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### Preparation and Copolymerization of Methacrylate-Terminated Ionic Liquid Rubbers

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## Preparation and Copolymerization of Methacrylate-Terminated Ionic Liquid Rubbers

HIDEAKI MATSUDA

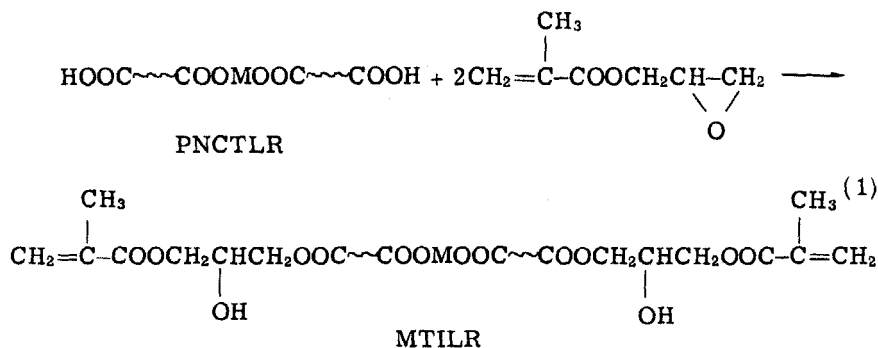
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### ABSTRACT

Preparation of methacrylate-terminated ionic liquid rubbers (MTILR) was investigated by the addition reaction of partially neutralized carboxyl-terminated liquid rubbers (PNCTLR) with glycidyl methacrylate. The PNCTLR were prepared from a polymer of butadiene (BD) (Hycar CTB 2000X162) and a copolymer of BD-acrylonitrile (Hycar CTBN 1300X8) by partial neutralization with MgO and CaO. The metal carboxylate groups of PNCTLR catalyzed the reaction. The Mg carboxylate group showed higher catalytic activities than the Ca carboxylate group. The MTILR obtained were copolymerized with styrene. The novel ionic copolymers obtained were evaluated for their physical properties. The copolymers containing Mg showed better physical properties than their reference copolymers not containing ionic links, an effect of introducing metal. The Ca-containing copolymers showed poor physical properties, probably due to lower interionic attraction of  $\text{Ca}^{2+}$ , to heterogeneity of the systems, and to lower overall cross-linking densities. Resistance to water and chemical attack, thermal behavior, and stress relaxation are also discussed.

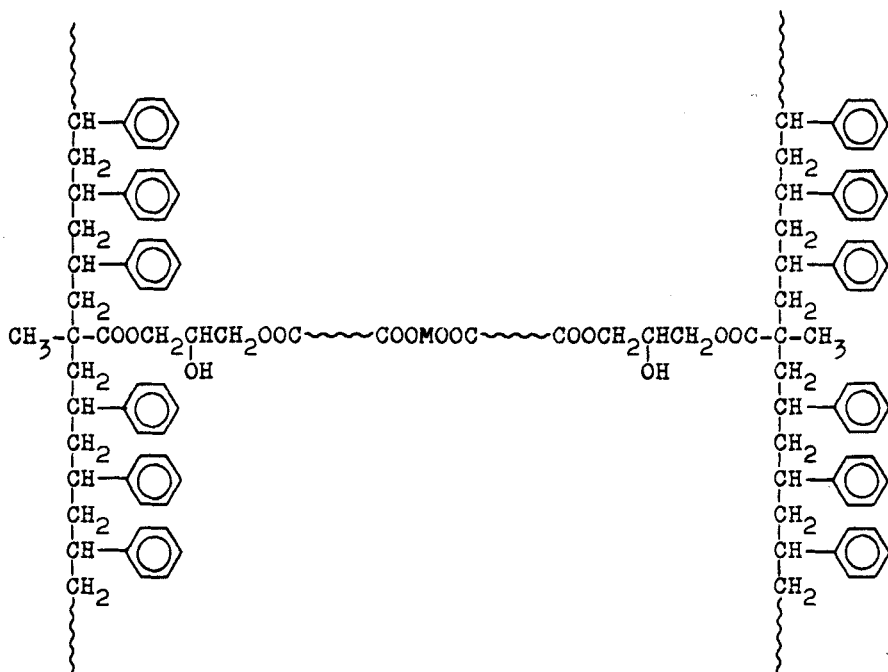
## INTRODUCTION

Recently, carboxyl-terminated liquid rubbers have attracted considerable interest from scientific and industrial standpoints. While complete neutralization of terminal carboxyl groups of liquid rubbers is difficult because of the low reactivities of the carboxyl groups toward metal ions [1], partial neutralization is comparatively easy [2, 3]. Partially neutralized carboxyl-terminated liquid rubbers (PNCTLR) are useful starting materials for the preparations of ionic rubbers into which metal is firmly incorporated. We have previously studied the preparation and properties of ionic cured rubbers by cross-linking (curing) of PNCTLR with anhydride and bisepoxide [2-4]. More recently we have reported chain extension of PNCTLR with bisepoxide [5]. In the present study the preparation of methacrylate-terminated ionic liquid rubbers (MTILR) was investigated by the addition reaction of PNCTLR with glycidyl methacrylate (GMA) as shown by



where M = Mg or Ca.

The carboxyl-terminated liquid rubbers used to prepare PNCTLR were a polymer of butadiene (BD) (Hycar CTB 2000X162) and a copolymer of BD-acrylonitrile (Hycar CTBN 1300X8). The MTILR obtained from them were copolymerized with styrene (St). The novel ionic copolymers obtained were evaluated for physical and other properties. They are considered to consist of the following two main blocks: a soft block based on MTILR and a hard block based on poly-St. The idealized main structure of the ionic copolymers obtained in the present study may be represented as



## EXPERIMENTAL

### Materials

The carboxyl-terminated liquid rubbers Hycar CTB 2000X162 and Hycar CTBN 1300X8 (B.F. Goodrich Chemical Co. products) were the same as those used in the previous studies [4, 5]. The PNCTLR from them were prepared by the same method as in a previous paper [2]. The degree of neutralization of the PNCTLR was 50%. A coded system for the PNCTLR will be used in this study. For example, CTB(0.5Mg) indicates that CTB 2000X162 was neutralized with MgO to the degree of neutralization equal to 50%. The acid values were 0.1874 equiv/kg for CTB(0.5Mg), 0.1864 equiv/kg for CTB(0.5Ca), 0.2690 equiv/kg for CTBN(0.5Mg), and 0.2609 equiv/kg for CTBN(0.5Ca).

Glycidyl methacrylate (GMA) was purified by distillation. Styrene (St) was a guaranteed reagent and was used as received.

## Preparation of Methacrylate-Terminated Ionic Liquid Rubbers (MTILR)

Into a 500-mL separable flask equipped with a stirrer, a thermometer, and a condenser were placed PNCTLR and GMA at a mole ratio of 1:14. 0.1 wt% of hydroquinone monomethyl ether as a polymerization inhibitor was added. The mixture was stirred at a fixed temperature. Samples were taken during reaction for analysis of acid. After the reaction the mixture was dissolved in chloroform-methanol (10:1) and the solution was poured into a large quantity of stirred methanol to precipitate the product. The product was washed with methanol and dried in vacuo at 50–55°C.

The same method was applied to prepare reference methacrylate-terminated liquid rubbers (MLTR) without ionic links. In this case, N,N-dimethylbenzylamine (DMBA) was used as the catalyst (0.5 wt% based on the total weight of reactants) and the products were purified by reprecipitation from chloroform solution in methanol.

## Copolymerization

In the copolymerization of MTILR or MLTR with St, 0.8 wt% of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (DBPH) was used as the initiator.

The mixtures to be copolymerized, which had been heated at 70°C for 3–7 h, were poured into molds and copolymerized under the following conditions: 70°C for 17 h, 90°C for 4 h, and 120°C for 4 h. The molds were kept in an atmosphere of nitrogen during copolymerization.

## Analytical Methods

Determination of acid values and infrared (IR) spectra, thermogravimetric analyses (TGA), and differential thermal analyses (DTA) were carried out by the same methods as in a previous paper [2].

## Determination of Physical and Other Properties

Tensile strength and elongation at break were determined by the same method as in previous papers [1, 2] at 23°C [relative humidity (RH) = 50%]. The samples were aged before testing for 24 h at 23°C in a room at 50% RH.

The effects of water on weight change and physical properties, and the resistance to chemical attack were determined by the previously reported methods [2].

Tear strength was determined using a Shimadzu Autograph IS-5000 at a strain rate of 100 mm/min.

Shore A or D hardness was determined using UF. Shore's durometer type A or D (Kamishima Seisakusho Co.) at 23°C (RH = 50%).

Stress relaxation was determined as follows: Dumbbell-shaped specimens of JIS Z 1702 were strained to 50% using the above autograph at a strain rate of 100 mm/min. The strained specimens were allowed to stand for 3 min, followed by determination of the initial stress. The stress was recorded continuously.

## RESULTS AND DISCUSSION

### Preparation of MTILR and MTLR

Figure 1 shows the addition reaction of PNCTLR with GMA in terms of conversion of acid. It is advantageous for the metal carboxylate groups in PNCTLR to catalyze this type of reaction [5]. The reactions of the systems containing Mg proceeded much more rapidly than those of the systems containing Ca, although the temperatures of the former systems were lower than those of the latter systems, indicating that Mg has a considerably higher catalytic activity than Ca toward this addition reaction. The difference in reactivity between the CTB and CTBN series was small. The viscosity of the system increased as the reaction proceeded, and in the latter stages of the reaction it was difficult to stir the system smoothly. Etherification of epoxide was considered negligible [5, 6].

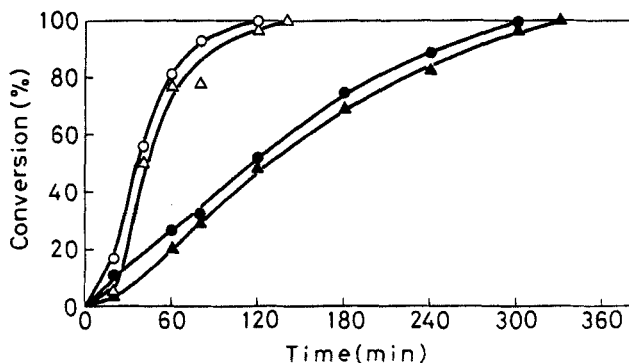


FIG. 1. Reaction of PNCTLR with GMA. (○) CTB(0.5Mg)-GMA at 70°C; (●) CTB(0.5Ca)-GMA at 80°C; (△) CTBN(0.5Mg)-GMA at 70°C; (▲) CTBN(0.5Ca)-GMA at 80°C. Feed mole ratio of PNCTLR: GMA = 1:14.

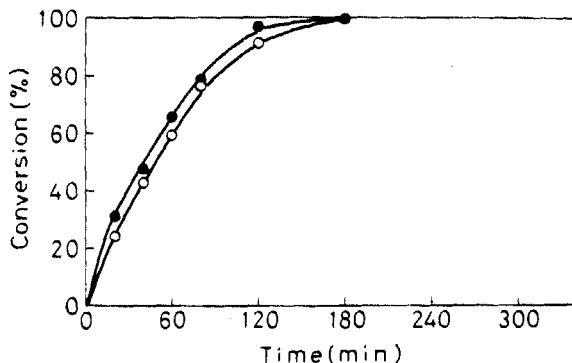


FIG. 2. Reaction of carboxyl-terminated liquid rubbers with GMA. (○) CTB 2000X162-GMA; (●) CTBN 1300X8-GMA. Temperature = 80°C. Catalyst = DMBA (0.5 wt% based on the total weight of reactants). Feed mole ratio of carboxyl-terminated liquid rubber:GMA = 1:14.

The reactions of the original carboxyl-terminated liquid rubbers with GMA without catalyst were very sluggish. However, reactions in the presence of DMBA as a catalyst proceeded smoothly, as shown by Fig. 2.

In Fig. 3 the IR spectra of representative MTILR and MTLR obtained

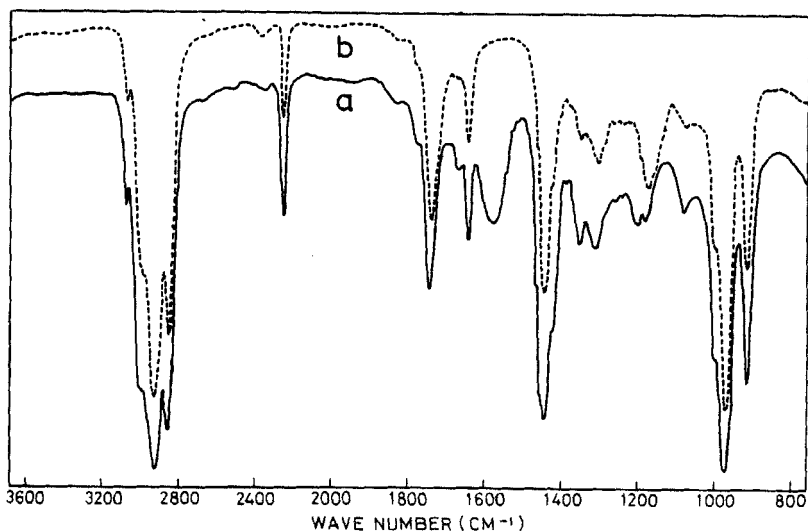


FIG. 3. Infrared spectra of (a) MTCTBN(Ca) and (b) MTCTBN.

in these addition reactions are shown as typical examples. The spectrum (a) of MTCTBN(Ca) exhibits an absorption band at  $1580\text{ cm}^{-1}$ , which is characteristic of the carboxylate group and cannot be observed in the spectrum (b) of MTCTBN without an ionic link. From this it is apparent that MTCTBN(Ca) has an ionic link. Both spectra have absorption bands at  $1640\text{ cm}^{-1}$  (C=C), at  $1740\text{ cm}^{-1}$  (C=O stretching) due to the ester group, and at  $2250\text{ cm}^{-1}$  (C≡N).

Table 1 summarizes the results of the preparation of MTILR and of MTLR. The addition reactions were carried out until the acid value became zero. The products were purified by the methods described in the Experimental Section. The yields were generally high. It is noteworthy that the IR absorption bands attributable to the metal carboxylate groups appear at  $1600\text{ cm}^{-1}$  for the Mg carboxylate group and at  $1580\text{ cm}^{-1}$  for the Ca carboxylate group. The MTILR obtained were slightly brownish semisolids and the MTLR were slightly brownish, very viscous liquids.

### Copolymerization

The MTILR were soluble in St, giving homogeneous solutions suitable for copolymerization. As a result of preliminary experiments, DBPH was found to be suitable for the copolymerization of MTILR with St because, in its presence, copolymerization proceeded at a convenient rate. In the presence of benzoyl peroxide or methyl ethyl ketone peroxide, copolymerization proceeded too rapidly, and was accompanied by a rapid viscosity increase of the system. Hence complete degasification and casting of the system were difficult. Therefore, DBPH was selected as the initiator in the present study.

The viscosities of the solutions containing MTILR were higher than those of the solutions containing MTLR, an effect on the viscosity of introducing metal. The copolymerizations were carried out under the conditions described in the Experimental Section. The MTILR content in the systems ranged from 30 to 50 wt%. The systems containing more than about 60 wt% MTILR were too viscous to permit bulk copolymerization to be carried out. Copolymerizations of MTLR with St were also conducted to obtain reference copolymers.

The copolymers containing Mg were transparent and those containing Ca were opaque. The reference copolymers were semitransparent at low MTLR content and transparent at high MTLR content.

### Physical Properties of Copolymers

Figures 4 and 5 show stress-strain curves of representative ionic copolymers and of reference copolymers, respectively. The curves show yield points characteristic of plastics. For the copolymers with low soft block content, a sharp decrease in the tensile stress after the yield point is accompanied by a necking down of the test specimen;



TABLE I. Preparation of MTILR by the Reaction of PNCTLR with GMA<sup>a</sup>

MTILR code	PNCTLR used	Synthesis condition		IR absorptions (cm <sup>-1</sup> )			External appearance	
		Temperature (°C)/ time (h)	Final acid value	Yield (%)	COO <sup>-</sup>	C=C		C≡N
MTCTB(Mg)	CTB(0.5Mg)	70/2 h	0	94	1600	1640	-	Semisolid
MTCTB(Ca)	CTB(0.5Ca)	80/5 h	0	92	1580	1640	-	Semisolid
MTCTB <sup>b</sup>	CTB 2000X162	80/3 h	0	92	-	1640	-	Very viscous liquid
MTCTBN(Mg)	CTBN(0.5Mg)	70/2.4 h	0	88	1600	1640	2250	Semisolid
MTCTBN(Ca)	CTBN(0.5Ca)	80/5.5 h	0	88	1580	1640	2250	Semisolid
MTCTBN <sup>b</sup>	CTBN 1300X8	80/3 h	0	85	-	1640	2250	Very viscous liquid

<sup>a</sup>Feed mole ratio of PNCTLR:GMA = 1:14.

<sup>b</sup>Reference methacrylate-terminated liquid rubber (MTLR) prepared using DMBA (0.5 wt% based on the total weight of reactants) as catalyst.

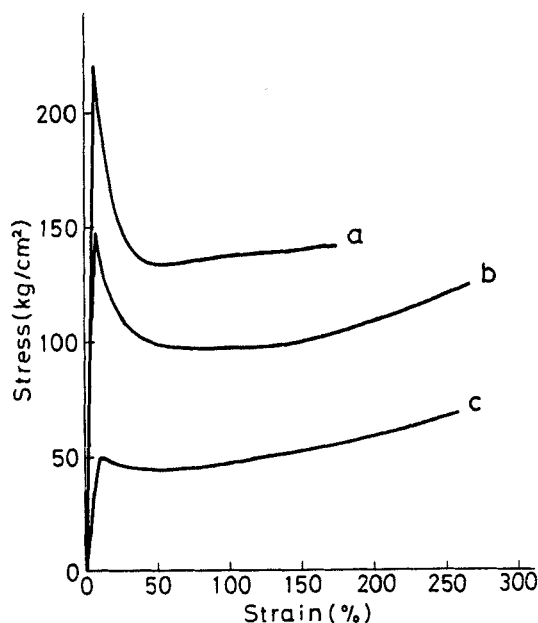


FIG. 4. Stress-strain curves for copolymers of MTCTB(Mg)-St at weight ratios of (a) 30:70; (b) 40:60; (c) 50:50.

cold-drawing with orientation and generally high elongation follows. With an increase in the soft block content, the copolymers become soft and tough.

Table 2 summarizes the physical properties of copolymers of various combinations of components. Tensile strength decreases markedly with an increase in the soft block content. It is noteworthy that the copolymers containing Mg showed higher tensile strength than their corresponding reference copolymers at the same soft block content. Thus the effect of introducing metal is clearly apparent. The Ca-containing copolymers showed poor tensile strength, especially for the MTCTB(Ca)-series. This is probably due to the lower interionic attraction of  $\text{Ca}^{2+}$ , to the heterogeneity of the copolymer systems, and to the lower overall cross-linking densities (mentioned later). Similar tendencies were also observed for tear strength and Shore hardness. The copolymers with 30 wt% soft block content showed Shore A hardness of above 100, hence Shore D hardness was determined for these copolymers. Elongations of the copolymers, except for those containing Ca, were 101-305%.

It is known that in the cured rubbers obtained by cross-linking of PNCTLR with bisepoxide and anhydride, the CTBN series has better physical properties than the CTB series due to a polarity effect of the

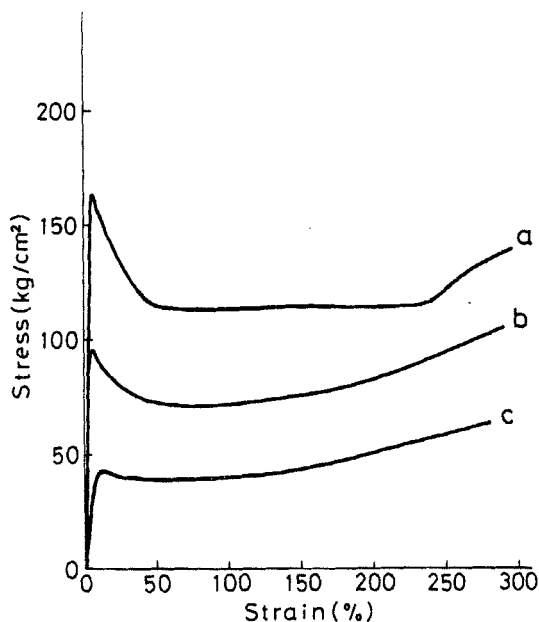


FIG. 5. Stress-strain curves for copolymers of MTCTB-St at weight ratios of (a) 30:70; (b) 40:60; (c) 50:50.

nitrile groups in the former rubbers [2]. Such a tendency is not observed for the above copolymers. In the copolymers containing Mg, the MTCTB(Mg) series showed slightly better physical properties than the MTCTBN(Mg) series. For the copolymers containing Ca, the MTCTB(Ca) series showed better physical properties than the MTCTB(Ca) series, probably due to the lower heterogeneity of the former copolymer systems.

It has been reported that the cross-linked polymers obtained from acid anhydride-adducted liquid poly-BD and GMA exhibit tensile strengths of 40-120 kg/cm<sup>2</sup> and elongations of 10-40% at soft block contents of 30-50 wt% [7]. Thus the ionic copolymers in the present study have higher tensile strengths and elongations than these cross-linked polymers at the same soft block contents. Moreover, the cross-linked polymer obtained by copolymerization of St and maleic anhydride-treated poly-BD has been reported to have a tensile strength of 128 kg/cm<sup>2</sup> and an elongation of 150% at 60 wt% St content [8].

#### Resistance of Copolymers to Chemical Attack

Table 3 shows the resistance of the copolymers to chemical attack. The copolymers showed much higher weight gains in benzene and diox-

TABLE 2. Physical Properties of Copolymers of MTLR or MTLR with St

Components	Weight ratio of components	Tensile strength (kg/cm <sup>2</sup> )	Elongation (%)	Tear strength (kg/cm)	Shore A or D hardness	External appearance
MTCTB(Mg)-St	30:70	228	169	140	D 72	Transparent
	40:60	148	264	83	A 98	Transparent
	50:50	73	273	35	A 95	Transparent
MTCTB(Ca)-St	30:70	73	< 5	-	D 52	Opaque
	40:60	12	< 5	-	A 93	Opaque
	50:50	7	159	4	A 46	Opaque
MTCTB-St	30:70	165	293	106	D 66	Semitransparent
	40:60	117	305	60	A 98	Semitransparent
	50:50	63	278	32	A 93	Transparent
MTCTBN(Mg)-St	30:70	217	260	136	D 75	Transparent
	40:60	146	280	74	A 97	Transparent
	50:50	63	256	17	A 87	Transparent
MTCTBN(Ca)-St	30:70	106	< 5	-	D 63	Opaque
	40:60	50	< 5	9	A 98	Opaque
	50:50	23	58	6	A 87	Opaque
MTCTBN-St	30:70	197	101	117	D 71	Semitransparent
	40:60	94	283	47	A 97	Transparent
	50:50	61	278	29	A 88	Transparent

TABLE 3. Resistances of Copolymers to Chemical Attack

Components	Weight ratios of components	Benzene		Dioxane		n-Hexane	
		Change in weight (%)	Soluble part (%)	Change in weight (%)	Soluble part (%)	Change in weight (%)	Soluble part (%)
MTCTB (Mg)-St	30:70	488	4.0	407	0	38	2.5
	40:60	450	4.7	361	1.7	46	2.7
	50:50	454	5.2	334	6.6	60	3.1
MTCTB (Ca)-St	30:70	2346	47.7	2172	37.5	51	10.3
	40:60	2088	55.5	1491	46.7	75	17.6
	50:50	1683	53.7	1358	49.5	96	19.5
MTCTB-St	30:70	544	9.9	415	4.1	35	7.3
	40:60	513	12.2	361	7.2	42	8.9
	50:50	472	11.5	319	9.0	50	9.0
MTCTBN (Mg)-St	30:70	484	3.6	485	5.6	17	0.2
	40:60	449	4.2	460	6.6	17	1.5
	50:50	404	4.5	416	7.9	19	1.7
MTCTBN (Ca)-St	30:70	1234	40.5	1833	22.7	17	1.8
	40:60	1475	42.8	1471	44.9	17	2.7
	50:50	2071	36.8	1161	48.6	19	3.0
MTCTBN-St	30:70	597	11.9	567	5.1	16	2.0
	40:60	538	14.4	495	12.9	18	2.5
	50:50	512	17.2	489	15.9	18	3.2

ane than in n-hexane. In benzene and dioxane the Ca-containing copolymers exhibited much higher weight gains and soluble parts than the other copolymers, indicating that the overall cross-linking densities of the former are considerably lower than those of the latter. Generally, the weight gain has a tendency to decrease with an increase in the soft block content. Thus the overall cross-linking density seems to increase with an increase in the soft block content.

It is noteworthy that the Mg-containing copolymers generally showed slightly lower weight gains in benzene and dioxane than their corresponding reference copolymers at the same soft block contents. This indicates that the former copolymers have slightly higher overall cross-linking densities than the latter ones. In the copolymers, except for those containing Ca, the benzene- and dioxane-soluble parts were generally very small. Most of the polymer molecules are considered to have taken part in the cross-linking.

Thus the Ca-containing copolymers were found to have considerably lower overall cross-linking densities, probably due to incomplete copolymerization. Therefore the copolymers, except for those containing Ca, were investigated further.

In addition, the weight gains in benzene and dioxane of the above copolymers are considerably higher than those of the cured rubbers from PNCTLR, bisepoxide, and anhydride in the previous study [2], suggesting that the former have lower overall cross-linking densities than the latter.

### Water Resistance of Copolymers

Figure 6 shows the effect of water on weight change of representative copolymers. Water absorption showed a tendency to increase with an increase in the soft block content, even for the reference copolymers without ionic links, although the copolymers with higher soft block contents have higher overall cross-linking densities. Thus the water absorption seems to be due mainly to the ester and hydroxyl groups in the soft block. The reference MTCTB series copolymers showed higher water absorption than the MTCTB(Mg) series copolymers, probably due to the lower overall cross-linking densities of the former. Meanwhile, a reverse trend was observed between the MTCTBN(Mg) series and MTCTBN series, although the MTCTBN(Mg) series has higher overall cross-linking densities. In this case the appearance of the effect of ionic links on water absorption is considered to be facilitated by the existence of polar nitrile groups. However, the water absorption of the above copolymers was considerably lower than that of the CTBN-based cured rubbers from PNCTLR, bisepoxide, and anhydride [2], although the former have lower overall cross-linking densities than the latter.

The above copolymers did not show significant changes in tensile strength; the changes after 14 d were not systematic and were generally within  $\pm 7\%$  of the initial values. Some of them exhibited a rather slight increase in tensile strength. In the cured rubbers the decrease

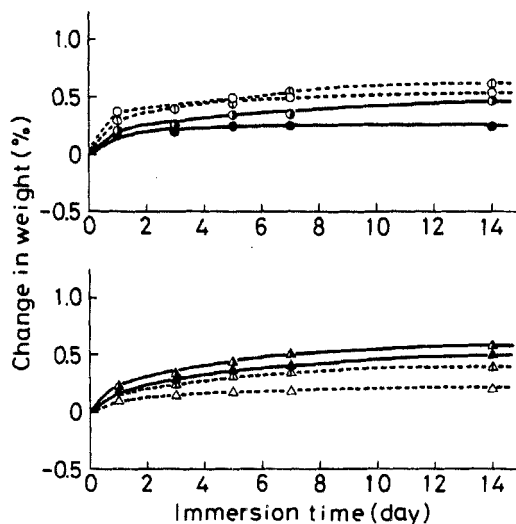


FIG. 6. Effect of water on weight change of copolymers. (●) MTCTB(Mg)-St (30:70); (◐) MTCTB(Mg)-St (40:60); (○) MTCTB-St (30:70); (⊕) MTCTB-St (40:60); (▲) MTCTBN(Mg)-St (30:70); (△) MTCTBN(Mg)-St (40:60); (◓) MTCTBN-St (30:70); (◔) MTCTBN-St (40:60).

in tensile strength was remarkable close to the order of water absorption [2]. In this case, even the hard block containing ester and hydroxyl groups would be subject to some degree of the plasticizing effect of water, thus contributing to the decrease in strength. In the case of the above copolymers, the hydrophobic poly-St block is not considered to suffer the plasticizing effect by water.

### Thermal Behavior

Figure 7 shows TGA and DTA curves in air of representative ionic copolymers as typical examples. In the TGA curves the copolymers are thermally stable up to about 300°C, above which a gradual weight loss begins. Above about 400°C, destruction proceeds rapidly. The temperatures for 50% weight loss were 440°C for the copolymer with 30% soft block content and 446°C for the copolymer with 50% soft block content. Thus thermal stability increased with an increase in the soft block content. The plateaus observed above 530°C correspond to the formation of MgO. The DTA curves showed several exothermic peaks, probably due to degradations occurring via oxidative modes.

Below 400°C the DTA curves showed no sharp endothermic peaks,

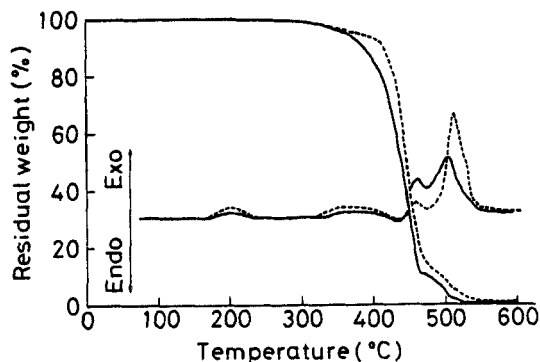


FIG. 7. TGA and DTA curves of ionic copolymers of MTCTB(Mg)-St at weight ratios of (—) 30:70 and (- -) 50:50.

indicating that the hard block domains in the polymer matrix have no melting point.

Other series copolymers showed similar tendencies in TGA and DTA curves.

### Stress Relaxation

Figure 8 shows the stress relaxation behavior of representative copolymers. At first, remarkable relaxation occurred, and then it gradually moderated. Ionically cross-linked rubbers are known to have a tendency to slowly relax because of reorganization of metal carboxylate bonds. For the copolymers in the present study, no appreciable difference in stress relaxation between the ionic copolymers and the reference copolymers was observed at the same soft block contents. In the MTCTB(Mg) and MTCTB series copolymers, stress relaxation showed a tendency to increase with an increase in the soft block content. Thus the ratio of soft block to hard block contents has a larger effect on stress relaxation of the copolymers than the metal carboxylate groups. On the other hand, in the cured rubbers from PNCTLR, bisepoxide, and anhydride in a previous study [2], those containing higher soft block contents showed lower relaxation.

As for aging resistance, the copolymers described in the present study have poor aging resistance. However, this can probably be improved by selecting suitable antioxidants.

### ACKNOWLEDGMENT

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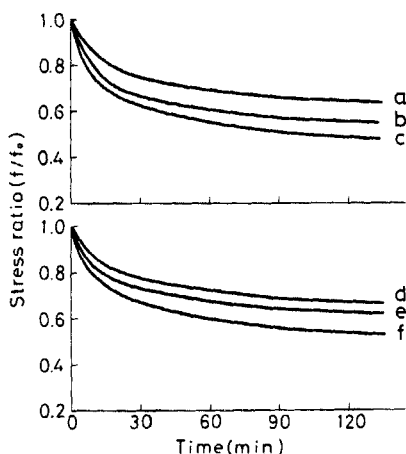


FIG. 8. Stress relaxation of copolymers. (a) MTCTB(Mg)-St (30:70); (b) MTCTB(Mg)-St (50:50); (c) MTCTB(Mg)-St (40:60); (d) MTCTB-St (30:70); (e) MTCTB-St (50:50); (f) MTCTB-St (40:60).

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