Separation of polycarbonate oligomers by high-performance size exclusion and reverse-phase liquid chromatography

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The separation of polycarbonate (PC) oligomers is achieved by high-performance size-exclusion chromatography (h.p.s.e.c.) with styrene–divinylbenzene microparticulate gel as stationary phase and methylene chloride as mobile phase. Oligomers were separated up to ten repeating units. H.p.s.e.c. is also shown to be useful for analysing the low-molecular-weight content of commercial PC samples. Retention times are significantly influenced by the nature of the end-groups (Ø– or OH–Ø–), indicating that adsorption occurs with hydroxy-terminated oligomers. H.p.s.e.c. separations are compared with results obtained by reverse-phase h.p.l.c. A simple method for determining the u.v. molecular absorption coefficient of the oligomers is proposed.

(Keywords: polycarbonate; oligomers; size-exclusion chromatography)

INTRODUCTION

Although size-exclusion liquid chromatography (s.e.c.) has been primarily used for high-molecular-weight substances, its applicability to small-molecule separation, in particular to oligomeric series, was recognized earlier. However, before the commercial availability of microparticulate gels, complete separation of low-molecular-weight mixtures could be achieved only by using very long columns or recycle systems, which required long analysis times. This situation changed dramatically with the appearance of high-efficiency columns packed with particles of 10 μm or less[1–3]. High-performance s.e.c. (h.p.s.e.c.) is now really convenient for rapid separations of low-molecular-weight compounds.

H.p.s.e.c. has a major advantage over other chromatographic techniques for evaluating the oligomer content of a polymer since it allows, with proper selection of pore sizes, the simultaneous analysis of low- and high-molecular-weight fractions. In contrast, reverse-phase h.p.l.c., while generally offering superior resolution, requires a preliminary extraction procedure and is often complicated by problems arising from the limited solubility of the oligomers in polar solvents.

Although the molecular weight of the bisphenol-A polycarbonate (PC) repeating unit is relatively high (254), the separation of PC oligomers by s.e.c. is difficult and has received little attention up to now[4,5]. The problem is further complicated by the existence of three oligomer families resulting from the addition of chain modifiers (monofunctional phenols) during the synthesis of the polymer by the usual interfacial method[6].

$$Ar–O–[–CO–O–Ø–C(Me)_2–Ø–O–]_n–CO–O–AR$$
Type I

$$Ar–O–[–CO–O–Ø–C(Me)_2–Ø–O–]_n–H$$
Type II

$$HO–Ø–C(Me)_2–Ø–O–[–CO–O–Ø–C(Me)_2–Ø–O–]_n–H$$
Type III

where Ar is a substituted phenyl group and Ø denotes a phenyl ring.

Throughout this paper, particular oligomers will be indexed as '*T,n*' compounds with *T* the type (I, II or III) and *n* the number of repeating units.

In this article, we will evaluate the feasibility of separating various PC oligomer mixtures by h.p.s.e.c. and try to determine the nature of the species present in some commercial polycarbonates. The problem of determining the u.v. molecular absorption coefficient of the oligomers will be discussed. H.p.s.e.c. results will be compared with those obtained by reverse-phase h.p.l.c. for the same systems.

EXPERIMENTAL

Materials

Type I oligomers. Bisphenol-A diphenyl carbonate (BADPC), i.e. oligomer I,1, was synthesized in the laboratory and allowed to react with 0.25% by weight of sodium *o*-chlorobenzoate (SOCB). This reaction produces sodium phenoxide end-groups, which undergo a fast interchange with the carbonate groups of BADPC[7]

$$Ø–O–CO–O–Ø–C(Me)_2–Ø–O–CO–O–Ø$$
BADPC

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If the reaction is effected under mild conditions (less than one hour at 180°C), a mixture consisting almost exclusively of type I oligomers is obtained. In a closed system, an equilibrium molecular distribution is rapidly attained. In an open system, the volatile product diphenyl carbonate evaporates and the molecular weight of the mixture increases. Experimental details are given elsewhere[7].

Type III oligomers. Low-molecular-weight hydrolysed PC ($\bar{M}_n = 1800$ measured by g.p.c.) containing 5.86×10^{-6} mol g^{-1} sodium phenoxide chain ends was mixed with an equal amount of bisphenol-A and reacted for 10 min at 200°C in a sealed d.s.c. pan. The interchange reaction between the phenoxide and carbonate groups produced an equilibrium mixture of almost pure type III oligomers.

Mixture of type I, II and III oligomers. A mixture of BADPC and bisphenol-A (1:1 molar ratio) was allowed to react for 15 min at 180°C with 1% (by weight) SOCB in a sealed d.s.c. pan. The interchange reaction between the sodium phenoxide groups thus produced, and the carbonates of BADPC resulted in an oligomer mixture of all three types.

Extracted oligomers. Low-molecular-weight PC supplied by General Electric (Lexan, batch 73-3-184-2) and Makrolon 2400 supplied by Bayer (batch 53903B) were dissolved in methylene chloride 1% (by weight). Ten volumes of acetone were added to the solutions to induce precipitation of the high-molecular-weight fractions. The oligomers still in solution were separated by filtration. The solvent was then evaporated and the oligomer fractions were extracted for several days in acetonitrile at ambient temperature.

Techniques

Size-exclusion chromatography. The h.p.s.e.c. system consisted of a Perkin–Elmer Series 2 pump, Waters Ultrastyragel columns (two 500 Å, two 1000 Å, 10^4 Å and 10^5 Å) and a Hewlett–Packard 1036A u.v. detector (254 nm). The column set was chosen to achieve a good separation of the oligomers in a reasonable time. The mobile phase was methylene chloride used at a 1 ml min^{-1} flow rate. The samples were dissolved in the same solvent (0.2% solution w/w; 25 μl injected). The columns were calibrated with PC broad standards characterized by light scattering at the Centre de Recherche sur les Macromolécules (Strasbourg, France) and by oligomer mixtures in the low-molecular-weight region. A Trivector Trilab 2000 microcomputer was used for data reduction. The software for the calculation of average molecular weights and molecular-weight distributions was developed in the laboratory. Sulphur was used as internal standard (retention time normalized to 4400 s) to correct for small variations of the flow rate as described by Hellman and Johnson[8].

Reverse phase h.p.l.c. The h.p.l.c. analyses were made either on a Hewlett Packard 1084A chromatograph equipped with a Waters U6K injector or on a modular system consisting of two Waters M6000 pumps controlled by a Waters System Controler Model 760 and equipped with a Rheodyne injector. A Perkin–Elmer LC55 u.v. detector was used at 240 nm. At this wavelength, a good sensitivity is obtained for all the oligomers, except for phenol. The column was a Merck Lichrosorb RP18 (7 μm particle size). A gradient elution with water and acetonitrile was made at a flow rate of 1 ml min^{-1}. The samples were dissolved in pure acetonitrile. The Trivector Trilab 2000 microcomputer mentioned earlier was used for data reduction.

RESULTS AND DISCUSSION

H.p.s.e.c. analyses

Type I oligomers. Figure 1 reports the chromatogram of a type I oligomer mixture at equilibrium (reaction effected for 15 min at 180°C in a closed system). Diphenyl carbonate (I,0) and BADPC (I,1) elute at 3675 and 3478 s, respectively. The higher oligomers are individually recognized up to seven repeating units. The small peak at 4156 s is associated with phenol (i.e. oligomer II,0), which is an hydrolysis product of BADPC.

It can be shown by using Bernoullian statistics that the equilibrium fraction of the nth oligomer in the mixture is $(0.5)^{n+1}$ (ref. 7). This is not obvious from the mere evaluation of the areas under the individual peaks since for the first oligomers, the molar extinction coefficient (ε) is not simply proportional to n. However, for the PC backbone the u.v. absorption of the chain can be assumed to result from an addition of the absorptions arising from individual phenyl groups. Without much error, only two kinds of phenyl groups have to be distinguished in type I oligomers: terminal and internal ones. Therefore, the assumption can be made that all the internal phenyl groups have the same absorption. The calibration curve $\varepsilon(n)$ can then be calculated on the basis of the experimental calibrations for diphenyl carbonate (DPC) and BADPC[7] and by using equation (1).

$$\varepsilon(\mathrm{I},n) = \varepsilon_{\mathrm{DPC}} + n(\varepsilon_{\mathrm{BADPC}} - \varepsilon_{\mathrm{DPC}})$$

or

$$\varepsilon(\mathrm{I},n) = \varepsilon(\mathrm{I},0) + n(\varepsilon(\mathrm{I},1) - \varepsilon(\mathrm{I},0)) \qquad (1)$$

Figure 2 shows that the molar fractions calculated from the experimental areas by using this simplifying assumption are in close agreement with the theoretical prediction.

By allowing the volatile product diphenyl carbonate to evaporate during the reaction, it is possible to obtain type

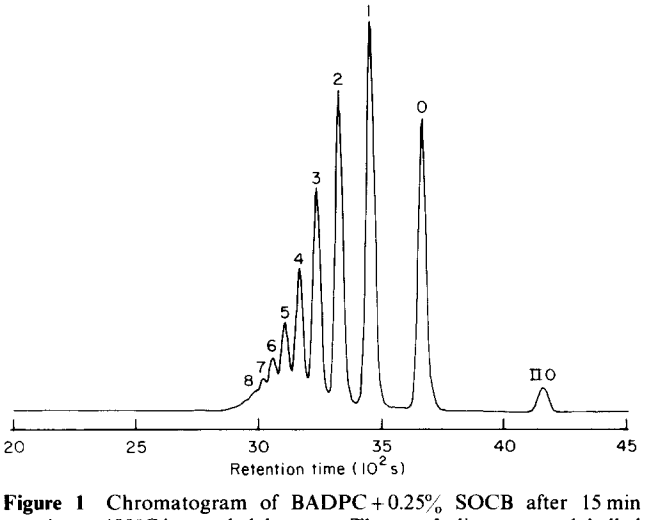

Figure 1 Chromatogram of BADPC + 0.25% SOCB after 15 min reaction at 180°C in a sealed d.s.c. pan. The type I oligomers are labelled with the corresponding number of repeating units.

I oligomers with a high molecular weight. The chromatogram of a system reacted for one hour at 180°C is presented in *Figure 3*. Individual contributions are clearly seen for components having up to ten repeating units. From the data reported in *Figures 1* and *3*, a molecular weight *versus* retention time calibration curve can be constructed (*Figure 4*, curve I) for the phenyl (type I) terminated polymer.

Type III oligomers. An equilibrium mixture of type III oligomers with a theoretical number-average molecular weight of 405 is separated in discrete species up to compounds with eight repeating units (*Figure 5*).

When compared with those of type I oligomers of similar molecular weight, the elution times of type III oligomers appear to be significantly higher (*Figure 4*, curve III). The relative difference decreases with increasing molecular weight. Moreover, in contrast with those of type I oligomers, elution times of type III oligomers are found to vary from analysis to analysis. This effect is the most important for bisphenol-A (oligomer III,0). For this compound, elution times ranging from 4250 to 4450 s (close to the permeation volume of the column set) are observed. Delayed elution of type III oligomers suggests that the presence of hydroxy terminal groups favours the reversible adsorption of these compounds on the columns. Adsorption significantly influences the separation of polar compounds by s.e.c. columns filled with silica particles[9-13]. Similar effects are less well documented for s.e.c. columns filled with polystyrene gels, although adsorption of phenolic compounds is known to occur on the surface of these gels[14].

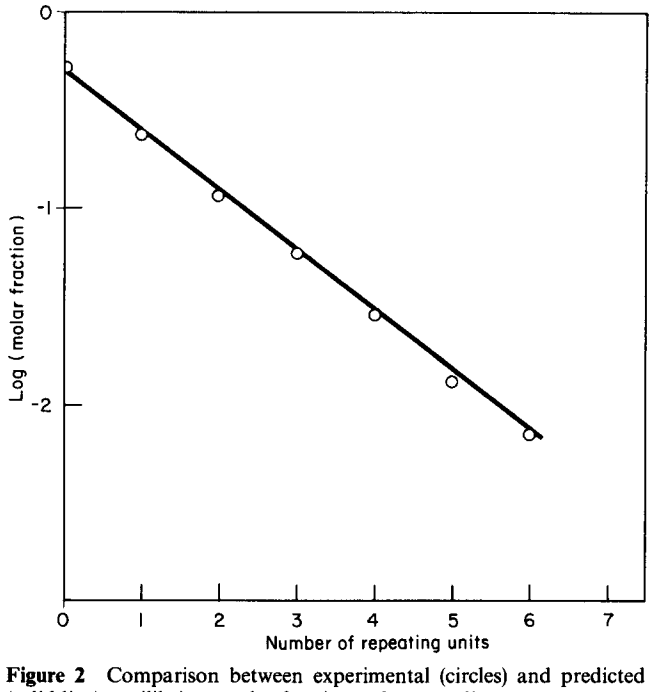

Figure 2 Comparison between experimental (circles) and predicted (solid line) equilibrium molar fractions of type I oligomers

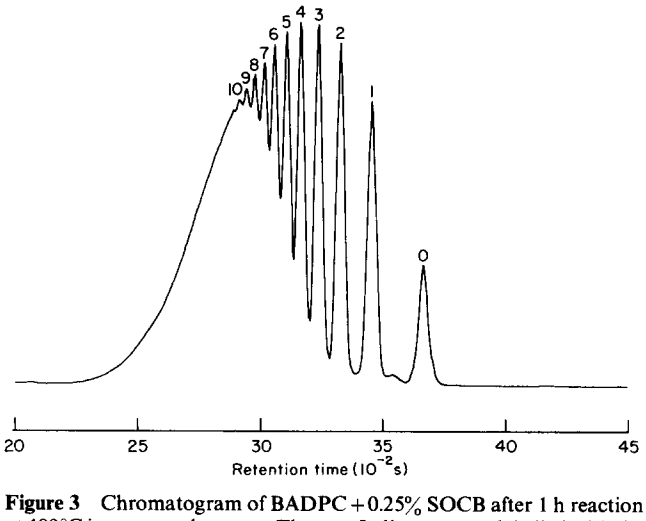

Figure 3 Chromatogram of BADPC + 0.25% SOCB after 1 h reaction at 180°C in an open d.s.c. pan. The type I oligomers are labelled with the corresponding number of repeating units

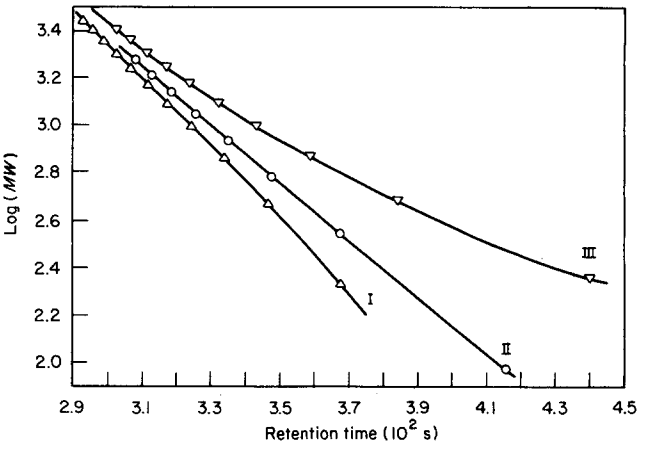

Figure 4 Molecular weight *versus* retention time relation for the three types of oligomers

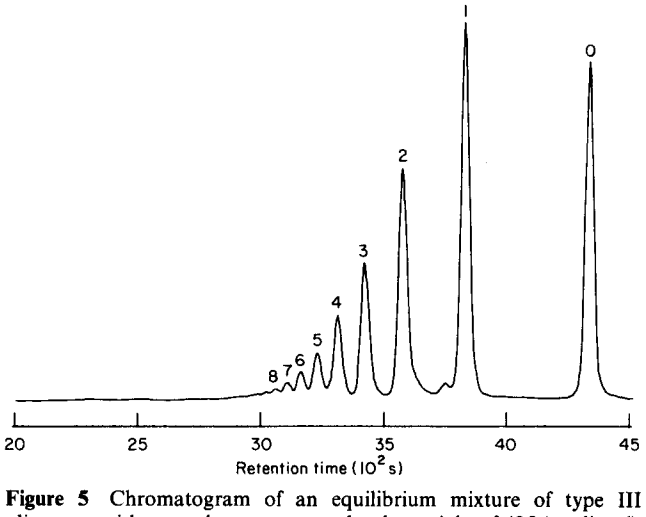

Figure 5 Chromatogram of an equilibrium mixture of type III oligomers with a number average molecular weight of 405 (predicted). The type III oligomers are labelled with the corresponding number of repeating units

The instability of elution time observed for the first type III oligomers is not very surprising when considering the molecular weight *versus* retention time relation for these compounds (*Figure 4*). In fact, the slope of the curve is small and minute temperature differences from run to run can explain the observed variations since adsorption effects are strongly dependent on temperature[15].

The theoretical equilibrium concentration of the oligomers is readily calculated. If x is the probability that a given bisphenol unit is a terminal one, the molar fraction of oligomer III,n is $(1-x)^n x$. Since $\bar{M}_n$, the number-average molecular weight of the mixture is

$$\sum_n (M_b + nM_u)x(1-x)^n$$

with M_b the molecular weight of bisphenol-A (228) and M_u the molecular weight of the PC repeating unit (254); x is equal to $(M_n - M_b)/M_u$. To obtain the experimental concentrations, an ε *versus* n curve is needed for type III oligomers. This can be calculated from the absorption values for BADPC, diphenyl carbonate and bisphenol-A, provided that the same simplifying assumptions are used as for type I oligomers.

$$\varepsilon(\mathrm{III},n) = \varepsilon(\mathrm{III},0) + n[\varepsilon(\mathrm{I},1) - \varepsilon(\mathrm{I},0)]$$

Figure 6 shows the close agreement existing between the theoretical and experimental equilibrium concentrations.

Mixtures of all types of oligomers. In a mixture of type I, II and III oligomers, only contributions from the first components can be uniquely assessed (*Figure 7*). However, since the mixture studied contains equal amounts of phenol and bisphenol groups, the dominant species are the type II oligomers. As a matter of fact, oligomers II,n having the same number of carbonate groups as oligomers I,$(n-1)$ and III,n will be twice as numerous as the latter. With this in mind, a tentative

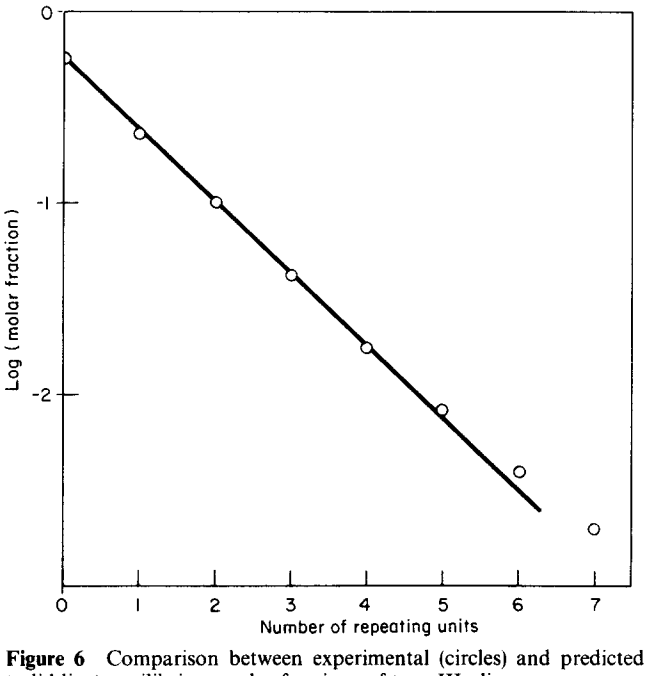

Figure 6 Comparison between experimental (circles) and predicted (solid line) equilibrium molar fractions of type III oligomers

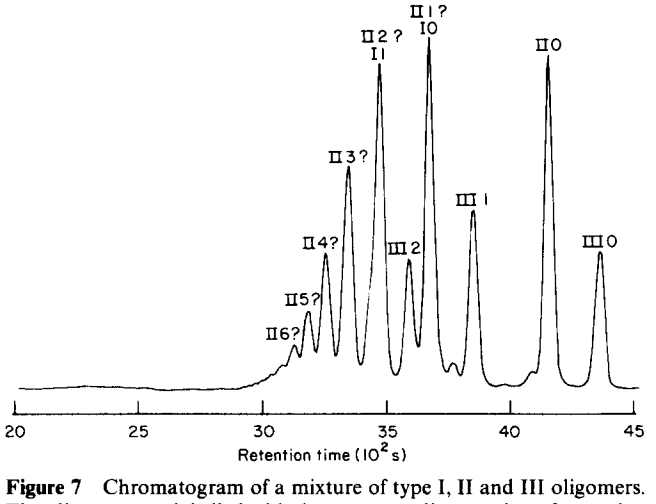

Figure 7 Chromatogram of a mixture of type I, II and III oligomers. The oligomers are labelled with the corresponding number of repeating units

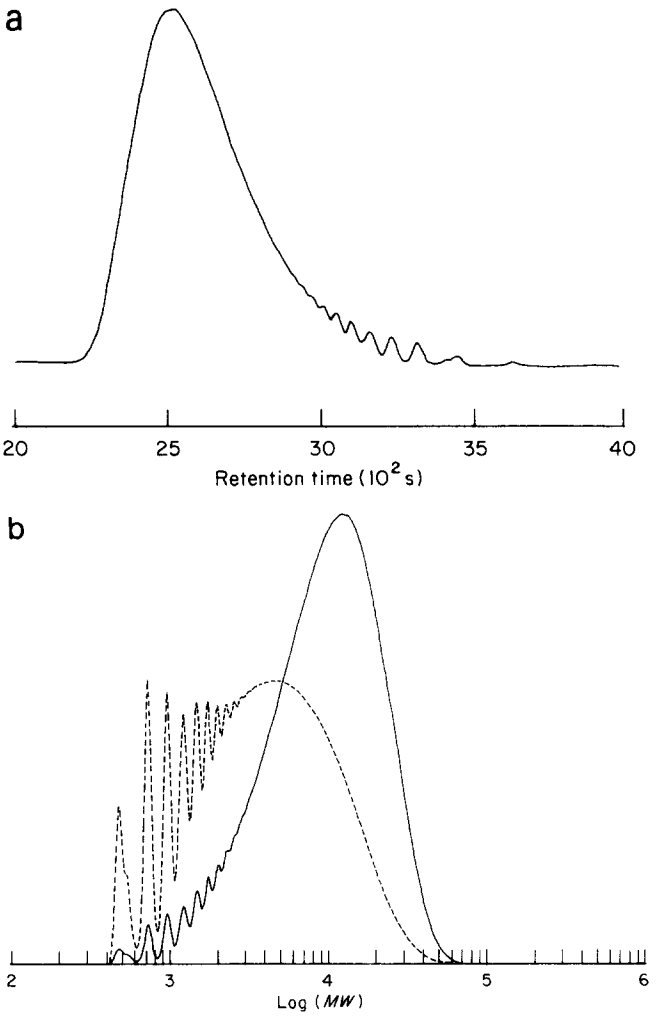

Figure 8 (a) Chromatogram of low-molecular-weight Lexan (sample L). (b) Number (broken line) and weight (solid line) molecular weight distributions of sample L. Diphenyl carbonate is not included in the distribution. The calibration in the low-molecular-weight region is based on the curve for type I oligomers. $\bar{M}_n = 5800$; $\bar{M}_w = 12\,000$ (light scattering gives $\bar{M}_w = 11\,500$)

interpretation of the chromatogram can be attempted (*Figure 7*). The molecular weight *versus* retention time relation for type II oligomers based thereon (*Figure 4*, curve II) is intermediate between those of type I and III oligomers, indicating that type II oligomers are less adsorbed than type III oligomers.

Polymer samples. The chromatograms of low-molecular-weight Lexan (sample L) and Makrolon 2400 (sample M) are reported in *Figures 8* and *9* along with the corresponding weight and number molecular weight distributions. The presence of oligomers, clearly visible on the chromatograms themselves, is even more evident on the number molecular weight distributions. In *Table 1*, the molecular weights corresponding to peak retention times are compared with those of type I oligomers. The agreement is striking and suggests that phenol is used during the synthesis of the polymers as a chain modifier. However, it should be noted that other species could be present since an 'all types' mixture cannot be completely resolved (cf. previous sections). For instance, oligomers II,1 and I,0 elute approximately at the same time as do oligomers II,2 and I,1. This could explain the presence of a shoulder at 3400 s in sample L (*Figure 8a*). Therefore, chromatograms of unknown oligomer mixtures should

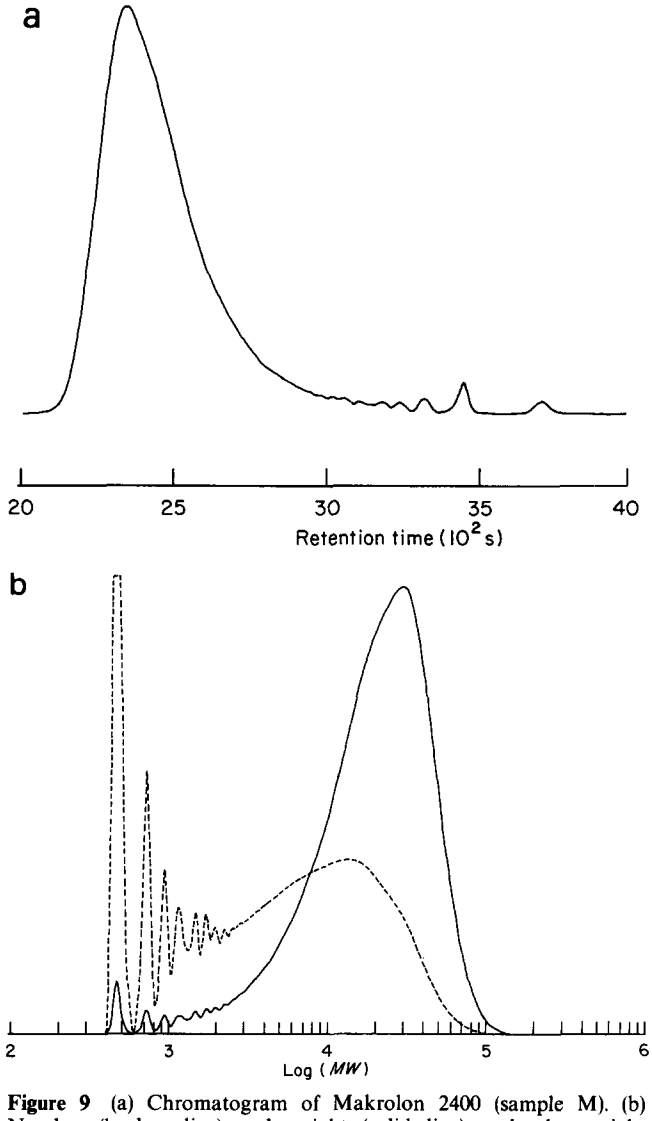

Figure 9 (a) Chromatogram of Makrolon 2400 (sample M). (b) Number (broken line) and weight (solid line) molecular weight distributions of sample M. Diphenyl carbonate is not included in the distribution. The calibration in the low-molecular-weight region is based on the curve for type I oligomers. $\bar{M}_n = 9500$; $\bar{M}_w = 24\,600$

Table 1 Comparison between retention times and molecular weights for type I oligomers and oligomers present in sample L and M

Type I oligomers		Sample L		Sample M	
RT (s)	*MW*	*RT* (s)	*MW**	*RT* (s)	*MW**
3464	468	3458	474	3465	468
3335	722	3333	729	3334	725
3243	976	3246	968	3253	947
3172	1230	3173	1229	3188	1190
3115	1484	3117	1479	3119	1468
3067	1738	3071	1722	3067	1738
3024	1992	3019	2049	3031	1964

* Based on calibration curve of type I oligomers

be interpreted only with caution. This point will be discussed in more detail in the next subsection.

Reverse-phase h.p.l.c. experiments

Oligomer mixtures. Oligomer mixtures similar to those studied by h.p.s.e.c. were analysed by reverse-phase h.p.l.c. The corresponding chromatograms are presented in *Figures 10–12*. The chromatograms of type III and 'all types' mixtures (*Figures 11* and *12*) cannot be interpreted quantitatively because the samples are not completely soluble in acetonitrile. Oligomers I,0; I,1; II,0; and III,0 are identified by cross injection. Other type I and III oligomers are identified by assuming that shorter species elute first. Type II oligomers are identified as the non-type I, non-type III oligomers in the 'all types' mixture. They are also present as minor species in the type I mixture (*Figure 10*), where they arise as hydrolysis and reaction products.

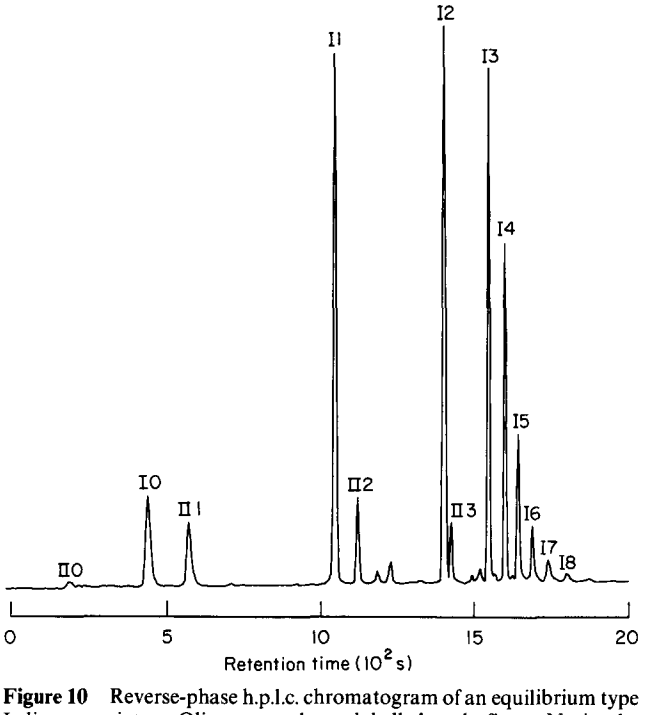

Figure 10 Reverse-phase h.p.l.c. chromatogram of an equilibrium type I oligomer mixture. Oligomer peaks are labelled on the figure. Notice the presence of small amounts of type II oligomers (hydrolysis and reaction products). Gradient elution from 65 to 100% acetonitrile between 0 and 1200 s, followed by isocratic elution at 100% acetonitrile

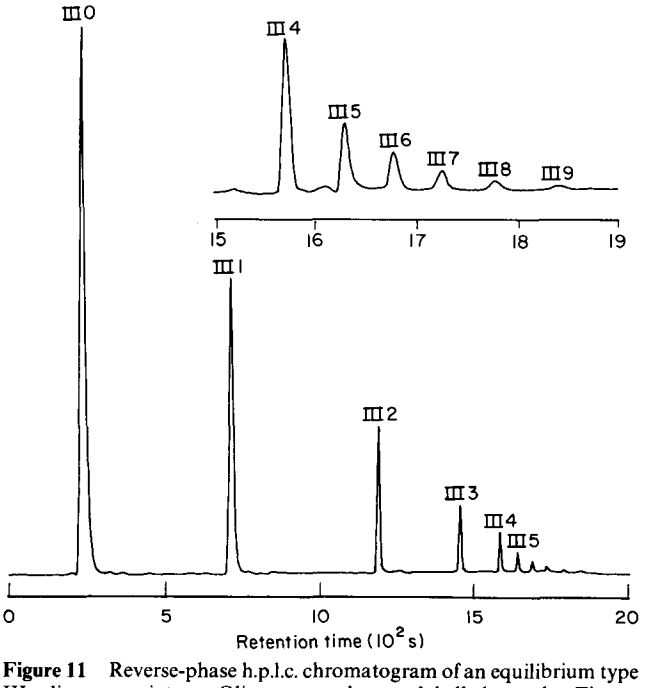

Figure 11 Reverse-phase h.p.l.c. chromatogram of an equilibrium type III oligomer mixture. Oligomer peaks are labelled on the Figure. Gradient elution as in *Figure 10*

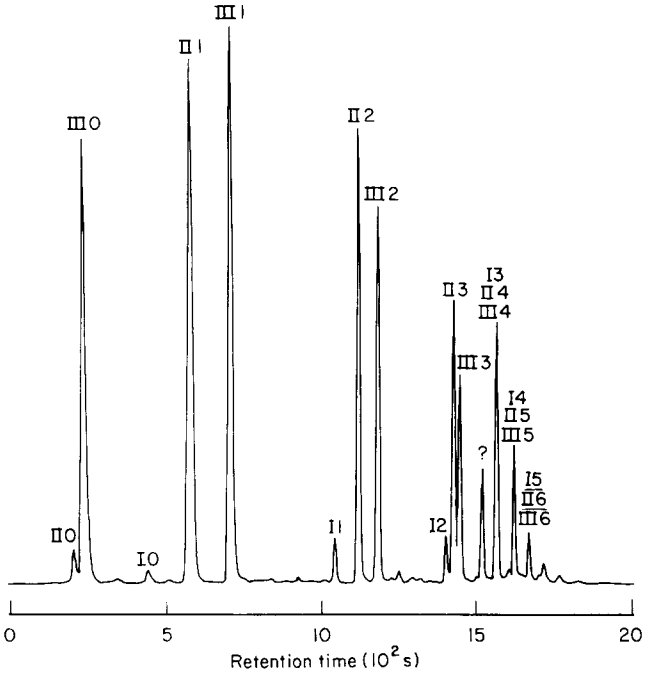

Figure 12 Reverse-phase h.p.l.c. chromatogram of an 'all types' oligomer mixture. Oligomer peaks are labelled on the Figure. Gradient elution as in *Figure 10*

Considering the chromatogram of the 'all types' mixture (*Figure 12*), it can be seen that oligomers are individually resolved up to I,2; II,3; and III,3. For higher oligomers, species I,n; II,$(n+1)$; and III,$(n+1)$, i.e. compounds having the same number of carbonate groups, elute at the same time. This can be interpreted as the consequence of a compensation between opposite influences from the terminal groups on the retention time of the oligomers. For species having the same number of carbonate groups, the polar hydroxy groups of type II and III oligomers tend to decrease the retention time with respect to that of type I oligomers whereas the bulkier bisphenol terminal groups tend to increase it.

Extracted samples. Oligomer fractions extracted in acetonitrile were analysed by reverse-phase h.p.l.c. The chromatogram of the extracted fraction of sample L is reported in *Figure 13*. The chromatogram corresponding to sample M is qualitatively similar.

The limited solubility of the oligomers in acetonitrile completely excludes a quantitative analysis of these data. However, the identification of a major portion of the extracted species is possible by cross-injecting the samples with solutions of known oligomers.

The proposed identification is reported in *Figure 13*. The presence of type I oligomers is clearly visible, confirming the h.p.s.e.c. results. Some type II oligomers are also observed, but almost no type III oligomers, at least the first ones that can be separated from type I and II species.

The presence of several unknown compounds (labelled ? in *Figure 13*) is more intriguing. Some of them could be assigned to polymer additive residues of synthesis. The possibility also exists that, along with phenol, another chain modifier was employed. It should be kept in mind that the observed concentration of a particular extracted oligomer does not necessary reflect its concentration in the polymer since extraction kinetics and solubility in acetonitrile may vary widely from species to species. Some of the unknown peaks are already present in type I oligomers mixtures (peaks of 1306 and 1580 s). It is therefore possible that the corresponding compounds are cyclic oligomers since the latter can be generated by the same interchange process that gives rise to type I oligomers.

In conclusion, reverse-phase h.p.l.c. of the extracted fractions of samples L and M reveals the great variety of oligomers present. Some more work is needed unambiguously to identify all the species observed. Although most of the unknown products could be very minor components of the samples, it appears that h.p.s.e.c. gives only a simplified view of the real situation.

CONCLUSION

It has been shown that h.p.s.e.c. is a powerful technique for separating PC oligomer mixtures. With the experimental system used, compounds with up to ten repeating units were resolved, following the nature of the oligomers present. By using special deconvolution techniques, it should even be possible to increase this number[16]. However, when several types of oligomers are simultaneously present, interpretation of the chromatograms becomes difficult and should be made with caution. This is particularly so when analysing the oligomer content of commercial PC samples. The resolution obtained by reverse-phase h.p.l.c. remains superior but in

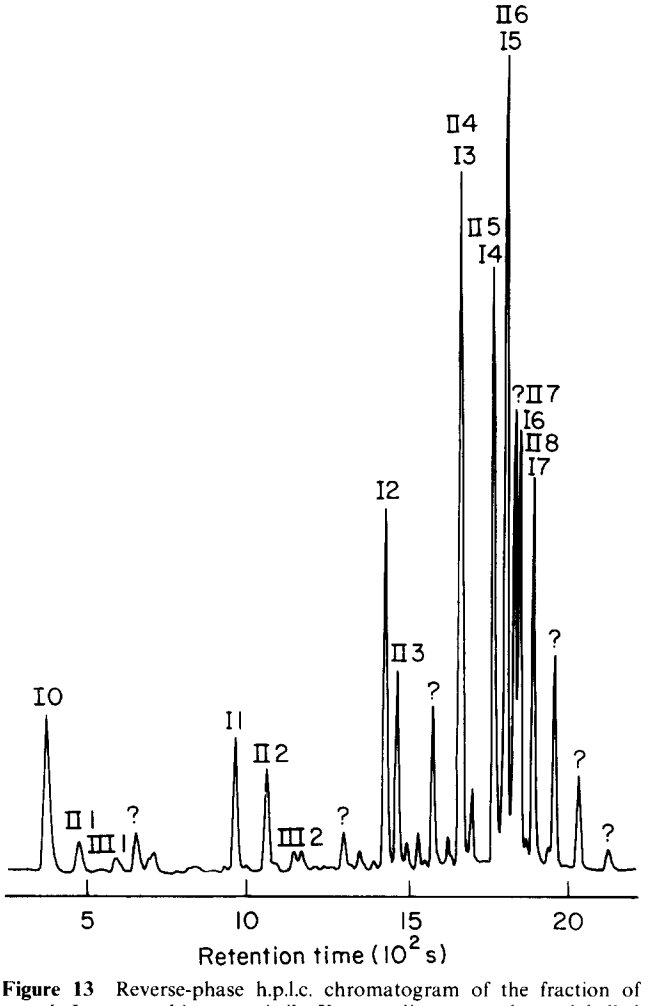

Figure 13 Reverse-phase h.p.l.c. chromatogram of the fraction of sample L extracted in acetonitrile. Known oligomer peaks are labelled on the Figure. Gradient elution from 65 to 100% acetonitrile between 0 and 1500 s, followed by isocratic elution at 100% acetonitrile

most cases, quantitative results cannot be obtained by this technique because of solubility problems.

In contrast with previous claims[5], the nature of the end-groups was observed significantly to influence the retention time of PC oligomers by s.e.c. The presence of hydroxy terminal groups induces a reversible adsorption of the compounds on the columns. This effect is very important for oligomers having two hydroxy end-groups (III,*n*), especially for bisphenol-A, which was found to elute close to the maximal permeation volume while its molecular weight is within the separation range of the column set used. This gives rise to different calibration curves for the three types of PC linear oligomers. The curves converge only at molecular weights close to 10 000. As a consequence, the precise determination of the number average molecular weight of PC samples by s.e.c. is possible only if the nature of the oligomers present is taken into account.

Finally, the problem of determining the u.v. molecular extinction coefficient of PC oligomers was shown to be easily solved by using the simplifying assumption that only two different types of phenyl groups give rise to the u.v. absorption: internal and terminal groups.

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