Chain Extension of Partially Neutralized Carboxyl-Terminated Liquid Polybutadiene with Bisepoxide

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Synopsis

Chain extension of partially neutralized carboxyl-terminated liquid polybutadiene (PB) with bisepoxide was investigated by the carboxyl–epoxide reaction. The partially neutralized liquid PB were prepared, by the partial neutralization with MgO and CaO, from a carboxyl-terminated liquid PB (Hycar CTB 2000X162). As the bisepoxide, hydroquinone diglycidyl ether was used. The metal carboxylate groups in the system catalyzed the reaction and, further, the Mg carboxylate group showed higher catalytic activity than the Ca carboxylate group. The chain-extended metal-containing PB obtained by the reaction were found to be elastic when subjected to a rapid impact, but plastic under slowly applied stress and their solution behavior in pyridine was examined. The viscosities were very low at very low concentrations but increased markedly as the concentration increased. This solution behavior is attributed to ionic associations of carboxylate anions and metal cations to longer chains. Further, thermal and other properties were evaluated.

INTRODUCTION

Previously, we have studied preparation of ionic rubbers by neutralization, with metal oxides and metal carbonates, of carboxyl-terminated liquid rubbers.[1] The liquid rubbers used were a polymer of butadiene (Hycar CTB 2000X162) and a copolymer of butadiene–acrylonitrile (AN) (Hycar CTBN 1300X8). This neutralization is the reaction of a weak acid and a weak base, and, hence, excess amounts of the metal compounds are necessary to attain higher molecular weights. However, complete neutralization was difficult even if large excess of the metal compounds was used.

On the other hand, partial neutralization of the liquid rubbers is easy. More recently, we have reported preparation of ionic cured rubbers by crosslinking (curing) of the partially neutralized carboxyl-terminated liquid rubbers (PNCTLR) with anhydride and bisepoxide,[2,3] as shown by eq. (1) (see Scheme I). The ionic cured rubbers have network structures by both covalent and ionic bonds. The PNCTLR were obtained by the partial neutralization, with MgO and CaO, of CTB 2000X162, CTBN 1300X8, and CTBNX 1300X9 (butadiene—AN copolymer having pendent carboxyl groups in addition to the terminal carboxyl groups). The functionalities of carboxyl groups are as follows[4]: 2.01 for CTB 2000X162, 1.8 for CTBN 1300X8, and 2.4 for CTBNX 1300X9. Theoretically, among them CTB 2000X162 is considered most suitable for the preparation of linear polymers of as high a molecular weight as possible by reaction with difunctional compounds. The microstructure of the liquid polybutadiene (PB) is as follows[4]: *cis*-1,4 = 22.1%, *trans*-1,4 = 53.4%, and vinyl

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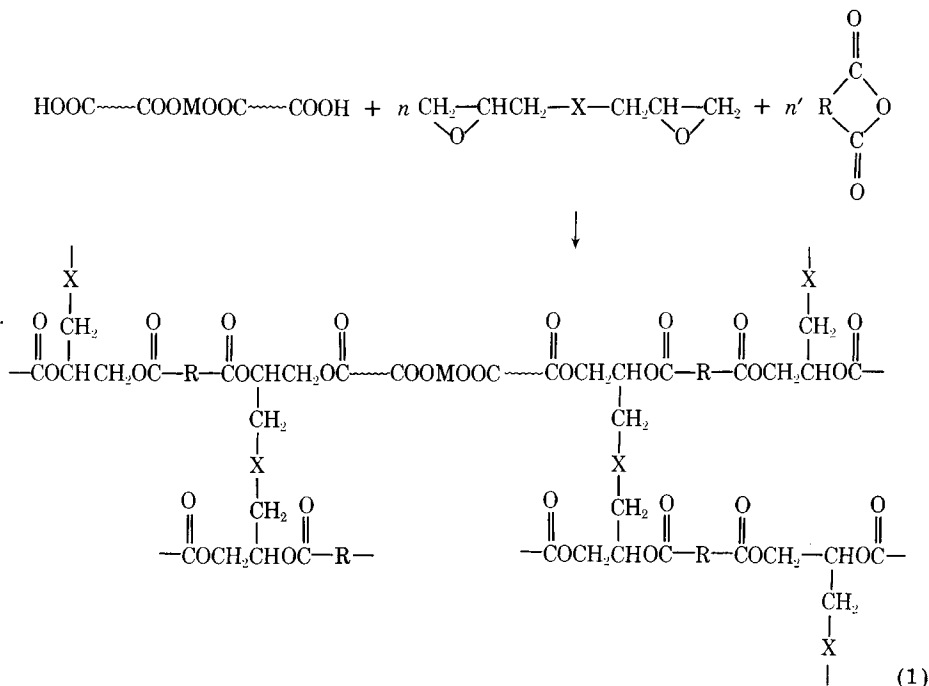
where M = Mg or Ca
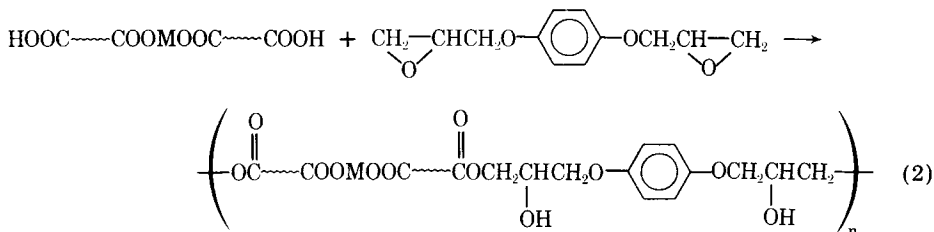
Scheme I.

structure = 24.5%. Therefore, in the present study chain extension of the PNCTLR from CTB 2000X162 with bisepoxide was investigated, as shown by eq. (2) (see Scheme I). The bisepoxide used was hydroquinone diglycidyl ether (HQDGE). Further, the chain-extended metal-containing PB obtained were evaluated for some properties.

EXPERIMENTAL

Materials

The carboxyl-terminated liquid PB, Hycar CTB 2000X162 (acid value = 0.3739 eq/kg, MW = 5349, by end-group analysis) (manufactured by B. F. Goodrich Chemical Co.) was used as received. The PNCTLR from CTB 2000X162 were prepared the same way as in the previous study.[2] The degree of neutralization was 50%. A coded system for the PNCTLR will be used in this discussion. For example, CTB (0.5Mg) indicates that CTB 2000X162 was neutralized with MgO to the degree of neutralization = 50%. The acid values were 0.1864 eq/kg for CTB (0.5Mg) and 0.1858 eq/kg for CTB (0.5Ca).

HQDGE was synthesized, according to the reported method,[5] by reacting hydroquinone, epichlorohydrin, and NaOH. The mixture of two optical isomers, mp = 87–90°C and 112–115°C, was used (epoxide value = 8.969 eq/kg; calcd = 8.999 eq/kg).

Chain Extension Reactions

In a 100-mL separable flask equipped with stirrer and nitrogen inlet and outlet adapter were placed fixed amounts of CTB (0.5M) and HQDGE, and the mixture was reacted at a desired temperature with stirring under a stream of nitrogen. Samples were taken during the reaction for determination of acidity. As the reaction proceeded, the mixture became viscous, and at the end of reaction the fluidity of the system was lost. After the reaction, the mixture was dissolved in diethyl ether and the solution was dropped into a large quantity of vigorously stirred acetone to precipitate the product. The product was further washed with acetone and dried *in vacuo* at 60°C.

The same method was applied to prepare reference chain-extended PB of CTB 2000X162—HQDGE (1:1) and adduct polymer of CTB 2000X162—HQDGE (2:1). *N,N*-dimethylbenzylamine was used as a catalyst for the former and triethylbenzylammonium chloride for the latter. The procedure after reaction was the same as above for the former. For the latter, the procedure was as follows: the reaction product was dissolved in chloroform and the solution was washed thoroughly with water to remove the catalyst. To the chloroform layer was added a suitable amount of Na_2SO_4 to remove water thoroughly. After filtering the solution by suction, the chloroform was removed by distillation at 90°C under reduced pressure, to obtain the slightly yellowish viscous product.

Measurements

Acidities were determined by titrating the solution of the sample in chloroform with $0.1N$ KOH—methanol using Thymol Blue–Cresol Red indicator.

Epoxide values of samples without metal were determined by titrating the solution of the sample in chloroform directly with $0.1N$ HBr—acetic acid using Crystal Violet–acetic acid indicator.

Viscosities were determined at concentrations of 0.01–0.2 g of sample/10 mL of pyridine at 30°C by use of an Ubbelohde viscometer.

Infrared spectra and physical properties were determined by the same method as in the previous study.[1]

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-20B at a heating rate of 10°C/min in air.

Water absorption was obtained by determining weight change of a 10 × 10 × about 2 mm sample (about 0.25 g) immersed in 100 mL water at 23°C.
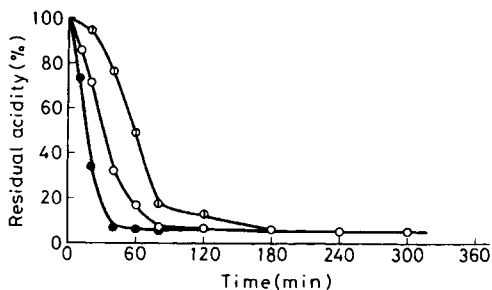
Fig. 1. Chain extension reaction of CTB (0.5Mg) with HQDGE at mole ratio of 1:1.   (⊕) at 90°C; (○) at 120°C; (●) at 150°C.

RESULTS AND DISCUSSION

Chain Extension Reactions

In the preparation of ionic rubbers by the neutralization of carboxyl-terminated liquid rubbers with metal ions, it is necessary that byproducts produced from hydrogen of carboxyl group and anion of metal compounds be removed effectively from the system.   Meanwhile, such byproducts are not formed in the chain extension reactions in the present study, and the reactions produce ionic polymers into which metal is firmly incorporated.

Figures 1 and 2 show the chain extension reactions of CTB(0.5M) with HQDGE at various temperatures in terms of residual acidity.   The chain extension proceeds through the addition reaction of the carboxyl group with the epoxide group to form a hydroxylalkyl ester.   With increase in temperature the rate of reaction increased.   Thus, the effect of temperature is clear.   In addition, as is obvious on comparing Figures 1 and 2, at the same temperature the reaction of the system containing Mg proceeded much more rapidly than that of the system containing Ca.   That is, Mg has considerably higher catalytic activity than Ca toward the addition reaction.   The catalytic activity of such metal carboxylate groups is clearly demonstrated also on comparing with the reaction of CTB 2000X162 with HQDGE without catalyst in Figure 3, where the reaction was very slow at 120°C.   However, the CTB 2000X162—HQDGE (1:1) reaction in the presence of N,N-dimethylbenzylamine proceeded smoothly at 120°C.

Previously, we have found[6] that the Ca carboxylate group in the Ca salt of monoethyl phthalate catalyzes the reactions of monoethyl maleate or hexahydrophthalate with phenyl glycidyl ether; moreover, the difference between
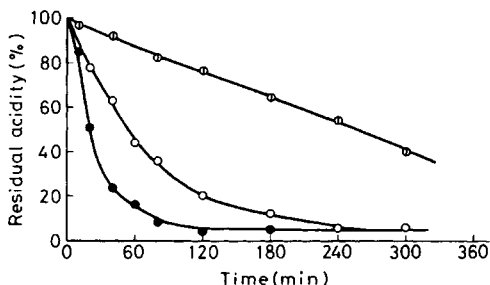

Fig. 2. Chain extension reaction of CTB (0.5Ca) with HQDGE at mole ratio of 1:1.   (⊕) at 90°C; (○) at 120°C; (●) at 150°C.
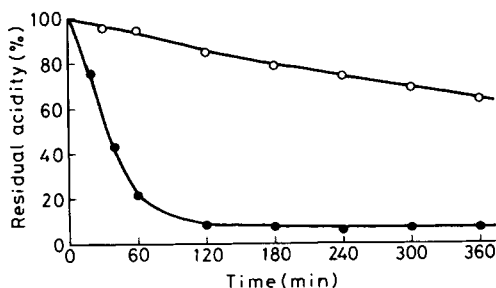
Fig. 3. Chain extension reaction of CTB 2000X162 with HQDGE at mole ratio of 1:1. (●) in the presence of N,N-dimethylbenzylamine (0.5 wt % based on the total weight of reactants); (○) without catalyst. Temp = 120°C.

conversion of epoxide and conversion of acid was very small. On the other hand, Iwakura and Matsuzaki reported[7] that bisphenol A diglycidyl ether reacts with dicarboxylic acids to produce insoluble, infusible polymers because of concomitant etherification. Similarly, Alvey reported[8] that in the reactions of bisphenol A diglycidyl ether with adipic acid in the presence or absence of base catalysts at 60–115°C, etherification also occurred as a side reaction.

In the present study, the reaction systems were generally homogeneous (did not gel) even if the conversion of acid reached final high conversion attainable of 95–96%. This indicates that etherification of epoxide is negligible. Equal degrees of acid and epoxide reaction would yield linear polymers. It was difficult to determine exactly epoxide values in case of the CTB(0.5M)—HQDGE systems because of influence of the metal carboxylate groups of CTB(0.5M). However, determination of epoxide values was possible for the reference CTB 2000X162—HQDGE system. In this system, epoxide value and acidity decreased equally, and no gelation was observed; at the end of reaction the difference was below 2%. Also, esterification between terminal carboxyl group and hydroxyl group of hydroxyalkyl ester is considered not to have occurred, because such a side reaction would result in gelation of the system.

If the catalytic action of the metal carboxylate groups of CTB(0.5M) is supposed to be due mainly to free ion mechanism, Ca with the lower electronegativity should have a greater catalytic activity than Mg. However, the reverse trend was observed as above with regard to the catalytic action of Mg and Ca, suggesting that the reaction proceeds by other mechanism than free ion mechanism. Ishii et al. proposed[9] that the reaction of oleic acid with ethylene oxide in the presence of KOH as a catalyst (without solvent) proceeded by a mechanism of an intermediate of termolecular complex. Also in the present study, the reaction is considered to proceed by a mechanism similar to that proposed by Ishii et al., and a complex mechanism where ion pair is concerned is supposed to be predominant.

In Table I are summarized the results of the chain extension reactions. The maximum conversion attainable in terms of COOH groups were generally 94–96%. However, in the CTB(0.5Ca)—HQDGE (1:1) reaction at 90°C, the conversion was 80% even after 9 h because of the lower catalytic activity of Ca; meanwhile, at 150°C the system slightly gelled at the latter stage of reaction, probably due to a slight degree of heat polymerization of the double bonds of the vinyl structure because of the high temperature. Therefore, a temperature of
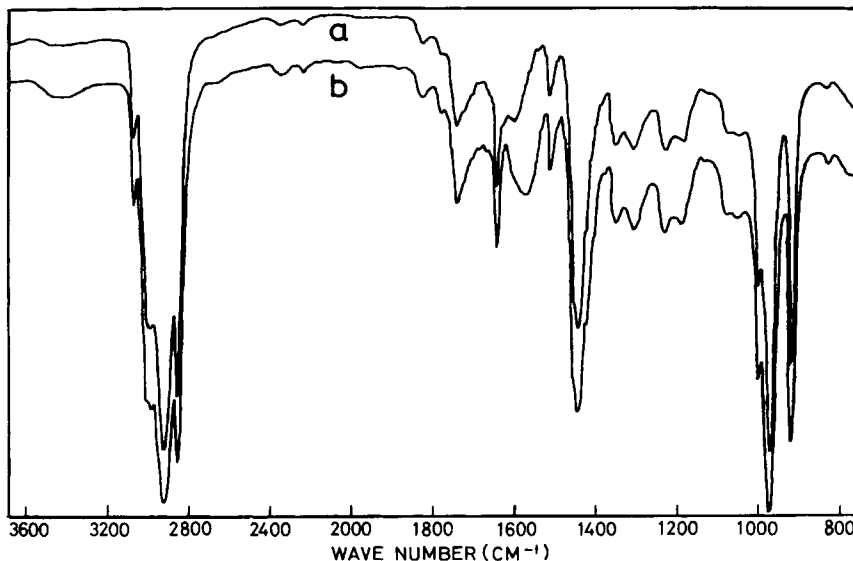
Fig. 4. Infrared spectra of chain-extended metal-containing PB of (a) CTB (0.5Mg)—HQDGE (1:1) and (b) CTB (0.5Ca)—HQDGE (1:1).

120°C seems to give a convenient reaction rate. The products obtained above were slightly brownish rubbery materials. The chain-extended Mg-containing PB obtained showed inherent viscosities (η_{inh}) in pyridine of 0.344–0.354, which were determined at a concentration of 0.5 g/100 mL pyridine. Similarly, the Ca-containing product obtained by the reaction at 120°C showed an η_{inh} value of 0.344, indicating that the extent of chain extension is almost equal to those of the Mg-containing products. However, the reaction at 90°C gave lower degree of chain extension for the Ca-containing product. On the other hand, the reference chain-extended PB of CTB 2000X162—HQDGE (1:1) showed an η_{inh} = 0.552, a value considerably higher than those of the metal-containing products. The molecular weight by the end-group analysis is about 82600. The adduct polymer of CTB 2000X162—HQDGE (2:1) showed an η_{inh} value of 0.234. This polymer is considered to be carboxyl-terminated. The molecular weight by the end-group analysis is about 10600. From the above facts, it is considered that in the metal-containing products the metal carboxylate groups are dissociated to an appreciable extent. Further detailed solution viscosity characteristics will be described in the next section.

Figure 4 shows the infrared spectra of the metal-containing products obtained by the reaction at 120°C. The spectra exhibit an absorption band at 1595 cm^{-1} for the Mg-containing product and at 1560 cm^{-1} for the Ca-containing one, which are characteristic of the carboxylate group and cannot be observed in the spectrum of the reference product in Figure 5. Also from this it is apparent that the metal-containing products have ionic links. Moreover, it is noteworthy that the band at 1740 cm^{-1} (due to C=O stretching) in Figure 4 is weaker than that in Figure 5, indicating that the concentration of ester groups is lower in the metal-containing products than in the reference one. All the spectra have a sharp band at 1640 cm^{-1} (C=C), showing that the double bonds are stable under the above reaction condition.

TABLE I
Chain Extension Reaction of CTB (0.5M) and CTB 2000X162 with HQDGE

Components	Mole ratio of components	Metal (%)	Reaction conditions		Conversion of COOH group (%)	Product		
			Temp (°C)	Time (h)		Yield (%)	Acidity (meq/kg)	η_{inh} in pyridine[a]
CTB (0.5Mg)—HQDGE	1:1	0.21	90	6	96	81	7.3	0.344
	1:1	0.21	120	5	95	82	5.8	0.353
	1:1	0.21	150	3	96	84	5.4	0.354
CTB (0.5Ca)—HQDGE	1:1	0.37	90	9	80	85	18.8	0.285
	1:1	0.37	120	9	96	87	7.3	0.344
	1:1	0.37	150	8	95	81	—[b]	—[b]
CTB 2000X162—HQDGE	1:1[c]	—	120	6	94	76	17.8[d]	0.552
	2:1[e]	—	120	6	96	95	189.0[f]	0.234

[a] Measured at a concentration of 0.05 g/10 mL pyridine at 30°C.
[b] The system slightly gelled at the latter stage of reaction.
[c] Catalyst = N,N-dimethylbenzylamine (0.5 wt % based on the total weight of reactants).
[d] Epoxide value = 6.4 meq/kg. Molecular weight by the end-group analysis = 82,645.
[e] Catalyst = triethylbenzylammonium chloride (0.5 wt % based on the total weight of reactants).
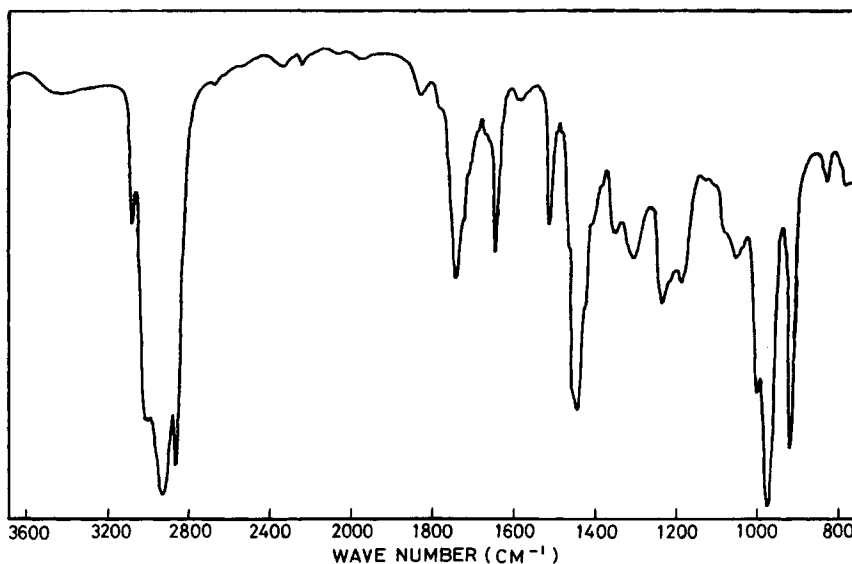[f] Molecular weight by the end-group analysis = 10,582.

Fig. 5. Infrared spectrum of reference chain-extended PB of CTB 20000X162—HQDGE (1:1).

The samples prepared by the reactions at 120°C were used for the investigations of the following various properties.

Solution Viscosities in Pyridine

Properties of ionic polymers have been extensively investigated until recently.[10–18] However, although ionomers containing comparatively few ionic groups have been commercially available, relatively little work has been reported on their dilute solution behavior because of very poor solubility in ordinary solvents. Also for carboxyl-terminated PB neutralized with various cations, the limited solubility of these ionomers precluded a detailed examination of their solution viscosities.[1]

The chain-extended metal-containing PB obtained in the present study are soluble in pyridine at relatively low concentrations. Therefore, the viscosities in pyridine solution of these polymers and related materials were investigated over a concentration range of 0.10–2.0 g/100 mL. The data are shown in Figure 6, where plots of η_{inh} and reduced viscosity ($\eta_{sp/C}$) against concentration were made. The data for the chain-extended metal-containing PB lie upon a curve which, at zero concentration, approaches the curve for the adduct polymer of CTB 2000X162—HQDGE (2:1), but becomes increasingly steeper as the concentation increases, especially so for $\eta_{sp/C}$. Meanwhile, the data for the reference chain-extended PB fall on essentially a straight line in respective η_{inh} and $\eta_{sp/C}$, from which the intrinsic visocisty ($[\eta]$) of 0.550 is obtained. In the case of CTB 2000X162 and adduct polymer, the increase in concentration does not substantially alter the viscosities and the following much lower viscosity values were observed: $[\eta] = 0.175$ for CTB 2000X162 and $[\eta] = 0.260$ for adduct polymer. Essentially the same viscosities were observed for CTB(0.5Mg) and CTB(0.5Ca). It is noteworthy that the data for respective CTB(0.5M) fall on a straight line which, at zero concentration, approaches the line for CTB 2000X162 but comes
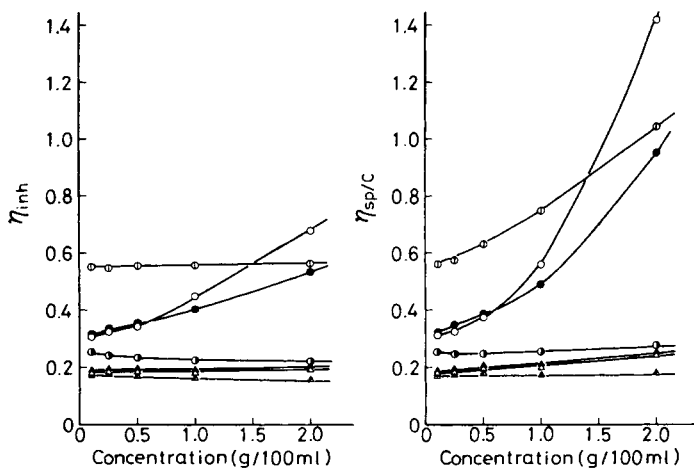
Fig. 6. η_{inh} and $\eta_{sp/C}$ vs. concentration in pyridine. (●) chain-extended PB of CTB (0.5Mg)—HQDGE (1:1); (O) chain-extended PB of CTB (0.5Ca)—HQDGE (1:1); (Φ) reference chain-extended PB of CTB 2000X162—HQDGE (1:1); (◑) adduct polymer of CTB 2000X162—HQDGE (2:1); (▲) CTB (0.5Mg); (△) CTB (0.5Ca); (▲) CTB 2000X162.

near to the line for adduct polymer as the concentration increases to 2.0 g/100 mL. This tendency is clearly demonstrated espeically in $\eta_{sp/C}$. It appears that in very dilute solution the apparent molecular weights of CTB(0.5M) are close to that of CTB 2000X162, suggesting a dissociation of metal carboxylate groups. In more concentrated solutions, the apparent molecular weights approach that of adduct polymer, suggesting an ionic association resulting in the formation of HOOC⌇COOMOOC⌇COOH which theoretically have about the same molecular weight as that of the adduct polymer.

Therefore, in case of the chain-extended metal-containing PB, it is considered that in very dilute solution the metal carboxylate groups dissociate to an appreciable extent, resulting in the remarkable decrease in apparent molecular weight; however, the apparent molecular weight is a little higher than that of adduct polymer. As the concentration increases, ionic association of carboxylate anions and metal cations occurs, leading to greater apparent molecular weight; the apparent molecular weight approaches that of reference chain-extended PB at concentrations near 1.5 g/100 mL for the chain-extended Ca-containing PB and 2.0 g/100 mL for that containing Mg. At concentrations near 2.0 g/100 mL, that containing Ca displays a high level of ionic association leading to considerably higher apparent molecular weight than that of the reference chain-extended PB.

The results somewhat similar to those observed above have been reported by Cowan and Teeter for the zinc salt of residual dimerized fat acids (zinc dimerate).[12] They carried out solution viscosity measurements on zinc dimerate in pyridine solution and found that, in very dilute solutions, zinc dimerate consisted of one zinc ion associated with one dimerate ion; however, in more concentrated solutions, more and more of these fundamental zinc ion–dimerate ion combinations associate, leading to greater apparent molecular weight. They estimated the apparent molecular weight of zinc dimerate in 10% solutions as somewhere between 10,000 and 20,000.
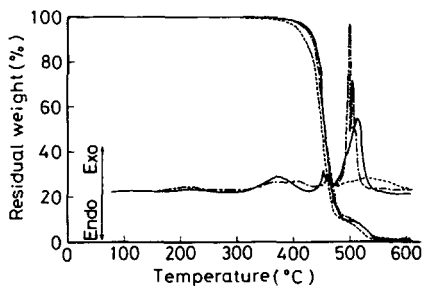
Fig. 7. TGA and DTA curves of chain-extended PB. (——) CTB (0.5Mg)—HQDGE (1:1); (-·-)
CTB (0.5Ca)—HQDGE (1:1); (-----) CTB 2000X162—HQDGE (1:1).

Thermal and Other Properties

Figure 7 shows TGA and DTA curves in air of the chain-extended metal-containing PB and of the reference one. In the TGA curves, they are thermally stable up to about 300°C, above which gradual weight loss begins; above about 400°C, destruction proceeds rapidly. The DTA curves of those containing metal show sharp exothermic peaks, probably due to degradations via oxidative modes. Moreover, the DTA curves show no sharp endothermic peaks, indicating that the polymer main chain have no melting point.

The chain-extended metal-containing PB are elastic when subjected to a rapid impact, but plastic under slowly applied stress, and show a tendency to slowly relax over a long time because of reorganization of the metal carboxylate bonds. As for their physical properties, the following data were obtained: for that containing Mg, tensile strength = 2.4 kg/cm^2, elongation = 65%, Shore A hardness = 37; for that containing Ca, tensile strength = 1.1 kg/cm^2, elongation = 625%, Shore A hardness = 37. Meanwhile, the reference chain-extended PB showed the following: tensile strength = 0.6 kg/cm^2, elongation = above 1400%, Shore A hardness = 28. Thus, the effect of introducing metal (ionic links) appears. As for the effect of the metal species on the properties, Mg imparts slightly better strength properties than Ca to the polymer, probably due to the higher interionic attraction of Mg^{++}. In addition, oxygen atoms of ester and OH groups of the polymer would coordinate to the Mg carboxylate to higher extent than to the Ca carboxylate. This seems to be further supported by the observation that the reaction system containing Mg showed considerably higher viscosity than that containing Ca.
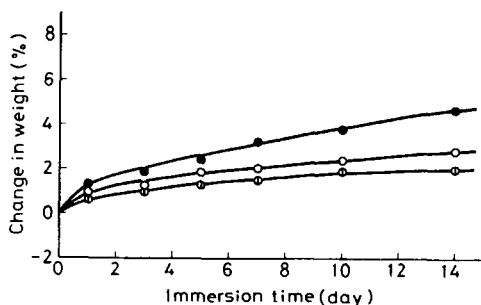

Fig. 8. Effect of water on weight change of chain-extended PB. (●) CTB (0.5Mg)—HQDGE
(1:1); (O) CTB (0.5Ca)—HQDGE (1:1); (◐) CTB 2000X162—HQDGE (1:1).

Figure 8 shows the effect of water on weight change of the chain-extended metal-containing PB and of the reference one. The incorporation of metal resulted in the increase in water absorption. Also in this case, Mg imparts higher water absorption than Ca.

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