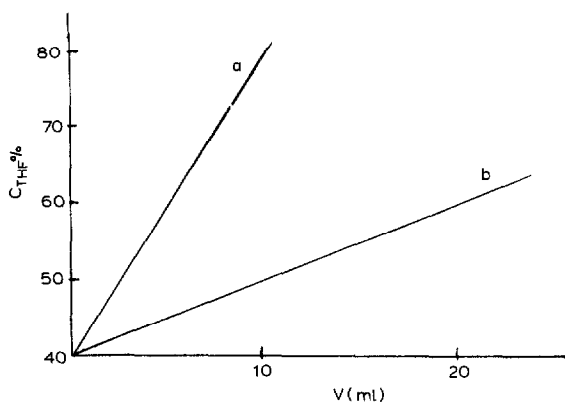


Fig. 4. Two arbitrarily chosen gradient programmes for a PBT oligomer separations, showing the variation of THF concentration C_{THF} with eluent volume V .

obtained by means of gradient elution to PBT and “machine experiment”, which facilitates calculation of the optimal eluent profile for simultaneous MMD and FTD determination, without experimental chromatography.

The parameters of adsorption interaction between oligomers and adsorbent are determined by means of the above critical conditions.

Calculated and experimental chromatograms for two arbitrarily specified gradient systems (Fig. 4) of the PBT oligomer sample containing three structural types with different end-groups are illustrated in Fig. 5. These figures show that as the C - V slope decreases the resolution by molecular mass increases, as does the functional type resolution. When the THF content in the eluent is changed at *ca.* 1%/min such a separation is achieved, provided that different functionality regimes do not overlap one another in a 2000 molecular mass range. The experimental chromatograms in Fig. 5 are similar to the theoretical ones, which confirms the possibility of evaluating different gradient programmes for analysis by “machine experiment”, with subsequent selection of the optimum conditions and experimental checking.

Thus, by using absorption chromatography, we have determined the content of different polymer oligomerization products and investigated the kinetics of their formation.

Analysis of polymers MMD

The next step in the present work is the adequate determination of MMD characteristics for the purpose of investigating the kinetics and mechanism of polymerization. It is known the relative error when determining molecular masses by gel-permeation chromatography is 10%. This may be due, for instance, to insufficient stability of the flow-rate, or to calculation difficulties that arise in chromatogram processing, particularly in connection with arbitrary selection of constants available in the literature for the Mark-Kun-Hawink equation. In some cases the error can be even greater: data reported from different laboratories vary by up to 40% for the same polycarbonate sample⁶. We believe that it is possible to avoid these errors, first by using an internal standard (*e.g.* toluene) and by using relative retention times in the calculated chromatogram programmes. Secondly, it is necessary to verify the calibration by correcting the calibration equation constants with the help of the ma-

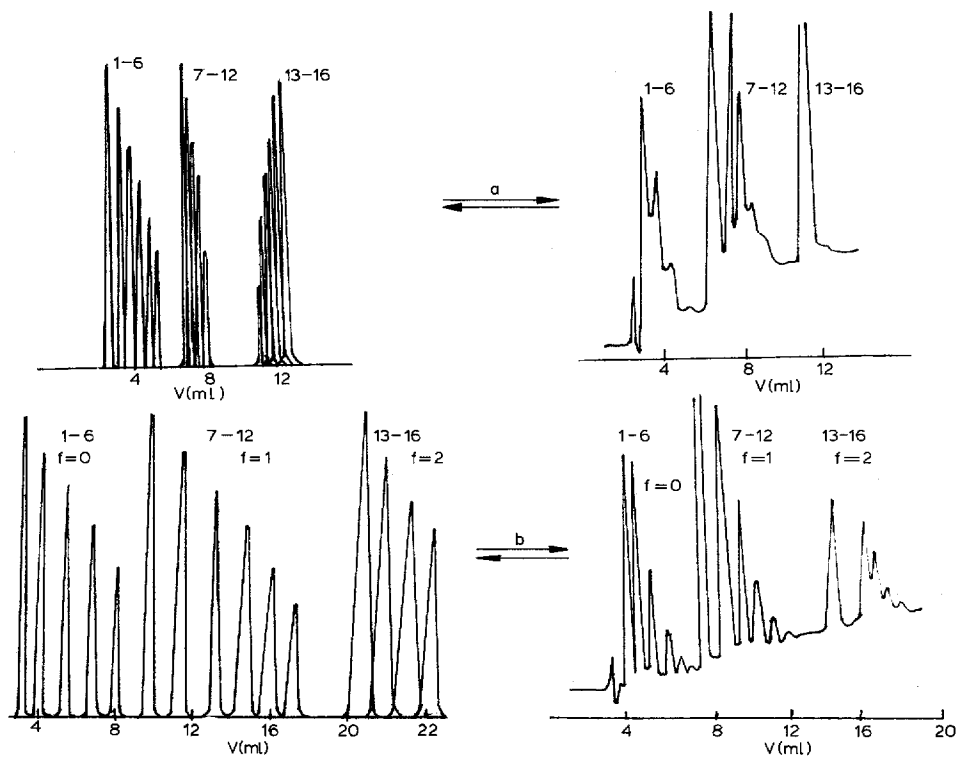


Fig. 5. Correlation between theoretical (left) and experimental (right) chromatograms, corresponding to gradient programmes a and b in Fig. 4. Peaks: 1-6 = zero-functional homologues; 7-12 = monofunctional; 13-16 = bifunctional.

chine method using gel chromatograms of one or several characterized samples with known \bar{M}_w and \bar{M}_n : for instance, for the polycarbonate Macrodon 2800 $\bar{M}_w = 3 \cdot 10^4$ and $\bar{M}_n = 1.5 \cdot 10^4$, and for Macrodon 2405 $\bar{M}_w = 2.6 \cdot 10^4$ and $\bar{M}_n = 1.07 \cdot 10^4$. The programme automatically corrects the first two coefficients so that the calculated molecular masses of the characterized samples coincide with the spe-

TABLE I

MOLECULAR MASS VALUES BEFORE AND AFTER CORRECTION OF THE CALIBRATED DEPENDENCE AND PEAK ELUTION TIME OF THE POLYMER ACCORDING TO INTERNAL STANDARD

The numerator is the non-corrected value and the denominator the corrected value; the sample was a polycarbonate.

$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_w \cdot 10^{-3}$	Toluene elution time (min)
7.9/10.5	23.2/25.8	24.35
13.1/10.8	29.7/26.2	24.7
12.0/10.8	28.0/26.0	24.5

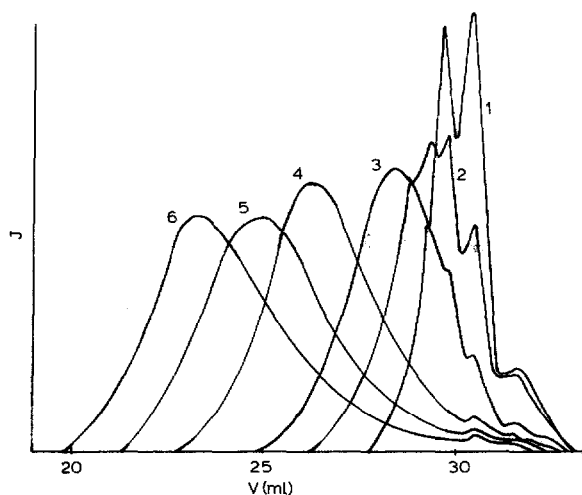


Fig. 6. Chromatograms of polysulphone samples, selected during synthesis. Curves 1–6 correspond to synthesis times of 1, 3, 5, 15, 30 and 60 min, respectively. Sorbent, microgel; pore sizes, 500, 10^3 and 10^5 Å.

cified ones. The correction results are given in Table I, which also shows the retention time of the toluene internal standard.

This technique made possible the study of the kinetics of polycondensation processes of polysulphone, polycarbonate and other polymers. Chromatograms of several polysulphone samples with molecular masses ranging from 500 to 50 000 are illustrated in Fig. 6. Fig. 7 shows the variation of the molecular mass with time of reaction. Also given are the rate constants for direct reaction of interaction of mac-

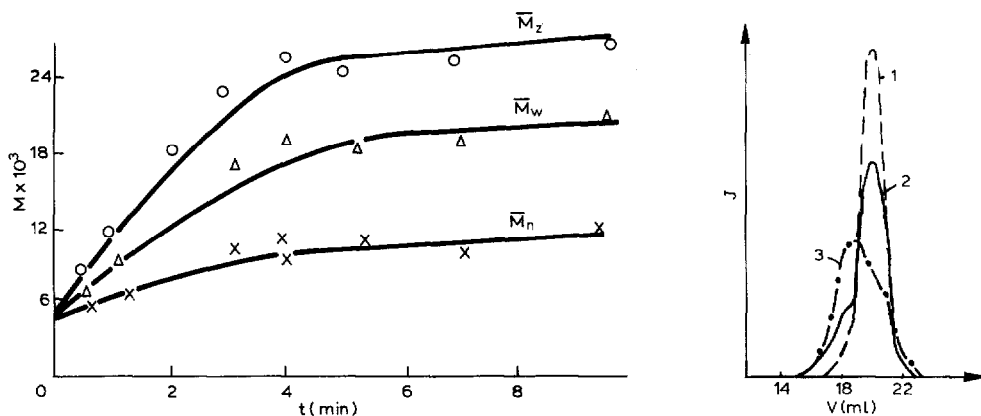


Fig. 7. Variation of polycarbonate molecular mass with reaction time. The lines represent calculated values, and the symbols represent the experimental values.

Fig. 8. Chromatograms of polysulphone fractions with $\bar{M}_w = 17\,000$ before (1) and after (2) heat treatment; detector, refractometer; sorbent, microstyrene gel with pore sizes $500 \cdot 10^4$ Å; eluent, chloroform. The chromatogram 3 of a heat-treated sample was obtained by UV detection at 330 nm.

romolecule end-groups and constants for hydrolysis reaction of end chloroformate groups calculated with the help of the generating functions method by MMD moments of polycarbonate which are relatively equal.

Correlation of polymers MMD and physicochemical (optical) properties

It is possible to make a polymer with a particular MMD both by varying the synthesis conditions and by additional treatment of the end-group. With the help of liquid chromatography, it is possible to ascertain the causes of change, in light transmission in optical polysulphone heated to 280°C and to choose the conditions for obtaining the polymer with the required MMD. UV-photometrical analysis of separate fractions of heat-treated polysulphone has revealed that the main part of the polymer is resistant to heat and oxygen, whereas in the low-molecular-weight region (up to 10 000) the polymer turns yellow. Gel chromatograms of the initial and heat-treated polysulphone fractions with $\bar{M}_w = 17\ 000$ are presented in Fig. 8. A two-detector system, consisting of a differential refractometer and a UV detector (set at 330 nm) connected in series, allowed observation of the change in the MMD of the sample after heat treatment (curve 2) and estimation of the contribution of individual fractions to the change in the sample optical density, using a UV detector. Fig. 8 shows that the conversion products are mainly responsible for the change in the optical characteristics of the polymer; these products, with $V = 15\text{--}16$ ml, corresponding to branched structures forming through the initiation of thermooxidative processes by hydroxyl end-groups. It is possible to avoid undesirable deterioration of the optical characteristics by blocking the hydroxyl end-groups and also by removing the low-molecular-weight part of the polymer by special treatment of the final polymer.

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