# Polymers Based on Divalent Metal Salts of *p*-Aminobenzoic Acid: A Review

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## ABSTRACT

*Divalent metal salts of p-aminobenzoic acid are useful starting materials for syntheses of ionic polymers into which metal is firmly incorporated. This paper is a review of a series of polymers that have been prepared using the metal salts. The salts can react with compounds having functional groups capable of reacting with amino groups.*

*By polyaddition reactions of the salt–aromatic diamine with diisocyanate, and with isocynate-terminated adducts of diisocyanate and dialkylene glycol, halatotelechelic polyureas and polyurethane-ureas are obtained. By amine–epoxy reactions of systems of the salt–diamine–bisepoxide, and addition reactions of systems of the salt–dicarboxylic acid anhydride–bisepoxide, metal-containing cured resins are obtained. In this case, the metal carboxylate groups of the salts have catalytic activities for the curing reactions, and also for etherification of epoxy groups as a side reaction. Therefore, crosslinking of bisepoxide with the salts, and with adducts of the salts and the anhydride, has been investigated by taking advantage of the catalytic activity of the metal carboxylate groups for the etherification of epoxy groups. Interestingly, the metal-containing cured resins obtained by crosslinking by etherification of bisepoxide with the adducts show very high impact strength.* © 1997 by John Wiley & Sons, Ltd.

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## INTRODUCTION

Divalent metal salts of *p*-aminobenzoic acid (ABA), that is, ABA(M) (where M is a divalent metal such as Mg or Ca), contain an ionic bond formed between $-COO^-$ and $M^{++}$, and two amino groups. The ABA(M) salts have been proposed to be useful as additivies [1, 2] for rubbers, and sunscreen materials [3]. However, polymers prepared by using ABA(M) salts were little known so far as we were aware.

$$H_2N- \langle\bigcirc\rangle -COOMOOC- \langle\bigcirc\rangle -NH_2$$

### ABA(M)
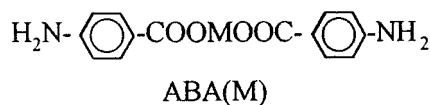
**M = divalent metal (Mg or Ca)**

In general, polymers containing ionic links formed between $-COO^-$ and $M^{++}$ in the main chain were prepared by neutralizing carboxyl-terminated low molecular weight compounds or oligomers with divalent metal ions. Well-known examples were metal dimerates obtained by the reaction of the K salts of dimerized fatty acids with a Zn, Ca or Mg salt [4]; metal dicarboxylates obtained by the reaction of organic dibasic acids with divalent metal ions [5, 6], and metal-containing unsaturated polyesters obtained by the reaction of carboxyl-terminated unsaturated oligoesters with MgO, CaO or ZnO [7–10]. The neutralization of styrene solutions of the carboxyl-terminated unsaturated oligoesters is the reaction of a weak acid with a weak base, and hence, for thickening, excess amounts of metal oxide are necessary to shift the equilibrium to higher molecular weights and viscosities [9].

Meanwhile, ordinary ion-containing monomers were generally based on labile acrylic, methacrylic or styrene structural units. Among them, some sulfonate group-containing monomers [11–14] and polyvalent metal salts of ethylene glycol–methacrylate–phthalate [15, 16] or maleate [17, 18] were well

known. However, generally it is very difficult to produce commercially available highly reactive and inexpensive ionic monomers in high yield and purity, because of spontaneous polymerization, which usually occurs during synthesis reactions.

The ABA(M) salts can be easily obtained by the neutralization of ABA with the respective metal oxides. The salts were considered to be useful as starting materials for the preparation of ionic polymers into which metal is firmly incorporated. Ionic polymers prepared by using such salts contain no excess unreacted metal compounds such as MgO and CaO.

We have been active in the syntheses of the ionic polymers by using the ABA(M) salt. In the following discussion, recent results from our laboratory bearing on the studies on syntheses and properties of ionic polymers by using ABA(M) will be surveyed.

## HALATO-TELECHELIC POLYUREAS BASED ON ABA(M)

By polyaddition reactions of 2,4-toluylene diisocyanate (TDI) with mixtures of ABA(M) and 4,4′-diaminodiphenylmethane (4,4′-methylenedianiline, MDA), a series of halato-telechelic polyureas has been prepared [19].

The polyureas obtained are slightly yellowish powders. Those obtained with ABA(M) contents below 10 mol% in feed diamines are soluble in dimethylacetamide (DMAc) and dimethylsulfoxide (DMSO), but insoluble in dimethylformamide (DMF).

The relationship beween inherent viscosity (concentration=0.5 g/100 ml) in DMAc and metal content of the polyureas incidated that the inherent viscosity decreases markedly as the ABA(M) content increases. This suggests that in a polar solvent such as DMAc, the ionic links in the polymer main chain dissociate into low molecular weight polymers when the concentration is very low. In addition, the higher the content of ionic links, the lower the polymer fragment molecular weights become. A similar tendency has been observed also for halato-telechelic polyurethanes and polyurethane-ureas [20, 21] based on divalent metal salts of mono(hydroxyethyl)phthalate (HEP).

Meanwhile, the reduced viscosity behavior of the polyureas was investigated for various concentrations in DMAc and DMSO, respectively. It was found that their apparent molecular weights become higher with an increase in concentration, perhaps by some degree of ionic association. The viscosity increase with concentration is higher in DMAc than in DMSO. It is known that in solvents of inceasing dielectric constant, dissociation of ionic links is enhanced and their aggregation depressed. The lower viscosity increase in DMSO is assumed to be due to higher depression of ionic association in DMSO, which has a higher dielectric constant ($\varepsilon=46.6$) than in DMAc, which has a low dielectric constant ($\varepsilon=37.8$). That is, in DMSO a considerable extent of dissociation of the metal carboxylate groups is considered to have occurred even at higher concentrations.

The polyelectrolyte behavior of the halato-telechelic polyureas in the solvents is suppressed by the addition of a simple salt (MgCl$_2$). At higher polymer concentrations, intermolecular aggregation is suppressed by the added MgCl$_2$. At very low concentrations, when the added salt amount is 0.40 mol/l, the viscosity is only slightly higher than that when no salt has been added. This might be attributable to only a slight degree of intermolecular association owing to the high salt concentration.

From the halato-telechelic polyureas, slightly yellow transparent films having a haze of 0.5–0.9% can be solvent-cast. The metal-containing polyurea films exhibit tensile strengths of 910–970 kg/cm$^2$ and elongations at break of 10–15%. Increasing the metal content makes the films more brittle, especially for the Ca-containing polyureas.

As for the dynamic mechanical properties, the polyureas show a peak of tan $\delta$ which shifts to higher temperature and becomes broader and more obscure as the metal content increases. This tendency coincides well with that of the shear modulus expressed in values ($G_r$) relative to a first measured value. This trend might be attributable to aggregation of ionic groups in the polymer main chain to form ionic clusters.

## HALATO-TELECHELIC POLYURETHANE-UREAS BASED ON ABA(M)

When isocyanate-terminated adducts of dialkylene glycol (1 mole) and TDI (2 mole) are subjected to the polyaddition reactions, halato-telechelic polyurethane-ureas can be obtained [22]. The polyaddition reactions are carried out by adding a mixture of ABA(M) and MDA dissolved in DMF into the isocyanate-terminated adducts in one portion and then stirring the system at room temperature for 5 hr.

The halato-telechelic polyurethane-ureas obtained are white solids when the metal content is low, and those with high metal content are slightly brown solids, or slightly brown or brown glassy materials. Further, those with a low metal content and the parent polymers are soluble in DMF and DMSO. Generally, they become insoluble in these solvents as the metal content increases.

The reduced viscosity of the polyurethane-ureas in DMF or DMSO increases as the concentration increases. In addition, the viscosity increase is higher in DMF than in DMSO, probably owing to the lower depression of ionic association in DMF because of its lower dielectric constant ($\varepsilon=36.7$) than in DMSO, which has a higher dielectric constant ($\varepsilon=46.6$).

The above-described added salt effect at very low polymer concentrations is observed as the distance between ionic groups increases. The viscosity behavior has been discussed theoretically as follows. So far, there has been only limited work concerning the salt effect on polyelectrolyte or aggregation behavior of ionomer solutions [23–25]. We have derived eq. (1) regarding theoretical treatment of viscosity behavior [22]:

$$[\eta_n] - [\eta] = [\eta]\,\frac{x}{100 - x} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity, $[\eta_n]$ is the intrinsic viscosity when viscosity-average molecular weight increased by a factor $n$, and $x$ is the degree of association of ionic groups.

Equation (1) implies that the difference between $[\eta_n]$ of partially associated polymers and $[\eta]$ of completely dissociated ones is proportional to $[\eta]$. Therefore, it can be said that the change of $\eta_{SP}/C$ by addition of $MgCl_2$ at very low polymer concentrations, hence, the difference between $[\eta_n]$ and $[\eta]$, becomes larger as the molecular weight between ionic groups, i.e. $[\eta]$ increases. Further, eq. (1) means that even if the molecular weight between ionic groups is constant, an increase in degree ($x$) of ionic association, caused by increasing the added amount of $MgCl_2$, leads to an increase in the difference between $[\eta_n]$ and $[\eta]$. Thus, eq. (1) clearly explains the viscosity behaviors of the halato-telechelic polyureas and polyurethane-ureas at low concentrations, suggesting that the behaviors are attributable mainly to partial reassociation of dissociated ions.

## CROSSLINKING OF BISEPOXIDE WITH ABA(M) AND DIAMINE

It is well known that epoxy resins are cured with amine compounds. However, there is the disadvantage of a slow curing rate in using the aromatic amines. The metal carboxylate groups of ABA(M) were anticipated to have catalytic activities for the amine cure. Therefore, crosslinking of bisepoxide with ABA(M) and MDA was investigated [26]. As the bisepoxide, bisphenol A diglycidyl ether (BADG) was used.

Although the complexity of the system is inevitably high, the degree of conversion has been followed by following residual epoxide, primary amine, produced secondary and tertiary amines, and produced ether group contents as a function of the curing time. It was found that the metal salts have catalytic activities for the cross-linking reaction and also for etherification of epoxy groups as a side reaction. In this case, the salt containing Ca with the lower electronegativity exhibits higher catalytic activities than that containing Mg. Hence, the crosslinking reaction is supposed to proceed via an ionic mechanism in which the carboxylate anion is concerned.

As for the physical properties of the cured resins, compressive strength is higher in the metal-containing cured resins than in the resin without metal, probably due to a formation of clusters of the metal carboxylate groups. Heat-distortion temperature (HDT) shows a tendency to decrease with increase in the metal content.

As for the dynamic mechanical properties, the metal-containing cured resins exhibit relaxations at ca. 150 and $-50°C$, and further at ca. 60°C. The relaxation at ca. 150°C is attributed to the glass transition temperature ($T_g$). The relaxation at ca. $-50°C$ is considered to be due to the lo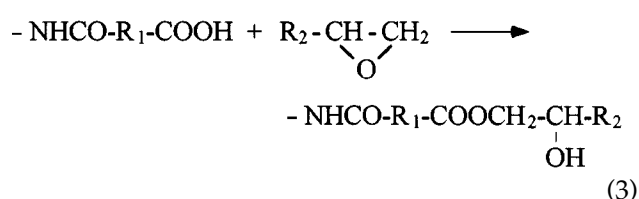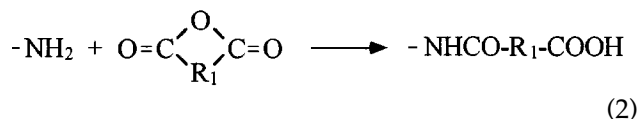cal mode of associated ionic linkages or diphenyl methane skeleton, in addition to the local mode of bisphenol A skeleton and the neighboring mobile structure parts [27–29]. Furthermore, the relaxation at ca. 60°C is supposed to be attributable to the linear chain structure [30].
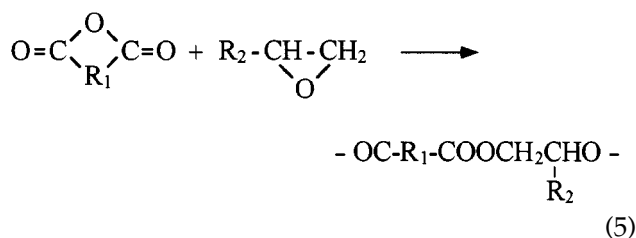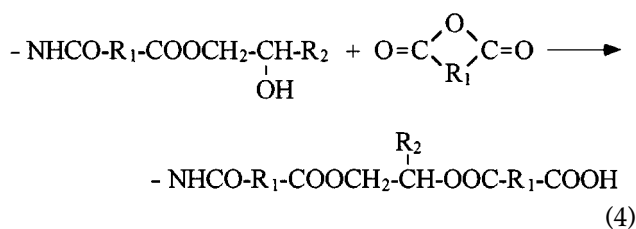
However, $T_g$ determined by the dynamic mechanical properties is not influenced by the metal content. This difference between the HDT and $T_g$ is supposed to be due to the difference in the determination methods. That is, the HDT is a temperature at which the sample is deformed as a whole by a fixed load. Hence, the HDT would depend on the proportion of each chemical structure existing in the cured resin sample. Meanwhile, the dynamic mechanical properties are considered to reflect a temperature of relaxation of each structure part in the sample, for example, $T_g$ is a temperature of relaxation of the main cross-linked structure part. The metal-containing amine-cured epoxy resins contained a large amount of unreacted secondary amines, in addition to the network structure part. The formation of the secondary amines is due to etherification. In this case, with an increase in the metal carboxylate groups, the degree of etherification becomes high; hence, the amounts of unreacted secondary amines increase. The secondary amine part is a component of a linear chain structure composed mainly of diphenylmethane. The $T_g$ of the main crosslinked structure part would not be affected even when there are many kinds of chemical structures in the cured resin sample.

## CROSSLINKING OF BISEPOXIDE WITH ABA(M) AND ANHYDRIDE

In crosslinking of epoxy resins with dicarboxylic acid anhydrides, tertiary amines such as N,N-dimethylbenzylamine (DMBA), etc., are widely used as a catalyst. Such tertiary amines are known to be toxic. ABA is much less toxic and the Mg and Ca carboxylate groups in ABA(M) were anticipated to have catalytic activities for the anhydride cure of epoxy resins. Therefore, crosslinking of BADG with ABA(M) and anhydride has been investigated to prepare metal-containing cured resins [31]. As the anhydride, hexahydrophthalic anhydride (HPAn) was used.

Although the complexity of the system is inevitably high, in principle, the curing of the ABA(M)–HPAn–BADG systems is considered to proceed as follows. First, reaction (2) should occur to produce a carboxyl group. In this case, adducts of

$$-NH_2 + O{=}C\underset{R_1}{\overset{O}{\diagdown\diagup}}C{=}O \longrightarrow -NHCO\text{-}R_1\text{-}COOH \tag{2}$$

$$-NHCO\text{-}R_1\text{-}COOH + R_2\text{-}CH\underset{O}{\diagup\diagdown}CH_2 \longrightarrow$$

$$-NHCO\text{-}R_1\text{-}COOCH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}R_2 \tag{3}$$

$$- NHCO\text{-}R_1\text{-}COOCH_2\text{-}CH\text{-}R_2 \ + \ O=C\underset{R_1}{\overset{O}{\diagup\diagdown}}C=O \longrightarrow$$
$$\underset{OH}{|}$$

$$\underset{R_2}{|}$$
$$- NHCO\text{-}R_1\text{-}COOCH_2\text{-}CH\text{-}OOC\text{-}R_1\text{-}COOH$$

$$(4)$$

$$O=C\underset{R_1}{\overset{O}{\diagup\diagdown}}C=O \ + \ R_2\text{-}CH\text{-}CH_2 \longrightarrow$$
$$\underset{O}{\diagdown\diagup}$$

$$- OC\text{-}R_1\text{-}COOCH_2CHO -$$
$$\underset{R_2}{|}$$

$$(5)$$

ABA(M) and HPAn are formed. The carboxyl group in the adducts is a starting point for chain extension. That is, the carboxyl group would enter into reaction (3) to produce a new hydroxyl group. Next, the hydroxyl group would immediately enter into reaction (4). Thus, these addition reactions are considered to repeat alternately, so that ample opportunity for further growth of a three-dimensional network structure will be provided. Meanwhile, reaction (5) is considered possible. However, reaction (5) would become less significant as the curing progresses because of a decrease in the anhydride content.
Also in this case, the degree of conversion depends on the acid, anhydride and epoxide contents as a function of the curing time.

It was found that the systems containing ABA(M) exhibit higher reaction rates than those without metal, indicating catalytic activities of the metal carboxylate groups of ABA(M). This tendency is especially remarkable for the system containing Mg. Thus, the reverse trend is observed in this case. In the curing reactions of the systems of divalent metal salts of HEP–anhydride–bisepoxide, the Mg salt exhibited higher catalytic activities than the Ca salt [32]. This curing was supposed to proceed mainly by a complex mechanism where ion pairs are

concerned [33]. Also, the curing reactions of the ABA(M)–HPAn–BADG systems are supposed to proceed via such a complex mechanism.

The idealized main structure part of the metal-containing cure resins obtained like this is represented in Fig. 1. As for the physical properties of the metal-containing cured resins, tensile and flexural strengths decrease with increase in the metal content. However, Rockwell hardness is not affected by the metal content.
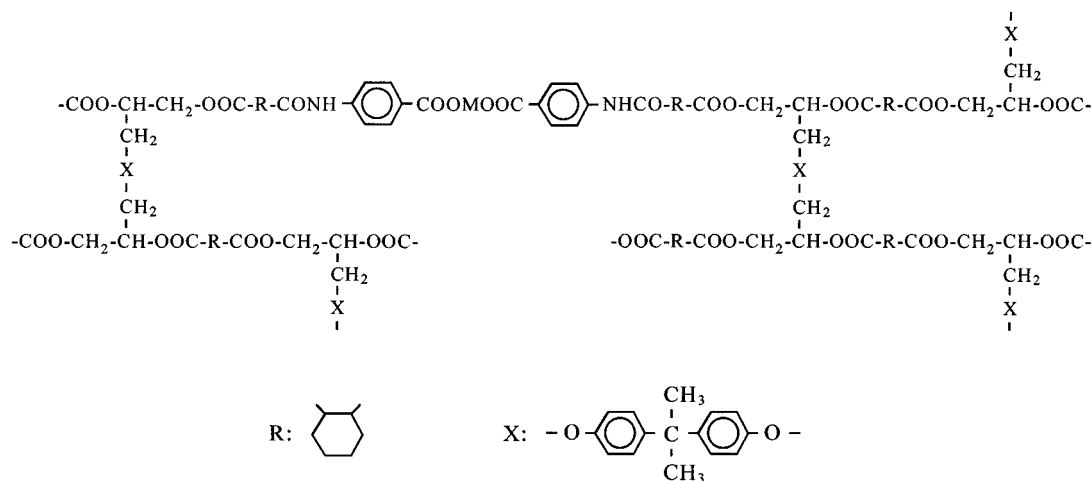
The metal-containing cured rsins exhibit relaxations at ca. 120–150°C ($T_g$) and ca. $-50$°C in the dynamic mechanical properties. In this case, there is a good correlation between the HDT and the $T_g$ determined by the dynamic mechanical properties. This suggests that the cured resins have uniform cross-linked structure and do not contain measurable amounts of linear chain structure part. Furthermore, the absence of linear chain structure parts is further supported by the absence of the relaxation at ca. 60°C.

In addition, the metal carboxylate groups act as a catalyst for the thermal decompositions and the salt containing Ca exhibits higher catalytic activities than that containing Mg. Therefore, the thermal decompositions are supposed to proceed via an ionic mechanism.
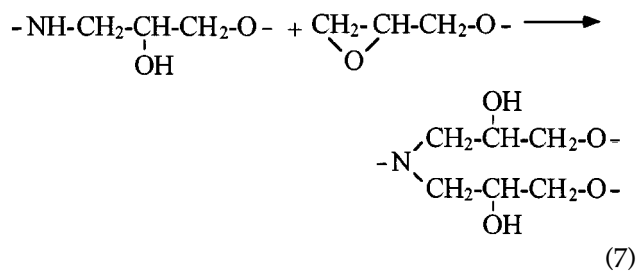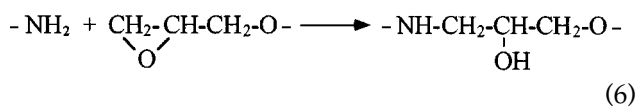
## CROSSLINKING BY ETHERIFICATION OF BISEPOXIDE WITH ABA(M)

As described above, the metal carboxylate groups in ABA(M) were also found to have catalytic activity for etherification of epoxy groups as a side reaction. It seemed of interest to prepare metal-containng cured resins by etherification of epoxy groups of BADG by the catalytic action of the metal carboxylate groups in ABA(M). Therefore, crosslinking of curable mixtures prepared from ABA(M) and a large excess of BADG was investigated by taking advantage of the catalytic activity of ABA(M) for the etherification of epoxy groups [34].

The curable mixtures can be obtained when a large excess of BADG is added to the solution of

$$-COO\text{-}\underset{\underset{\underset{X}{|}}{\overset{|}{CH_2}}}{\overset{|}{CH}}\text{-}CH_2\text{-}OOC\text{-}R\text{-}CONH-\hexagon-COOMOOC-\hexagon-NHCO\text{-}R\text{-}COO\text{-}CH_2\text{-}\underset{\underset{\underset{X}{|}}{\overset{|}{CH_2}}}{\overset{|}{CH}}\text{-}OOC\text{-}R\text{-}COO\text{-}CH_2\text{-}\underset{\underset{X}{|}}{\overset{|}{CH}}\text{-}OOC-$$

$$-COO\text{-}CH_2\text{-}\underset{\underset{X}{|}}{\overset{|}{CH}}\text{-}OOC\text{-}R\text{-}COO\text{-}CH_2\text{-}CH\text{-}OOC- \qquad -OOC\text{-}R\text{-}COO\text{-}CH_2\text{-}\underset{\underset{X}{|}}{\overset{|}{CH}}\text{-}OOC\text{-}R\text{-}COO\text{-}CH_2\text{-}CH\text{-}OOC-$$

$$R: \ \hexagon \qquad\qquad X: \ -O-\hexagon-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\hexagon-O-$$

**FIGURE 1.** Idealized main structure part of metal-containing cured resins prepared by crosslinking of BADG with ABA(M) and HPAn.

$$-NH_2 + CH_2\text{-}CH\text{-}CH_2\text{-}O- \longrightarrow -NH\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}O-$$
$$\underset{O}{\diagdown\diagup} \qquad\qquad\qquad \underset{OH}{|}$$

$$(6)$$

$$-NH\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}O- + CH_2\text{-}CH\text{-}CH_2\text{-}O- \longrightarrow$$
$$\underset{OH}{|} \qquad\qquad \underset{O}{\diagdown\diagup}$$

$$-N\diagup\overset{\overset{OH}{|}}{CH_2\text{-}CH\text{-}CH_2\text{-}O-}_{\diagdown CH_2\text{-}CH\text{-}CH_2\text{-}O-}$$
$$\underset{OH}{|}$$

$$(7)$$

ABA(M) in DMF and then the DMF is removed after the mixture is heated at 100°C for 1 hr. In this case, one or two amino groups in ABA(M) are considered to have reacted with the epoxy groups in BADG, as shown by eqs (6) and (7), forming soluble adducts of ABA(M) and BADG:

It was found that the salt containing Ca exhibits higher catalytic activity than that containing Mg. Therefore, the curing reactions are supposed to proceed via an ionic mechansm. The order of reaction with respect to carboxylate anion concentration is one order for the both systems, suggesting the participation of one $-COO^-$ group in the curing reactions. The overall activation energies of the crosslinking reaction are 13.4 kcal/mol for the system containing Mg and 23.0 kcal/mol for the system containing Ca.

The idealized main structure part of the metal-containing cured resins obtained is represented in Fig. 2. The metal-containing cured resins show higher flexural strength, Rockwell hardness and compressive strength than the resins without metal. Thus, the effect of introducing metal appears in this case.

As for the dynamic mechanical properties, the metal-containing cured resins exhibit relaxations at

ca. 110–140°C ($T_g$) and $-70$°C. The HDT and the $T_g$ (determined by the dynamic mechanical properties) increase with an increase in the metal salt content in the feed. Therefore, the good correlation between the HDT and the $T_g$, observed in this case, suggests that the cured resins have a uniform crosslinked structure.

Thermal decomposition is accelerated by the incorporated metal. In addition, the metal-containing cured resins have high boiling water and water resistances.

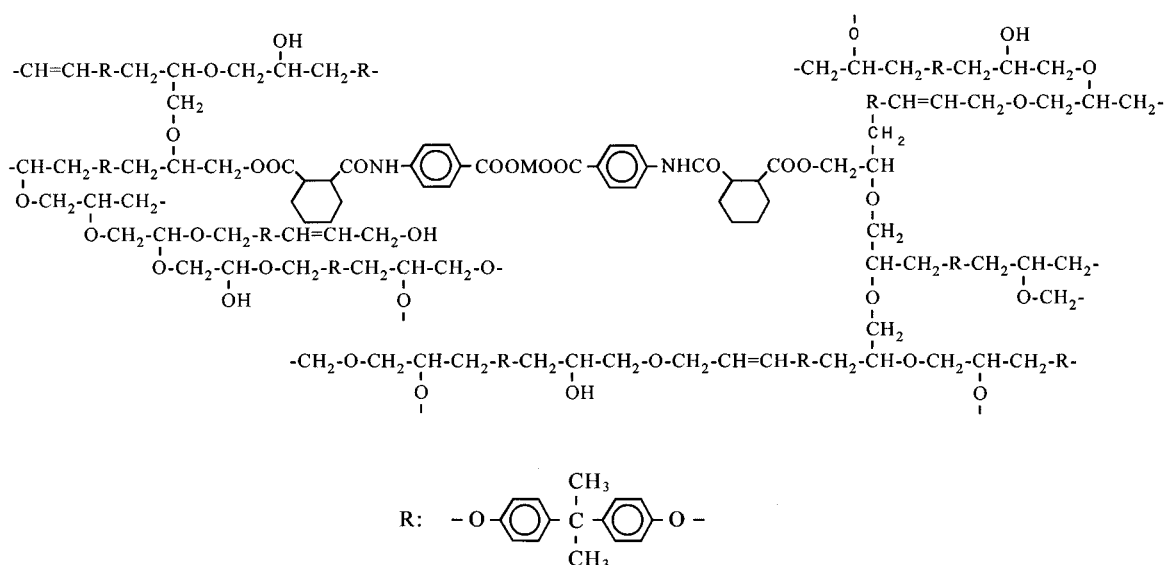## CROSSLINKING BY ETHERIFICATION OF BISEPOXIDE WITH ADDUCTS OF ABA(M) AND ANHYDRIDE

As described above, in the initial stage of the curing reactions of BADG with ABA(M) and HPAn, adducts of ABA(M) and HPAn are formed. The adducts contain amide and carboxyl groups in addition to the metal carboxylate group. It seemed of interest to prepare metal-containing cured resins by etherification of epoxy groups of BADG by the catalytic action of the metal carboxylate groups in the adducts of ABA(M) and HPAn.

Therefore, crosslinking of curable mixtures prepared from ABA(M), HPAn and a large excess of BADG was investigated by taking advantage of the catalytic activity of the ABA(M)–HPAn adducts for the etherification of epoxy groups [35]. In the initial stage of the curing reaction, the epoxy groups in BADG are considered to react dominantly with the carboxyl groups in the adducts. Also in this case, the Ca carboxylate group shows higher catalytic activity than the Mg carboxylate group, suggesting an ionic mechanism in which the carboxylate anion is concerned.

Figure 3 shows the idealized main structure part of the metal-containing cured resins thus obtained. The metal-containing cured resins show relaxations at ca. 100–120°C ($T_g$) and $-70$°C in the dynamic
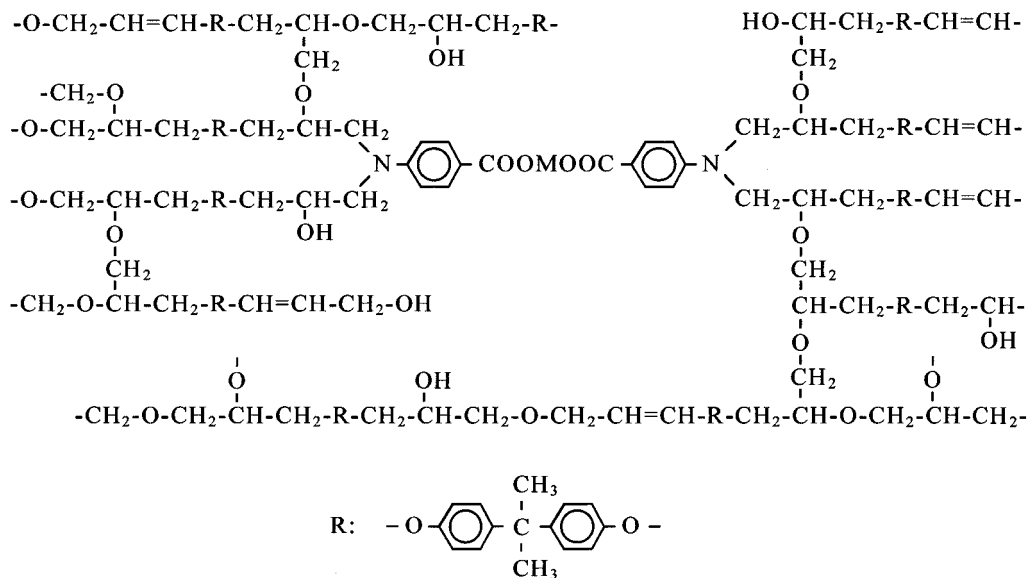
**FIGURE 2.** Idealized main structure part of metal-containing cured resins prepared by crosslinkng by etherification of BADG with ABA(M).

$$-CH=CH-R-CH_2-\overset{OH}{\underset{|}{CH}}-O-CH_2-\overset{|}{CH}-CH_2-R-$$
$$\overset{|}{CH_2}$$
$$\overset{|}{O}$$
$$-\overset{|}{CH}-CH_2-R-CH_2-\overset{|}{CH}-CH_2-OOC \qquad CONH-\bigcirc-COOMOOC-\bigcirc-NHCO \qquad COO-CH_2-\overset{|}{CH}$$
$$\overset{|}{O}-CH_2-\overset{|}{CH}-CH_2-$$
$$O-CH_2-CH-O-CH_2-R-CH=CH-CH_2-OH$$
$$O-CH_2-\overset{|}{CH}-O-CH_2-R-CH_2-\overset{|}{CH}-CH_2-O-$$
$$\overset{|}{OH} \qquad \overset{|}{O}$$

$$\overset{|}{O} \qquad OH$$
$$-CH_2-\overset{|}{CH}-CH_2-R-CH_2-\overset{|}{CH}-CH_2-O$$
$$R-CH=CH-CH_2-O-CH_2-\overset{|}{CH}-CH_2-$$
$$\overset{|}{CH_2}$$
$$\overset{|}{O}$$
$$\overset{|}{CH_2}$$
$$\overset{|}{CH}-CH_2-R-CH_2-CH-CH_2-$$
$$\overset{|}{O} \qquad \overset{|}{O}-CH_2-$$
$$\overset{|}{CH_2}$$

$$-CH_2-O-CH_2-\overset{|}{CH}-CH_2-R-CH_2-\overset{|}{CH}-CH_2-O-CH_2-CH=CH-R-CH_2-\overset{|}{CH}-O-CH_2-\overset{|}{CH}-CH_2-R-$$
$$\overset{|}{O} \qquad \overset{|}{OH} \qquad \overset{|}{O}$$

$$R: \quad -O-\bigcirc-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\bigcirc-O-$$

**FIGURE 3.** Idealized main structure part of metal-containing cured resins prepared by crosslinking by etherification of BADG with adducts of ABA(M) and HPAn.

**TABLE 1.** $T_g$ and Impact Strengths of Various Types of ABA(M)-based Cured Resins

| Component | Type of curing | Tg (°C) | Impact strength (kg cm/cm) | Reference |
|---|---|---|---|---|
| ABA(M)–MDA–BADG | Amine–epoxy reactions | 162–163 | 1.20–1.40 | 26 |
| ABA(M)–HPAn–BADG | Addition esterification | 126–143 | 1.12–1.16 | 31 |
| ABA(M)–BADG | Etherification of epoxy groups | 111–139 | 0.98–1.46 | 34 |
| ABA(M)–HPAn–BADG | Etherification of epoxy groups | 103–118 | 4.8–6.3 | 35 |

mechanical properties. The $T_g$ of the metal-containing cured resins increases with an incrase in the ABA(M) content. Thus, the effect of introducing metal appears clearly. This might be attributed to a possible aggregation of the metal carboxylate groups.

It has been reported that crosslinking density of cured epoxy resins is proportional to shear modulus ($G$) at a temperatue above $T_g$ [36]. The $T_g$ for these cured resins [35] is nearly proportional to the $G$ of the resins at the region above the $T_g$. That is, the $T_g$ of the cured resins increases with an increase in the crosslinking density. Further, as a whole, the $G$ and the $T_g$ of the cured resins are lower than those of the ABA(M)–BADG resins cured by the etherification of epoxy groups [34]. This suggests that, in general, the former cured resins have lower cross-linking densities than the latter.

As for the physical properties, the HDT of the metal-containing cured resins increases with an increase in the mole ratio of ABA(M) in the feed. Thus, there is a good correlation between the HDT and the $T_g$ of these cured resins, again suggesting that these cured resins have a uniform cross-linking structure and do not contain a measurable amount of linear chain structure part.

It is noteworthy that the impact strengths of the cured resins are 4.8–6.3 kg cm/cm, very high values for the cured epoxy resins. Table 1 shows $T_g$ and impact strengths of various types of ABA(M)-based cured resins. It is apparent that the cured resins [35] exhibit lower $T_g$ and much higher impact strengths than do the ABA(M)–MDA–BADG and ABA(M)–HPAn–BADG resins cured by the addition reactions [26, 31], and the ABA(M)–BADG resins cured by the etherification of epoxy groups [34].

It is generally said that the impact strength of cured resins increases with decrease in the crosslinking density of the cured resins. For the ABA(M)–HPAn–BADG resins cured by the etherification of epoxy groups [35], the impact strength increases markedly as the $T_g$ decreases. Such a remarkable increase in the impact strength might be due not only to the decrease in the cross-linking density, but also to some interaction between molecular chains, i.e. the hydroxyl groups and the amide linkages in the molecular chains are supposed to form hydrogen bonding, resulting in an interaction between molecular chains, contributing, to some extent, to the increase in the impact strength.

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