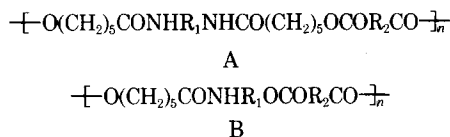


# Synthesis of Alternating Polyamide Esters by Melt and Solution Polycondensations of N,N'-Di(6-hydroxycaproyl)diamines and N-6-Hydroxycaproyl Aminoalcohol with Terephthalic and Adipic Dimethyl Esters and Dichlorides

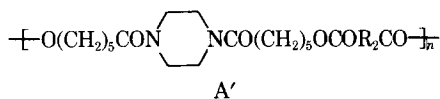
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## Synopsis

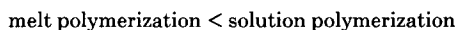
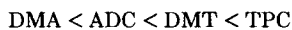
Alternating polyamide esters of structures A and B were obtained by melt polymerization of dimethyl adipate and terephthalate or by solution polymerization of adipoyl and terephthaloyl chlorides, with N,N'-di(6-hydroxycaproyl)diamines and an N-6-hydroxycaproyl aminoalcohol:



where R<sub>1</sub> is selected from dimethylene, hexamethylene, and *p*-phenylene radicals, and R<sub>2</sub> is selected from tetramethylene or *p*-phenyl radical. Polyamide esters of structure A' were also prepared:



Average values of melting points of the resulting polyamide esters were dependent on the starting diacid derivatives, amide diols, and methods of polymerizations as follows:



where CPZ, CHD, CED, and CPPD are N,N'-di(6-hydroxycaproyl)-, each in this order: piperazine, hexamethylenediamine, ethylenediamine, and *p*-phenylenediamine. ECA is N-(2-hydroxyethyl)6-hydroxycaproamide. For a given polyamide ester obtained from the same starting materials and by the same method of polymerization, the melting points increased with inherent viscosities. Polyamide esters of high molecular weight were obtained from CHD with both adipic and terephthalic derivatives both by melt and solution polymerizations. Polymerizations of

the other amide diols gave lower molecular weights. Solution polymerization gave colorless or light-colored polymers, while melt polymerization gave deeper-colored polymers.

## INTRODUCTION

There are a number of studies on alternating polyamide esters. The authors would like to propose a method of classification of alternating polyamide esters. The repeating unit of a polyamide ester molecule consists of amide and ester linkages, each separated by polycarbon linkages. Considering the directions of such linkages, there are four basic directions, i.e., CA which is —CONH—, AC which is —NHCO—, CO which is —COO—, and OC which is —OCO—. The combinations of these four directions give the following possible configurations of polyamide esters:

Polymonoamide monoester (MAME): (i) CA CO; (ii) CA OC.

Polymonoamide diester (MADE) (similar to polydiameter monoester): (i) CA CO CO; (ii) CA CO OC; (iii) CA OC CO; (iv) CA OC OC.

Polytriamide monoester (TAME) (similar to polymonoamide triester): (i) CA CA CA CO; (ii) CA CA CA OC; (iii) CA CA AC CO; (iv) CA CA AC OC; (v) CA AC CA CO; (vi) CA AC CA OC; (vii) CA CA CO AC; (viii) CA CA OC AC.

Polydiameter diester (DADE): (i) CA CA CO CO; (ii) CA CA CO OC; (iii) CA CA OC CO; (iv) CA CA OC OC; (v) CA CO CA CO; (vi) CA CA CO OC; (vii) CA OC CA OC; (viii) CA AC CO CO; (ix) CA AC CO OC; (x) CA AC OC CO; (xi) CA CO AC CO; (xii) CA CO AC OC; (xiii) CA CO CO AC; (xiv) CA CO OC AC; (xv) CA OC CO AC.

This classification indicates methods of preparation and properties of alternating polyamide esters. MAME polymers of the type MAME-(i) are rare,<sup>1</sup> while MAME-(ii) polymers have been widely studied.<sup>2-6</sup> DAME-(ii)<sup>7</sup> and TAME-(viii)<sup>8</sup> polymers are also rare. DADE polymers have been most intensively studied, and the typical types are DADE-(ix),<sup>9-12</sup> DADE-(x),<sup>13</sup> DADE-(xiii),<sup>14,15</sup> DADE-(xiv),<sup>8,16,17</sup> and DADE-(xv).<sup>18-21</sup> Thus, the many studied polyamide esters are reduced in their structures to only several types of the above classification with too many unstudied types.

In this study, the authors have obtained polyamide esters A, A' corresponding to the type DADE-(x), and B corresponding to the type MADE-(iii), as described in the synopsis of this paper. This study follows the authors' previous paper<sup>22</sup> on polyamide urethanes from N,N'-di(6-hydroxycaproyl)alkylenediamines and N-hydroxylalkyl-6-hydroxycaproamide. The resulting interest of our previous study has led us to study the melt polymerization of these amide diols with dimethyl dicarboxylates such as dimethyl adipate (DMA) and terephthalate (DMT), and the solution polymerization with dicarboxyloyl chlorides such as adipoyl (ADC) and terephthaloyl (TPC) chlorides.

## EXPERIMENTAL

### Starting Materials

**ECA, CED, and CHD.** ECA, CED, and CHD were prepared according to the method in our previous paper.<sup>22</sup>

**CPZ and CPPD.** Our previous method<sup>22</sup> using acetonitrile as solvent did not give CPZ nor CPPD. Higher reaction temperatures and longer reaction time were necessary to obtain the amide diols as crystals, but when temperatures were too high and reaction times too long, amide-ester interchange reactions occurred which resulted in difficulty in product isolation. Therefore, yields were low. Better examples are as shown below.

**CPZ:** In a 1-liter flask equipped with a stirrer, a dropping funnel with a nitrogen inlet, and a condenser with a nitrogen outlet was placed 77.5 g (0.9 mole) anhydrous piperazine, which was then melted at the bath temperature of 120°C in a nitrogen atmosphere.  $\epsilon$ -Caprolactone, 205.2 g (1.8 mole), in the dropping funnel was added dropwise into the agitated piperazine during 30 min, and the mixture was reacted at 120°C in the nitrogen atmosphere for the further 20 hr. An oil viscous even at room temperature was obtained, and it was allowed to stand at room temperature for ten days until fine crystals precipitated. The crystals were recrystallized in aqueous ammonia; yield 25.0%; mp 78.0–79.0°C. Obsd. C, 60.52; H, 9.42; N, 9.76. Calcd. C, 61.12; H, 9.62; N, 8.92. IR key bands by KBr tablet, 3400  $\text{cm}^{-1}$  (OH stretching), 1620  $\text{cm}^{-1}$  (C=O stretching), 1050  $\text{cm}^{-1}$  (C—O stretching and OH deformation).

**CPPD:** In the same flask as used for the preparation of CPZ was placed 108.0 g (2 moles)  $\epsilon$ -caprolactone in the dropping funnel dropwise into the agitated *p*-phenylenediamine during 1 hr, and the mixture was reacted at 160°C in the nitrogen atmosphere for the further 17 hr. After the reaction, a condensed powdery cake was obtained on cooling to the room temperature. It was recrystallized several times with a total of 30 liters of water. Yield, 22.0%; mp 197–199°C. Obsd. C, 64.22; H, 5.91; N, 9.03. Calcd. C, 64.27; H, 8.39; N, 8.32. IR key bands by KBr tablet, 3300  $\text{cm}^{-1}$  (OH and NH stretchings), 1640  $\text{cm}^{-1}$  (amide I band), 1560  $\text{cm}^{-1}$  (amide II band), 1050  $\text{cm}^{-1}$  (C—O stretching and OH deformation).

**DMA and DMT.** Freshly prepared DMA (bp 76–78°C/1 mm Hg) and DMT recrystallized from ethanol (mp 142–143°C) were used.

**ADC and TPC.** ADC and TPC were prepared according to the method of Fuson et al.<sup>23</sup> ADC: bp 89–90°C/2–3 mm; TPC: bp 115–116°C/3 mm, mp 81–82°C.

**Solvents.** Nitrobenzene was washed with water, dried over calcium chloride, and distilled in the presence of phosphorous pentoxide, bp 207°C. Pyridine was dried over sodium hydroxide and distilled, bp 115°C. Tetrachloroethane was dried over potassium carbonate and distilled, bp 145°C. Dimethylformamide was distilled in the presence of 2,4-tolylene diisocyanate, bp 74–75°C/4–5 mm.

**Catalyst.** Commercially available best-grade antimony trioxide (ATO) and calcium acetate (CAC) were fully dried under vacuum at room temperature without further treating.

### Polymerization Procedure

**Melt Polymerization.** One mole dimethyl carboxylate and 1 to 2 moles amide diol were placed together with antimony trioxide and calcium acetate in a polymerization glass tube equipped with a nitrogen inlet leading to the bottom of the tube and a nitrogen outlet which also worked as the outlet of

TABLE I  
 Polymerization of Amide Diols with Dimethyl Carboxylates<sup>a</sup>

Polymerization conditions							
Run no.	Amide diol, mole	Temp., °C (hr)	Temp., °C/mm Hg (hr)	Color and state	mp, °C	$\eta_{inh}$ , dl/g	Density, g/cm <sup>3</sup>
ECA-DMA							
1	0.015	197(4)	197/0.4(4)	light yellow wax	33-45	0.06	1.15
2	0.022	197(4)	197/0.5(4)	light brown liquid	—	0.07	—
ECA-DMT							
3	0.015	197(2), 225(2)	255/0.4(4)	black solid	—	—	—
4	0.015	197(4), 197(4)	(4)	brown solid	30-39	0.16	1.22
5	0.022	197(2), 283(2)	283/0.3(4)	black solid	84-95	0.10	1.217
6	0.022	197(2), 255(2)	255/0.5(4)	black solid	39-46	0.19	1.223
CED-DMA							
7	0.015	197(4)	197/0.4(4)	light yellow solid	123-130	0.12	1.16
8	0.022	197(4)	197/0.3(4)	milky white solid	124-130	0.14	1.171
9	0.022	197(2), 283(2)	283/0.5(4)	black solid	—	—	1.143
CED-DMT							
10	0.015	197(2), 255(2)	255/0.3(3)	black solid	—	—	—
11	0.015	197(4)	197/0.5(4)	brown solid	150-164	0.06	1.18
12	0.022	197(4)	197/0.3(4)	black solid	148-163	0.11	1.196
13	0.022	197(2), 283(2)	283/0.5(4)	black solid	122-134	0.39	1.188
14	0.022	197(2), 255(2)	255/0.5(4)	black solid	71-81	0.11	1.189

<sup>a</sup> Antimony trioxide, 0.0082g, and calcium acetate, 0.0031g, were used as catalysts.

 TABLE II  
 Polymerizations of Amide Diols with Dimethyl Carboxylates<sup>a</sup>

Polymerization conditions							
Run no.	Amide diol, mole	Temp., °C (hr)	Temp., °C/mm Hg (hr)	Color and state	mp, °C	$\eta_{inh}$ , dl/g	Density, g/cm <sup>3</sup>
CHD-DMA							
15	0.015	197(2), 283(2)	283/0.4(4)	brownish solid	116-127	0.20	1.12
16	0.020	197(2), 283(2)	283/0.4(4)	brownish solid	98-108	0.20	1.035
17	0.020	197(2), 255(2)	255/0.4(4)	light gray solid	92-98	0.12	1.121
18	0.022	197(2), 283(2)	283/0.5(4)	black solid	112-119	0.165	1.148
CHD-DMT							
19	0.020	197(2), 283(2)	283/0.4(4)	colorless solid	144-153	0.74	1.15
20	0.022	197(2), 283(2)	283/0.4(4)	colorless solid	161-170	1.02	1.078
CPZ-DMA							
21	0.020	197(2), 283(2)	283/0.4(4)	dark green gum	visc. liq.	0.25	1.076
CPZ-DMT							
22	0.020	197(2), 283(2)	283/0.4(4)	black gum	visc. liq.	0.24	1.180
CPPD-DMA							
23	0.02	197(2), 283(2)	283/0.4(4)	black solid	—	—	—
CPPD-DMT							
24	0.020	197(2), 283(2)	283/0.4(4)	brown solid	221-233	—	1.248

<sup>a</sup> Antimony trioxide, 0.0082g, and calcium acetate, 0.0031g, were used as catalysts.

TABLE III  
 Polymerization of Amide Diols with Dicarboxyloyl Chlorides

Run no.	Dicarboxyloyl chloride, mole	Amide diol, mole	Polymerization temp., °C	Color and state	Yield, wt-%	mp, °C	$\eta_{inh}$ , dl/g	Density, g/cm <sup>3</sup>
ECA-ADC								
1	0.010	0.010	140-148	oily liquid	53.5	42-47	0.13	1.16
2	0.010	0.012	140	brown liquid	105.88	—	0.0538	—
3	0.010	0.022	142-148	brown liquid	81.21	—	0.0521	—
4	0.012	0.010	140	brown liquid	85.90	—	0.0408	—
ECA-TPC								
5	0.010	0.010	140-148	white solid	65.5	84-92	0.20	1.12
6 <sup>a</sup>	0.010	0.010	60-70	white solid	62.5	119-127	0.12	1.12
7 <sup>c</sup>	0.010	0.012	140	white powder <sup>b</sup>	3.165	—	—	1.189
				brown liquid	69.10	—	0.0638	—
8	0.010	0.022	143-147	brown liquid	76.58	—	0.0158	—
9 <sup>c</sup>	0.012	0.010	140	white powder <sup>b</sup>	17.00	—	—	—
				brown liquid	23.88	—	0.073	—

<sup>a</sup> The polymerization was carried out by method (b), with 0.010 mole amide diol/20 ml trichloroethylene and 0.010 mole TPC/20 ml pyridine, polymerizing 1 (run no. 6) or 1.5 (run no. 20) hr.

<sup>b</sup> Soluble part in methanol.

<sup>c</sup> Polymerization in 20 ml DMF. Other polymerizations were carried out in 20 ml nitrobenzene for 6 hr by method (a).

methanol and lower molecules. Nitrogen was slowly introduced into the tube and the mixture was melted and reacted at a lower temperature with continuous slow bubbling of nitrogen for a few hours until no methanol evolved. The temperature was then elevated and the polymerization was continued for a further few hours. Finally, the nitrogen inlet was replaced by a capillary, and several more hours' polymerization in a reduced pressure was carried out. Detailed polymerization conditions are tabulated in Tables I and II.

**Solution Polymerization.** Solution polymerization was carried out by either of two methods. Method (a): Amide diol and carboxyloyl chloride were dissolved together in a solvent and polymerized. Method (b): Carboxyloyl chloride or its solution was added dropwise into a solution of amide diol during the polymerization time.

A general example of method (a) is as follows: A three-necked flask equipped with a stirrer, a condenser leading to a nitrogen outlet, and a dropping funnel leading from a nitrogen inlet was flamed thoroughly with passing nitrogen inside the flask to remove any trace of moisture. After cooling the flask to room temperature, amide diol and carboxyloyl chloride dissolved in a solvent in the dropping funnel were poured into the flask. The mixture was polymerized with stirring in nitrogen atmosphere for a few to several hours at 100-150°C. Detailed polymerization methods are tabulated in Tables III to VI. The resulting polyamide ester was dissolved in DMF and precipitated in water. Polyamide esters from CPD were precipitated in methanol instead of in water.

TABLE IV  
 Polymerization of Amide Diols with Dicarboxyloyl Chloride

Run no.	Dicarboxyloyl chloride, mole	Amide diol, mole	Polymerization temp., °C	Color and state	Yield, wt-%	mp, °C	$\eta_{inh}$ , dl/g	Density, g/cm <sup>3</sup>
10	0.010	0.010	140-148	CED-ADC —	76.7	152-157	0.38	1.18
11 <sup>a</sup>	0.010	0.010	80-90	—	59.5	151-156	0.20	1.18
12	0.010	0.010	140	brown liquid	90.40	—	0.191	—
13	0.010	0.012	140	brown gum	75.61	—	0.0329	—
14	0.010	0.012	140	brown powder	76.09	152-210	0.0673	1.189
15	0.010	0.012	140	brown gum	70.90	—	0.0523	—
16	0.010	0.022	143-147	brown powder	40.55	136-141	0.152	1.176
17	0.012	0.010	140	black liquid	112.1	—	0.0328	—
18	0.012	0.010	140	black liquid	83.51	—	0.0904	—
19	0.010	0.010	142-148	CED-TPC white powder	76.4	206-213	0.18	1.24
20 <sup>b</sup>	0.010	0.010	80-90	white powder	77.7	230-237	0.25	1.24
21	0.010	0.012	140	brown solid	49.23	177-187	0.101	1.235
22	0.010	0.022	142-149	white powder	55.47	208-214	0.191	1.244

<sup>a</sup> CED without solvent and ADC/20 ml pyridine were polymerized for 1 hr by method (b).

<sup>b</sup> The polymerization was carried out by method (b), with 0.010 mole amide diol/20 ml trichloroethylene and 0.010 mole TPC/20 ml pyridine, polymerizing 1 (run no. 6) or 1.5 (run no. 20) hr. Other polymerizations were carried out in 20 ml nitrobenzene for 6 hr by method (a).

TABLE V  
 Polymerization of Amide Diols with Dicarboxyloyl Chlorides

Run no.	Dicarboxyloyl chloride, mole	Amide diol, mole	Polymerization temp., °C	Color and state	Yield, wt-%	mp, °C	$\eta_{inh}$ , dl/g	Density, g/cm <sup>3</sup>
23	0.010	0.022	140-143	CED-TPC white powder	19.44	175-187	0.133	1.270
24	0.012	0.010	140	brown solid	66.20	168-179	0.0805	1.353
25	0.010	0.010	140-147	CHD-ADC white solid	74.2	138-142	0.66	1.15
26 <sup>a</sup>	0.010	0.012	140	light brown	40.2	136-138	0.23	1.182
27	0.010	0.012	140	white	44.5	139-141	0.70	1.140
28	0.010	0.0125	140	white	54.7	133-134	0.95	1.135
29	0.010	0.022	142-149	white powder	50.87	131-138	0.456	1.166
30	0.010	0.010	140-148	CHD-TPC white powder	80.0	197-202	0.34	1.20
31 <sup>b</sup>	0.010	0.010	115-125	white powder	79.4	196-204	0.22	1.20
32	0.010	0.012	140	white powder	71.13	179-188	0.133	1.190
33	0.010	0.015	140	white powder	49.68	171-179	0.186	1.250
34	0.010	0.012	140	white powder	86.2	190-198	0.33	1.114

<sup>a</sup> Polymerized for 1.5 hr.

<sup>b</sup> CHD/10 ml nitrobenzene and TPC/10 ml nitrobenzene were polymerized by method (b) for 3 hr. Other polymerizations were carried out in 20 ml nitrobenzene for 6 hr by method (a).

TABLE VI  
 Polymerization of Amide Diols with Dicarboxyloyl Chlorides

Run no.	Dicarboxyloyl chloride, mole	Amide diol, mole	Polymerization temp., °C	Color and state	Yield, wt-%	mp, °C	$\eta_{inh}$ , dl/g	Density, g/cm <sup>3</sup>
35	0.010	0.022	143-148	CHD-TPC white powder	64.26	182-196	0.611	1.216
36	0.010	0.022	140-145	white powder	53.27	171-179	0.421	1.247
37	0.010	0.030	140	white powder	96.80	161-174	0.0113	1.241
38	0.011	0.010	140	white powder	77.19	176-186	0.160	1.245
39	0.010	0.0125	140	brown CPZ-ADC	32.6	—	0.19	1.163
40	0.010	0.012	140	GPZ-TPC light brown	24.7	—	0.04	1.202
41 <sup>a</sup>	0.010	0.012	140	CPPD-ADC white	67.0	160-167	0.13	1.120
42 <sup>a</sup>	0.010	0.012	140	CPPD-TPC white	81.1	242-254	0.11	1.065

<sup>a</sup> Precipitated in methanol. Polymerizations were carried out in 20 ml nitrobenzene for 6 hr by method (a).



### Characterization of Polyamide Esters

Melting point, thermal gravimetric analysis, solution viscosity, density, IR, and x-ray powder diffraction were measured by the same methods and apparatus as in our previous study.<sup>22</sup>

**Differential Thermal Analysis.** A Shimadzu (Japan) DTA analyzer Model DT-2A was used with aluminum oxide as the standard compensator at the rate of temperature elevation of 6°C/min in nitrogen atmosphere.

**X-Ray Diffraction Photography.** A  $\text{CuK}_\alpha$  beam was projected into the bunch of stretched polymer filaments (cold-drawn to five times of the undrawn) at an incidence angle of 90° on the direction of fiber axis.

## RESULTS AND DISCUSSION

### Polymerizability

As shown in Tables I and II, by melt polymerization high molecular weight polymers were obtained from CHD–DMT couples. These polymers were colorless and could be cast into films both by melt and solution methods. The order of polymerizability, judging from the inherent viscosity, is:

CHD–DMT > CED–DMT > CPZ–DMA, CPZ–DMT > CHD–DMA  
> ECA–DMT > CED–DMA > ECA–DMA > CPPD–DMT > CPPD–DMA.

Classifying the order from the points of amide diols and dimethyl carboxylate,

DMT > DMA

and

CHD > CED > CPZ > ECA > CPPD.

Except for CHD–DMT polymers, all the polymers were colored, and increasing polymerization temperature and time deepened the color to black. High molecular weight polymers were obtained only from DMT and N,N'-di(6-hydroxycaproyl)alkylene primary diamine such as CHD and CED. N-Hydroxyalkyl-6-hydroxycaproamide such as ECA, the molecular structure of which is not symmetrical in regard to the center of the molecule, did not give a high molecular weight polymer, probably because of the different reactivities of the two hydroxy groups and also because of the random configuration of the amide and ester linkages due to the amide–ester interchange reaction. N,N'-Di(6-hydroxycaproyl) secondary diamine such as CPZ should give a rather high molecular weight polymer, but the smaller inherent viscosity may be due to the lack of the hydrogen bonding of the polymer. N,N'-Di(6-hydroxycaproyl) aromatic diamine such as CPPD gave a low molecular weight polymer because of the thermal decomposition. The better reactivity of DMT compared with DMA gave higher molecular weight DMT polymers. The double or a little more than double amount of amide diol over the amount of dimethyl carboxylate gave higher molecular weight polymers in case of DMT. This fact indicates polymerization of DMT via ester interchange reaction, while DMA directly polymerizes without ester interchange

to give low molecular weight polymers due to the unequivalent ester-hydroxy balance.

The polymerizability of solution polymerization as tabulated in Tables III, IV, V, and VI is of the following order:

$$\text{CHD-ADC} > \text{CHD-TPC} > \text{CED-ADC} > \text{CED-TPC} > \text{ECA-TPC} \\ > \text{CPZ-ADC} > \text{ECA-ADC} > \text{CPPD-ADC} > \text{CPPD-TPC} > \text{CPZ-TPC}$$

and

$$\text{CHD} > \text{CED} > \text{ECA, CPZ, CPPD}$$

and also

$$\text{ADC} > \text{TPC.}$$

CHD-ADC and CHD-TPC gave colorless polymers which could be cast into films both by melt and solution methods. CED-ADC also gave a rather high molecular weight polymer. Polymers by solution polymerization were less colored and had higher molecular weights than those by melt polymerization. These should be due to the high reactivity of dicarboxyloyl chlorides and milder polymerization conditions such as lower temperature and shorter time. The smaller inherent viscosities of TPC polymers than those of ADC polymers are due to the smaller reactivity of TPC. It is remarkable that the maximum inherent viscosities of CHD and CED polymers are obtained not only at a OH/COCl index near 1 but also at an index near 2.

### Melting Point

The melting points of the melt-polymerized polymers are of the following order:

$$\text{CPPD-DMT} > \text{CHD-DMT, CED-DMT} > \text{CED-DMA} > \text{CHD-DMA} \\ > \text{ECA-DMT} > \text{ECA-DMA, CPZ-DMT, CPZ-DMA.}$$

On classifying by the diols,

$$\text{CPPD} > \text{CHD, CED} > \text{ECA} > \text{CPZ.}$$

On classifying by the carboxyls,

$$\text{DMT} > \text{DMA.}$$

The melting points of the solution-polymerized polymers are of the following order:

$$\text{CPPD-TPC} > \text{CED-TPC} > \text{CHD-TPC} > \text{CPPD-ADC} > \text{CED-AC} \\ > \text{CHD-ADC} > \text{ECA-TPC} > \text{ECA-ADC} > \text{CPZ-TPC, CPZ-ADC}$$

On classifying by the diols,

$$\text{CPPD} > \text{CED} > \text{CHD} > \text{ECA} > \text{CPZ.}$$

On classifying by the carboxyl chlorides,

$$\text{TPC} > \text{ADC.}$$

TABLE VII  
Korshak-Phrynze's Constants  $a$  of Polyamide esters

Polyamide ester	$a$	Polyamide ester	$a$
ECA-DMA	-2.38	ECA-ADC	-2.31
CED-DMA	0.800	CED-ADC	1.64 ± 0.44
CHD-DMA	0.15 ± 0.75	CHD-ADC	1.50 ± 0.10

It is interesting that these orders are consistent with the orders of the melting points of the amide diols, dimethyl carboxylates, and dicarboxyloyl chlorides, similar to the case of polyamide urethanes in our previous paper.<sup>22</sup> To evaluate the melting points, Korshak-Phrynze's constants<sup>22,24</sup> on melting points were calculated and are tabulated in Table VII. The order of Korshak-Phrynze's constants  $a$  is CED > CHD > ECA in both melt-polymerized and solution-polymerized polymers. Comparing the methods of polymerization: solution polymerization > melt polymerization. This difference of the melting points of polymers by melt polymerization and by solution polymerization is probably due to the amide-ester interchange reaction of the polymers on melt polymerization at high temperatures. Korshak-Phrynze's constant of polyamide ester is in the following order compared with those of other polymers:

polyurea > polyamide > polyamide urethane > polyurethane  
> polyamide ester > polyester.

### Density

Densities of the polyamide esters are of the following order:

CPPD-DMT > CED-TPC > ECA-DMT > CHD-TPO > CPZ-TPC  
> CED-DMT CED-ADC > CPZ-DMT > CPZ-ADC > ECA-ADC  
> CHD-ADC, CED-DMA > ECA-DMA, CHD-DMT > CHD-DMA  
> CPZ-DMA, CPPD-ADC, ECA-TPC > CPPD-TPC.

With some exceptions, the densities, classifying by the kind of dimethyl dicarboxylates and dicarboxyloyl chlorides, are of the following order:

TPC  $\approx$  DMT > ADC > DMA.

Also with some exceptions, the densities, classifying by the amide diols are of the following order:

CED > CHD, CPZ, ECA > CPPD on solution polymerization

and

CPPD > CED, ECA > CPZ, CHD on melt polymerization.

The density dependence on the kind of dimethyl dicarboxylates and dicarboxyloyl chlorides indicates higher regularities of the solution-polymerized polymers than those of the melt-polymerized polymers and higher rigidities of the terephthalic polymers than those of the adipic polymers. CED, having the highest amide density, gave the highest polymer density on solution poly-

merization, probably because of high crystallinity; but on melt polymerization, a lower polymer density was obtained due to the more irregularly alternating configuration. CPPD, having a bulky rigid benzene ring, gave the highest density on melt polymerization, while giving the smallest density on solution polymerization, probably because on solution polymerization the alternating amide linkages may overcome the benzene rigidity.

### Thermal Stability

In Figures 1 and 2 are shown TGA of polyamide esters, and polymer decomposing temperatures are tabulated in Table VIII. Polymer decomposing temperatures  $T_d$  are of the following order:

CPZ-DMT > CED-TPC > CHD-TPC > CHD-DMT  
 > CPZ-DMA > CHDD-ADC > CED-ADC > CPPD-TPC  
 > CPPD-ADC > ECA-DMT > ECA-DMA.

Classifying the polymer decomposing temperatures by the dimethyl carboxylates and dicarboxyloyl chlorides, the order becomes

TPC, DMT > ADC, DMA

regardless of the kind of amide diols. Classifying the polymer decomposing temperatures by the amide diols, the order of  $T_d$  becomes

CPZ > CHD, CED > CPPD > ECA.

The higher  $T_d$  of TPC and DMT polymers are due to the aromatic stability of the ester linkage. The highest  $T_d$  of CPZ may be probably due to the lack of the N-hydrogen of the amide linkage, since the N-hydrogen may cause the initiation of thermal decomposition. The lowest  $T_d$  of ECA polymer should

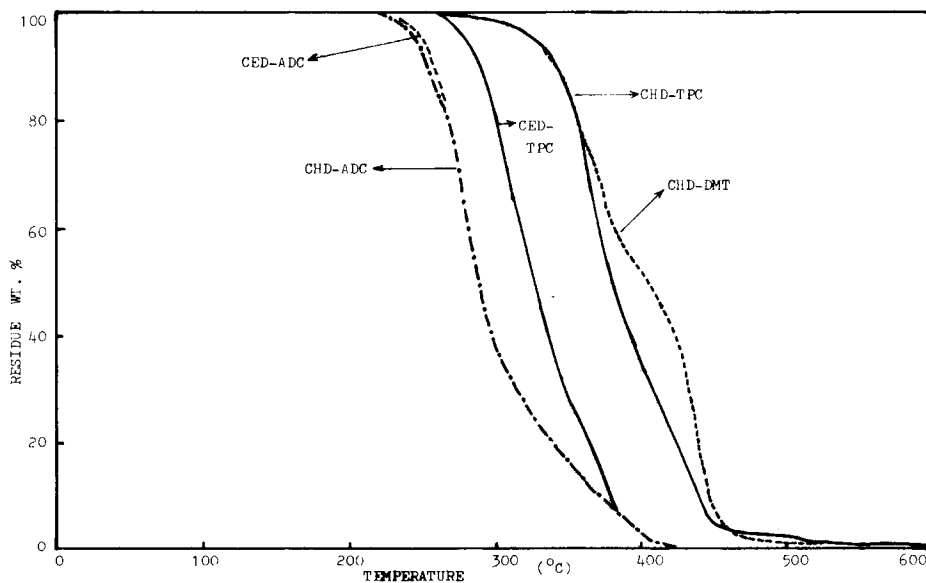
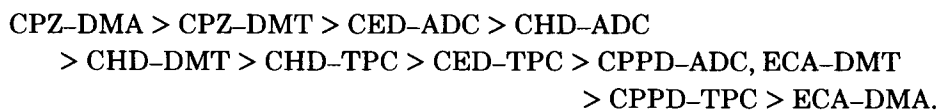


Fig. 1. TGA curves of polyamide esters—I.

be due to the impure quality of the resinous polymer. All the other polymers are dry powders showing far higher  $T_i$  values. The smaller  $T_d$  of CPPD polymers may be due to the more acidic N-hydrogen which causes the thermal decomposition of the ester linkage since the ester linkage is weaker to acid than the amide linkage.<sup>22</sup> The difference of  $T_i$  and  $T_m$  is of the following order:



Thus, melt-casting and melt-spinning of ECA-DMA polymer and CPPD-TPC polymer would be difficult. The double melting points annotated (b) in Table VIII are noteworthy. The three polymers are characteristic in their high intermolecular action since CED polymers have high concentration of amide and ester linkages, and CPPD-TPC polymer has the most rigid structure due to the benzene rings. The concentrations of amide linkages of CHD polymers are diluted with the longer methylene chains, and CPZ polymers have the lowest intermolecular action because of the absence of hydrogen bonding.

The authors would like to consider the lower endothermic temperatures as the melting points due to the ester linkage and the higher endothermic temperatures as the melting points due to the amide linkage. As shown in Figure 1, the modes of the thermal decomposition of CHD-DMT polymer and CHD-TPC polymer are different, i.e., the former has two steps in its thermal degradation curve, while the latter has only one step. This may be due probably to the more random configuration of the amide-ester linkages of the CHD-DMT polymer and the more alternating configuration of the amide-

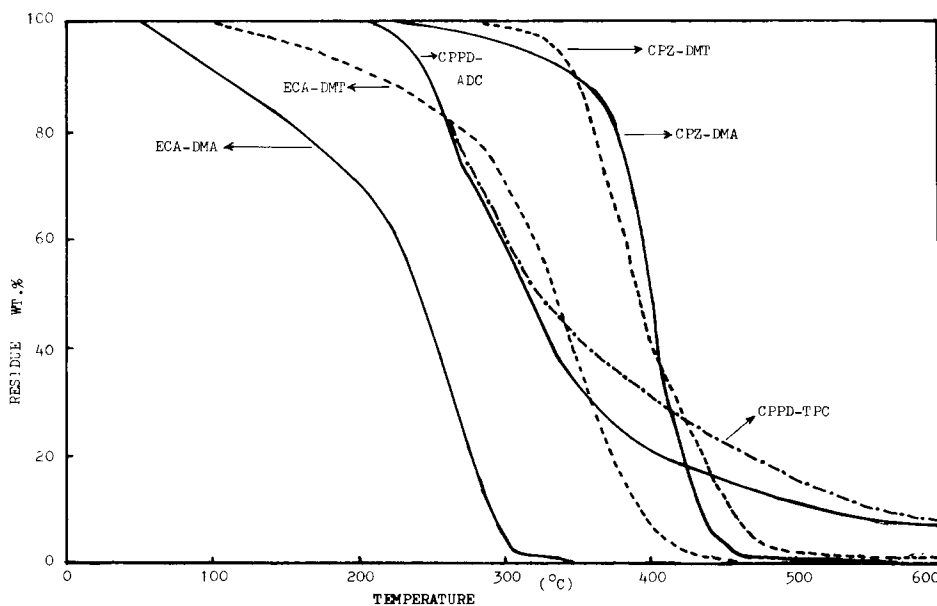


Fig. 2. TGA curves of polyamide esters—II.

TABLE VIII  
Initiating Temperatures of Thermal Decomposition and the Corresponding Melting Points of Polyamide Esters<sup>a</sup>

Polymer	$T_i$ , °C	$T_m$ , °C	$T_i - T_m$ , °C
ECA-DMA	50	70	-20
ECA-DMT	100	60	40
CED-ADC	218	120, 180 <sup>b</sup>	98, 38
CED-TPC	255	200, 220 <sup>b</sup>	55, 35
CHD-ADC	225	133	92
CHD-TPC	250	190	60
CHD-DMT	250	165	85
CPZ-DMA	230	80	150
CPZ-DMT	290	147	143
CPPD-ADC	210	170	40
CPPD-TPC	215	140, 230 <sup>b</sup>	75, -15

<sup>a</sup> The initiating temperatures of thermal decomposition  $T_i$  were obtained by thermal gravimetric analysis, and the melting points  $T_m$  were obtained by differential thermal analysis.

<sup>b</sup> Though the polymers melt at the higher temperatures, endothermic transitions at the lower temperatures were observed.

ester linkages of the CHD-TPC polymer. The ester sequence of the CHD-DMT polymer will decompose in the first step, and in the second step the amide sequence will decompose. The alternating polymer CHD-TPC has a regularly alternating configuration of the amide-ester linkage, so that the decomposition of the ester linkage will accompany the subsequent decomposition of the neighboring amide linkage. This two-step mode decomposition is not observed in low melting point polymers, such as CPZ-DMA, CPZ-DMT, ECA-DMA, and ECA-DMT.

ECA, CED, and CHD gave higher thermal stabilities when polymerized with DMT and TPC than with DMA and ADC, while, on the other hand, CPZ and CPPD showed the same order of stability regardless whether they were polymerized with DMA and ADC or DMT and TPC. In the case of CPZ polymers, the absence of an N-hydrogen cannot accelerate the cleavage of the ester linkage which is weak to proton, so that the stability of the ester linkage will become of the same order as that of the amide linkage. Similarly, the difference of the stabilities of the terephthalic ester and adipic esters is small. In CPPD polymers, the active, considerably acidic N-hydrogen of the amide linkage strongly initiates the decomposition of not only the adipic ester linkage but also the terephthalic ester linkage without the difference in rates of the two decompositions.

### Solubility

Solubilities of the polyamide esters are tabulated in Table IX. Dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), formic acid, and *m*-cresol dissolve most of the polyamide esters. Except for two kinds of polymers, *m*-cresol dissolves polyamide esters very easily. CPZ polymers are easily soluble in chloroform, probably because of the absence of hydrogen bonding. It

TABLE IX  
Solubilities of Polyamide Esters

Polymer	Solvent Action <sup>a</sup>							
	DMSO	DMF	Formic acid	<i>m</i> -Cresol	Methanol	Ethylene glycol	Chloroform	Benzene
ECA-DMA	4	4	4	4	5	3	0	0
ECA-DMT	4	4	4	4	4	3	0	0
CED-DMA	3	3	3	4	3	3	0	0
CED-DMT	3	3	3	4	3	3	0	0
CHD-DMA	3	3	3	4	3	3	0	0
CHD-DMT	3	3	3	4	3	3	0	0
CPZ-DMA	5	5	5	4	5	2	5	5
CPZ-DMT	5	5	5	4	2	2	5	0
CPPD-DMA	2	2	1	0	0	1	0	0
CPPD-DMT	2	2	1	1	0	1	0	0
ECA-ADC	5	5	5	5	4	4	1	1
ECA-TPC	3	3	3	4	3	4	0	0
CED-ADC	3	3	3	4	3	3	0	0
CED-TPC	3	3	3	4	3	3	0	0
CHD-ADC	3	3	3	4	3	3	0	0
CHD-TPC	3	3	3	4	3	3	0	0
CPZ-ADC	5	5	5	4	5	4	5	1
CPZ-TPC	5	5	5	4	2	2	5	0
CPPD-ADC	5	5	4	5	0	2	0	0
CPPD-TPC	5	5	0	5	4	0	0	0

<sup>a</sup> 0 = insoluble; 1 = swelling; 2 = partially soluble when hot; 3 = soluble when hot, but reprecipitates on cooling; 4 = soluble when hot and keeps solution state even after cooling; 5 = soluble even when cold.

is interesting that these polyamide esters are soluble in DMSO which dissolves polyesters but does not dissolve polyamides. On the other hand, chloroform does not dissolve polyamide esters, while it dissolves polyesters and does not dissolve polyamides. It is also remarkable that the solubility of polyamide esters in formic acid is not so good in spite of the good solubility of polyamides and polyesters in formic acid, while *m*-cresol dissolves all polyamide esters, polyamides, and polyesters. Thus, it should be concluded that these polyamide esters have solubilities which are not the mathematical sum of the solubilities of polyamides and polyesters due to the regularly alternating amide-ester linkages which have different characteristics from those of the individual amide and ester linkages. Films could be cast from the *m*-cresol solutions of CHD polymers, but not from DMSO, DMF, or formic acid.

### Infrared Absorption Spectra and X-Ray Diffraction

In Figures 3 and 4, typical examples of IR spectra of polyamide esters are shown. Characteristic key bands appear at 3280–3350  $\text{cm}^{-1}$ , 3070–3080  $\text{cm}^{-1}$  (both NH stretchings of the secondary amide linkage), 1640–1660  $\text{cm}^{-1}$  (secondary amide I band), 1540–1560  $\text{cm}^{-1}$  (secondary amide II band), 1730–1740  $\text{cm}^{-1}$  (C=O stretching of the ester), 1250–1290  $\text{cm}^{-1}$  (the CO—O stretching of the ester linkage), 1000–1180  $\text{cm}^{-1}$  (two or three absorptions, C—O and

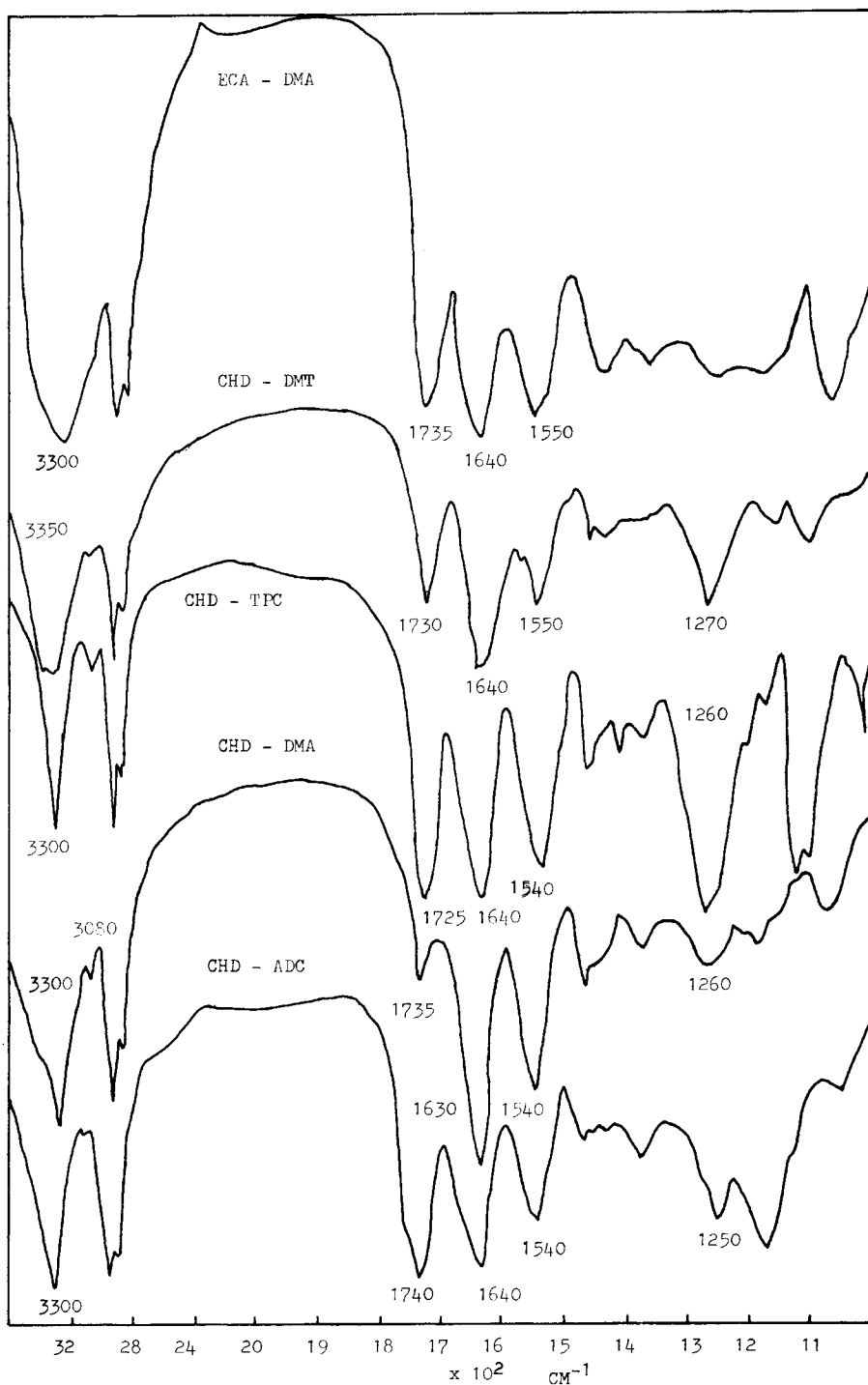


Fig. 3. IR of polyamide esters—I.



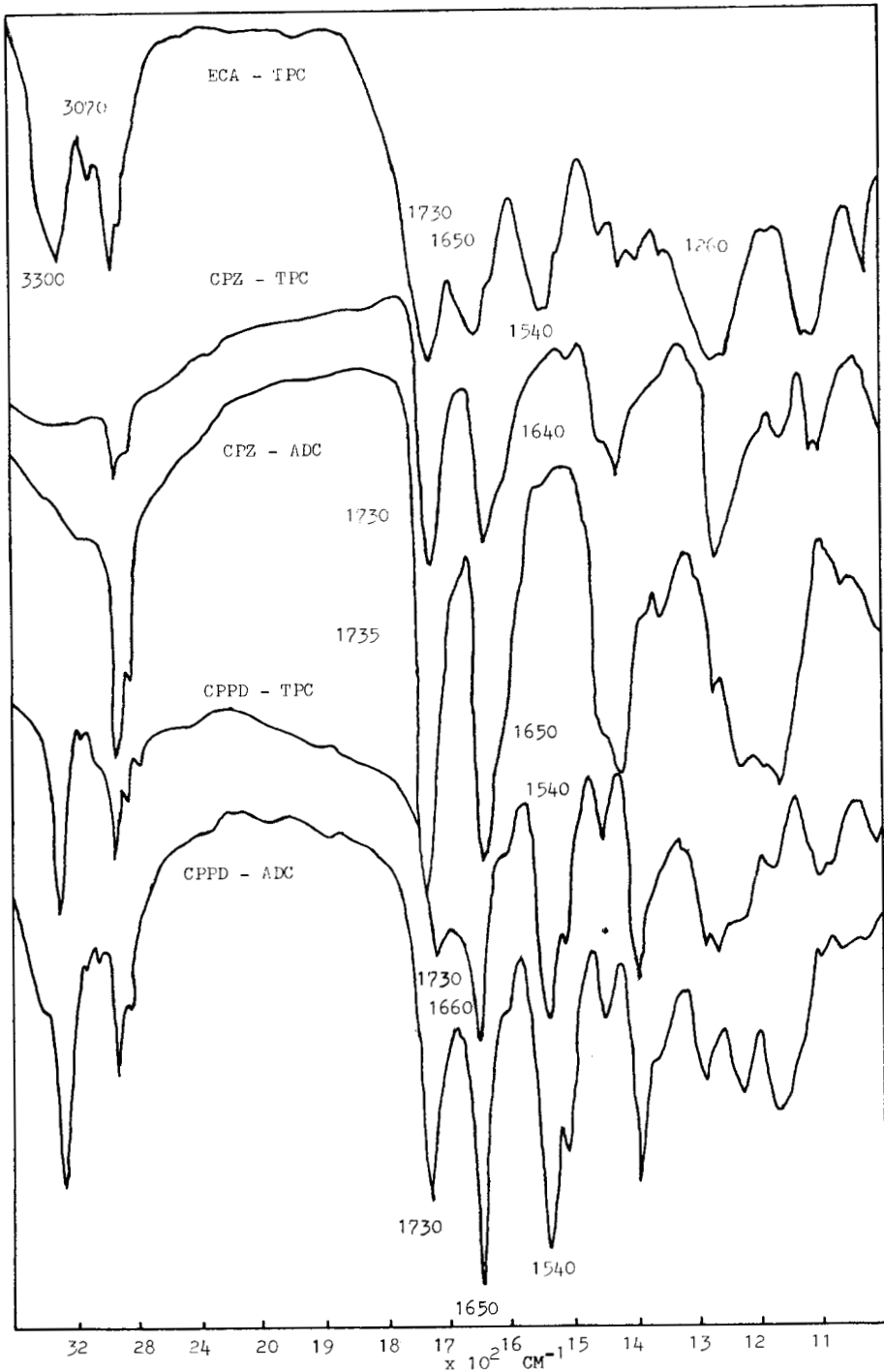


Fig. 4. IR of polyamide esters—II.

C—N stretchings of the ester and amide linkages), and at  $700\text{--}750\text{ cm}^{-1}$  (amide V band and polymethylene band).

The above absorptions are all strong bands. Comparing the IR charts of melt-polymerized polyamide esters with those of solution-polymerized polyamide esters, the bands at  $1730\text{--}1740\text{ cm}^{-1}$  and  $1250\text{--}1290\text{ cm}^{-1}$  and a band

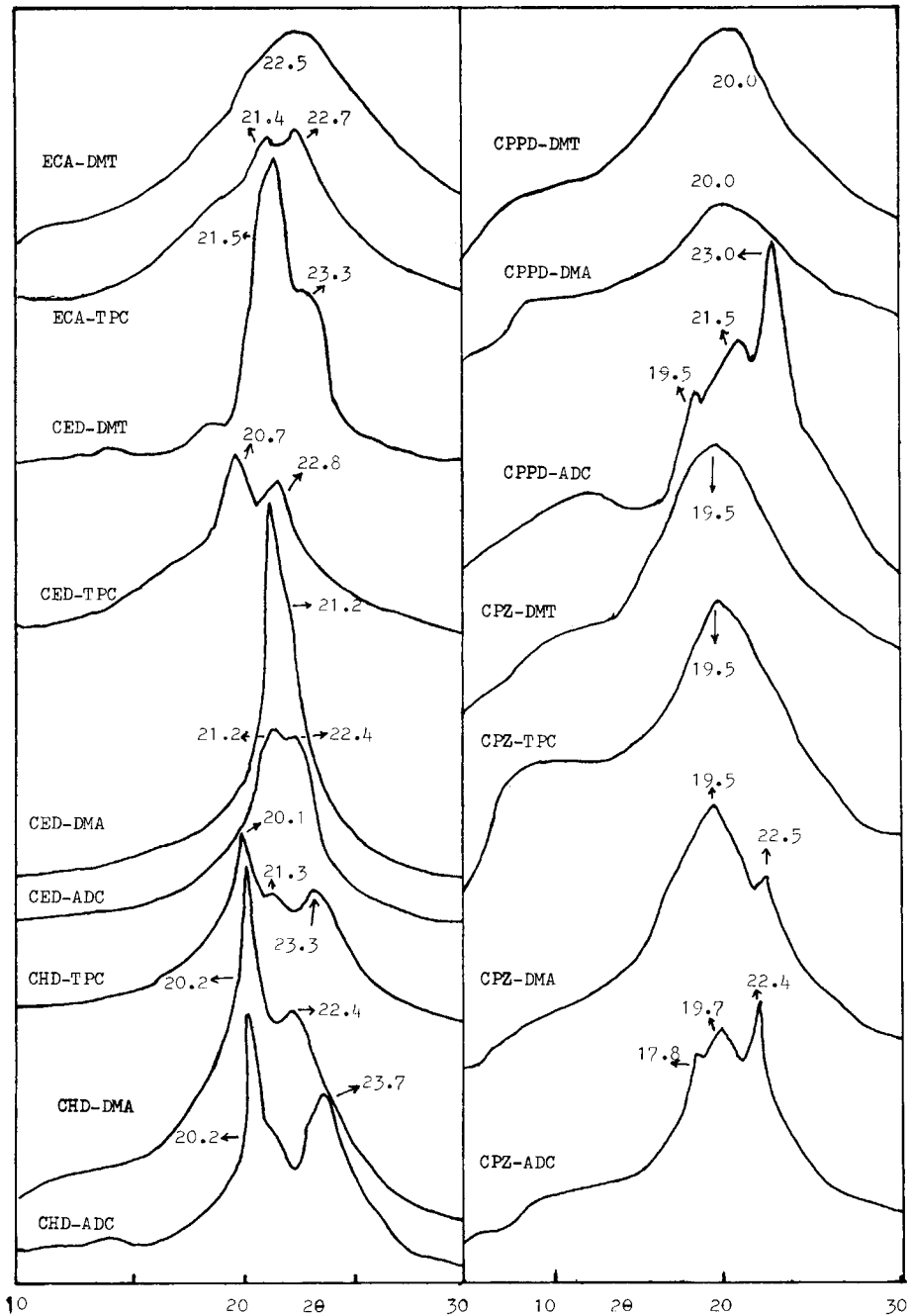
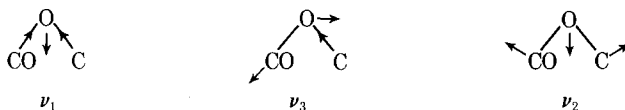


Fig. 5. X-Ray diffractions of polyamide esters.

among the 1000–1180  $\text{cm}^{-1}$  region decrease in intensity in some melt-polymerized polyamide esters, i.e., the ester linkages are partially lost by the thermal decomposition as was already discussed in the former sections. An interesting phenomenon on the relationship of the intensities between the 1250–1290  $\text{cm}^{-1}$  and 1000–1180  $\text{cm}^{-1}$  regions is observed. In these regions, polyethylene adipate has key bands at 1260  $\text{cm}^{-1}$ , 1175  $\text{cm}^{-1}$ , and 1085  $\text{cm}^{-1}$ . The basic vibrations of the ester linkage can be drawn as shown:



$\nu_1$  is the symmetric stretching vibration,  $\nu_3$  is the antisymmetric stretching vibration, and  $\nu_2$  is the deformation vibration. Thus, assignment of each vibration to each band should be as follows:  $\nu_3$  at 1260  $\text{cm}^{-1}$ ,  $\nu_2$  at 1175  $\text{cm}^{-1}$ , and  $\nu_2$  at 1085  $\text{cm}^{-1}$  in poly(ethylene adipate). Poly(ethylene terephthalate) absorbs at 1250  $\text{cm}^{-1}$ , 1100  $\text{cm}^{-1}$ , and 1010  $\text{cm}^{-1}$ , each assigned as  $\nu_3$ ,  $\nu_1$ , and  $\nu_2$ . The intensities of each absorption are of the following order: in poly(ethylene adipate),  $\nu_1 > \nu_3 > \nu_2$ ; and in poly(ethylene terephthalate),  $\nu_3 > \nu_1 > \nu_2$ . This difference is due to the rigid configuration of the terephthalate ester linkage and the elastic configuration of the adipate ester linkage. The  $\nu_3$  bands of DMA and ADC polyamide esters increase their intensities much higher than the  $\nu_3$  intensities, so that in some DMA and ADC polyamide esters the order of the intensities becomes  $\nu_3 > \nu_1 > \nu_2$ . This indicates hydrogen bonding of the ester carbonyl with the N-hydrogen of the amide linkage. CPZ-DMA and CPZ-ADC polymers have the same order of intensity as that of poly(ethylene adipate) since these polymers have no hydrogen bonding.

It is interesting that the intensity of the  $\nu_3$  band is higher in DMA polyamide esters than in ADC polyamide esters. In the regularly alternating ADC polyamide esters, the hydrogen bonding should be formed between the amide carbonyl and the N-hydrogen, so that the ester carbonyl would not take part in the hydrogen bonding. In the randomly configured DMA polyamide esters, there are many chances of the hydrogen bonding between the ester carbonyl and the N-hydrogen.

In Figures 5A and 5B, several examples of x-ray diffraction of polyamide esters are presented. ECA polymers and CPZ polymers are mostly of amorphous patterns, the former due to their random configuration and the latter due to the absence of N-hydrogen bonding. Solution-polymerized polyamide esters are all more highly crystalline than melt-polymerized polyamide esters, because the former are much more regularly alternating than the latter.

Crystalline polyamide esters are as follows: ECA-TPC; CED-ADC, CED-TPC, CED-DMA, CED-DMT; CHD-ADC, CHD-TPC, CHD-DMA, CHD-DMT; CPPD-ADC, CPPD-TPC.

Amorphous polyamide esters are as follows: ECA-ADC, ECA-DMA, ECA-DMT; CPZ-ADC, CPZ-TPC, CPZ-DMA, CPZ-DMT; CPPD-DMA, CPPD-DMT. A good fiber x-ray photograph was obtained from the melt-cast and drawn film five times its original. The observed fiber identity distance was 37.50 Å, which is very near the calculated value for the fully extended zig-zag structure of CHD-ADC polymer.

## References

1. S. Katayama, I. Goodman, and R. H. Peters, paper presented at 26th Meeting of Japan Chem. Soc., 1972, Abstr. IV, 3S12, p. 1982.
2. (to Chiyoda-kako Co. Ltd.), Jap. Pat. 36-5748 (1961).
3. (to B.A.S.F.), U.S. Pat. 3,036,974 (1962).
4. I. M. Panaiotov, *C. R. Acad. Bulgare Sci.*, **16**, 39 (1963); *C. A.*, **60**, 3108 (1964).
5. J. R. Caldwell, Brit. Pat. 1,126,824 (1969); *C. A.*, **70**, 12246t (1969).
6. E. Cislak Francis, U.S. Pat. 3,409,597 (1969); *C. A.*, **70**, 12153k (1969).
7. S. Nishizaki and A. Fukami, *Mitsubishi Denka Lab. Rep.*, **10**(2), (1969), 141; *C. A.*, **72**, 101167b (1970).
8. T. M. Phrynze, V. V. Korshak, and R. V. Kozrov, *Izv. An. CCCP*, **OXN**, 535 (1959).
9. J. L. R. Williams, T. M. Laakso, and L. E. Contois, *J. Polym. Sci.*, **61**, 353 (1962).
10. J. L. R. Williams, J. M. Carlson, and G. A. Reynolds, *Makromol. Chem.*, **65**, 541 (1963).
11. K. Ateya, *Angew. Makromol. Chem.*, **7**, 79 (1969); *C. A.*, **71**, 91955v (1969).
12. T. Kubota, T. Tsuda, S. Minami, and M. Watanabe, Jap. Pat. 7,001,831 (1970); *C. A.*, **72**, 101379x (1970).
13. (to U.C.C.), U.S. Pat. 3,036,974 (1960).
14. H. Kobayashi, K. Yamaguchi, and T. Yamashita, Jap. Pat. 68 13,230 (1969); *C. A.*, **70**, 48053s (1969).
15. H. Kobayashi et al., Jap. Pat. 6,813,230 (1969); *C. A.*, **70**, 48053s (1969).
16. C. S. Cleaver and B. C. Pratt, *J. Amer. Chem. Soc.*, **77**, 1541 (1955).
17. T. M. Laakso and D. D. Reynolds, *J. Amer. Chem. Soc.*, **82**, 3640 (1960).
18. T. Managi and Mizutani, *Kogyo Kagaku Zasshi*, **65**, 78 (1962).
19. S. Nishizaki and A. Fukami, *Kogyo Kagaku Zasshi*, **71**, 299 (1968); *C. A.*, **70**, 4679w (1969).
20. M. F. Sorokin and V. A. Yamskii, *Tr. Mosk. Khim. Tekhnol. Inst.*, 171 (1968); *C. A.*, **70**, 88862m (1969).
21. Nishizaki et al., *Kogyo Kagaku Zasshi*, **71**, 1299 (1968); *C. A.*, **70**, 4679w (1969).
22. S. Katayama, H. Horikawa, Y. Ito, N. Gomyo, and Y. Obuchi, *J. Appl. Polym. Sci.*, **15**, 775 (1971).
23. R. C. Fuson and J. T. Waker, *Org. Synth. Coll.*, **II**, 169 (1950).
24. V. V. Korshak, *Progrecc Polimernoii Ximii* (Japanese translation), Izdatelictvo "Nayka," Moscow, 1965, p. 287.

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