BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(6), 1943—1944 (1975)

On the Phase Transition of Cyclic Tris(ethylene terephthalate)

Yukishige Kitano,* Michio Kashiwagi,** and Yasuyuki Ebata
Basic Research Laboratories, Toray Industries, Inc., Tebiro, Kamakura 248

(Received October 31, 1974)

Synopsis. The crystal data of the Type B modification of the cyclic tris(ethylene terephthalate) showed it to be hexagonal, with the unit-cell dimensions of $a=15.42\pm0.03$ and $c=20.78\pm0.05$ Å (space group, $P6_1$ or $P6_5$). The effects of some organic reagents on the stability of Type B were studied qualitatively, and some information about the phase changes was obtained by the X-ray-diffraction and thermal-analysis techniques.

Because of their industrial importance and structural interest, the oligomers of poly(ethylene terephthalate), especially the cyclic trimer, have been investigated by many workers. The existence of two different forms, Type A and Type B,*** of the cyclic trimer was first found by Binns *et al.*,[1] and the discrepancies among the data previously reported[2-5] have been adjusted. Further observations were made by Ito and Okajima.[6] However, the Type B structure has not yet been unequivocally described. In this study we prepared stable Type B single crystals at room temperature and obtained crystal data on this material and some information concerning the effects of several organic reagents on the stability of the material.

The samples of the Type A cyclic trimer were extracted from a piece of poly(ethylene terephthalate) film with chloroform and were recrystallized repeatedly from a DMF solution. The samples of Type B were prepared by heating the Type A powder above 200 °C and by subsequently cooling it to room temperature. The X-ray diffraction data taken on the Type A samples were generally in agreement with those of Farrow *et al.*[7] and of Ito and Okajima.[6] The data for the Type B samples were similar to those of Binns *et al.*[1] and of Ito and Okajima,[6] but the X-ray pattern contained a number of reflections other than those previously reported. Single crystals of the Type B cyclic trimer were also prepared by the sublimation of the Type A powder. They are white platelet crystals of a size between 3 and 5 mm. The single-crystal X-ray pattern was identical to that of the Type B sample prepared by heating Type A and was completely indexed on the basis of the computer-refined hexagonal lattice parameters of $a=15.42\pm0.03$ and $c=20.78\pm0.05$ Å. The results are shown in Table 1. On the basis of six cyclic tris(ethylene terephthalate) per unit cell, the theoretical density is calculated to be 1.342 $\mathrm{g\cdot cm^{-3}}$; this should be compared with the observed density of 1.351 $\mathrm{g\cdot cm^{-3}}$ obtained by floatation in a $ZnCl_2$ solution. Systematic absences are observed on the Weissenberg photographs for the (00*l*) reflections with $l=6n$, where *n* is any integer. These data, combined with the Laue symmetry, 6/m, indicated the space group to be $P6_1$ or $P6_5$. Moreover, it is quite remarkable that the (00*l*) reflections with $l=6n$ show a diffuse scattering elongated in the direction perpendicular to [001]. Such diffuse scattering is undoubtedly due to some disordering in the packing of molecules in the crystal.

Next, the stability of Type B at room temperature was investigated. The endothermic transition peaks from Type A to B in the differential thermal analysis of

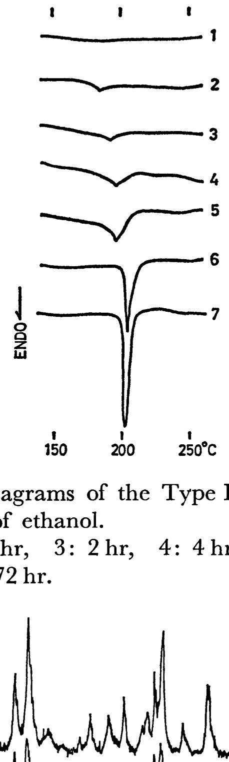

Fig. 1. DTA diagrams of the Type B samples exposed in the vapor of ethanol.
1: 0 hr, 2: 1 hr, 3: 2 hr, 4: 4 hr, 5: 6 hr, 6: 24 hr, 7: 72 hr.

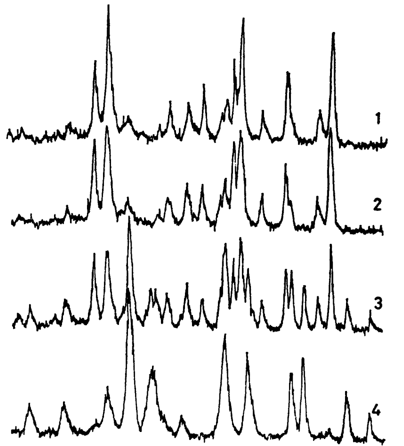

Fig. 2. X-Ray diffraction diagrams of the Type B samples exposed in the vapor of ethanol.
1: 0 hr, 2: 1 hr, 3: 4 hr, 4: 24 hr.

---

* Present address: Pioneering Research and Development Laboratories, Toray Industries, Inc., Sonoyama, Otsu 520.

** Present address: Engineering Research Laboratories, Toray Industries, Inc., Sonoyama, Otsu 520.

*** Type A and Type B, which have been designated by Binns *et al.*,[1] are stable at low and high temperatures respectively. The transition point of Type A to Type B is about 200 °C.

Table 1. X-Ray powder diffraction data for type B cyclic tris(ethylene terephthalate)[a)]

h	k	l	d_{obsd}	d_{calcd}	I_{obsd}
0	1	1	11.200	11.231	9
0	1	2	8.194	8.188	3
1	1	0	7.687	7.708	56
1	1	1	7.225	7.227	20
0	2	1	6.354	6.355	12
1	1	2	6.172	6.190	56
0	1	3		6.147	
0	2	2	5.615	5.616	13
1	1	3	5.149	5.151	60
1	2	0	5.032	5.046	70
1	2	1	4.901	4.904	21
2	1	1			
0	2	3	4.795	4.806	12
1	2	2	4.540	4.539	17
2	1	2			
0	3	1	4.353	4.352	8
1	1	4	4.312	4.307	23
0	2	4	4.114	4.099	7
0	3	2	4.080	4.091	16
1	2	3		4.078	
0	1	5	3.969	3.967	7
0	3	3	3.745	3.744	3
1	3	0	3.703	3.703	4
1	1	5	3.658	3.657	18
1	3	1		3.645	
1	2	4	3.612	3.619	9
2	1	4			
2	2	2		3.613	
0	2	5	3.527	3.527	13
3	1	2	3.488	3.488	25
0	0	6	3.463	3.463	100
0	3	4	3.373	3.379	30
2	2	3		3.368	
0	1	6	3.353	3.352	60
0	4	0	3.339	3.338	5
0	4	1	3.298	3.295	5
1	3	3	3.265	3.265	3
3	1	3			
1	2	5	3.206	3.208	3
2	1	5			
0	4	2	3.179	3.178	7
1	1	6	3.156	3.158	9
2	2	4	3.081	3.095	8
0	2	6		3.074	
2	3	0		3.063	
0	4	3	3.006	3.007	4
0	1	7	2.897	2.897	3
1	4	1	2.885	2.885	3
4	1	1			
1	2	6	2.856	2.855	8
2	1	6			
2	2	5	2.825	2.826	3
0	4	4	2.805	2.808	3
1	4	2		2.805	
4	1	2			
1	2	7	2.557	2.558	4
0	1	8	2.550	2.549	3
1	5	1	2.383	2.382	3
5	1	1			
4	2	3	2.373	2.371	3
4	3	1	2.182	2.183	3
0	2	9		2.182	
2	5	1	2.127	2.127	3
5	2	1			
0	6	3	2.118	2.118	9
5	2	2	2.093	2.094	3
4	3	3		2.092	
4	1	7	2.080	2.079	3
5	2	3	2.041	2.043	3
2	4	6		2.039	3
4	2	6			
1	6	0	2.036	2.036	4
1	6	1	2.026	2.026	3
0	6	5	1.962	1.962	3
0	1	12	1.717	1.717	3

a) $d=_{obsd}$, From diffractometer pattern calibrated by silicon powder; d_{calcd}, based on hexagonal lattice parameters, $a=15.42$ and $c=20.78$ Å; I_{obsd}, peak intensities from diffractometer pattern (Cu$K\alpha$ radiation).

the samples were found to vary when Type B was exposed to the vapor of such reagents as methanol, ethanol, acetone, DMF, benzene, and chloroform. Figure 1 shows the DTA diagrams of a sample treated with ethanol. After the sample had been treated for one hour, a small peak appeared at 187 °C. This peak grew larger and sharper, and, moreover, it shifted to high temperatures with time. After 24 hr of treatment, the peak reached 204 °C. In the course of this treatment, structural changes occurred, as assessed by X-ray diffraction. As is shown in Fig. 2, initial Type B structure gradually changed with time; finally it was almost entirely transformed into the Type A structure. Similar phenomena were observed when the samples were treated with other organic reagents.

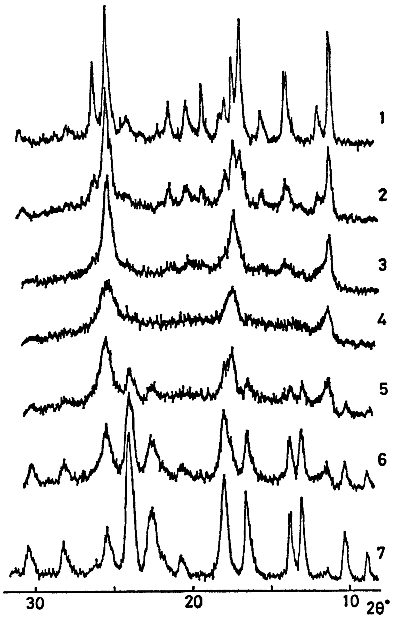

Fig. 3. X-Ray diffraction diagrams of the Type B samples kept in the air of 30 to 50% relative humidity.
1: 0 hr, 2: 1 day, 3: 2 days, 4: 7 days,
5: 10 days, 6: 15 days, 7: 30 days.

X-Ray diffraction diagrams taken after the samples had been kept in air with a relative humidity of 30 to 50% for different lengths of time are given in Fig. 3. The peaks gradually broadened, showing that the samples became amorphous with time; one month later the Type B structure completely changed into Type A. On the other hand, when the Type B samples were kept in a desiccator over silica gel, no such phenomena were observed. This means that the Type B cyclic trimer is stable at room temperature in dry air.

References

1) G. L. Binns, J. F. Frost, F. S. Smith, and E. C. Yeadon, *Polymer*, **7**, 583 (1966).

2) I. Goodman and B. F. Nesbitt, *ibid.*, **1**, 384 (1960).

3) D. Grime and I. M. Ward, *Trans. Faraday Soc.*, **54**, 959 (1958).

4) B. Seidel, *Z. Elektrochem.*, **62**, 214 (1958).

5) H. Zahn and B. Seidel, *Makromol. Chem.*, **29**, 70 (1959).

6) E. Ito and S. Okajima, *Polymer Lett.*, **7**, 483 (1969), *Polymer*, **12**, 650 (1971).

7) G. Farrow, J. McIntosh, and I. M. Ward, *Makromol. Chem.*, **38**, 147 (1960).