polymer communications

Cyclic oligomers in poly(1,4-butylene terephthalate)

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The cyclic oligomers present in poly(1,4-butylene terephthalate) have been extracted and quantitatively determined by high pressure liquid chromatography.

Keywords Analysis; oligomers; polyesters; cyclic compounds; liquid chromatography

Introduction

The cyclic oligomer content of poly(ethylene terephthalate) (PET) has been extensively investigated over the past twenty years[1]. Most of the studies were stimulated by the problems caused during the dyeing of PET fibres due to the migration of the cyclic trimer (the predominant cyclic species) from the interior of the fibre to the fibre surface. The other interest, exemplified by the work of Cooper and Semlyen[2], has been in comparing the equilibrium cyclic oligomer content with that predicted by theory. The use of poly(1,4-butylene terephthalate) (PBT) as a textile fibre prompted us to investigate the cyclic oligomer content of this polyester. After we had begun our investigation, Burzin and co-workers[3] reported values for the equilibrium amounts of cyclic dimer, trimer and tetramer in PBT. Whilst our study is not yet complete, we wish to report our findings on the cyclic species present in PBT since we believe that the results presented by Burzin *et al.* are seriously in error.

Experimental

PBT in chip form was supplied by I.C.I. Plastics Division; $[\eta]$ was 0.95 dl g^{-1} in 60:40 phenol:tetrachlorethane at 30°C. Two separate procedures for isolation of the cyclic oligomers were used. In the first, the chips were dissolved in *o*-dichlorobenzene (10 g in 150 ml) at the boil. Upon cooling, the precipitated polymer was recovered by filtration and washed extensively with chloroform. The chloroform washings were combined with the *o*-dichlorobenzene extract and the oligomers were recovered by evaporation of the solvents. The second procedure entailed solution of the polymer in trifluoroacetic acid (1 g in 10 ml) at room temperature, followed by precipitation, as described by Hudgins *et al.*[4] for PET.

The extracts were examined qualitatively using thin layer chromatography and preparative t.l.c. was used to obtain milligram quantities of the three most plentiful species. Quantitative analysis of the extracts was carried out by high pressure liquid chromatography using a Pye-Unicam LC-XP instrument. A good resolution of the mixture was obtained using a Lichrosorb Si 60 (5 μ) column (250 × 3.2 mm), with hexane-dioxan (70:30) as the mobile phase at a flow rate of 1.5 ml min^{-1}. The effluent was monitored at 249 nm and the cyclic trimer of PET was used as an internal standard. Calibration experiments were performed with the cyclic dimer, trimer and tetramer of PBT (recovered by preparative t.l.c.) and with the internal standard; these showed that peak height varied linearly with concentration for all four species, though with quite different response factors. The response factors for the higher species were estimated by extrapolation.

Results and Discussion

The extracts obtained using the *o*-dichlorobenzene procedure varied between 1.5 and 1.8% on the weight of polymer taken. Repeating the procedure on the same polymer samples gave a further 0.2–0.4% o.w.p. The trifluoroacetic acid procedure, carried out in duplicate, gave an extract of 1.5% o.w.p. Resolution of the extracts on t.l.c. was achieved by using much the same conditions as used earlier in studies of cyclic oligomers in PET[5]. *Figure 1* shows a typical chromatogram, obtained by successive developments with chloroform hexane (10:5) and chloroform hexane (10:3). Preparative t.l.c. allowed samples of the components assigned as 1, 2 and 3 in *Figure 1* to be recovered and they were identified as the cyclic

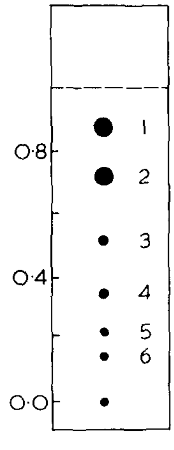

Figure 1 Schematic thin layer chromatogram of PBT extract, developed successively with chloroform/hexane (10 : 5) and chloroform/hexane (10 : 3) on silica gel G60

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dimer, trimer and tetramer respectively. The identification was based on extensive characterization of each component. Thus component 1 was assigned as cyclic dimer on the basis of molecular weight (451) and the correspondence of the melting point (193°C), n.m.r. spectrum and mass spectrum with published data[6,7]. Similarly component 2 was identified *via* molecular weight (661), mass spectrum (parent mass 660) and the agreement of melting point (167.5°C) and n.m.r. spectrum with published values[6]. Component 3, on the basis of a molecular weight of 858 and a melting point of 247°8°C (literature values being 243°–7°C[6] and 246°–9°C[8]) was assigned as the cyclic tetramer. In all cases, elemental analysis and infra-red spectra were in complete agreement with the assignments as cyclic esters of PBT. In the light of these assignments, it seemed reasonable to conclude that components 4, 5 and 6 (*Figure 1*) corresponded to the cyclic pentamer, hexamer and heptamer respectively. Indeed, such a conclusion was supported by the linear relationship which then existed between log R_f and number of units in the ring[9].

A typical h.p.l.c. trace is shown in *Figure 2* and the quantitative results obtained are shown in *Table 1*, together with the data of Burzin *et al.* and their theoretical estimates. The reproducibility of the analysis is satisfactory and the agreement between the two extraction procedures is excellent. The discrepancy between our data and that of Burzin *et al.* is obvious and results, we believe, from their use of an inefficient extraction procedure. They extracted the finely ground polymer with methylene chloride, despite the conclusions of earlier workers[1,2] that such procedures fail to remove the cyclics completely (at least with PET) and that dissolution of the polymer is essential for efficient extraction of cyclics. Indeed, Burzin *et al.* failed to obtain any cyclic species higher than tetramer in all three polyesters they examined, nor did they show that extraction was complete. In our study, the extracted polymer was re-extracted using the *o*-dichlorobenzene procedure and the second extract was examined by both t.l.c. and h.p.l.c. Only very small traces of the cyclics could be detected, confirming the efficiency of the extraction procedure.

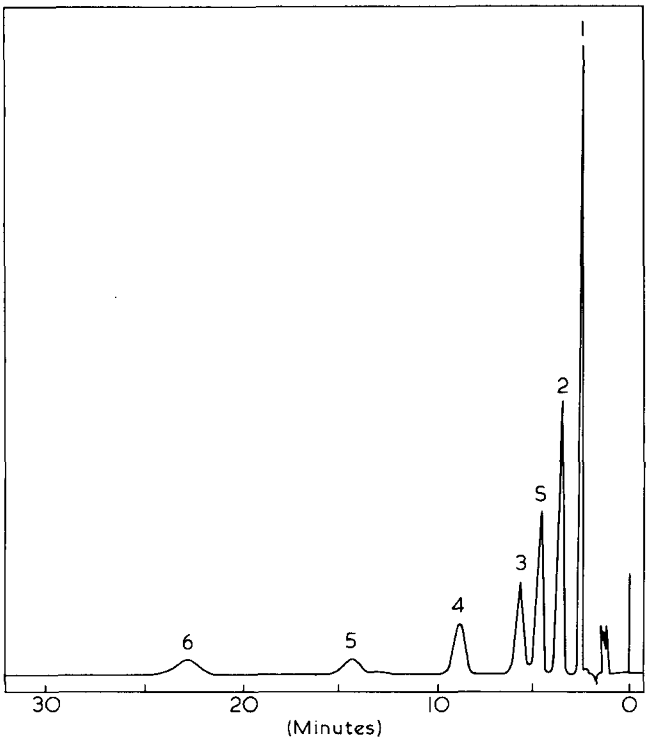

Figure 2 H.p.l.c. trace of PBT extract; peaks 1–6 correspond to the numbered components in *Figure 1*; S corresponds to the cyclic trimer of PET, present as internal standard

Quite interestingly, the amounts of the cyclic trimer, tetramer and pentamer observed in our study are in good agreement with the theoretical estimates made by Burzin *et al.* Such theoretical values apply to equilibrium conditions only, and if it is accepted that quite long periods of time (e.g. 10–15 h)[2] are required for equilibration, the sample of PBT examined is not necessarily equilibrated. Preliminary attempts have been made to establish equilibrium by holding the polymer in the melt at 255°C for lengths of time up to 15 h, with and without added titanium tetraisopropoxide. In all cases, the effect of this has been to lower the cyclic content, the loss being greater the longer the time the polymer is held in the melt. It is tempting to conclude that the polymer is already at equilibrium or that equilibrium cannot be attained due to decomposition processes.

Acknowledgements

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Table 1 Distribution of cyclic oligomers in PBT (% on weight of polymer)

	o-Dichlorobenzene procedure		Trifluoroacetic acid procedure		Data of Burzin *et al.*[3]	
Cyclic species	Run 1	Run 2	Run 1	Run 2	Expt.	Theory
Dimer	0.49	0.48	0.49	0.47	0.43	0.97
Trimer	0.44	0.46	0.45	0.44	0.17	0.45
Tetramer	0.21	0.24	0.23	0.22	0.10	0.27
Pentamer	0.16	0.18	0.17	0.16	–	0.18
Hexamer	0.07	0.03	0.02	0.02	–	0.13
Heptamer	0.07	0.02	0.02	0.02	–	0.10