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Synthesis of Polymers by Using Divalent Metal Salts of Mono(hydroxyethyl)phthalate: Metal-Containing Unsaturated Polyesters with Pendent Methacrylate Groups

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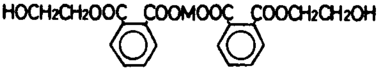
ABSTRACT

Syntheses of novel metal-containing unsaturated polyesters having pendent methacrylate groups obtained by use of divalent metal salts of mono(hydroxyethyl)phthalate–maleic anhydride (MA)–glycidyl methacrylate (GMA) reactions were investigated. The yields were generally high. The metal-containing polyesters obtained were slightly yellow-brown solids, and the molecular weights ranged from 1546 to 2174, depending on the mole ratio of feed. Among them, the polyesters obtained at a feed mole ratio of metal salt:MA:GMA of 1:8:8 were miscible with methyl methacrylate (MMA), giving homogeneous solutions suitable for copolymerization, and the polyesters could be easily cross-linked with MMA to give cured resins. The metal-containing cured polyester resins showed excellent physical properties. Resistance of the resins to chemical attack and boiling water and thermal behavior are also discussed.

INTRODUCTION

Divalent metal salts of mono(hydroxyethyl)phthalate (HEP), that is, $(HEP\text{-})_2M$, where HEP- denotes the hydroxyethylphthalate residue and M is a divalent metal, contain an ionic bond between $-COO^-$ and M^{2+}, and two hydroxyl groups. Therefore, compounds of the type I



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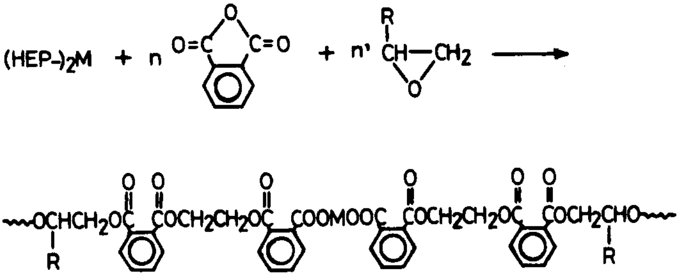
where M is a divalent metal (Mg or Ca) are considered to be of interest as ionic monomers from the scientific and industrial standpoints. The author has been active in the syntheses of ionic polymers by using $(HEP\text{-})_2M$ [1-6]. In a previous paper [5], it was shown that metal-containing polyesters were synthesized by the $(HEP\text{-})_2M$–phthalic anhydride (PA)–epoxide reaction, as shown by Eq. (1).



(1)

Phenyl glycidyl ether (PGE) and 1,2-butylene oxide (BO) were the epoxides used. The polyesters obtained contained ionic links in the main chain. By applying the above synthetic route to the synthesis of unsaturated polyesters, unsaturated polyesters have been prepared from $(HEP\text{-})_2M$, ethylene glycol (EG), PA, maleic anhydride (MA) and epoxides [6].

It seemed of interest to prepare metal-containing unsaturated polyesters containing substituents available for further reactions by the same synthetic route [Eq. (1)]. In the present study, the synthesis of novel metal-containing unsaturated polyesters having pendent methacrylate groups from $(HEP-)_2M$, MA and glycidyl methacrylate (GMA) was investigated.

The curable metal-containing unsaturated polyesters obtained were crosslinked with methyl methacrylate (MMA). Further, the cured resins were evaluated for physical and other properties.

EXPERIMENTAL

Materials

$(HEP-)_2M$ were prepared according to the method reported in the previous paper [1]. MA was a reagent-grade chemical and used as received. GMA and MMA were purified by distillation. Chloroform, used as the solvent, was a reagent grade chemical and used as received (purity > 99.5%).

Synthesis of Metal-Containing Unsaturated Polyesters Having Pendent Methacrylate Groups

Into a flask equipped with a stirrer, thermometer, condenser and dropping funnels, were placed fixed amounts of $(HEP-)_2M$ and MA, and the mixture was stirred at 110-130°C for 1-1.5 hr. Next, the temperature was kept at 90-130°C and a given amount of GMA was gradually added dropwise to the flask. When the mixture became viscous, chloroform as a solvent was added to the flask to reduce the viscosity and the temperature of the system. The additions of given amounts of GMA and chloroform were over after about 2 hr, and then the mixture was stirred at the reflux temperature (63° C) of chloroform. The reaction was continued until unreacted reactants were almost consumed.

After the reaction, additional chloroform was introduced into the mixture to make the viscosity suitable for filtration, and the solution was filtered by suction. The filtrate was poured into a large quantity of stirred diethyl ether to precipitate the product (polyester). The product was washed with diethyl ether and dried in vacuo.

Analytical Methods

Acidities were determined as follows: About 1.0 g of sample was dissolved in 10 ml of DMF and then 10 ml of water was added to it.

After standing for about 15 min, the solution was titrated with standard methanolic potassium hydroxide.

Epoxide values were determined according to the HCl-dioxane method [7].

OH values were determined in the same manner as in the previous study [5].

Ester values were determined as follows. A 0.3-0.5 g sample was weighed to the nearest milligram into a 100-ml flask, and 10 ml of 0.5 N KOH was added by pipet. The mixture was heated to boiling for 1.5-2 hr. When the mixture was cooled to room temperature, 10 ml of 0.5 N HCl was added by pipet. It was titrated with 0.5 N methanolic potassium hydroxide. A blank experiment was also run. OH values were obtained by calculating by usual method.

Bromine numbers were determined by a known method [8].

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

Thermogravimetric analyses (TGA) were carried out in a Shimazu microthermobalance TGA-20 at a heating rate of 5°C/min in air.

Differential thermal analyses (DTA) were carried out in a Shimazu thermal analyzer DT-20 B at a heating rate of 5°C/min in air.

Copolymerization

In the copolymerization of the polyester with MMA, 0.5 wt % of a 60% dimethyl phthalate solution of methyl ethyl ketone peroxide and 0.5 wt % of a 10% solution of cobalt naphthenate in styrene were added to the mixtures of the polyester and MMA.

To obtain time-yield curves, copolymerization was carried out in bulk by using a glass ampoule containing a fixed amount of the above mixture. After the desired polymerization time at a fixed temperature, the mixture, if soft, was swollen with chloroform containing 0.5 wt % of hydroquinone (HQ) at room temperature for 24 hr, to give an insoluble portion (crosslinked polyester); when the mixture was hard, it was broken up into small particles and extracted with chloroform containing 0.5 wt % of HQ in a Soxhlet apparatus for 3 hr, obtaining the insoluble portion, which was dried at 80°C. Meanwhile, the soluble portion, as a chloroform solution, was poured into benzene to precipitate unreacted polyester. The unreacted polyester was filtered, and the filtrate was poured into methanol to obtain poly-MMA, if present. However, PMMA was not obtained.

The resin boards for determining physical and other properties were prepared as follows. The mixtures to be cured were poured into molds consisting of two stainless boards, laminated with Teflon sheets, separated by a rubber gasket, and, after degasification, polymerized at fixed temperature for fixed periods.

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 (M scale) was determined according to ASTM-D 785-62.

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

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

RESULTS AND DISCUSSION

Synthesis of Metal-Containing Unsaturated Polyesters Having Pendent Methacrylate Groups

In the $(HEP-)_2M-PA-$ epoxide reactions in the previous study [5], DMF was used as solvent. On the other hand, the $(HEP-)_2M-MA-GMA$ reactions in the present study could be initiated without solvent, because MA has low melting point (52.8° C) and hence worked as solvent in the initial stages of the reaction. In the composition of the feeds investigated, the following molar ratios were selected: $(HEP-)_2M:MA:GMA = 1:4:4$ and $1:8:8$.

In the synthesis reaction of the polyesters, given amounts of $(HEP-)_2M$ and MA were first heated together at 110-130° C for 1-1.5 hr with stirring in a reaction vessel, giving a homogeneous mixture; in this case, most of the $(HEP-)_2M$ was considered to have reacted with the MA to form carboxyl-terminated adducts. Next, a fixed amount of GMA was gradually added dropwise into the mixture at 90-130° C. The reaction started immediately with the addition, accompanied by an exotherm. The reaction proceeded rapidly in the initial stages of reaction, due to the catalytic effect of metal carboxylate groups in $(HEP-)_2M$. As the reaction progressed, the viscosity of the mixture increased, and hence chloroform as solvent had to be added to the mixture to reduce the viscosity and the temperature;

without solvent, the viscosity was too great to permit the mixture to be stirred. Moreover, the viscosity increase was more marked in systems containing Mg than in those containing Ca. The addition of chloroform was started when about 10% of the amount of GMA to be used had been added in the case of the mixtures containing Mg, and about 30% in the case of those containing Ca. After about 2 hr the additions of GMA and chloroform were completed, and then the mixture was stirred at the reflux temperature (63° C) of chloroform. The viscosity of the system increased again as the reaction proceeded to completion. About 10-13 hr after the end of the addition of GMA, titration indicated that acidities and epoxide values approached zero.

The polyesterification in the present study is considered to proceed by the following main reactions as in the case of the previous study [5]: (1) the reaction of a carboxyl group with an epoxide group to produce an OH group; (2) the reaction of the OH group with an acid anhydride group to form a terminal carboxyl group; (3) the reaction of the acid anhydride group with an epoxide to form the ester linkage. It is advantageous that the metal carboxylate groups in $(HEP-)_2M$ catalyze this type of reaction. Moreover, homopolymerization of the epoxide as side reaction is not considered to have occurred, because acidity and epoxide values decreased at almost equal rates. On the other hand, in the $(HEP-)_2M$–PA–epoxide reactions in DMF in the previous study [5], epoxide homopolymerization occurred to slight degree.

Table 1 shows the results of the syntheses. The products (polyesters) were obtained by precipitation with diethyl ether; they were slightly yellow brown solids. The yields were generally high. Acidities were extremely small as compared to OH values, indicating that the polyesters are almost all OH-terminated. Further, it is apparent from the results of elemental analyses and bromine number determination that the polyesters obtained contain metal and pendent methacrylate groups. The molecular weights, as obtained by end-group analysis, ranged from 1546 to 2174; with increase in $(HEP-)_2M$ content in the feed the molecular weight of the polymer decreased. The GMA used was unsymmetrical, and undirected opening of the ring is considered to have occurred. Hence, the product must be a mixture of closely related stereoisomers.

Figure 1 shows the infrared spectra of the metal-containing unsaturated polyesters. They are essentially identical, having absorption bands at 3350-3550 cm^{-1} (OH stretching), about 1730 cm^{-1} (C=O stretching), 1630-1640 and 940 cm^{-1} (terminal vinyl group), 1580-1590 cm^{-1} (carboxylate group and phenyl ring), and 1400 cm^{-1} (carboxylate group). The weak band at about 1400 cm^{-1} due to the maleate group is considered to be hidden by the strong band of metal

TABLE 1. Synthesis of Metal-Containing Unsaturated Polyesters Having Pendent Methacrylate Groups by the $(HEP\text{-})_2M-MA-GMA$ Reactions

			Product							
								Found (calcd)		
Poly-ester	Metal M	Mole ratio of components in feed $(HEP\text{-})_2M$:MA:GMA	Yield (%)	OH value (eq/kg)	Acidity (eq/kg)	Ester value (calcd) (eq/kg)	Bromine number (calcd)	Mol wt[a]	C (%)	H (%)	M (%)
M-144	Mg	1 : 4 : 4	78	1.246	0.029	9.265 (9.975)	36.9 (45.6)	1546	52.13 (54.77)	4.65 (4.74)	1.80 (1.73)
M-188	Mg	1 : 8 : 8	70	0.928	0.010	10.421 (10.997)	47.2 (54.1)	2133	52.25 (54.86)	4.85 (4.86)	1.04 (1.03)
C-144	Ca	1 : 4 : 4	61	1.134	0.070	9.269 (9.864)	36.3 (45.0)	1662	51.55 (54.16)	4.35 (4.69)	2.85 (2.82)
C-188	Ca	1 : 8 : 8	81	0.874	0.046	10.242 (10.924)	50.7 (53.7)	2174	52.60 (54.50)	4.65 (4.83)	1.58 (1.68)

[a] Molecular weights were obtained by endgroup analysis.

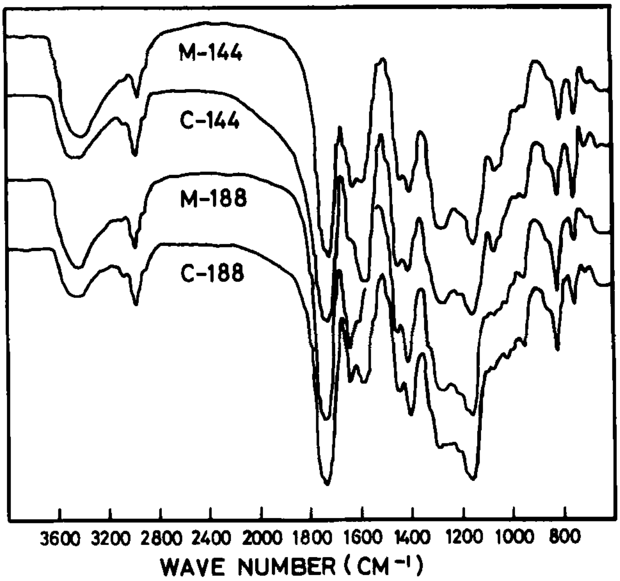


FIG. 1. Infrared spectra of metal-containing unsaturated polyesters.

carboxylate group. It is apparent from the spectra that the polyesters have ionic links in the molecule.

Figure 2 shows the TGA curves of the polyesters. They are thermally stable up to about 200° C, above which gradual weight loss begins, and remarkable weight loss occurs above about 320° C. The plateau observed above 550° C corresponds to the formation of MgO in case of the Mg salt and to the formation of $CaCO_3$ in case of the Ca salt. The DTA curves, although not shown here, showed exothermic peaks, among which the peak at about 500° C was very sharp, probably due to degradation occurring via oxidative modes. As is clear from Figure 2, the polyester of C-188 is thermally most stable.

As shown in Table 2, the metal-containing polyesters are soluble in chloroform, DMF, and THF and are insoluble in benzene, methanol, and diethyl ether.

Copolymerization

The polyesters M-144 and C-144 were immiscible with MMA and styrene. On the other hand, polyesters M-188 and C-188, although

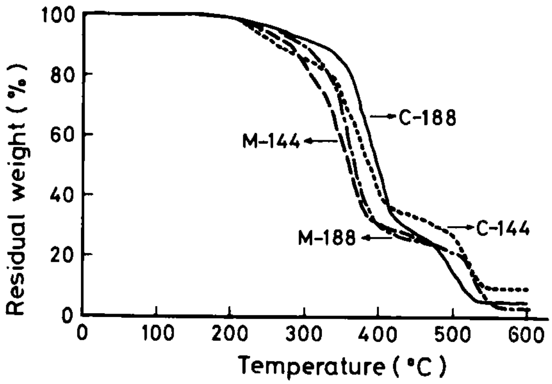


FIG. 2. TGA curves of metal-containing unsaturated polyesters.

immiscible with styrene, were miscible with MMA, giving homogeneous solutions suitable for copolymerization, in the range of M-188:MMA = 30:70 - 40:60 (wt. ratio) and C-188:MMA = 20:80 - 40:60. Therefore, these two polyesters were selected for the copolymerization with MMA.

Figure 3 shows the time-yield curves for the copolymerization of M-188 or C-188 with MMA. The copolymerization was accompanied with crosslinking reaction. During the whole course of the copolymerization, the formation of homopolymer of MMA (PMMA) was not detected. Therefore, in the present study, the yields of crosslinked polymers may be regarded as corresponding to conversion. The copolymerization proceeded fairly rapidly at 40° C, and the rates of copolymerization increased markedly as the concentration of the polyester in the mixture increased. This tendency is a phenomenon often observed in bulk polymerization; it is considered that, as the concentration of the polyesters which are polyfunctional compounds increases, the viscosity of polymerization system increases, so that the rate of polymerization increases by means of the so-called "gel effect." Moreover, mixtures containing more than 50 wt % polyester were too viscous to permit bulk copolymerization to be carried out. On the other hand, it was difficult to prepare solutions containing 20 wt % M-188, because the M-188 was not completely soluble in MMA below this concentration.

At 40 C, the yield of the systems with high polyester content reached nearly the maximum yield attainable after 9-10 hr, after which polymerization appeared to proceed no further. On the other

TABLE 2. Solubility Characteristics of Metal-Containing Unsaturated Polyesters Having Pendent Methacrylate Groups

Polyester	Solubility[a]							
	Chloroform	Acetone	DMF	Benzene	Ethyl acetate	THF	Methanol	Ethyl ether
M-144	+	±	+	-	-	+	-	-
M-188	+	+	+	-	±	+	-	-
C-144	+	±	+	-	-	+	-	-
C-188	+	±	+	-	±	+	-	-

[a] Solubility: (+) soluble; (±) partially soluble; (-) insoluble.

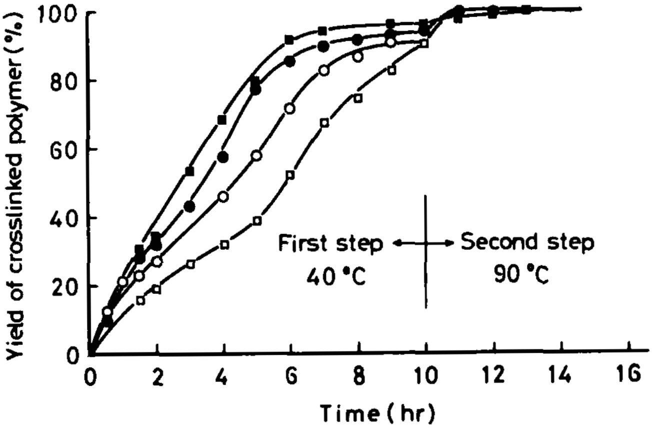


FIG. 3. Time-yield curves for the copolymerization of M-188 or C-188 with MMA: (○) M-188/MMA, (30/70); (●) M-188/MMA, (40/60); (□) C-188/MMA (20/80); (■) C-188/MMA, (40/60).

hand, when the concentration of polyester was lower, the yield did not reach the maximum yield. Successively, second-step polymerizations were carried out at 90 C; it was found that, in all cases, polymerization proceeded further and yield seemed to approach 100% within 1-3 hr. In all cases, the yields of crosslinked polymers immediately after gelation of the systems were 10-20%.

The fact that PMMA was not formed in the copolymerization is considered due to the high polyfunctionality of the polyesters and also the high copolymerizability of the polyesters with MMA. Thus, MMA is very effective as a crosslink carrier.

It is generally known that unsaturated polyesters generally have relatively poor copolymerization tendencies toward MMA. Therefore, the maleate groups in the polyesters in the present study can be considered to have taken very little part in the copolymerization with methacrylate groups. This may be expected also from the very large difference in the reactivity ratios in the copolymerization of diethyl maleate (M_1) with MMA (M_2); for example, $r_1 = 0$, $r_2 = 20$ at 60 C [9].

The copolymers obtained under the above-described polymerization conditions were transparent, hard materials.

TABLE 3. Physical Properties of Metal-Containing Cured Polyester Resins

		Physical properties					
Composition of resin (wt. ratio)	Viscosity before curing (cps)	Heat distortion temp (°C)	Tensile strength (kg/cm^2)	Flexural strength (kg/cm^2)	Rockwell hardness	Impact strength (kg-cm/cm)	Compressive strength (kg/cm^2)
M-188/MMA							
30/70	204	110	656	1228	110	1.54	1257
40/60	4670	109	537	1279	110	1.55	1270
C-188/MMA							
20/80	6	109	607	1141	109	1.55	1266
30/70	33	106	604	1221	109	1.47	1245
40/60	92	101	598	1139	110	1.49	1233

Physical Properties

The physical properties of the metal-containing cured polyester resins are summarized in Table 3, together with the viscosity data for the resin solutions before curing. The viscosity of the resin solutions increases markedly with increasing polyester content, that is, metal content, in the solution. In addition, it is of interest to note that the resin solutions containing Mg with the higher electronegativity show much higher viscosity than those containing Ca. Thus, the effect of introducing a metal on the viscosity is pronounced.

The resin solutions were cured under the following conditions to give resin boards for determining physical and other properties: room temperature for 15 hr, 40° C for 7 hr, 80° C for 5 hr, and 110° C for 2 hr.

The resins thus cured showed considerably higher HDT values than the metal-containing cured resins in previous studies [4, 6]. In the C-188/MMA resins, the HDT shows a tendency to decrease slightly with increasing the C-188 content.

The M-188/MMA (30/70) resin showed the highest tensile strength. In case of the C-188/MMA resins, tensile strength is not affected by resin composition as markedly as in case of the M-188/MMA resins.

The M-188/MMA resins showed slightly higher flexural strength values than the C-188/MMA resins did.

No wide variations by resin species or by resin composition were observed in Rockwell hardness, impact strength, or compressive strengths.

In general, the cured resins in the present study have excellent physical properties. The influence of the metal species on physical properties of the cured resins is small, while in the metal-containing cured resins in the previous study [6], Mg was generally more effective in improving physical properties than Ca, due to the larger interionic attraction of Mg^{2+}. In case of the cured resins in the present study, the crosslinking density due to covalent bonds is considered to be so high as to mask the effect of interionic attraction on physical properties.

Resistance to Chemical Attack

Table 4 shows resistance of metal-containing cured polyester resins to chemical attack. The resins were unaffected in external appearance by 30% H_2SO_4, 10% NaOH, 95% ethanol, 10% NaCl, benzene, and distilled water.

TABLE 4. Resistance of Metal-Containing Cured Polyester Resins to Chemical Attack

Reagent	Change in weight (%) and external appearance[a]				
	M-188/MMA (30/70)	M-188/MMA (40/60)	C-188/MMA (20/80)	C-188/MMA (30/70)	C-188/MMA (40/60)
30% H_2SO_4	+0.41 (UA)	+0.36 (UA)	+0.29 (UA)	+0.41 (UA)	+0.37 (UA)
10% NaOH	+0.38 (UA)	+0.27 (UA)	+0.31 (UA)	+0.26 (UA)	+0.11 (UA)
95% Ethanol	-0.06 (UA)	-0.23 (UA)	-0.01 (UA)	-0.05 (UA)	-0.18 (UA)
Acetone	+12.29 (SS)	+2.46 (UA)	+48.84 (CS)	+8.65 (SS)	+3.89 (UA)
$ClCH_2CH_2Cl$	+29.29 (SD)	+4.42 (UA)	– (DI)	+26.26 (SD)	+6.03 (UA)
10% NaCl	+0.67 (UA)	+0.75 (UA)	+0.01 (UA)	+0.63 (UA)	+0.59 (UA)
Benzene	+0.09 (UA)	+0.10 (UA)	+0.04 (UA)	+0.16 (UA)	+0.07 (UA)
Distilled water	+0.79 (UA)	+1.07 (UA)	+0.69 (UA)	+0.80 (UA)	+0.84 (UA)

[a] UA = Unaffected; SD = sample disintegrated slightly; DI = sample disintegrated; SS = sample was slightly swollen; CS = sample was considerably swollen.

TABLE 5. Boiling Water Resistance of Metal-Containing Cured Polyester Resins

Composition of resin (wt. ratio)	Metal in cured resin (%)	Change in thickness (%)	Change in weight (%)	External appearance[a]
M-188/MMA				
30/70	0.31	+0.93	+1.44	UA
40/60	0.42	+1.46	+1.66	UA
C-188/MMA				
20/80	0.32	+0.74	+1.04	UA
30/70	0.47	+0.91	+1.26	UA
40/60	0.63	+1.07	+1.28	UA

[a] UA = Unaffected.

The cured resins having the lower polyester contents were swollen by acetone, and disintegrated on contact with ethylene dichloride. The degrees of swelling and of disintegration became marked with decreasing polyester content, due to the decrease in crosslinking density. However, the M-188/MMA (40/60) and C-188/MMA (40/60) resins, i.e., the resins having the highest polyester content, showed high resistance to these reagents. On the other hand, cured resins in previous studies [4, 6] were disintegrated by acetone; such a tendency is often observed in the case of conventional polyester resins. In distilled water, weight gain showed a tendency to increase slightly with increase in the polyester content, namely, metal content.

Resistance to Boiling Water

Table 5 shows the boiling water resistance determined by immersing samples in boiling water for 2 hr. Water absorption and change in thickness increased with increase in the polyester content, namely, metal content. In addition, the cured resins containing Mg showed considerably higher water absorption than did those containing Ca. The external appearance of none of the cured resins was affected by boiling water. Generally, the above resins have better boiling water

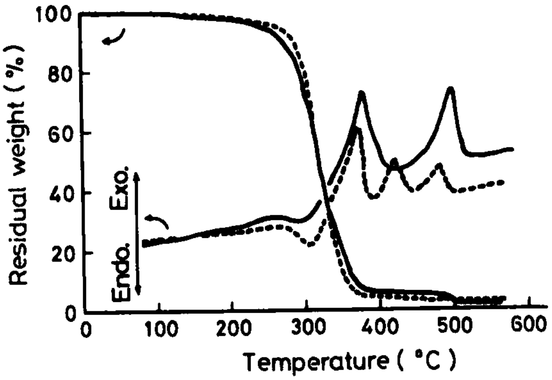


FIG. 4. TGA and DTA curves of metal-containing cured polyester resins: (——) M-188/MMA, 30/70; (- -) C-188/MMA, (20/80).

resistance than the cured resins in the previous studies [4, 6], which became slightly white or white on the surface.

Thermal Behavior

Figure 4 shows representative TGA and DTA curves in air of the cured resins. The DTA curves show two or three exothermic peaks, probably due to degradations occurring via oxidative modes. In the TGA curves, a marked weight loss begins above about 280° C, and the temperature of 50% weight loss is 320° C. The plateau observed above about 500° C corresponds to the formation of MgO in the case of Mg and to the formation of $CaCO_3$ in the case of Ca. As is obvious on comparing Figs. 2 and 4, the metal-containing unsaturated polyesters are thermally more stable than the cured resins.

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