Polymer Vol. 37 No. 15, pp. 3427–3429, 1996

0032-3861/96/$15.00 + 0.00

polymer communications

X-ray crystallographic structure of cyclic tetramer ester based on bisphenol-A and *o*-phthaloyldichloride

Hongyan Jiang, Tianxi Liu, Hongfang Zhang, Tianlu Chen and Zhishen Mo*
Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China
(Received 26 October 1995)

The polycrystalline powder of the cyclic tetramer ester based on bisphenol-A and *o*-phthaloyldichloride has been prepared by recrystallization from nitrobenzene and its crystal structure determined by wide-angle X-ray diffraction. The unit cell is orthorhombic and has dimensions $a = 0.967$ nm, $b = 0.8699$ nm, $c = 2.0859$ nm. With two tetramers per unit cell, the crystal density is 1.36 g cm^{-3}. Indices of crystal diffraction peaks are also detailed in the present work. Copyright © 1996 Elsevier Science Ltd.

(Keywords: cyclic tetramer ester; wide-angle X-ray diffraction; unit cell parameters)

Introduction

Polyarylates constitute an important class of engineering polymers. They are tough materials having excellent mechanical and thermal properties. However, these polymers generally suffer the problem of very high melt viscosity, which limits their applications in some areas. Therefore the use of low-molecular-weight macrocyclic precursors to prepare these polymers via ring-opening polymerization during processing has received considerable attention in recent years[1-4]. Macrocyclic precursors have the advantage of a lower viscosity at processing temperature than the final polymer, and may find applications in such areas as compositions for reaction injection moulding[5].

A research programme on the synthesis and ring-opening polymerization of cyclic ester oligomers was initiated in our laboratory several years ago, and an efficient way to prepare cyclic ester oligomers was found. The cyclic oligomers obtained by this method are a mixture of ring sizes, ranging from dimer to octomer, with the cyclic tetramer being the main product. Although the latter has been reported by Tyuzyo and Harada[6], its crystal structure has not been determined so far. The dimensions of the single-crystal sample prepared in our laboratory are not suitable for X-ray diffraction. The present communication reports the preparation, isolation and X-ray crystal structure of the polycrystalline powder of the cyclic tetramer prepared from bisphenol-A and *o*-phthaloyldichloride.

Experimental

The cyclic oligoesters were prepared as a mixture of different ring sizes in 70–80% yields via a PTC catalysed interfacial condensation of bisphenol-A and *o*-phthaloyldichloride using CH_2Cl_2 and NaOH under pseudo-high-dilution conditions[7] (see *Scheme 1*).

On the basis of the solubility difference on the cyclics and high-molecular-weight linear polymer in CH_2Cl_2, a mixture of cyclic tetramer and a small amount of cyclic dimer was obtained; the cyclic tetramer was then purified as an individual species by recrystallization as follows. The cyclic oligomer mixture (~0.20 g) was dissolved in hot nitrobenzene (analytical grade, 10 ml). The solution was then brought to room temperature over a period of at least 2 h, and the crystals of cyclic tetramer were obtained by gently tapping the outside of the flask. The colourless crystals of the tetramer were removed by filtration and washed with cold nitrobenzene (2 × 10 ml).

The wide-angle X-ray diffraction (WAXD) pattern was taken on a Rigaku D/max-IIB diffractometer from $2\theta = 5$ to 55°. Cu$k_{\alpha 1}$ radiation was provided by a 2 kW Philips X-ray tube (40 kV, 20 mA). As monochromator and analyser we used curved graphite crystals.

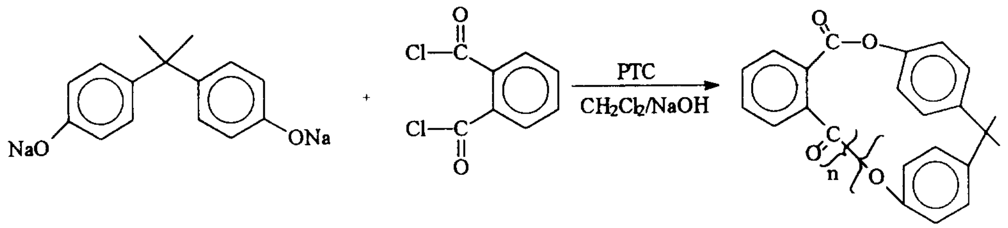
Results and discussion

The cyclic tetramer (*Scheme 2*) is a crystalline solid that melts at 302.8–304.0°C, and has been characterized by gel permeation chromatography (g.p.c.), fast atom bombardment mass spectrometry (f.a.b.-m.s.), Fourier transform infra-red spectroscopy (*FT*i.r.) and elemental analysis. The g.p.c. trace shown in *Figure 1* indicates that the cyclic tetramer is isolated, recrystallized as a pure compound. F.a.b.-m.s.: m/z 717 (M^+ molecular ion), 701 ($M^+ - CH_3 - H$). *FT*i.r. absence of phenolic stretching and all other peaks are common to the corresponding polymer. Elemental analysis: calcd for the cyclic tetramer C, 77.16; H, 5.03. Found: C, 77.08; H, 5.06. The density of the cyclic tetramer was determined using the suspension method as 1.26 g cm^{-3}.

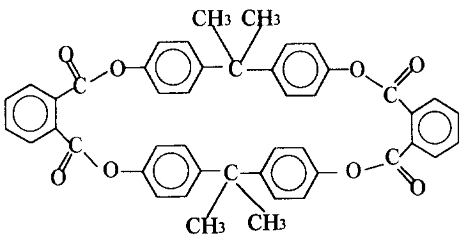
Using a trial-and-error method, the orthorhombic unit cell was determined with cell dimensions $a = 0.9676$ nm, $b = 0.8699$ nm, $c = 2.0859$ nm. Comparing the observed d-spacing with the calculated ones, the results were quite satisfactory (*Table 1*). *Figure 2* shows the WAXD pattern of the cyclic tetramer. The diffraction pattern with 30 diffraction peaks was indexed in terms of an orthorhombic unit cell. The Miller indices of all the reflections and relative intensities are also displayed in *Table 1*. Using

---

* To whom correspondence should be addressed



Scheme 1



Scheme 2 Chemical structure of cyclic tetramer

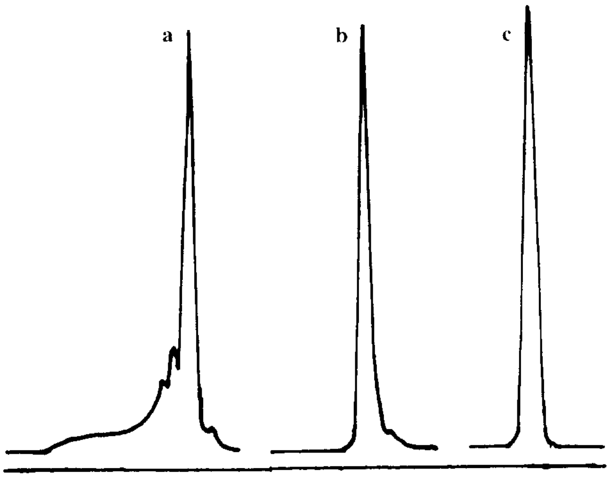


Figure 1 G.p.c. trace of the reaction product (a), cyclic mixture (b) and cyclic tetramer (c)

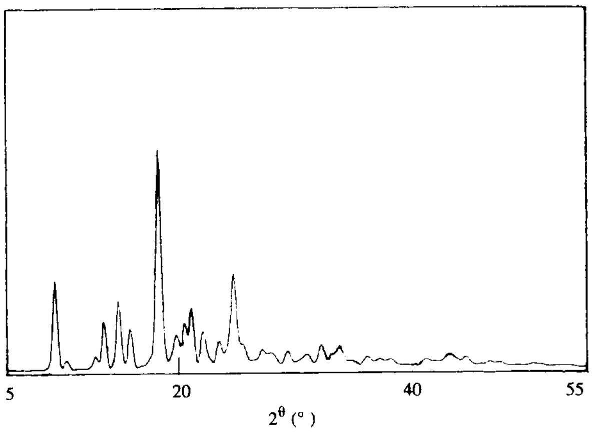
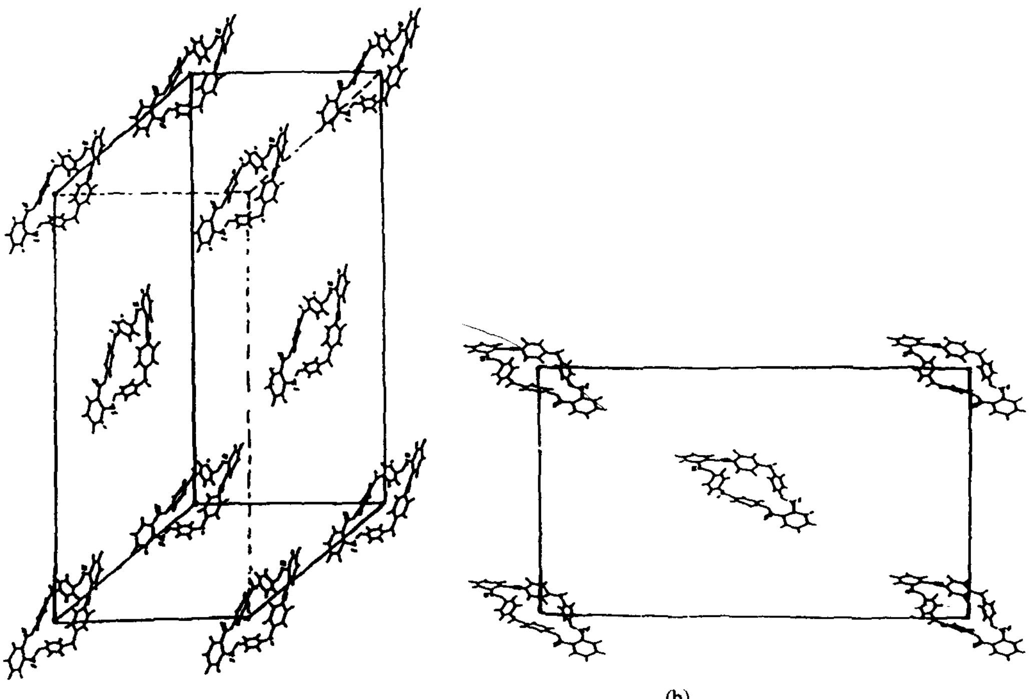


Figure 2 WAXD diffractogram of cyclic tetramer

these data, a model of the crystal structure of an orthorhombic unit cell (*Figure 3*) was proposed. There are two tetramers per unit cell: 1/2 × 2 tetramer lying in the *ac*-plane, the other (1/8 × 8) tetramer positioning at the eight vertices of the unit cell. A projection on the (0 1 0) plane of the tetramer, in keeping with the symmetry

Table 1 Observed and calculated *d*-spacings and relative intensities of reflections for cyclic tetramer

No.	2θ (°)	d_{obs} (nm)	d_{calc} (nm)	I/I_o	*h k l*
1	9.18	0.963	0.968	42	1 0 0
2	10.16	0.870	0.870	6	0 1 0
3	12.72	0.695	0.695	8	0 0 3
4	13.50	0.655	0.647	23	1 1 0
5	14.76	0.600	0.618	33	1 1 1
6	15.80	0.560	0.565	20	1 0 3
7	18.32	0.484	0.484	100	2 0 0
8	19.84	0.447	0.447	18	0 1 4
9	20.60	0.431	0.435	23	0 2 0
10	21.24	0.418	0.423	30	2 1 0
11	22.26	0.399	0.397 0.397 0.401	19	2 0 3 1 2 0 0 2 2
12	23.70	0.375	0.369	15	3 2 0
13	24.98	0.356	0.355	45	2 0 4
14	25.90	0.344	0.345	11	1 2 3
15	27.38	0.325	0.324 0.323 0.328	11	2 2 0 3 0 0 2 1 4
16	28.38	0.314	0.319 0.309	9	3 0 1 2 2 2
17	29.60	0.302	0.302 0.299	10	3 1 0 3 1 1
18	31.16	0.287	0.287 0.290	9	0 3 1 0 3 0
19	32.46	0.276	0.278 0.275 0.277 0.279 0.275	13	1 3 0 1 3 1 3 1 3 0 3 2 2 2 4
20	33.96	0.264	0.268	13	0 3 3
21	34.92	0.257	0.257 0.259 0.258	6	3 2 1 3 2 0 1 3 3
22	36.20	0.248	0.249	8	2 3 0
23	37.26	0.241	0.242 0.240 0.242 0.243	7	4 0 0 4 0 1 2 3 2 3 2 3
24	38.20	0.235	0.236 0.233	6	4 0 2 4 1 0
25	41.42	0.218	0.219 0.218 0.216 0.216 0.215	6	4 0 4 0 4 0 0 4 1 3 3 0 1 4 0
26	43.32	0.209	0.208 0.211 0.211 0.207	8	0 4 3 4 2 0 1 4 1 4 2 2
27	44.64	0.203	0.203 0.201	7	1 4 3 0 4 4
28	46.68	0.194	0.195 0.196	5	2 4 2 4 2 4
29	47.54	0.191	0.186	5	4 3 0
30	50.54	0.180	0.180 0.180	5	3 4 0 3 4 1



(a)

(b)

Figure 3 (a) Sterodiagram of unit cell of cyclic tetramer; (b) b-axis projection of unit cell of cyclic tetramer

constraints is shown in *Figure 3*. It can be seen that there are three symmetry elements of this space group, i.e. two-fold rotation axis, mirror plane and centre of symmetry.

With the above unit cell parameters, the calculated crystal density is 1.36 g cm^{-3} assuming two cyclic tetramers per unit cell. A density measurement of the as-synthesized sample is 1.26 g cm^{-3}. This represents satisfactory agreement with the calculation since the density of the partially amorphous material in the oligomer is expected to be less than that of the completely crystalline polymer. The density measurement together with the crystallographic data establish the model of two cyclic tetramers per unit cell.

Acknowledgements

This work was supported by the National Natural Science Foundation of China, and The National Key Projects for Fundamental Research, 'Macromolecular Condensed State', of The State Science and Technology Commission of China. It was also supported by the Ford Motor Company and NSFC No. 09415308.

References

1 Brunell, D. J. and Shannon, T. G. *Macromolecules* 1991, **24**, 3035
2 Brunell, D. J., Boden, E. P. and Shannon, T. G. *J. Am. Chem. Soc.* 1990, **112**, 2399
3 Calquhoun, H. M., Dudman, C. C., Thomos, M. and Williams, D. J. *J. Chem. Soc. Chem. Commun.* 1990, 336
4 Brunell, D. J. and Shannon, T. G. *US Patent 4 829 114* 1989
5 Guggenheim, T. L., McCormick, S. J., Kelly, J. J., Brunelle, D. J., Colley, A. M., Boden, E. P. and Shannon, T. G. *Polym. Prepr.* 1990, **30**(2), 579
6 Tyuzyo, K. and Harada, K. *Polym. Lett.* 1964, **2**, 43
7 Rossa, L. and Vogtle, F. 'Topics in Current Chemistry' (Ed. F. L. Boschke), Springer-Verlag, New York, 1983, No. 113, Ch. 1