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Synthesis of Polymers by Using Divalent Metal Salts of Mono(hydroxyethyl) Phthalate: Unsaturated Polyesters from Metal Salts, Glycol, Anhydrides, and Epoxides

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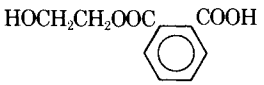
Synopsis

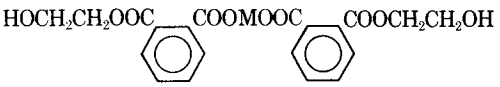
Syntheses of unsaturated polyesters were investigated by the divalent metal salts of mono(hydroxyethyl) phthalate–ethylene glycol–anhydrides–epoxide reactions. As anhydrides, phthalic anhydride and maleic anhydride were used, and propylene oxide and 1,2-butylene oxide were the epoxides used. The metal carboxylate groups of the above metal salts catalyzed the reaction. Viscosities of styrene solutions of the polyesters obtained showed a tendency to increase with increase in metal content. The styrene solutions could be cured to give metal-containing cured polyester resins. The cured resins were evaluated for physical properties. Generally, Mg was more effective than Ca in improving the physical properties. Further, resistance to chemical attack and boiling water and thermal behavior were also discussed.

INTRODUCTION

The author has been active in the syntheses of ionic polymers by using divalent metal salts of mono(hydroxyethyl) phthalate (HEP),

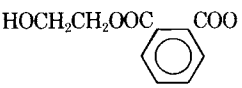


that is, $(HEP—)_2M$,



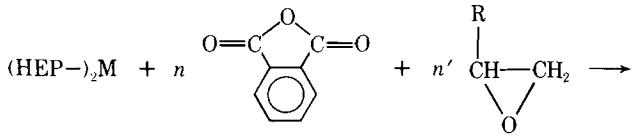
where M = divalent metal (Mg or Ca)

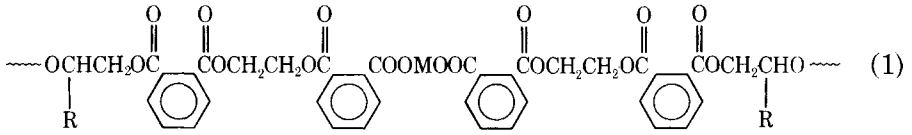
where HEP— denotes, as in the previous papers,[1–5] HEP residue,



and M is divalent metal.[1–5] These compounds contain an ionic bond formed between $—COO^-$ and M^{2+} and two hydroxyl groups, and, therefore, they are

considered to be of interest as ionic monomers from the scientific and industrial standpoints. In a previous study,[5] syntheses of metal-containing polyesters were investigated by the (HEP—)$_2$M–phthalic anhydride (PA)–epoxide reactions, as shown eq. (1):

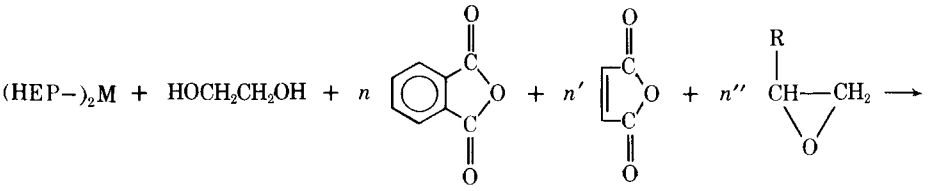


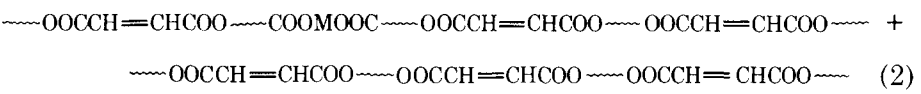


(1)

It was found that the metal carboxylate groups of these metal salts catalyze the above reactions. The metal-containing polyesters obtained contained ionic links in the main chain.

In the present study, applying the above synthetic route to the synthesis of unsaturated polyesters, the author investigated the synthesis of unsaturated polyesters from (HEP—)$_2$M, ethylene glycol (EG), PA, maleic anhydride (MA), and epoxides.





(2)

Since, in the polyesterification of the above five components, MA and PA have similar reactivities, these anhydrides are considered to be randomly distributed along the polyester chain. Hence, products obtained in eq. (2) are considered to consist of metal-containing unsaturated polyesters containing ionic links in the main chain and those not containing metal. Moreover, as the epoxides, propylene oxide (PO) and 1,2-butylene oxide (BO) were used. Unsaturated polyesters prepared by the above reaction are little known, so far as the author is aware. The metal-containing cured polyester resins obtained in the present study were evaluated for physical and other properties.

EXPERIMENTAL

Materials

(HEP—)$_2$M were prepared according to the method reported in a previous paper.[1]

EG, PA, MA, PO, and styrene were reagent chemicals and used as received. BO of extrapure grade was used as received.

Synthesis of Unsaturated Polyesters

In a 1-liter flask equipped with a stirrer, a thermometer, a condenser, and a dropping funnel were placed fixed amounts of $(HEP—)_2M$, EG, PA, and MA, and the mixture was stirred at 110–140°C for 30–60 min. Next, a given amount of PO or BO was dropped very gradually into the mixture with stirring at the same temperature over 3–16 hr. After dropping, the mixture was further stirred at the same temperature for an additional 1 hr.

Where isomerization of maleate groups into fumarate homologs was attempted, the mixture was further heated to 210°C, at which temperature stirring was continued for a fixed time. (In this case, hydroquinone as a polymerization inhibitor was added at an amount of 100 ppm before isomerization.)

Generally, the product (polyester) was semisolid or solid at room temperature.

Curing Reaction

To the solutions of unsaturated polyesters in styrene, 0.5 wt-% of 60% dimethyl phthalate solution of methyl ethyl ketone peroxide and 0.5 wt-% of 10% styrene solution of cobalt naphthenate were added. The solutions were cured under the following condition, giving cured polyester resins: 40°C for 15 hr, 80°C for 4 hr, and 120°C for 2 hr.

Determination of Physical and Other Properties

Heat distortion temperature (HDT) was determined according to ASTM-D 648-56. Tensile strength was determined according to ASTM-D 638-68. Flexural strength was determined according to ASTM-D 790-66. Compressive strength was determined according to ASTM-D 695-69. Impact strength was determined according to ASTM-D 256-56 (with Izod notch). Rockwell hardness was determined according to ASTM-D 785-62 (M or R scale).

Resistance to chemical attack was determined according to ASTM-D 543-67.

Boiling water resistance was determined according to ASTM-D 570-63.

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

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

RESULTS AND DISCUSSION

Synthesis of Unsaturated Polyesters

Conventional-type unsaturated polyesters are generally prepared by the polycondensation reactions of dibasic acids or anhydrides with glycols, which reactions have widely been studied in detail. In addition, communications have recently appeared on the synthesis of unsaturated polyesters by the reaction of epoxides with anhydrides.[6–8] Tertiary amines, alkylammonium

compounds, lithium halides, phosphoric acid, aluminum salts, etc., are used as catalysts in this reaction, which otherwise is slow.

On the other hand, the reaction, eq. (2), in the present study offers the following peculiarities: (1) the metal carboxylate groups of $(HEP—)_2M$,which are used as one component of glycols, have catalytic activities for the reaction; (2) the reaction proceeds at comparatively low temperatures without evolution of volatile matters; (3) the reaction gives products (polyesters) which copolymerize with styrene to give metal-containing cured polyester resins containing ionic links.

Table I summarizes the results of synthesis of unsaturated polyesters from $(HEP—)_2M$, EG, PA, MA, and epoxides. In the compositions of the polyesters, the molar ratio of PA/MA was maintained constant at 1:1, but the $(HEP—)_2M$ amount in the diols varied.

In the synthetic reactions, given amounts of $(HEP—)_2M$, EG, PA, and MA were first heated together at 110–140°C for 30–60 min with stirring in a reaction vessel, giving a homogeneous (transparent) mixture; in this case, most of the diols were considered to have reacted with the anhydrides to form carboxyl-terminated adducts. Next, a fixed amount of epoxide was slowly added dropwise into the mixture at the same temperature. The initiation of the reaction was manifested by a rapid consumption of the epoxide added, and also by about 20–30°C temperature exotherm, which, after approximately 1 hr, had reached a maximum temperature.

Thus, in the initial stages of reaction, the reaction proceeded fairly rapidly. As the reaction proceeded, the viscosity of the mixture increased and reflux of the epoxide added came to occur. Then, it was necessary that the addition of epoxide be at such a rate that the reflux of the epoxide added was not vigorous. In the latter stages of reaction, the temperature was generally raised to about 150–165°C. After the end of addition of epoxide, the mixture was stirred at the same temperature range for an additional 1 hr, at which time titration showed complete disappearance of epoxide.

The increase in viscosity of the reaction mixture was remarkable when the $(HEP—)_2M$ amount, that is, the metal content, was high. When the metal content in feed was above 0.8%, it was generally difficult to carry out the synthetic reaction because of very high viscosity of the reaction mixture. Meanwhile, in case of the reaction mixtures not containing $(HEP—)_2M$, there was no reaction. From this it is apparent that $(HEP—)_2M$ catalyzes the reaction in the present study.

A previous study[5] disclosed that, in the $(HEP—)_2M$–PA–epoxide reaction, the following main reactions occur: (1) the reaction of carboxyl group with epoxide to form OH group; (2) the reaction of the OH group with acid anhydride group to form terminal carboxyl group; (3) the reaction of acid anhydride group with epoxide to form ester linkage. Also in the present study, the polyesterification is considered to proceed by the same main reactions as above. Homopolymerization of the epoxides might have occurred to a slight degree, but appears least serious in the present study. The polyesters obtained showed very low acid values, indicating that the polymers are almost OH-terminated.

In the synthetic reactions of usual unsaturated polyesters, the temperature is comparatively high (generally 160–200°C), and maleate groups are largely

isomerized into fumarate homologs during esterification; with increase in temperature, the degree of isomerization generally becomes higher.[9] It is generally known that fumarates are much more reactive than maleates toward styrene. The progress of the conversion of maleate to fumarate is generally followed by infrared measurement.[10] In the present study, isomerization of polyesters obtained was attempted by heating the polyesters at high temperatures. At 200°C, the shift from the maleate to the fumarate form was not recognized by infrared spectra. It is known that the acidity of the reaction mixture has a significant influence upon the rate of isomerization; polyesters with acid number in the range of 40 to 60 isomerize in 2 to 3 hr, while a much longer time is needed when the acid number is lower.[6,11] Infrared spectra showed that at 210°C, maleate fully isomerized to fumarate in 4–5 hr in case of the polyesters based on PO; meanwhile, in case of the polyesters based on BO, the occurrence of isomerization was not clear by infrared spectra. When the metal content in the feed was above 0.5 wt-%, the polyesters obtained showed a tendency to gelation in several hours at 210°C.

The polyesters obtained were semisolids or solids at room temperature of slightly brown or brown color; the color was more remarkable in the polyesters based on $(HEP—)_2Ca$ than in those based on $(HEP—)_2Mg$. They are soluble in styrene. As is clear from Table I, the viscosity of solutions in 30% styrene increased markedly with increase in the metal content; this tendency is characteristic of polymers containing ionic links. Moreover, the viscosity and the peak exotherm of the styrene solutions generally increased by heating the polyesters at 210°C, indicating that the polyesters based on BO also isomerized. Since heating at 210°C resulted in no change in acid value, chain extension of the polyesters is considered not to have occurred. It has been stated[12] that, in the same solvent, polyesters containing predominantly fumarates have higher viscosities than those containing maleates.

Also, the styrene solutions of the polyesters obtained without heating at 210°C showed high peak exotherms when the metal contents were high, suggesting that the metal carboxylate groups of $(HEP—)_2M$ accelerate the curing reactions.

Physical Properties

The styrene solutions (resin solutions) of the polyesters in Table I were cured in the manner described in the experimental section. The physical properties of the cured polyester resins are summarized in Table II. Generally, the cured resins of MP and CP series, namely, the resins based on PO, showed better physical properties than the cured resins of MB and CB series, namely, the resins based on BO. Thus, pendent methyl groups impart better physical properties to the cured resins than pendent ethyl groups.

In the MP and CP series, HDT, Rockwell hardness, and compressive strength of the cured resins of the maleate-based polyesters (not isomerized) showed a tendency to increase with increase in $(HEP—)_2M$ content, namely, metal content; this tendency is remarkable in the resins containing Mg. As is obvious on comparing resins with the same metal content, heating the polyesters at 210°C resulted in improvement in these physical properties, due to the increase in crosslinking density of the cured resins. Meanwhile, tensile, flex-

TABLE I
Synthesis of Unsaturated Polyesters from (HEP—)$_2$M, EG, PA, MA, and Epoxides

Polyester code	Molar ratio of components					Metal content in feed, %	Addition of epoxide		Heating time at 210°C, hr	Polyester		
											Solution in 30% St	
							Temp., °C	Time, hr		Acid value, mg KOH/g	Viscosity at 23°C, cps	Peak exotherm,[a] °C
MP-1	0.096	0.904	4	4	8.4	0.15	120–150	7	—	2.72	1165	94
MP-1′	0.096	0.904	4	4	8.4	0.15	120–167	4	5	5.68	4225	149
MP-2	0.196	0.804	4	4	8.4	0.30	120–150	10	—	3.06	3320	89
MP-2′	0.196	0.804	4	4	8.4	0.30	120–161	6.5	5	8.88	4640	157
MP-3	0.337	0.663	4	4	8.4	0.50	130–164	10	—	11.81	21800	126
	(HEP—)$_2$Mg	EG	PA	MA	BO							
MB-1	0.103	0.897	4	4	8.16	0.15	130–143	6.5	—	11.70	1960	102
MB-1′	0.103	0.897	4	4	8.16	0.15	120–152	3	5	7.72	1823	113
MB-2	0.210	0.790	4	4	8.16	0.30	130–150	7.5	—	9.28	2500	105
MB-2′	0.210	0.790	4	4	8.16	0.30	120–161	3.5	5	10.60	2340	125
MB-3	0.362	0.638	4	4	8.16	0.50	140–162	8	—	19.28	44700	129

	$(HEP—)_2Ca$	EG	PA	MA	PO							
CP-1	0.057	0.943	4	4	8.4	0.15	120–153	8	—	2.62	2090	113
CP-1′	0.057	0.943	4	4	8.4	0.15	120–153	4.5	4.5	2.88	2775	134
CP-2	0.117	0.883	4	4	8.4	0.30	120–150	5	—	1.99	3655	128
CP-2′	0.117	0.883	4	4	8.4	0.30	120–150	4.5	4	2.76	17750	161
CP-3	0.198	0.802	4	4	8.4	0.50	130–161	3	—	2.81	3100	125
CP-4	0.328	0.672	4	4	8.4	0.80	130–160	3.5	—	1.95	9100	130
	$(HEP—)_2Ca$	EG	PA	MA	BO							
CB-1	0.062	0.938	4	4	8.16	0.15	110–120	5.5	—	9.75	692	92
CB-1′	0.062	0.938	4	4	8.16	0.15	120–149	3	5	8.73	2360	127
CB-2	0.125	0.875	4	4	8.16	0.30	120–150	6	—	3.11	995	88
CB-2′	0.125	0.875	4	4	8.16	0.30	120–152	3	5	2.68	2500	116
CB-3	0.213	0.787	4	4	8.16	0.50	120–142	6.5	—	3.00	2685	109
CB-4	0.352	0.648	4	4	8.16	0.80	130–160	15.5	—	2.10	4900	125

[a] Determined according to JIS K 6901.

TABLE II
Physical Properties of Cured Polyester Resins (70% Polyester–30% Styrene)

Polyester	Heat distortion temp., °C	Tensile strength, kg/cm²	Flexural strength, kg/cm²	Rockwell M or R hardness	Impact strength, kg·cm/cm	Compressive strength, kg/cm²
MP-1	38	274	795	M 90.1	1.10	741
MP-1′	63	789	1052	M 109.3	1.60	1479
MP-2	58	580	1299	M 108.1	1.84	1433
MP-2′	59	598	1314	M 112.0	1.70	1545
MP-3	65	469	1139	M 110.6	1.61	1487
MB-1	43	400	—	M 92.7	1.10	528
MB-1′	47	614	—	M 95.3	1.43	1078
MB-2	45	482	—	M 94.4	1.60	943
MB-2′	52	658	—	M 99.5	1.23	1138
MB-3	59	512	1001	M 102.2	1.45	1179
CP-1	43	465	—	M 94.9	1.47	981
CP-1′	50	496	1036	M 102.9	1.20	1276
CP-2	53	612	1212	M 105.3	1.51	1393
CP-2′	64	499	1139	M 109.7	1.47	1430
CP-3	49	547	977	M 105.2	1.18	1310
CP-4	58	567	889	M 107.6	1.32	1365
CB-1	28	148	—	R 87.8	0.97	328
CB-1′	46	459	827	M 91.5	1.28	925
CB-2	31	186	—	R 99.3	1.02	385
CB-2′	46	436	762	M 92.1	1.14	971
CB-3	46	415	849	M 93.1	1.19	939
CB-4	57	593	946	M 101.0	1.23	1107

ural, and impact strengths showed the maximum values in case of the MP-2 and CP-2 resins, respectively. In case of the MP series, when the metal content was low, these physical properties increased markedly in value by isomerization (MP-1 vs. MP-1′). The previous study[4] showed that, in the polyesters obtained by the polycondensation reaction of $(HEP—)_2Mg$–EG–propylene glycol with MA–PA, the polyester with Mg content of 0.32% gave excellent physical properties of the cured resin.

On the other hand, in the MB and CB series, the physical properties of the cured resins of the maleate-based polyesters were improved markedly with increase in metal content. Thus, in the BO-based resins, the effect of introducing metal appears clearly. In addition, over a wide range of metal content, the resins containing Mg showed better physical properties than the resins containing Ca. Also, in these series, heating the polyesters at 210°C resulted in remarkable improvement in physical properties of the cured resins. From this, it is apparent that the BO-based polyesters fully isomerized at 210°C, though the occurrence of isomerization was not clear by infrared spectra. The MB series resins, except for MB-3, did not break during flexural strength measurement because of flexibility of the resins.

The observations described above lead to the conclusion that the physical properties of the cured resins become worse in the following order: MP > CP > MB > CB series. Generally, Mg is more effective than Ca in improving the physical properties of the resins, probably because of higher interionic attraction of Mg^{2+}.

TABLE III
Resistance of Cured Polyester Resins (70% Polyester–30% Styrene) to Chemical Attack

Reagent	External appearance[a] and change in weight, %						
	MP-2	MB-2	MB-2′	CP-2	CP-4	CB-2	CB-4
30% H_2SO_4	UA, +0.22	UA, +0.23	UA, +0.28	UA, +0.18	UA, +0.21	UA, +0.23	UA, +0.16
10% NaOH	UA, −0.25	UA, +0.07	UA, −0.27	UA, −0.13	UA, −1.21	UA, −0.10	UA, −0.21
95% Ethanol	UA, +1.39	UA, +3.43	UA, +1.97	UA, +1.74	UA, +1.98	UA, +5.44	UA, +2.22
Acetone	DI	DI	DI	DI	DI	DI	DI
$ClCH_2CH_2Cl$	DI	DI	DI	DI	DI	DI	DI
10% NaCl	UA, +0.39	UA, +0.44	UA, +0.53	UA, +0.31	UA, +0.40	UA, +0.37	UA, +0.29
Benzene	DI	DI	DI	DI	DI	DI	DI
Distilled water	UA, +0.52	UA, +0.58	UA, +0.45	UA, +0.40	SW, +0.51	UA, +0.72	UA, +0.41

[a] UA = Unaffected; SW = surface of sample became slightly white; DI = sample was disintegrated.

TABLE IV
Boiling Water Resistance of Cured Polyester Resins (70% Polyester–30% Styrene)

Polyester	Change in thickness, %	Change in weight, %	External appearance[a]
MP-2	+0.65	+1.39	UA
MB-2	+1.59	+1.26	UA
MB-2′	+0.62	+1.50	SW, ND
CP-2	+1.52	+1.14	SW, ND
CP-4	+0.91	+1.28	SW, ND
CB-2	+0.37	+1.03	SW, ND
CB-4	+0.83	+0.92	SW, ND

[a] UA = Unaffected; SW = surface of sample became slightly white; ND = sample showed no deformation.

Resistance to Chemical Attack and Boiling Water

Table III shows the resistance of representative cured polyester resins to chemical attack. They were unaffected in external appearance by 30% H_2SO_4 and 10% NaOH, and changes in weight were generally small.

In 95% ethanol, while they were unaffected in external appearance, the resins based on BO generally showed higher weight gain than those based on PO; in the CB series, with increase in Ca content in the resin the weight gain decreased (CB-2 vs. CB-4), and also, in the MB series, the effect of isomerization of polyester appears, that is, heating the polyester at 210°C resulted in decrease in weight gain of the cured resin, due to the increase in crosslinking density (MB-2 vs. MB-2′).

All cured resins were disintegrated by acetone, ethylene dichloride, and benzene. In 10% NaCl and distilled water, they were unaffected in external appearance, except for the CP-4 resin, the surface of which became slightly white.

Table IV shows the boiling water resistance of the resins. The MP-2 and MB-2 resins were unaffected in external appearance by boiling water, while the surfaces of other resins became slightly white. No resins showed deformation.

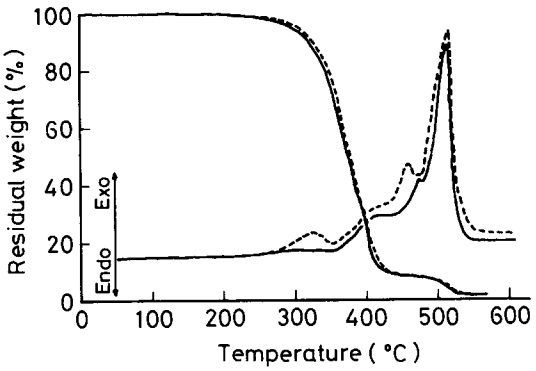


Fig. 1. TGA and DTA curves of cured polyester resins: (—) MP-2 polyester resin; (- - -) CB-4 polyester resin.

Thermal Behavior

Figure 1 shows TGA and DTA curves in air of representative cured polyester resins. In the TGA curves, the MP-2 and CB-4 resins showed 50% weight loss temperatures of 370° and 375°C, respectively. The plateaus observed above 520°C correspond to the formation of MgO in case of the MP-2 resin, and to the formation of $CaCO_3$ in case of the CB-4 resin. The DTA curves showed several exothermic peaks, probably because of degradation occurring via oxidative modes.

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