Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Matsuda, Hideaki(1977) 'Synthesis of Polymers by Using Divalent Metal Salts of Mono(hydroxyethyl) Phthalate: Metal-Containing Three-Dimensional Polyesters from Metal Salts, Pyromellitic Dianhydride, and Epoxides', Journal of Macromolecular Science, Part A, 11: 2, 431 — 447

To link to this Article: DOI: 10.1080/00222337708061278

URL: http://dx.doi.org/10.1080/00222337708061278

J. MACROMOL. SCI.–CHEM., A11(2), pp. 431-447 (1977)

Synthesis of Polymers by Using Divalent Metal Salts of Mono(hydroxyethyl) Phthalate: Metal-Containing Three-Dimensional Polyesters from Metal Salts, Pyromellitic Dianhydride, and Epoxides

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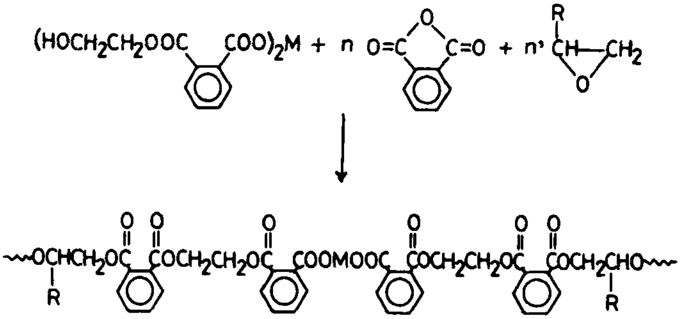
ABSTRACT

Syntheses of metal-containing three-dimensional polyesters were investigated by the reactions of divalent metal salts of mono(hydroxyethyl) phthalate–pyromellitic dianhydride–epoxide in DMF at 90° C. The metal carboxylate groups of these metal salts catalyzed the reactions. Systems with low metal salt content gelled during reaction. The yield of the products obtained by precipitating or washing with water increased with decreasing metal salt content in the feed. The products were metal-containing, three-dimensional polyesters containing ionic links; they were slightly yellow powdery materials. Hydroxyl values of the products were much higher than the values of acidity. Inherent viscosities (in DMF at 30° C) of the products obtained from the systems which did not gel were low, ranging

from 0.031 to 0.083. The thermal stability of the products showed a tendency to increase with decreasing metal salt content in the feed.

INTRODUCTION

Syntheses of a number of ionic polymers by using divalent metal salts of mono(hydroxyethyl) phthalate (HEP), that is, $(\text{HEP-})_2\text{M}$ (where HEP- denotes HEP residue and M is divalent metal) have been reported previously [1-7]. These compounds are considered to be of interest in that they contain an ionic bond formed between $-\text{COO}^-$ and M^{2+} and also two hydroxyl groups. Previously, it was shown [5] that metal-containing polyesters containing ionic links in the main chain were synthesized by the $(\text{HEP-})_2\text{M}$–phthalic anhydride (PA)–epoxide reaction, as shown by Eq. (1), where M denotes a divalent metal (Mg or Ca).



(1)

When dianhydride such as pyromellitic dianhydride (PMDA) is subjected to the above synthetic route, it is expected that three-dimensional polymers could be obtained. Therefore, in the present study, the syntheses of novel metal-containing three-dimensional polyesters by the $(\text{HEP-})_2\text{M}$-PMDA-epoxide reaction were investigated. Phenyl glycidyl ether (PGE), 1,2-butylene oxide (BO), and propylene oxide (PO) were used as the epoxides.

EXPERIMENTAL

Materials

$(HEP\text{-})_2M$ salts were synthesized according to the method reported in a previous paper [1]. PMDA was purified by washing with diethyl ether. PGE and dimethylformamide (DMF) were purified by distillation. BO, PO, and isopropyl alcohol (i-PrOH) were of extra pure grade and were used as received. Diethyl pyromellitate (DEP) was synthesized by the reaction of PMDA with ethanol (1:2). The Ca salt of monoethyl phthalate (EP), $(EP\text{-})_2Ca$, was synthesized by a reported method [2]. Diethylene glycol (DEG) and N,N-dimethylbenzylamine (DMBA) were purified by distillation under reduced pressure.

Model Reactions

As model reactions, the reactions between DEP and PGE, i-PrOH and PMDA, PMDA and PGE, and DEP and i-PrOH were carried out with $(EP\text{-})_2Ca$ in DMF solvent at 90°C.

The general procedure was as follows. Into a 100-ml flask equipped with a stirrer, a thermometer, and a condenser were placed the given amounts of reactants, $(EP\text{-})_2Ca$, and DMF as a solvent; the mixture was stirred at 90°C for a given time. Aliquots were removed during the reaction for analyses of acid and/or epoxide.

$(HEP\text{-})_2M$–PMDA–PGE Reactions

Into a 100-ml flask of the same type as above, were placed given amounts of $(HEP\text{-})_2M$, PMDA, PGE, and DMF, and the mixture was stirred at 90°C for 7 hr. Aliquots were taken during the reaction for analyses of acid and epoxide. After the reaction, small quantities of DMF were added to the mixture, and the solution was slowly poured into 1 liter of vigorously stirred water to precipitate the product (polyester). The product was further washed with water and dried in vacuo. In a few cases, the products were obtained by precipitating with acetone. In the case where the reaction mixture gelled, the gelled mixture was kept at 90°C without stirring. After the total reaction time of 7 hr, the mixture was broken up into small particles and thoroughly washed with water; the crosslinked product which was obtained was dried in vacuo.

In case of the DEG–PMDA–PGE reactions which were carried out for comparison, the same procedure was applied. In this case, DMBA (0.2 mole-% referred to the quantity of DEG) was used as a catalyst.

$(HEP\text{-})_2M$–PMDA–BO or PO Reactions

Into a 100-ml flask equipped with a stirrer, a thermometer, a condenser, and a dropping funnel were placed given amounts of $(HEP\text{-})_2M$, PMDA, and DMF, and the mixture was stirred at 90° C for 15 min, giving a homogeneous solution. Next, a fixed amount of BO or PO was added dropwise over about 10 min. After the addition, the reaction was continued at this temperature for 7 hr. The products were obtained by the same procedure as above.

Analytical Methods

Acidity

Acidities of the reaction systems were determined in the same manner as in the previous study [5].

Alternatively, acidities of products were determined as follows. A 0.1-0.3-g portion of sample which had been broken up into small particles was weighed to the nearest milligram into a flask, and 10 ml of DMF was added. The mixture was heated at 70° C for 3 hr. When the mixture was cooled to room temperature, 2 ml of water was added. It was titrated with 0.1 N methanolic potassium hydroxide.

Epoxide Value

Epoxide values of reaction systems were determined according to the method reported in the previous paper [5].

OH Value

OH values of products were determined as follows. A 0.3-0.5-g portion of sample which had been broken up into small particles was weighed to the nearest milligram into a flask, and 10 ml of acetic anhydride–pyridine (1 : 7) was added by pipet. The mixture was heated at 70° C for 3 hr. When the mixture was cooled to room temperature, 10 ml of DMF was added and then 10 ml of water was further added. This solution was titrated with 0.5 N methanolic potassium hydroxide.

A blank experiment including all reagents, but omitting the sample, was also run. OH values were obtained by calculating by usual method.

Ester Value

Ester values of products were determined as follows. About 0.3 g of sample in the form of small particles was weighed to the nearest milligram into a flask, and 10 ml of 0.5 N KOH was added. The mixture was heated at 90° C for 2 hr. When the mixture was cooled to room temperature, 10 ml of 0.5 N HCl was added by pipet and the resultant solution titrated with 0.5 N KOH. A blank experiment was also run. Ester values were obtained by calculating by usual method.

Infrared Spectra

Infrared spectra were determined with a Shimazu IR-400 instrument.

Inherent Viscosity

Inherent viscosities were determined at a concentration of 0.05 g polymer/10 ml of DMF at 30° C by use of an Ubbelohde viscometer.

Thermogravimetric Analyses (TGA)

TGA were carried out in air in Shimazu TGA-20 microthermobalance at a heating rate of 10° C/min.

Differential Thermal Analyses (DTA)

DTA were carried out in air in a Shimazu DT-20 B thermal analyzer at a heating rate of 10° C/min.

RESULTS AND DISCUSSION

$(HEP-)_2M$–PMDA–Epoxide Reactions

The $(HEP-)_2M$–PMDA–epoxide reactions were carried out, in the same manner as in the reactions of previous study [5], in DMF at 90° C. In other solvents, such as dioxane, chloroform, benzene, or toluene, the reactions did not proceed smoothly because of poor solubility of $(HEP-)_2M$ and PMDA. It is known that such an aprotic dipolar solvent as DMF, owing to its high polarity, assists in dissociation of the metal carboxylate groups and easily solvates the releasing cations, keeping the carboxylate anions in an unsolvated and, therefore, highly reactive state.

For this type of reaction, generally, the following reactions are first theoretically anticipated: (1) reaction of carboxyl group with epoxide group to produce hydroxyl group; (2) reaction of the hydroxyl group with acid anhydride group to form terminal carboxyl group; (3) reaction of acid anhydride group with epoxide group to form ester linkage; (4) polymerization of epoxide group; (5) reaction of the hydroxyl group with epoxide group to form ether linkage; (6) reaction of the hydroxyl group with carboxyl group to produce ester linkage.

To obtain information on the above elementary reactions, some model reactions were conducted with the use of $(EP-)_2Ca$ in DMF at 90°C. DEP, i-PrOH, and PGE were chosen as model carboxylic acid, secondary alcohol, and epoxide, respectively. Figures 1-3 show the results.

At the initial stage of the $(HEP-)_2M$–PMDA–epoxide reactions, the reaction of $(HEP-)_2M$ with a large excess of PMDA to form adducts containing carboxyl and acid anhydride groups must occur. Therefore, the reactions of the carboxyl group with epoxide group, that is, reaction (1) is considered to be important. As the model reaction for this, DEP–PGE reactions were carried out. As is clear from Fig. 1, the reaction in the presence of $(EP-)_2Ca$ proceeded more rapidly than that without $(EP-)_2Ca$, indicating that $(EP-)_2Ca$ catalyzes the reaction. Moreover, the fact that the conversion of

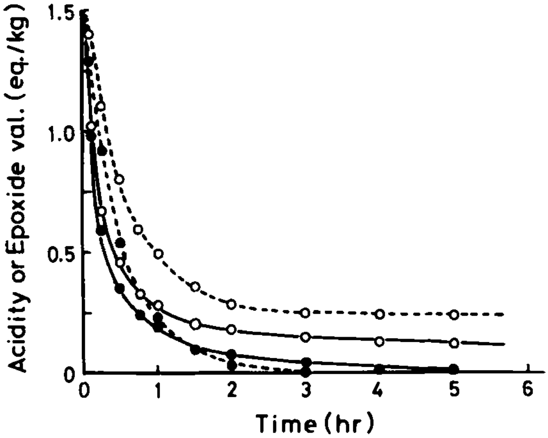


FIG. 1. Effect of $(EP-)_2Ca$ on (○) acidity and (●) epoxide conversion in DEP–PGE (1 : 2) reaction in DMF at 90°C: (--) without $(EP-)_2Ca$; (——) mole ratio of $(EP-)_2Ca$:DEP:PGE = 1:5:10.

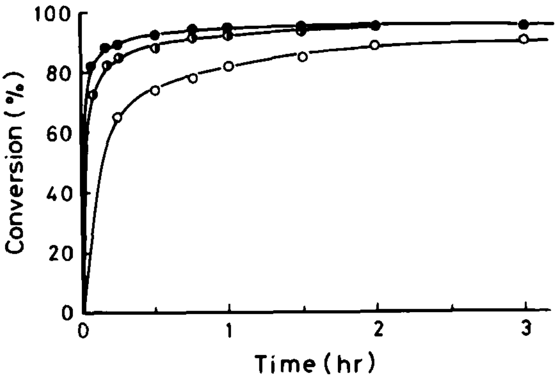


FIG. 2. Effect of $(EP-)_2Ca$ on reaction of PMDA with i-PrOH (1:2) in DMF at 90° C: (○) without $(EP-)_2Ca$; (◑) mole ratio of $(EP-)_2Ca$:PMDA:i-PrOH = 1 : 20 : 40; (●) mole ratio of $(EP-)_2Ca$:PMDA:i-PrOH = 1 : 10 : 20. Initial [PMDA] = 0.75 mole/kg; [i-PrOH] = 1.5 mole/kg.

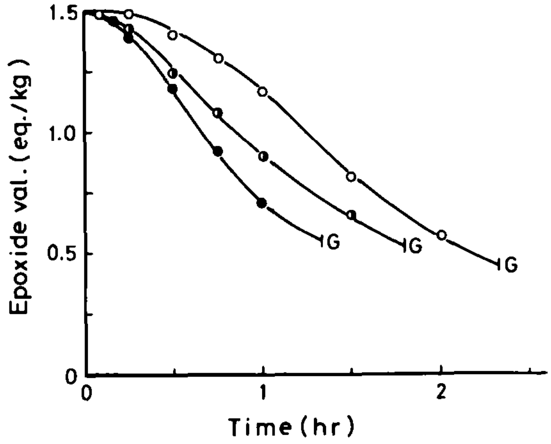


FIG. 3. Effect of $(EP-)_2Ca$ on PMDA–PGE (1:2) reaction in DMF at 90° C: (○) without $(EP-)_2Ca$; (◑) mole ratio of $(EP-)_2Ca$:PMDA:PGE = 1:20:40;(●) mole ratio of $(EP-)_2Ca$:PMDA:PGE = 1:10:20. G denotes the gelation point.

epoxide was consistently greater than that of acid suggests that etherification of epoxide occurred as a side reaction. From Fig. 1, it is apparent that reaction (1) readily occurs in the $(HEP-)_2M$–PMDA–epoxide reactions.

Reaction (1) results in formation of a new hydroxyl group. Hence, the reaction of the hydroxyl group so produced with acid anhydride group, that is, reaction (2) is considered to occur. Figure 2 shows the results of the model reaction (PMDA–i-PrOH reaction) for this; the reaction proceeded very rapidly and was catalyzed by $(EP-)_2Ca$. In the $(HEP-)_2M$–PMDA–epoxide system, reaction (2) will occur as soon as a new hydroxyl group is formed. Meanwhile, the carboxyl group produced by reaction (2) is considered to enter into reaction (1), thus providing ample opportunity for further growth of three-dimensional polymer.

As the model reaction for reaction (3), PMDA–PGE reactions were carried out. Figure 3 shows the epoxide data; the reaction is catalyzed by $(EP-)_2Ca$; however, the systems gelled when epoxide value decreased to 63-70%. Meanwhile, the decrease of acidity at the gel point was 12-16% lower than that of epoxide value, suggesting that etherification occurred to some degree. Also, the fact that gelation occurred during reaction suggests that both of the acid anhydride groups in PMDA took part in the reaction and that crosslinking occurred randomly. It has been reported [8] that, when the reactions of PMDA with cyclic ethers such as PGE and epichlorohydrin were carried out in dilute solution with DMBA as catalyst to obtain copolymers having mainly a ladder structure, etherification of cyclic ether also occurred to some extent, in addition to copolymerization of acid anhydride group with cyclic ether group. Since the concentration of acid anhydride group is high in the initial stages of the $(HEP-)_2M$–PMDA–epoxide reactions, reaction (3) is considered to occur.

On comparing Figs. 1, 2, and 3 with each other, the following may be inferred. In the $(HEP-)_2M$–PMDA–epoxide reactions, reaction (1) would proceed much more rapidly than reaction (3); similarly, reaction (2) is considered to proceed much more rapidly than reaction (3). With progress of the reaction, the concentration of acid anhydride group decreases and unreacted anhydride groups enter into reaction (2) rather than into reaction (3) because of higher rate of reaction (2).

As stated above, etherification occurs to some extent as a side reaction. This etherification has been found [5] to be due to reaction (4) rather than to reaction (5). In the $(HEP-)_2M$–PMDA–epoxide reactions, a new hydroxyl group formed is considered to react much more easily with acid anhydride group than with epoxide group. Therefore, reaction (5) is not considered to be important.

The possibility of reaction (6) can be omitted from the results of the model reaction (DEP–i-PrOH reaction), where there was no reaction at all.

The above observations lead to the following conclusion: in the $(HEP-)_2$ M–PMDA–epoxide reactions, reactions (1), (2), and (3) are the main reactions. This is consistent with that obtained from our previous investigations devoted to the $(HEP-)_2$ M–PA–epoxide reactions [5].

Figure 4 shows, as the typical example, results of the $(HEP-)_2$ Ca–PMDA–PGE reactions at mole ratios of 1:1.2:2.4 and 1:2:4. The reactions were carried out by adding all reactants to the reaction system at the beginning of the reaction. The acidity determined by nonaqueous titration is due to acid anhydride and carboxyl groups. The reaction rate increased with increasing content of $(HEP-)_2$ Ca, indicating that $(HEP-)_2$ Ca catalyzes the reaction. Further, the decrease of epoxide value was consistently greater than that of acidity. This tendency agrees with the consistently greater conversion of epoxide observed in the model reactions, also suggesting that etherification of epoxide occurred as side reaction. Figure 4 indicates that about 86% of the epoxide groups react with carboxyl and acid anhydride groups rather than with each other.

On the other hand, for comparison, DEG–PMDA–PGE reactions were conducted at DEG:PMDA:PGE mole ratios of 1:1.2:2.4 and

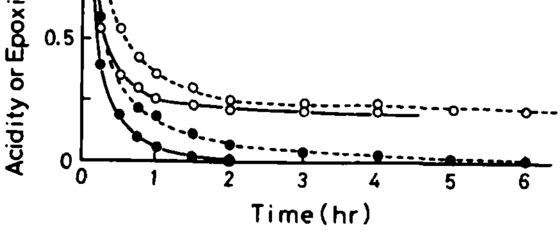


FIG. 4. $(HEP-)_2$ Ca–PMDA–PGE reaction at mole ratios of (——) 1:1.2:2.4 and (--) 1:2:4 at 90°C in DMF: (○) acidity; (●) epoxide conversion.

1:2:4 with DMBA as catalyst in DMF at 90° C. When the mole ratio was 1:1.2:2.4, the result obtained was similar to that obtained with the $(HEP-)_2$ Ca–PMDA–PGE reaction at a mole ratio of 1:1.2:2.4. Theoretically, the reaction system at the mole ratio of 1:2:4 should gel when crosslinking occurs randomly. Indeed, when the ratio was 1:2:4, the system gelled during reaction. Therefore, the fact that the system $(HEP-)_2$Ca–PMDA–PGE at the mole ratio of 1:2:4 was apparently homogeneous during reaction is considered to be due to the dissociation in DMF solution of ionic links introduced into the resulting three-dimensional polymers.

However, in case of the systems with lower $(HEP-)_2$ Ca content, that is, in the systems of $(HEP-)_2$ Ca–PMDA–PGE at the mole ratios of 1:3:6, 1:4:8, 1:6:12, and 1:10:20, gelation occurred during reaction. In this case, the time for gelation to occur became shorter with increasing $(HEP-)_2$ Ca content. The decrease of epoxide value at the gel point was to 47-63%. Similar tendencies were observed also in case of the $(HEP-)_2$ Mg–PMDA–PGE reactions.

When BO or PO was used as the epoxide, BO or PO was added dropwise to the reaction system over about 10 min. The reactions proceeded smoothly, with tendencies similar to those observed in the above reactions.

Products

Table 1 summarizes the results of syntheses of metal-containing three-dimensional polyesters by the $(HEP-)_2$ M–PMDA–epoxide reactions in DMF at 90° C. Reaction time was 7 hr. Initial concentrations of PMDA and epoxide were [acid anhydride group] = [epoxide group] = 1.5 equiv/kg. The products were obtained by precipitating or washing with water, except in a few cases where the products were obtained by precipitating with acetone.

As stated earlier, the systems with low $(HEP-)_2$ M content gelled during reaction. For the same molar ratio of $(HEP-)_2$ M–PMDA–epoxide in the feed, the gelation times of the systems containing Ca were a little shorter than those of the systems containing Mg; further, the gelation time showed a tendency to become shorter, depending on the epoxide, in the order PGE $>$ BO $>$ PO. The yields of the products obtained by precipitating or washing with water increased with decreasing $(HEP-)_2$ M content in the feed.

The products from the $(HEP-)_2$ M–PMDA–PGE systems were generally obtained in good yield, while the BO or PO-containing systems with high $(HEP-)_2$ M content gave products in poor yield; these products, except for that obtained by precipitating with acetone,

TABLE 1. Metal-Containing Three-Dimensional Polyesters Obtained by the $(HEP-)_2M$–PMDA–Epoxide Reactions in DMF at 90°C

		Product								
								Analyses (calcd)		
Reactants and mole ratio of reactants in feed	Reaction system[a]	Yield (%)	OH value (equiv/kg)	Acidity (equiv/kg)	Ester value (calcd) (equiv/kg)	η_{inh}[b]	Temp of 10% wt loss (°C)	C (%)	H (%)	M (%)
$(HEP-)_2Ca$–PMDA–PGE										
1:1.2:2.4	H	76	2.398	0.796	5.539 (6.293)	0.041	275	59.20 (59.57)	4.50 (4.14)	3.06 (3.71)
1:1.5:3.0	H	84	2.248	0.901	5.502 (6.472)	0.050	304	60.15 (60.24)	4.25 (4.30)	2.91 (3.24)
1:2:4	H	85	1.952	0.678	5.916 (6.685)	0.057	285	60.60 (61.04)	4.40 (4.18)	2.32 (2.68)
1:2:4	H	47[c]	1.890	0.233	6.158 (6.685)	0.050	287	58.75 (61.04)	4.15 (4.18)	3.90 (2.68)
1:3:6	G	95	1.794	0.326	6.486 (6.951)	–	300	60.85 (62.03)	4.30 (4.20)	2.14 (1.99)
1:4:8	G	98	1.532	0.315	6.658 (7.095)	–	303	62.25 (62.61)	4.20 (4.22)	1.12 (1.58)
1:6:12	G	99	1.017	0.227	6.923 (7.265)	–	315	61.85 (63.26)	4.30 (4.24)	1.23 (1.12)

(continued)

TABLE 1 (continued)

Reactants and mole ratio of reactants in feed	Reaction system[a]	Product								
		Yield (%)	OH value (equiv/kg)	Acidity (equiv/kg)	Ester value (calcd) (equiv/kg)	η_{inh}[b]	Temp of 10% wt loss (°C)	Analyses (calcd)		
								C (%)	H (%)	M (%)
1:10:20	G	100	1.034	0.201	6.989 (7.445)	–	328	63.15 (63.85)	4.50 (4.25)	0.56 (0.71)
$(HEP-)_2Mg$–PMDA–PGE										
1:1.2:2.4	H	71	2.588	0.920	5.481 (6.379)	0.031	246	60.15 (60.46)	4.60 (4.20)	2.03 (2.28)
1:1.5:3.0	H	77	2.272	0.964	5.558 (6.552)	0.044	255	60.10 (61.02)	4.35 (4.21)	1.92 (1.99)
1:2:4	H	82	2.080	0.847	5.734 (6.748)	0.050	248	60.25 (61.68)	4.25 (4.24)	1.39 (1.64)
1:2:4	H	42[c]	1.781	0.342	6.031 (6.748)	0.048	249	59.10 (61.68)	4.25 (4.24)	1.97 (1.64)
1:3:6	G	92	1.902	0.478	5.942 (7.028)	–	272	60.80 (62.51)	4.45 (4.24)	1.07 (1.22)
1:4:8	G	95	1.281	0.308	6.684 (7.186)	–	287	62.25 (63.00)	4.20 (4.25)	0.90 (0.97)
1:6:12	G	97	1.088	0.251	6.767 (7.275)	–	294	63.05 (63.54)	4.40 (4.26)	0.73 (0.68)

1:10:20	G	100	0.814	0.191	6.839 (7.432)	–	317	63.15 (64.03)	4.25 (4.26)	0.25 (0.43)
(HEP-)$_2$Ca–PMDA–BO										
1:1.5:3.0	H	31	2.692	0.896	8.155 (7.985)	0.060	275	57.30 (56.34)	5.35 (4.53)	1.91 (4.00)
1:2:4	H	67	2.223	0.775	8.005 (8.453)	–	275	56.00 (56.85)	4.90 (4.60)	2.40 (3.39)
1:3:6	G	83	2.065	0.934	8.209 (9.059)	–	300	56.55 (57.51)	4.90 (4.70)	2.46 (2.59)
1:6:12	G	99	1.260	0.392	9.269 (9.877)	–	299	57.10 (58.40)	5.05 (4.82)	1.54 (1.52)
(HEP-)$_2$Mg–PMDA–BO										
1:1.5:3.0	H	28	2.804	0.973	8.215 (8.113)	0.054	262	56.75 (57.13)	5.15 (4.60)	1.05 (2.47)
1:2:4	H	59	2.403	1.162	8.061 (8.567)	0.073	260	56.15 (57.62)	5.00 (4.66)	1.14 (2.08)
1:3:6	G	82	2.034	0.852	8.514 (9.153)	–	288	57.60 (58.10)	4.85 (4.74)	1.28 (1.59)
1:6:12	G	98	0.904	0.201	9.613 (9.934)	–	289	57.90 (58.82)	4.90 (4.85)	0.90 (0.93)
(HEP-)$_2$Ca–PMDA–PO										
1:1.5:3.0	H	23	2.419	0.935	8.360 (8.335)	0.069	263	53.10 (55.06)	4.85 (4.10)	2.27 (4.18)

(continued)

TABLE 1 (continued)

Reactants and mole ratio of reactants in feed	Reaction system[a]	Product								
		Yield (%)	OH value (equiv/ kg)	Acidity (equiv/ kg)	Ester value (calcd) (equiv/ kg)	η_{inh}[b]	Temp of 10% wt loss (°C)	Analyses (calcd)		
								C (%)	H (%)	M (%)
1:2:4	H	52	2.078	0.881	8.591 (8.873)	–	268	54.65 (55.42)	4.50 (4.11)	2.52 (3.56)
1:3:6	G	80	1.527	0.478	9.356 (9.581)	–	314	55.50 (55.89)	4.35 (4.14)	2.56 (2.74)
1:6:12	G	98	0.968	0.184	10.055 (10.552)	–	307	55.70 (56.53)	4.25 (4.17)	1.57 (1.63)
$(HEP-)_2Mg-PMDA-PO$										
1:1.5:3.0	H	45[c]	1.553	0.334	7.480 (8.474)	0.049	246	51.70 (55.98)	3.95 (4.16)	3.57 (2.57)
1:2:4	H	36	2.274	1.072	8.583 (8.999)	0.083	252	55.50 (56.20)	4.50 (4.17)	1.02 (2.19)
1:3:6	G	69	1.673	0.855	8.852 (9.686)	–	280	55.30 (56.50)	4.55 (4.18)	0.89 (1.68)
1:6:12	G	97	0.827	0.235	10.138 (10.620)	–	297	55.60 (56.90)	4.30 (4.20)	0.85 (0.99)

[a] H = reaction system was homogeneous during reaction; G = reaction system gelled during reaction.

[b] Determined at a concentration of 0.05 g/10 ml in DMF at 30°C.

[c] Obtained by precipitating with acetone.

showed considerably lower metal content than calculated value, indicating that the portions which are rich in metal were washed away by water.

Ester value and elementary analyses show that the products contain ester linkages and metal. The OH values of the products were much higher than the values of acidity, indicating that hydroxyl termination predominates. The concentrations of these terminal groups generally decrease with decreasing $(HEP-)_2M$ content in the feed. It is considered that with decrease in the $(HEP-)_2M$ content in feed the crosslinking density of the products increases. The products obtained from the systems which did not gel showed higher values of acidity than the values (0.3-0.55 equiv/kg) anticipated from the final acidities (0.2-0.3 equiv/kg) of the reaction systems. On the other hand, the products obtained by precipitating with acetone, although the yields were not good, showed acidity values almost corresponding to the values anticipated from the final acidities of the reaction systems. Moreover, the total concentrations of terminal groups of the latter products are lower than those of the former products. From the above observations it would be inferred that, at the time of precipitation with water, some of the ester linkages of the resulting polyesters were hydrolyzed by the catalytic effect of the metal carboxylate groups. However, it is considered that the gelled products which have high crosslinking density are stable to the hydrolysis.

Inherent viscosities (in DMF at 30° C) of the products obtained from the systems which did not gel were low, ranging from 0.031 to 0.083, tending to increase slightly with a decrease in the $(HEP-)_2M$ content in the feed. Moreover, it is considered that in a polar solvent such as DMF the ionic links in the polyester dissociate into low molecular weight polymer when the concentration is very low.

The epoxides used are unsymmetrical, and undirected opening of the ring is considered to have occurred. The products obtained are slightly yellow, powdery materials. Among them, those from the systems which did not gel showed a broad endothermic peak at 50-60° C in DTA in air. Meanwhile, no such peak was observed in the gelled products or in the products obtained by precipitating with acetone. All the products showed exothermic peaks above 340° C, probably due to degradation occurring via oxidative modes. Generally, the 10% weight loss temperatures show a tendency to increase with decreasing $(HEP-)_2M$ content in the feed, that is, with an increase in crosslinking density of the polyester. Moreover, the polyesters containing Ca are, in general, thermally more stable than those containing Mg.

In Fig. 5 are shown the infrared spectra of representative metal-containing three-dimensional polyesters. They are essentially

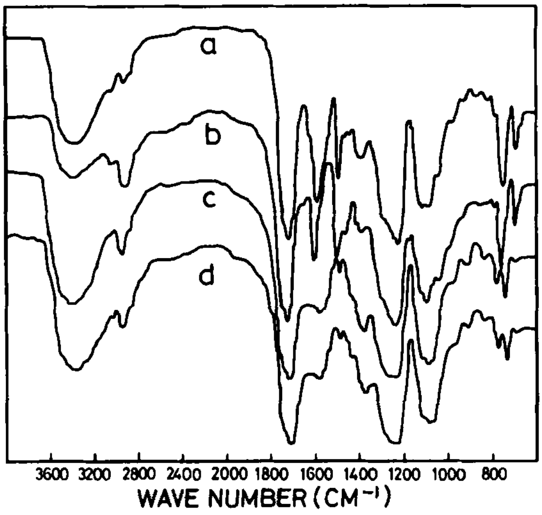


FIG. 5. Infrared spectra of metal-containing three-dimensional polyesters from (a) $(HEP-)_2Ca$–PMDA–PGE (1:3:6); (b) $(HEP-)_2Mg$–PMDA–PGE (1:3:6); (c) $(HEP-)_2Ca$–PMDA–PO (1:3:6); (d) $(HEP-)_2Mg$–PMDA–PO (1:3:6).

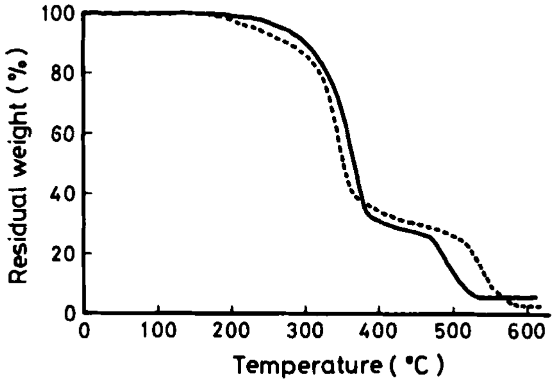


FIG. 6. TGA curves of metal-containing three-dimensional polyesters: (——) from $(HEP-)_2Ca$–PMDA–PGE (1:3:6); (--) from $(HEP-)_2Mg$–PMDA–PO (1:3:6).

identical, having absorption bands at 3400 cm^{-1} (OH stretching), 1730 cm^{-1} (C=O stretching), 1570-1600 cm^{-1} (carboxylate and phenyl ring), and 1400 cm^{-1} (carboxylate group). Further, the sharp bands attributable to ether linkage (aliphatic ether) appear at 1070-1130 cm^{-1}. From this it is apparent that the polyesters have ionic links in the molecule.

Figure 6 shows the TGA curves of representative metal-containing three-dimensional polyesters. Gradual weight loss begins about 200° C, and destruction proceeds rapidly above 280-310° C. At 350-370° C the residual weight approaches 50%. Between 380 and 480°C the weight loss is gradual, and above 500°C marked degradation proceeds again. The plateau observed about 600°C corresponds to the formation of MgO in case of the Mg salt and to the formation of $CaCO_3$ in the case of the Ca salt.

ACKNOWLEDGMENTS

The author wishes to thank Mr. H. Dohi for technical assistance and Mr. F. Yamauchi for performing elemental analyses. The author also wishes to thank Dr. T. Kume for his continued interest and encouragement.

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Accepted by editor May 26, 1976
Received for publication July 22, 1976