# Preparation and Copolymerization of Polyvalent Metal Salts of Ethyleneglycol–Methacrylate–Phthalate

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Synopsis

Preparation of polyvalent metal salts of ethyleneglycol–methacrylate–phthalate (EMP) was investigated by the reaction of the Na salt of EMP and chlorides of polyvalent metals such as Al^{3+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Co^{2+}, and Cu^{2+}. It was found that, among the metal salts obtained, the Cr salt could be obtained in the form of $(EMP—)_2$-Cr(OH) in high purity and good yield where EMP— means EMP residue: $(EMP—)_2$-

$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-COOCH_2CH_2OOC\underset{\bigcirc}{}COO$$
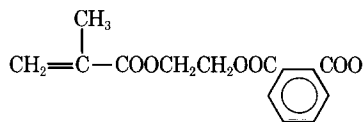
Cr(OH) is soluble in chief organic solvents and vinyl monomers such as styrene (St) and MMA. $(EMP—)_2$Cr(OH) was then copolymerized with St and MMA. As for the physical properties of the copolymers obtained, heat distortion temperature, compressive strength, and Rockwell hardness were generally improved by introducing $(EMP—_2)$Cr-(OH) into the polymers. Tensile strength, flexural strength, and impact strength were also improved by selecting the most suitable concentration of $(EMP—)_2$Cr(OH) according to the species of vinyl monomers. Moreover, the physical properties of $(EMP—)_2$Cr(OH)–MMA copolymers are generally superior to those of $(EMP—)_2$Cr-(OH)–St copolymers. TGA and boiling water resistance of the copolymers were also discussed.

INTRODUCTION

In recent years, there have been many studies[1] on polymers ionically crosslinked by metal ions; and such polymers have attracted fair interest from scientific and industrial standpoints. Usually, most of the ionically crosslinked polymers have been prepared by the following method: First, a base polymer containing a functional group capable of forming an ionic crosslink, such as a carboxylic acid group at a side chain, is prepared and then the polymer is neutralized with metal salts. On the other hand, except for our previous paper[2] there are few reports about the one-step-preparation of ionically crosslinked polymers by copolymerization of a polymerizable monomer already containing an ionic bond with vinyl monomers. In the previous report,[2] divalent metal salts (I) of ethyleneglycol–methacrylate–phthalate (EMP) were prepared as the polymerizable

monomers containing an ionic bond, and these salts were copolymerized
with other vinyl monomers and the chief properties of copolymers obtained
were discussed. From this investigation, interesting results were obtained.
The divalent metals used in the previous report were Mg, Ca, Zn, Cd, Ba,
and Pb:

$$(CH_2\!=\!\underset{\underset{CH_3}{|}}{C}\!-\!COOCH_2CH_2OOC\!-\!\!\!\bigcirc\!\!\!-\!COO)_2M$$

I

where M = divalent metal.

In the present study, extending the species of metals further to other
polyvalent metals such as Al^{3+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Co^{2+}, and Cu^{2+}, we in-
vestigated metalation of EMP by these polyvalent metals and found that
the Cr salt could be obtained in high purity and good yield. So the Cr
salt obtained was copolymerized with other vinyl monomers and chief
properties of copolymers obtained were discussed.

EMP can be prepared easily by the addition reaction of commercially
available hydroxyethyl methacrylate (HEMA) and phthalic anhydride.
By the reaction of Na salt of EMP and chlorides of polyvalent metals,
preparation of polyvalent metal salts of EMP was investigated. MMA
and styrene (St) were used as vinyl monomers.

EXPERIMENTAL

EMP was prepared by the addition reaction of HEMA and phthalic
anhydride, according to the method reported in the previous paper;[2] the
acid value was 193.2 (calcd. 191.7).

Preparation of Polyvalent Metal Salts of EMP

Preparation of Al, Cr, Fe, Ni, and Co Salts. To a three-necked flask in
which 100 g of EMP was placed was added dropwise a solution of an
equivalent amount of Na_2CO_3 dissolved in 100 g water with stirring at
room temperature, to obtain the Na salt. To the aqueous solution of the
Na salt of EMP so prepared, a solution of fixed amount of metal chloride
($AlCl_3 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot$
$2H_2O$) dissolved in 100 g of water with stirring at room temperature was
added dropwise. When the mixture became partially solid, 30 g chloro-
form was added to dissolve the solid. After the addition, stirring was con-
tinued for 40 min, and then 170 g chloroform was added to the mixture
with stirring to extract the product. After the separation of the organic
and the aqueous layers, 200 g 8% aqueous solution of $NaHCO_3$ was added
for neutralization to the organic layer (the extracted mixture). After
neutralization, the organic layer was separated and washed with water
several times to remove excess alkali.

TABLE I
Synthesized Metal Salts of EMP

Metal	Expt. no.	Mole ratio of reactants	Method of treatment	Yield,[a] g	External appearance	Metal, %	
						Found	Calcd.
Al	1	$EMP/AlCl_3 \cdot 6H_2O = 2$	A	84	slightly yellow, glassy material	5.67	7.98 for (EMP—)$Al(OH)_2$, 4.51 for (EMP—)$_2$Al(OH), 3.14 for (EMP—)$_3$Al
	2	$EMP/AlCl_3 \cdot 6H_2O = 2$	B	69	white powder	6.37	
	3	$EMP/CrCl_3 \cdot 6H_2O = 3$	A	74	deep-blue glassy material	7.64	14.32 for (EMP—)$Cr(OH)_2$, 8.34 for (EMP—)$_2$Cr(OH), 5.89 for (EMP—)$_3$Cr
Cr	4	$EMP/CrCl_3 \cdot 6H_2O = 3$	B	66	deep-blue powder	8.27	
	5	$EMP/CrCl_3 \cdot 6H_2O = 2$	B	65	deep-blue powder	8.33	
	6	$EMP/CrCl_3 \cdot 6H_2O = 2$	A	73	deep-blue, glassy material	7.52	
Fe	7	$EMP/FeCl_3 \cdot 6H_2O = 2$	B	69	light-brown powder	12.45	15.21 for (EMP—)$Fe(OH)_2$, 8.90 for (EMP—)$_2$Fe(OH), 6.29 for (EMP—)$_3$Fe
	8	$EMP/FeCl_3 \cdot 6H_2O = 2$	A	73	brown, glassy material	10.15	
Ni	9	$EMP/NiCl_2 \cdot 6H_2O = 2$	B	47	slightly green powder	17.37	16.63 for (EMP—)Ni(OH), 9.57 for (EMP—)$_2$Ni
	10	$EMP/NiCl_2 \cdot 6H_2O = 2$	A	64	green, glassy material	13.61	
Co	11	$EMP/CoCl_2 \cdot 6H_2O = 2$	B	43	slightly pink powder	19.31	16.69 for (EMP—)Co(OH), 9.61 for (EMP—)$_2$Co
	12	$EMP/CoCl_2 \cdot 6H_2O = 2$	A[b]	62	pink, glassy material	16.12	
Cu	13	$EMP/CuCl_2 \cdot 2H_2O = 2$	c	75	green, glassy material	10.21	17.76 for (EMP—)Cu(OH), 10.28 for (EMP—)$_2$Cu

[a] EMP amount used 100 g.
[b] Synthesized in methanol.
[c] Synthesized in methanol and crystallized without alkali ($NaHCO_3$) treatment.

The organic layer thus obtained was treated by the following two methods to obtain the product: (A) The chloroform was removed by distillation under reduced pressure from the organic layer to yield the product. (B) The product obtained in A was dissolved in acetone, and then the solution was added dropwise to a great quantity of vigorously stirred water, precipitating the product. The product was dried in vacuo at 40°C.

The symbols A and B in Table I refer to, the methods of treatment mentioned above. Moreover, when the reaction was carried out in methanol, the procedure was based upon the one mentioned above. However, in this case, to the methanol solution of the Na salt of EMP was added dropwise a fixed amount of metal chloride dissolved in methanol with stirring at 45°C for 30 min, and then the stirring was continued for another 2 hr. After the reaction, the methanol was removed by distillation under reduced pressure, and then the product was dissolved in chloroform. The solution was then treated in the same way as mentioned above.

Preparation of the Cu Salt. A solution of 100 g EMP in 100 g methanol was added dropwise into a solution of an equivalent amount of Na_2CO_3 in 60 g methanol with stirring at 50°C, to yield the Na salt. To the methanol solution of the Na salt of EMP so prepared, a solution of fixed amount of $CuCl_2 \cdot 2H_2O$ in 90 g of methanol was added dropwise with stirring at 50°C. After the addition, the stirring was continued for 30 min, and then the mixture was filtered to remove NaCl (by-product). Upon standing, the product was separated as green crystals from the filtrate, washed with 350 g water–methanol (3/1) mixture, and dried. The bromine numbers of the products were determined according to the bromination method.[3]

Copolymerization of Cr Salt with Vinyl Monomers

The ampoule polymerization for determining the conversion in the copolymerization of the Cr salt with MMA and St were carried out according to the usual method.

The method of preparation of resin boards for determining the physical properties was as follows: To the mixture of Cr salt and vinyl monomers, 0.5 wt-% of 60% dimethyl phthalate solution of methyl ethyl ketone peroxide (MEKPO) and 0.5 wt-% of 10% styrene solution of cobalt naphthenate were added. After the atmosphere was replaced by nitrogen, the mixture was poured into molds consisting of two stainless boards laminated with Teflon sheets, separated by a rubber gasket, and, after degassification, polymerized at a fixed temperature for a fixed period.

MMA and St of chemically pure grade were used without further purification.

Determination of Physical Properties

Heat distortion temperature (HDT) was determined in accordance with ASTM-D 648-56. Tensile strength was determined in accordance with ASTM-D 638-64 T. Flexural strength was determined in accordance with ASTM-D 790-63. Compressive strength was determined in accordance

with ASTM-D 695-63 T. Impact strength was determined in accordance with ASTM-D 256-56 (with Izod notch). Rockwell hardness was determined in accordance with ASTM-D 785-62 (M scale).

Thermogravimetric Analyses

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

RESULTS AND DISCUSSION

Preparation of Polyvalent Metal Salts of EMP

Table I summarizes the preparation of the polyvalent metal salts of EMP. "Yield" is expressed by "gram" (weight) of product obtained from 100 g EMP. Hereafter, EMP residue will be denoted by EMP—.

The preparation of polyvalent metal salts of EMP in the present study was investigated by the reaction of the Na salt of EMP and chlorides of polyvalent metals. The reaction proceeded generally in aqueous solution. Since in the reaction in aqueous solution the mixture often became partially solid which made stirring difficult, it was necessary to add small quantities of chloroform to dissolve the solid. After the reaction, chloroform was added to the mixture to extract the product. When the organic layer was treated with aqueous solution of $NaHCO_3$, carbon dioxide evolved. The organic layer washed with water after alkali treatment is considered to consist of chloroform and the products. The products could be obtained by treating the organic layer according to method A or B mentioned above.

In case of the Al salt, the found values of metal content did not agree with any of the calculated values. The products are considered to be a mixture of (EMP—)Al(OH)$_2$ and (EMP—)$_2$Al(OH). In case of the Cr salt, the found values of metal content of the products obtained by method B agreed well with the calculated value for (EMP—)$_2$Cr(OH), regardless of the mole ratios of the reactants. On the other hand, the products obtained by method A are considered to be a mixture of (EMP—)$_2$Cr(OH) and (EMP—)$_3$Cr, judging from the found values of metal content. In case of the Fe salt, the found values of metal content did not agree with any of the calculated values. The products are considered to be a mixture of (EMP—)Fe(OH)$_2$ and (EMP—)$_2$Fe(OH). In case of the Ni salt, the found value of metal content of the product obtained by method B agreed considerably well with the calculated value for (EMP—)Ni(OH). The product obtained by method A is considered to be a mixture of (EMP—)-Ni(OH) and (EMP—)$_2$Ni, judging from the found value of metal content. In case of the Co salt, the found value of metal content of the product obtained by method B did not agree with any of the calculated values. However, the found value of metal content of the product obtained by method A after being synthesized in methanol agreed well with the calculated value for (EMP—)Co(OH). In case of the Cu salt, the synthetic re-

TABLE II
Analysis of Synthesized Cr and Cu Salts of EMP

Metal salt	Calcd. for	C, %	H, %	M, %[a]	Bromine no.
Cr salt (no. 4)		53.29	4.85	8.27	53
	(EMP—)Cr(OH)$_2$	46.29	4.16	14.32	44
	(EMP—)$_2$Cr(OH)	53.93	4.36	8.34	51
	(EMP—)$_3$Cr	57.08	4.45	5.89	54
Cu salt (no. 13)		52.03	4.75	10.21	36
	(EMP—)Cu(OH)	46.99	3.94	17.76	45
	(EMP—)$_2$Cu	54.41	4.24	10.28	52

[a] M = Metal.

action was carried out in methanol. Since the product crystallized from methanol after the reaction, it was possible to separate the product. The found value of metal content of the product agreed well with the calculated value for (EMP—)$_2$Cu.

The products obtained by method A were glassy materials, and those obtained by method B were powders. Among the metal salts obtained, the Cr salt and the Cu salt were considered to contain two EMP residues per molecule. The Cr salt (no. 4) and the Cu salt (no. 13) were then analyzed, and the analytical data are shown in Table II. In case of the Cr salt, the found values of elemental analysis and bromine number agreed well with the calculated values for (EMP—)$_2$Cr(OH). In case of the Cu salt, the found bromine number was considerably lower than the calculated value for (EMP—)$_2$Cu. Moreover, in the infrared spectra of the Cr salt, an absorption band about 1550 cm^{-1} which is characteristic of carboxylate and cannot be seen in case of EMP was observed, and, in addition, absorption bands about 1620 and 940 cm^{-1} which are characteristic of the terminal vinyl group were observed.

The Cr salt obtained are soluble in chief organic solvents such as benzene, chloroform, acetone, dioxane, and ethyl acetate, and in vinyl monomers such as St, MMA, and HEMA.

In summary, it was found that, among the above metal salts, the Cr salt can be obtained in the form of (EMP—)$_2$Cr(OH) in high purity and good yield.

Therefore, copolymerizations of Cr salt with St and MMA were carried out. The Cr salt used in the copolymerization was prepared in experiment no. 4 in Table 1. The Cr salt will be denoted hereafter by (EMP—)$_2$Cr-(OH).

Copolymerization

Since (EMP—)$_2$Cr(OH) is soluble in St and MMA, homogeneous compositions for copolymerization could be obtained. Figure 1 shows the time–conversion curves for the copolymerization of (EMP—)$_2$Cr(OH)–MMA and (EMP—)$_2$Cr(OH)–St. The first step of the polymerization was
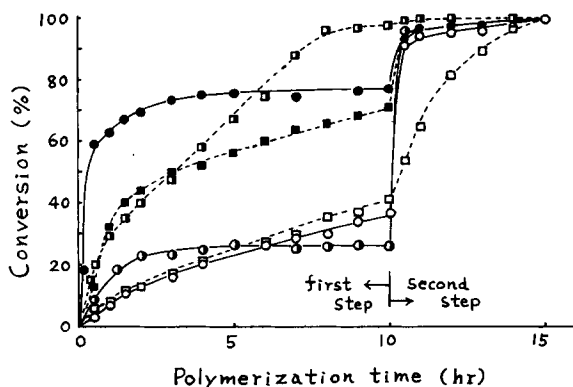
Fig. 1. Time–conversion curves for the copolymerization of (EMP—)$_2$Cr(OH)–vinyl monomer: (○) (EMP—)$_2$Cr(OH) 10 wt-%, MMA 90 wt-%; (◐) (EMP—)$_2$Cr(OH) 30 wt-%, MMA 70 wt-%; (●) (EMP—)$_2$Cr(OH) 50 wt-%, MMA 50 wt-%; (□) (EMP—)$_2$- Cr(OH) 10 wt-%, St 90 wt-%; (◧) (EMP—)$_2$Cr(OH) 30 wt-%, St 70 wt-%; (■) (EMP—)$_2$Cr(OH) 50 wt-%; St 50 wt-%. First step polymerization: 55°C, 10 hr, second step polymerization: 100°C (except EMP—)$_2$Cr(OH)(10 wt-%)—St (90 wt-%) system, whose second step polymerization temperature was 90°C), 5 hr.

carried out at 55°C, for 10 hr. In the (EMP—)$_2$Cr(OH)–MMA system, the initial rate of polymerization increased as the concentration of (EMP—)$_2$Cr(OH) increased; however, the conversion after 10 hr is not always proportional to the concentration of (EMP—)$_2$Cr(OH). Although the conversions at 30% and 50% (EMP—)$_2$Cr(OH) reached the maximum attainable after about 5 hr, the conversion at 10% (EMP—)$_2$Cr(OH) continued to increase even after 10 hr. In the copolymerization of MMA with the divalent metal salts in the previous report,[2] the rates of polymerization and the maximum conversions attainable were very high. However, in the (EMP—)$_2$Cr(OH)–MMA system, the maximum conversion attainable was no more than 77% even at the high concentration of 50% (EMP—)$_2$Cr(OH). On the other hand, in the (EMP—)$_2$Cr(OH)–St system, the conversion at 30% (EMP—)$_2$Cr(OH) reached 98% after 10 hr, but that at the high concentration of 50% (EMP—)$_2$Cr(OH) was no more than 70% even after 10 hr. As mentioned above, the conversions generally did not reach high values at 55°C for 10 hr. Next, the second-step polymerizations were carried out at 100°C, except that the second-step polymerization of the (EMP—)$_2$Cr(OH)–St system containing 10% (EMP—)$_2$- Cr(OH) was carried out at 90°C; as a result, it was found that the conversions reached maximum conversion attainable after 5 hr.

In all cases, the observed gelation of polymerization systems occurred at 10–20% conversion. Moreover, at the beginning of polymerization the copolymer obtained contained a large quantity of chloroform-soluble part, but as the conversion increased the chloroform-soluble part decreased markedly and became negligible above 25% conversion. The copolymers obtained were deep blue, hard materials.

According to the results of copolymerization mentioned above, the polymerization condition for obtaining samples for determining physical properties was set up as follows: 55°C for 15 hr, 80°C for 3 hr, 100°C for 5 hr, and 110°C for 2 hr.   For the very slow polymerization systems containing 5% (EMP—)₂Cr(OH), 55°C for 40 hr, 80°C for 3 hr, 100°C for 5 hr, and 110°C for 2 hr.

Physical Properties of Copolymers

HDT.   As shown in Figure 2, in the copolymers of (EMP—)₂Cr(OH)–MMA, HDT increases gradually with increase of (EMP—)₂Cr(OH); for instance, about 10°C increase is observed at 20% (EMP—)₂Cr(OH).   On the other hand, in the copolymers of (EMP—)₂Cr(OH)–St, an approximate 5°C increase in HDT is observed in the region of 5–15% (EMP—)₂Cr(OH); however, HDT decreases at 20% (EMP—)₂Cr(OH).

Tensile Strength.   As is clear from Figure 2, in the copolymers of (EMP—)₂Cr(OH)–MMA, tensile strength reaches peak of 800 kg/cm² at 10% (EMP—)₂Cr(OH).   On the other hand, in the copolymers of (EMP—)₂Cr(OH)–St, a slight increase in tensile strength is observed at 5% (EMP—)₂Cr(OH); however, above 10% (EMP—)₂Cr(OH), tensile strength decreases with increase in (EMP—)₂Cr(OH).

Rockwell Hardness.   As shown in Figure 3, in the copolymers of (EMP—)₂Cr(OH)–MMA, the Rockwell hardness reaches a peak of 110.5 at 10% (EMP—)₂Cr(OH).   In the copolymers of (EMP—)₂Cr(OH)–St, Rockwell hardness increases almost linearly with increase in (EMP—)₂Cr-(OH), and in this case the effect of introducing (EMP—)₂Cr(OH) is apparent.
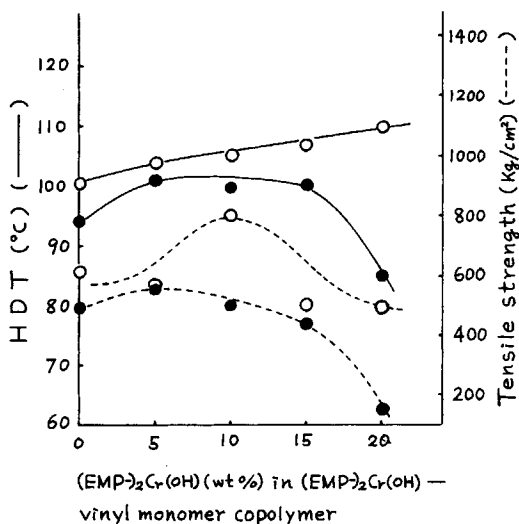
Fig. 2.   Effect of (EMP—)₂Cr(OH) on HDT and tensile strength of (EMP—)₂Cr(OH)–vinyl monomer copolymer: (O) (EMP—)₂Cr(OH)–MMA;   (●) (EMP—₂)Cr(OH)–St.
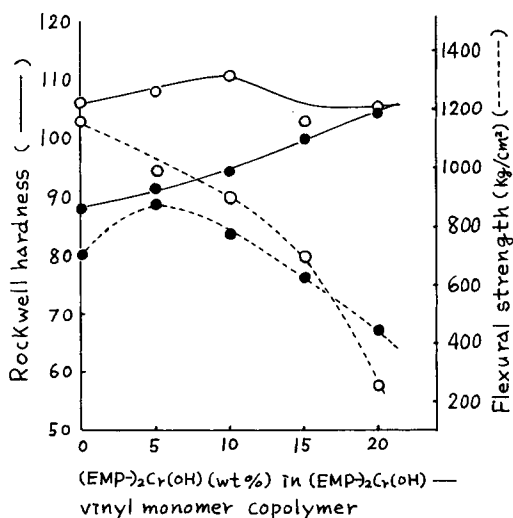
Fig. 3. Effect of (EMP—)₂Cr(OH) on Rockwell hardness and flexural strength of (EMP—)₂Cr(OH)-vinyl monomer copolymer: (O) (EMP—)₂Cr(OH)–MMA; (●) (EMP—)₂Cr(OH)–St.
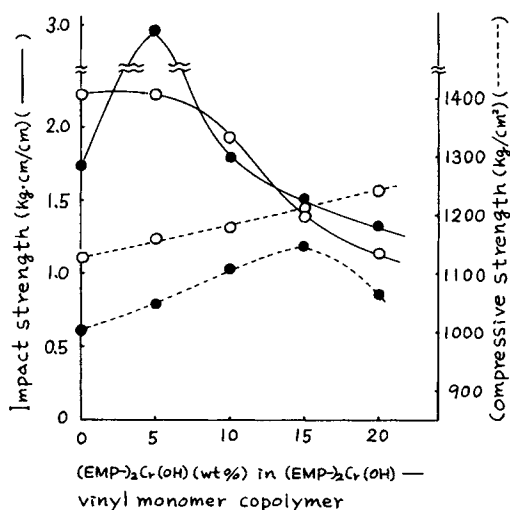
Fig. 4. Effect of (EMP—)₂Cr(OH) on impact strength and compressive strength of (EMP—)₂Cr(OH)-vinyl monomer copolymer: (O) (EMP—)₂Cr(OH)–MMA; (●) (EMP—)₂Cr(OH)–St.

Flexural Strength. As is clear from Figure 3, in the copolymers of (EMP—)₂Cr(OH)–MMA, flexural strength decreases markedly with increase in (EMP—)₂Cr(OH). On the other hand, in the copolymers of (EMP—)₂Cr(OH)–St, flexural strength reaches peak at 5% (EMP—)₂Cr-(OH), at which a 170 kg/cm² increase is observed.

Impact Strength. As shown in Figure 4, in the copolymers of (EMP—)₂-Cr(OH)–MMA, above 5% (EMP—)₂Cr(OH), impact strength decreases

with increase in (EMP—)$_2$Cr(OH). On the other hand, it is noteworthy that, in the copolymers of (EMP—)$_2$Cr(OH)–St, impact strength reached a peak of 2.96 kg·cm/cm at 5% (EMP—)$_2$Cr(OH). Such a tendency was not observed in the previous copolymers containing St.[2]

Compressive Strength. As is clear from Figure 4, in the copolymers of (EMP—)$_2$Cr(OH)–MMA, compressive strength increases linearly with increase in (EMP—)$_2$Cr(OH); for instance, a 110 kg/cm^2 increase in compressive strength was observed at 20% (EMP—)$_2$Cr(OH). In the copolymers of (EMP—)$_2$Cr(OH)–St, compressive strength reached a peak at 15% (EMP—)$_2$Cr(OH), at which a 140 kg/cm^2 increase in compressive strength was observed. In compressive strength, the effect of introducing (EMP—)$_2$Cr(OH) is clearly apparent.

In summary, the following may be concluded. Generally, HDT, Rockwell hardness, and compressive strength can be improved by introducing (EMP—)$_2$Cr(OH) into the polymers, and tensile strength, flexural strength, and impact strength are also improved by selecting the most suitable concentration of (EMP—)$_2$Cr(OH) according to the species of vinyl monomers. Moreover, the physical properties of (EMP—)$_2$Cr(OH)–MMA copolymers are generally superior to those of (EMP—)$_2$Cr(OH)–St copolymers.

TGA

Figure 5 shows the TGA curves for representative copolymers. The decomposition temperature was defined, as described in the previous report,[2] as the intersection of the two lines drawn on the curve before and after the major change in slope. The temperatures at 50% loss at which considerable weight loss occurred were also determined. The copolymer of (EMP—)$_2$Cr(OH)–MMA and blank polymer (poly-MMA) showed decomposition temperatures of 250°C and 270°C, respectively, and temperatures of 279°C and 320°C, respectively, at 50% loss. The copolymer of (EMP—)$_2$Cr(OH)–St and blank polymer (poly-St) showed

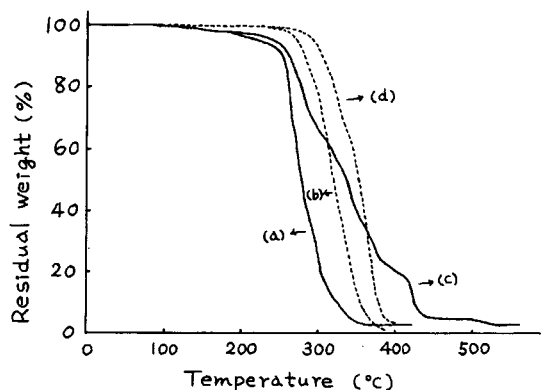Fig. 5. TGA curves of polymer obtained: (a) (EMP—)$_2$Cr(OH) (20 wt-%)–MMA; (b) poly-MMA; (c) (EMP—)$_2$Cr(OH) (20 wt-%)–St; (d) poly-St.

decomposition temperatures of 250°C and 292°C, respectively, and temperatures of 336°C and 352°C, respectively, at 50% loss.   From this, it is apparent that the copolymers containing (EMP—)$_2$Cr(OH) are thermally inferior to those not containing (EMP—)$_2$Cr(OH).

On the other hand, in the previous report[2] it was observed that introducing (EMP—)$_2$Zn into the MMA–HEMA copolymer increased thermal stability.

Boiling Water Resistance

The samples were immersed in boiling water for 30 hr.   The change of state was observed visually.   Copolymers of (EMP—)$_2$Cr(OH)–MMA showed no change, except for the 5% (EMP—)$_2$Cr(OH)-containing copolymer, the surface of which became white a little.   Blank polymer (poly-MMA) showed no change.   Similarly, the copolymers of (EMP—)$_2$Cr(OH)–St showed no change, except for the 5% (EMP—)$_2$Cr(OH)-containing copolymer, the surface of which became somewhat white.   In the blank polymer (poly-St), the surface became white.

On the other hand, at room temperature, none of the samples showed any change at all in water.

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