

X-RAY CRYSTALLOGRAPHIC STRUCTURE OF Meta- AND Para-DIMETHYL ESTER OF PYROMELLITIC ACID

HUANG Wenxi (黄文溪) LIU Tianxi (刘天西) GAO Lianxun (高连勋)

ZHANG Xin (张欣) XU Jiping (徐纪平) and DING Mengxian (丁孟贤)*

(Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022)

ABSTRACT

The polycrystalline powder of para- and meta-dimethyl ester of pyromellitic acid (PMDE) have been prepared by fractional crystallization, and their crystal structures have been determined by Wide-Angle X-ray Diffraction (WAXD). Both p-PMDE and m-PMDE was found to be orthorhombic crystal system, and their unit cell parameters $a = 0.840$ nm, $b = 0.707$ nm, $c = 1.136$ nm and $a = 1.032$ nm, $b = 0.835$ nm, $c = 0.714$ nm, respectively. Space group all belongs to P_{mmm} . p-PMDE has two molecules per unit cell with crystal density $1.388 \text{ g} \cdot \text{cm}^{-3}$, while m-PMDE has two molecules per unit cell with crystal density $1.522 \text{ g} \cdot \text{cm}^{-3}$. Indices of crystal diffraction peaks are also detailed in the present work. The difference in crystal structures between p-PMDE and m-PMDE has thus been used to explain the curing behavior of isomerically pyromellitic dianhydride-based poly(amic ester)s.

INTRODUCTION

The synthesis of poly(amic ester)s has been encouraged^[1-8] by their increased hydrolytic stability in solution, improved solubility, higher and broader imidization temperature regime which results in a significant improvement in the processability of these polymers for their applications. The ring closure reaction to form the polyimides from these poly(amic ester)s proceeds through elimination of the corresponding alcohol.

Initial step of the synthesis of pyromellitic dianhydride (PMDA)-based poly(amic ester)s involves the esterification of PMDA. Two aromatic diester-diacid isomers may appear as a result of the opening selectivity of anhydride groups towards the alcohol (Fig. 1), and the resulting poly(amic ester)s are a copolymer containing meta- and

* To whom all correspondence should be addressed.

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para-linkages whose isomerism come from the diester-diacids starting material. The possibility of separating respective diester-diacid isomers of pyromellitic acid and the preparation of the corresponding isomerically pure poly(amic ester)s has led us to investigate the effect of the isomerism of the repeat units on the curing behavior of the polymer. Theoretical considerations have led to the predication that the percentage of imidization expected for pure para-, meta- and mixed meta-/para-additions of the polyamic acids are 100, 82 and 91% respectively^[9]. This effect is predicted to arise from the relative difficulty of bringing the amide functionally into the correct geometry to react with the —OH group of the acid. The meta-poly(amic ethyl ester) of PMDA-ODA has showed lower viscosity in concentrated solution, and higher imidization temperature than the randomized chain^[10].

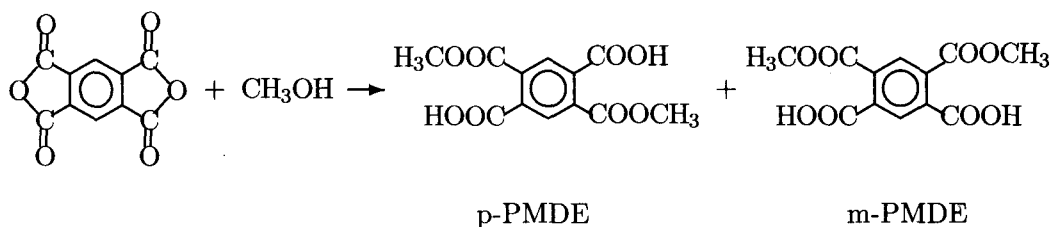


Fig. 1 Synthesis of two isomers of PMDE

The cycloimidization reaction of poly(amic ester) precursors can most often occur in the absence of solvent and chain conformations in the solid state will, therefore, play an important role in the imidization reaction. In order to investigate in detail both the reaction kinetics and stereochemistry of poly(amic ester)s, it is necessary to investigate separately the chemistry, in particular, the crystal structures of the monomers from which the poly(amic ester)s are prepared. To this end, we have obtained the polycrystalline powder of the two isomers of dimethyl ester of pyromellitic acid (PMDE) and have studied their crystal structures using Wide-Angle X-ray Diffraction (WAXD).

EXPERIMENTAL

Starting materials

PMDA was available commercially and purified by sublimation. Methanol was distilled under nitrogen over CaH₂.

Preparation of dimethyl ester of pyromellitic acid (PMDE)

A 200 ml methanol solution containing 40.0 g of freshly sublimed PMDA was refluxed under nitrogen. The reaction was carried out for an additional hour after

all solids have gone into the solution. Finally the methanol was distilled off to yield 50.7 g (98%) of the desired diester-diacid after vacuum drying at 60°C for 24 h.

Separation of isomers

PMDE (40.0 g) was suspended in ethyl acetate (400 ml) and stirred for 24 h at room temperature. The resulting suspension was filtered and the filtrate was evaporated under vacuum. This procedure yielded 14.2 g (35.5%) of ethyl acetate soluble material corresponding mainly to the meta-isomer and 24.4 g (61.0%) of ethyl acetate insoluble material corresponding mainly to the para-isomer. HPLC was used to determine the purity of isomers. The para-rich isomer was recrystallized several times from methanol/water by staying overnight in a refrigerator, 7.2 g p-PMDE crystal was yielded with an isomeric purity of > 99.5%. The meta-rich material was recrystallized several times from ethyl acetate and 2.2 g m-PMDE crystal was yielded with an isomeric purity of > 99%. After vacuum drying at 40°C for 24 h, the polycrystalline powder of both p-PMDE and m-PMDE was obtained and was ready for X-ray experiment.

Measurement

Densities were measured by suspension method. WAXD patterns were taken on a Rigaku D/max-IIB diffractometer from $2\theta = 4 \sim 55^\circ$. $\text{CuK}\alpha_1$ radiation is provided by a 2 kW PHILIPS X-ray Tube (40 kV, 20 mA). As monochromator and analyzer we used cured graphite crystals.

High performance liquid chromatography (HPLC) was performed on a GILSON HPLC system with a GILSON model 306 pump.

RESULTS AND DISCUSSION

The esterification of PMDA can lead to the formation of two isomers (Fig.1). The separation of these two isomers is achieved by taking advantage of the much greater solubility of m-PMDE in organic solvent. HPLC results showed that both m-PMDE and p-PMDE are pure after recrystallization (Fig.2).

The densities of m-PMDE and p-PMDE were found to be $1.506 \text{ g}\cdot\text{cm}^{-3}$ and $1.385 \text{ g}\cdot\text{cm}^{-3}$, respectively. Fig.3 is the WAXD diffractograms of m-PMDE and p-PMDE. With the help of trial and error method, both isomers were found to be orthorhombic crystal system. Using the following orthorhombic relation:

$$\frac{1}{d_{hkl}^2} = \frac{a^2}{h^2} + \frac{b^2}{k^2} + \frac{c^2}{l^2}$$

the unit cell dimensions were calculated as $a = 1.032 \text{ nm}$, $b = 0.835 \text{ nm}$, $c = 0.714 \text{ nm}$ for m-PMDE and $a = 0.840 \text{ nm}$, $b = 0.707 \text{ nm}$, $c = 1.136 \text{ nm}$ for p-PMDE. The diffraction pattern with 43 diffraction peaks was indexed in terms of an orthorhombic

unit cell for *m*-PMDE. The Miller indices of all the reflections and relative intensities are displayed in Table 1. It can be seen, by comparing the observed *d*-spacings with the calculated ones, that the results are quite satisfactory. Using these above data, a model of the crystal structure of an orthorhombic unit cell for *m*-PMDE (Fig.4(1)) is proposed. There are two molecules per unit cell, one molecule ($1/2 \times 2$) lying in the *bc* plane, the other one ($1/8 \times 8$) positioning at the 8 vertexes of the unit cell. From the symmetry and reflection conditions, only the space group P_{mmm} is possible. Three symmetry elements of this space group i.e. two fold rotation

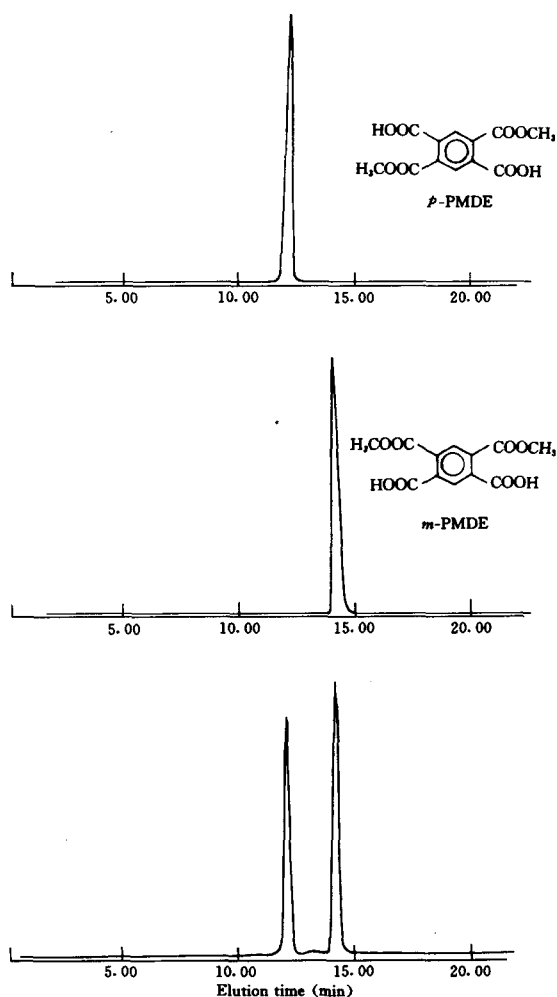


Fig. 2 HPLC separation of the two isomers of PMDE

Mobile phase: 5/95 CH_3CN /buffer (pH= 3), Flow rate 1ml/min

Column: 250 $\times$ 1.6mm, Spherisorb ODS-2,

Detector: UV254nm, at 0,1 AUFS

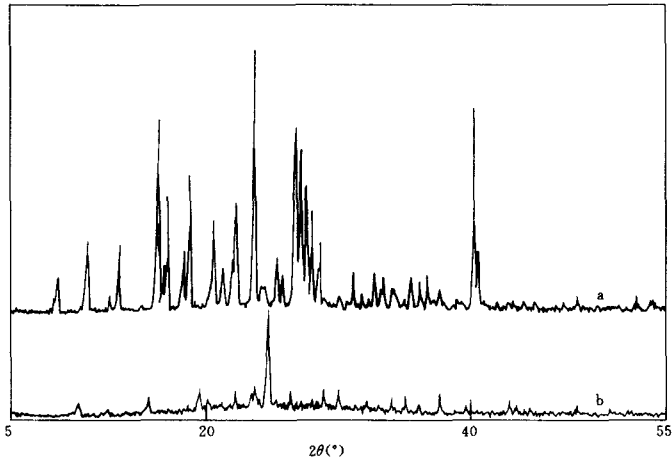


Fig. 3 WAXD diffractograms of (a) m-PMDE and (b) p-PMDE

Table 1 Observed and calculated d-spacings and relative intensities of reflections for m-PMDE

No.	hkl	d_o (nm)	d_c (nm)	2θ (°)	I_{norm}^a
1	100	1.032	1.032	8.56	6
2	010	0.835	0.835	10.58	21
3	001	0.714	0.714	12.38	5
4	110	0.651	0.649	13.12	21
5	101	0.584	0.587	15.98	57
6	011	0.547	0.543	16.42	15
7	200	0.518	0.516	16.78	42
8	111	0.479	0.480	18.50	42
9	210	0.435	0.439	20.38	41
10	201	0.419	0.418	21.10	27
	020		0.418		
11	120	0.380	0.387	23.38	88
12	211	0.367	0.374	24.22	15
	021		0.361		
13	002	0.354	0.357	25.14	27
14	300	0.348	0.344	25.54	8
15	102	0.337	0.338	26.42	45
16	012	0.331	0.328	26.88	100
17	220	0.326	0.325	27.34	46
18	310	0.320	0.318	27.86	72
19	112	0.315	0.313	28.32	20
20	301	0.306	0.309	29.18	4
21	221	0.298	0.296	29.92	5
22	311	0.291	0.291	30.72	13
23	202	0.288	0.289	31.04	4
24	022	0.274	0.271	32.60	5
	212		0.277		
25	130	0.269	0.269	33.34	17
26	122	0.262	0.262	34.24	40
27	131	0.253	0.252	35.46	27

(to be continued)

28	321	0.247	0.249	36.28	7
	302		0.248		
	410		0.247		
29	230	0.244	0.245	36.80	17
	401		0.243		
30	222	0.241	0.240	37.22	5
31	003	0.239	0.238	37.64	5
	312		0.238		
32	411	0.233	0.233	38.60	4
33	231	0.231	0.232	38.96	4
	103		0.232		
34	013	0.229	0.229	39.30	5
35	113	0.224	0.224	40.12	45
36	420	0.221	0.220	40.86	7
37	132	0.215	0.215	41.98	2
	330		0.216		
38	421	0.211	0.210	42.86	6
	213		0.209		
	040		0.209		
	402		0.209		
39	331	0.206	0.207	43.94	3
	023		0.207		
	140		0.205		
40	412	0.202	0.203	44.88	5
	123		0.203		
	232		0.202		
	041		0.201		
41	430	0.189	0.189	48.08	3
42	431	0.184	0.183	49.56	3
	332		0.185		
43	403	0.174	0.175	52.46	3
	014		0.175		
	341		0.173		

^a Normalized intensity, here, it is the height of diffraction peak, $I_{\max} = 100$

axis, mirror plane and centre of symmetry are also shown in Fig.4(1). With the above unit cell parameters, the calculated crystal density is $1.522 \text{ g}\cdot\text{cm}^{-3}$ assuming two molecules per unit cell, which is well agreed with the density measured ($1.506 \text{ g}\cdot\text{cm}^{-3}$), since the density of the partially amorphous materials in the products is expected to be less than that of the fully crystalline material. The measured density together with the crystallographic data does establish the two molecules per unit cell.

The same method was used to calculate the unit cell parameters for p-PMDE, and the results are shown in Table 2. The calculated crystal density is $1.388 \text{ g}\cdot\text{cm}^{-3}$ with two molecules per unit cell, and the unit cell model of p-PMDE was thus proposed (Fig.4(2)). By comparing the calculated crystal density ($1.388 \text{ g}\cdot\text{cm}^{-3}$) with the measured one ($1.385 \text{ g}\cdot\text{cm}^{-3}$), the results are also satisfactory.

It is clear from these studies that m-PMDE and p-PMDE have different

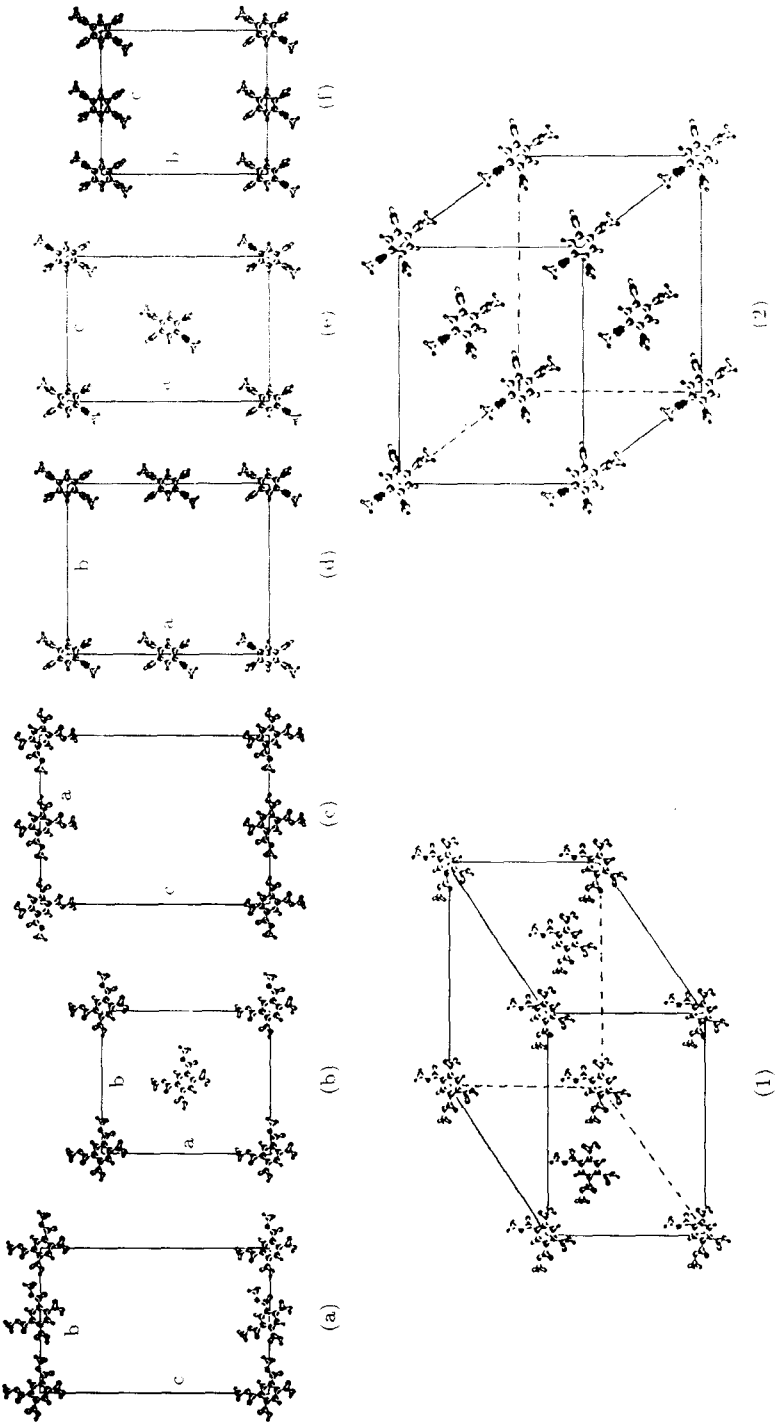


Fig.4 Projection and stereodiagram of unit cell of (1) m-PNIDE (a, b, c) and (2) p-PNIDE (d, e, f)

crystal structure. The WAXD pattern indicated that p-PMDE has a shift of diffraction peaks toward higher angle position than m-PMDE, which will result in different

Table 2 Observed and calculated d-spacings and relative intensities of reflections for p-PMDE

No.	hkl	d_o (nm)	d_c (nm)	2θ (°)	I/I_0
1	100	0.849	0.840	10.41	16
2	010	0.712	0.707	12.42	12
3	002	0.572	0.568	15.46	20
4	102	0.465	0.470	19.07	28
5	012	0.440	0.442	20.16	20
6	200	0.420	0.420	21.14	19
7	201	0.397	0.394	22.38	28
	112		0.392		
8	003	0.380	0.379	23.36	28
9	210	0.361	0.361	24.62	100
10	020	0.354	0.354	25.16	22
11	021	0.338	0.338	26.36	28
	202		0.338		
12	121	0.318	0.313	28.02	23
13	113	0.309	0.310	28.90	27
14	212	0.304	0.305	29.38	18
15	022	0.297	0.300	30.02	32
16	004	0.289	0.284	30.90	16
17	203	0.278	0.281	32.22	20
	300		0.280		
18	301	0.273	0.272	32.82	16
19	104	0.270	0.269	33.16	16
	220		0.270		
20	213	0.262	0.261	34.14	24
	310		0.260		
	221		0.263		
	014		0.263		
21	331	0.255	0.254	35.16	21
22	123	0.248	0.247	36.22	16
23	312	0.237	0.237	37.84	23
	030		0.237		
24	130	0.227	0.227	39.68	15
	303		0.225		
25	132	0.210	0.211	43.06	20
	400		0.210		
26	230	0.208	0.206	43.06	13
	401		0.206		
27	410	0.203	0.201	44.62	12
	322		0.205		
	231		0.202		
28	412	0.188	0.189	48.28	15
	232		0.190		
29	233	0.180	0.181	50.66	13
	420		0.180		
	330		0.180		
30	040	0.176	0.177	52.00	11
	241		0.175		
	134		0.177		

^a Normalized intensity, here, it is the height of diffraction peak, $I_{\max} = 100$

d-spacings. p-PMDE has larger unit cell dimensions than m-PMDE, which indicates a larger unit cell volume. As a consequence, m-PMDE has a larger density than p-PMDE, i.e. the packing in unit cell for m-PMDE molecules is denser and tighter than p-PMDE molecules.

Attempts to obtain the enthalpies of crystallization of the two isomers were unsuccessful due to their decomposition before melting.

It is possible that in the view of molecular structure the bulky COOCH_3 group in the 1, 4 position increase the spacing between molecules of the para-isomer, and it is disadvantageous for p-PMDE molecule to arrange tightly, para-monomer is, therefore, less crystalline (or has a looser crystal structure) than does the meta-monomer.

In a previous work, Volksen et al.^[10] has shown that the meta-poly(amic ethyl ester)s has a lower viscosities in concentrated solution, a better solubilities and higher imidization temperatures than the para-analogues. Considering the difference in crystal structure between para and meta monomers, we think that these two observations are closely related.

The difference in viscosity between para- and meta- isomers of poly(amic ester)s is characteristic of many other types of polymers and is due to the fact that the meta geometry has a more kinked main chain structure than the para geometry^[10-12]. It is known from the above results that the meta monomer which has a more compact packing, when incorporated in the poly(amic ester)s it tends to form kinked chain structure because of the position and bulkiness of the COOCH_3 group, and it is responsible for the difference in viscosity between para and meta isomers of poly(amic ester)s. The para isomer of poly(amic ester)s is more extended in solution than the meta isomer, and it would, therefore, has a looser structure than that of meta isomer in solid state. These differences could cause meta geometry to be more difficult in attaining correct conformations for cycloimidization, which result in a higher imidization temperature for meta isomer of poly(amic ester)s, predicted in a previous theoretical considerations^[9].

Keywords:

WAXD; Orthorhombic; Polyimide; Aromatic diester-diacids

REFERENCES

- [1] Kharkov, S.N.; Vinogradova, S.V.; Vygodskii, Y.S., et al., *Vysokomol. Soyed.*, **1971**, A-13: 1190.
- [2] Kharkov, S.N.; Krasnov, Ye P.; Lavrova, Z.N., et al., *Vysokomol. Soyed.*, **1971**, A-13: 833.

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- [3] Becker, K.H. and Schmidt, H-W., *Macromolecules*, **1992**, 25: 6784.
 - [4] Nishizaki, S. and Moriwaki, T., *Kogyo Kagaku Zasshi.*, **1970**, 73: 1873.
 - [5] Koltsov, A.I.; Dauengauer, S.A.; Denisov, V.M., et al., *Akad. Nauk SSSR*, **1984**, B278: 1380.
 - [6] Kim, K.; Ryou, J.H.; Kim, Y., et al., *Polymer Bulletin*, **1995**, 34: 219.
 - [7] Volksen, W.; Hofer D. and Cheng, Y.Y., Proc. 2nd European Technical Symposium on Polyimides & High Temperature Polymers, **1991**, 45.
 - [8] Volksen, W.; Yoon, D.Y.; Hedrick J.L., et al., "Materials Science of High Temperature Polymers for Microelectronics", MRS Symposia Proceedings, Anaheim, **1991**, 227: 23.
 - [9] Milevshaya, I.; Lukasheva, N.V. and Yel'Yashevich, A.M., *Vysokomol. Soyed., Ser A*, **1979**, 21: 1302.
 - [10] Volksen, W., Recent Advances in Polyimide and Other High Performance Polymers Interdisciplinary Symposium. ACS, San Diego, **1990**, C-1.
 - [11] Chin, E.; Yoshikiyo, M.; Houlihan, F.E., et al., Proc. 2nd European Technical Symposium on Polyimides & High Temperatures Polymers, **1991**, 19.
 - [12] Houlihan, F.M.; Bachman, B.J.; Wilkins, C.W., et al., *Macromolecules*, **1989**, 22: 4477.