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# Functional copolymers of isobutylene and acrylic ester

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Reactive copolymers of isobutylene and acrylic ester were successfully synthesized by the incorporation of acryloyl chloride or maleic anhydride into alternating copolymers of isobutylene and acrylic ester by means of complexed copolymerization catalysed with alkylboron halide. The terpolymers of isobutylene, acrylic ester and acryloyl chloride (AILM) and isobutylene, acrylic ester and maleic anhydride (AIHM) reacted with many compounds. Via the polymer reactions based on AILM and AIHM, various functional copolymers of isobutylene and acrylic ester were synthesized, which contained carboxyl group, amide group, hydroxyl group, nitrile group, epoxy group and so forth on the pendant of the polymer chains.

**(Keywords: isobutylene; acrylic ester; functional copolymer)**

## INTRODUCTION

The authors have already found that alternating copolymers of isobutylene (IB) and acrylic ester (AE) can be obtained by means of complexed copolymerization catalysed with alkylboron halide in much higher activities than with alkylaluminium halide[1].

Among the alternating copolymers IB–methyl acrylate copolymer has intermediate properties between plastics and rubber. IB–ethyl acrylate and IB–n-butyl acrylate copolymers show rubber-like properties and IB–2-ethylhexyl acrylate copolymer is tacky[2]. If the alternating copolymers are to be used as the raw materials for textile treatment agents, paints, adhesives and so forth, solvent resistance, dry-cleaning resistance, high mechanical strength and other properties are demanded. For these purposes it is necessary to incorporate a third reactive monomer into the alternating copolymers to make them crosslinking-type (thermosetting-type) polymers. Acryloyl chloride (ACL) and maleic anhydride (MAH) are very reactive monomers that react with many functional groups via acid chloride or acid anhydride group.

This report describes first the synthesis of the terpolymers of IB, AE and ACL (AILM) and IB, AE and MAH (AIHM), and then the introduction of various functional groups via polymer reactions based on AILM and AIHM.

## EXPERIMENTAL

### *Materials*

ACL, obtained from Osaka Organic Chemical Ltd, was distilled and dried with 4 Å molecular sieves. MAH, obtained from Nakarai Chemical Ltd, was purified by eliminating the benzene-insoluble part (maleic acid). Other materials were described in the previous paper[1].

### *Polymerization*

The polymerization was conducted following the method described in the previous paper[1] under an oxygen ($O_2$)–nitrogen ($N_2$) mixed gas flow or $N_2$ atmosphere.

### *Measurements*

The conversions of AE, ACL and MAH were measured by gas chromatograph analyses and polymer yields. Intrinsic viscosity measurements were carried out in benzene at 30°C using Ubbelohde viscometers. In the case of AILM, the acid chloride group was esterified beforehand with alcohol corresponding to the ester group of AE component. For elemental analyses of AILM, the acid chloride group was changed to amide group with aqueous ammonia beforehand. Other measurements were described in the previous papers[1,2].

## RESULTS AND DISCUSSION

### *Synthesis of the reactive copolymers*

*Terpolymerization of isobutylene, acrylic ester and acryloyl chloride. Table 1* shows the results of copolymerization or terpolymerization of IB, ACL and/or methyl acrylate (MA). The polymerization was conducted under $N_2$ atmosphere. ACL copolymerized with IB (run No. 1) but the conversion of ACL was lower than that of MA in IB–MA copolymerization (run No. 3) in spite of twice of catalyst concentration. The intrinsic viscosity of IB–ACL copolymer was also lower than that of IB–MA copolymer. In IB–ACL copolymerization the produced

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**Table 1** Copolymerization or terpolymerization of isobutylene (IB), acryloyl chloride (ACL) and/or methyl acrylate (MA)[a]

| Run No. | Monomer IB (mmol) | Monomer MA (mmol) | Monomer ACL (mmol) | Catalyst $BEtCl_2$ (mmol) | Polymerization yield (g) | Polymer $[\eta]$ ($dl\,g^{-1}$) | Polymer Composition[b] (mol%) IB | Polymer Composition[b] (mol%) MA | Polymer Composition[b] (mol%) ACL | Polymer Conv. (%) on IB | Polymer Conv. (%) on MA | Polymer Conv. (%) on ACL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 400 | | 200 | 4 | 4.87 | 1.16[c] | 47.8 | | 52.2 | 8 | | 17 |
| 2 | 400 | 180 | 20 | 4 | 18.61 | 2.14 | 49.2 | 46.1 | 4.7 | 32 | 67 | 60 |
| 3 | 400 | 200 | | 2 | 26.15 | 5.67 | 49.6 | 50.4 | | 46 | 93 | |

[a] Conditions: toluene, 150 ml; temp., −30°C; time 3 h; order of addition, toluene → IB → $BEtCl_2$ → the mixture of MA and ACL; under $N_2$ atmosphere; vessel, a glass flask

[b] By elemental analysis of the reaction product with ammonia (run Nos. 1 and 2)

[c] Esterified with methanol

copolymer contained about equimolar IB and ACL though the feed molar ratio of IB to ACL was 2/1. In the terpolymerization the produced polymer comprised about 50 mol% of IB and about 50 mol% of the sum of MA and ACL. The feed monomer ratios were not so widely varied and the structure of polymers was not analysed. Therefore we cannot say clearly but perhaps ACL reacted as an acceptor monomer in the present complexed copolymerization to replace a part of the AE in the alternating sequences. *Figure 1* shows the i.r. spectra of the copolymer of IB and ACL, and the terpolymer of IB, MA and ACL. Both spectra have an absorption at 1790 $cm^{-1}$ ascribed to acid chloride group, indicating the existence of ACL unit in the polymers.

Though ACL is such a reactive monomer that it reacts with moisture in the air, unexpectedly it did not react and deactivate alkylboron halide catalyst and was incorporated well into the alternating copolymers of IB and AE. It is known that ACL copolymerizes with AE[3] or ethylene[4] by conventional radical polymerization, but it has never been reported that ACL copolymerized with IB by complexed copolymerization. In the complex copolymerization with alkylaluminium halide catalyst, ACL did not polymerize successfully. There are many similarities between organoaluminium and organoboron compounds, but several differences exist between them. For example, trialkylaluminium reacts readily with water but trialkylboron is not decomposed by water; and alkylboron halide is more sensitive to $O_2$ than alkylaluminium halide. Besides there exists a 'sesqui' type in alkylaluminium halide, but not in alkylboron halide, i.e. an equimolar mixture of triethylaluminium and aluminium trichloride easily forms $Al_2Et_3Cl_3$ even at room temperature, but in the case of boron the mixture of triethylboron and boron trichloride does not show any change at room temperature. These differences are perhaps ascribed to the differences of electronegativity and size of p orbital of both metals and the difference of Lewis acidity of both compounds.

The reactivity of ACL and MA was compared in the terpolymerization catalysed with the 1:1 mixture of $BEtCl_2$ and $BEt_2Cl$. The polymerization was conducted under the existence of co-catalytic $O_2$, i.e. under an $O_2$–$N_2$ mixed gas flow. The molar ratio of IB/MA/ACL/catalyst was 100/45/5/1. The results are shown in *Figure 2*. In the binary system of IB and MA the conversion of MA reached 100% in 30 min. In the case of the ternary system, in the early stage ACL polymerized selectively and MA hardly polymerized. On the contrary, in the latter period the conversion of MA increased rapidly after which ACL was considerably consumed. In the ternary system the time that the conversion of MA reached 100% was 60 min, i.e. twice that of the binary system. The intrinsic viscosity of the copolymer was almost constant through the polymerization. On

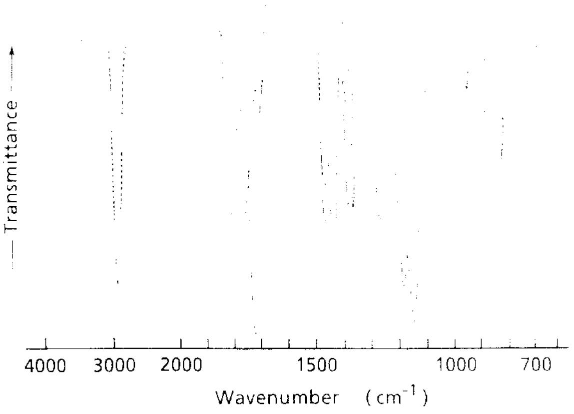


**Figure 1** I.r. spectra of the copolymer of isobutylene (IB) and acryloyl chloride (ACL) and the terpolymer of IB, methyl acrylate (MA) and ACL: (---) IB–ACL, molar composition, 48.2/51.8; (——) IB–MA–ACL, molar composition, 49.0/45.9/5.1

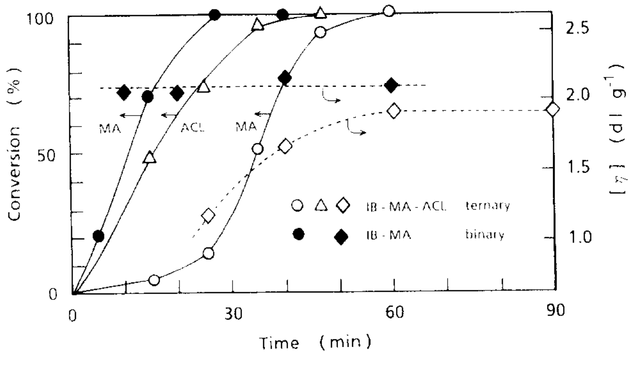
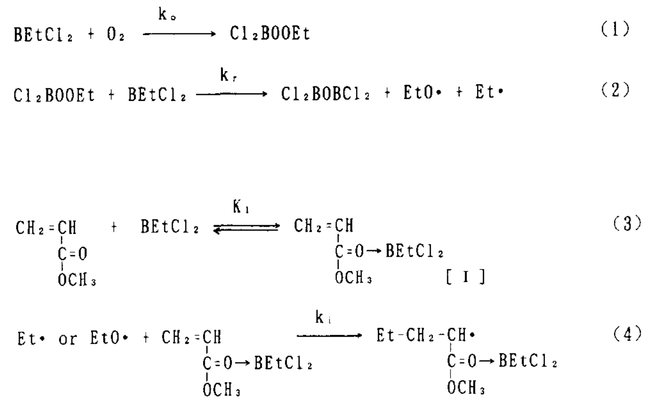
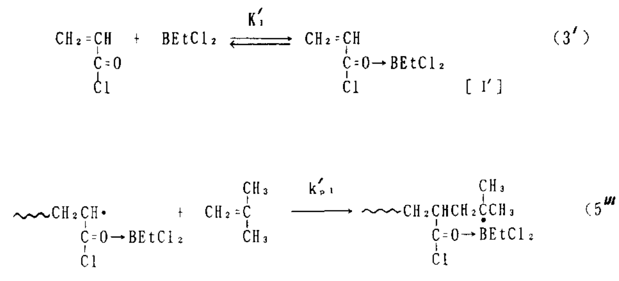


**Figure 2** Time course of the terpolymerization of isobutylene (IB), methyl acrylate (MA) and acryloyl chloride (ACL). Conditions: IB, 666 mmol; MA, 300 mmol; ACL, 33 mmol; $BEtCl_2$/$BEt_2Cl$, 3.3/3.3 mmol; toluene, 400 ml; temp., −20°C; order of addition, toluene → IB → the mixture of MA and ACL → $BEtCl_2$ → $BEt_2Cl$; 20 $cm^3\,min^{-1}$ of $O_2$–$N_2$ mixed gas ($O_2$ 2.5%) was flowed through the vapour part of the flask; vessel, a glass flask



**Scheme 1**



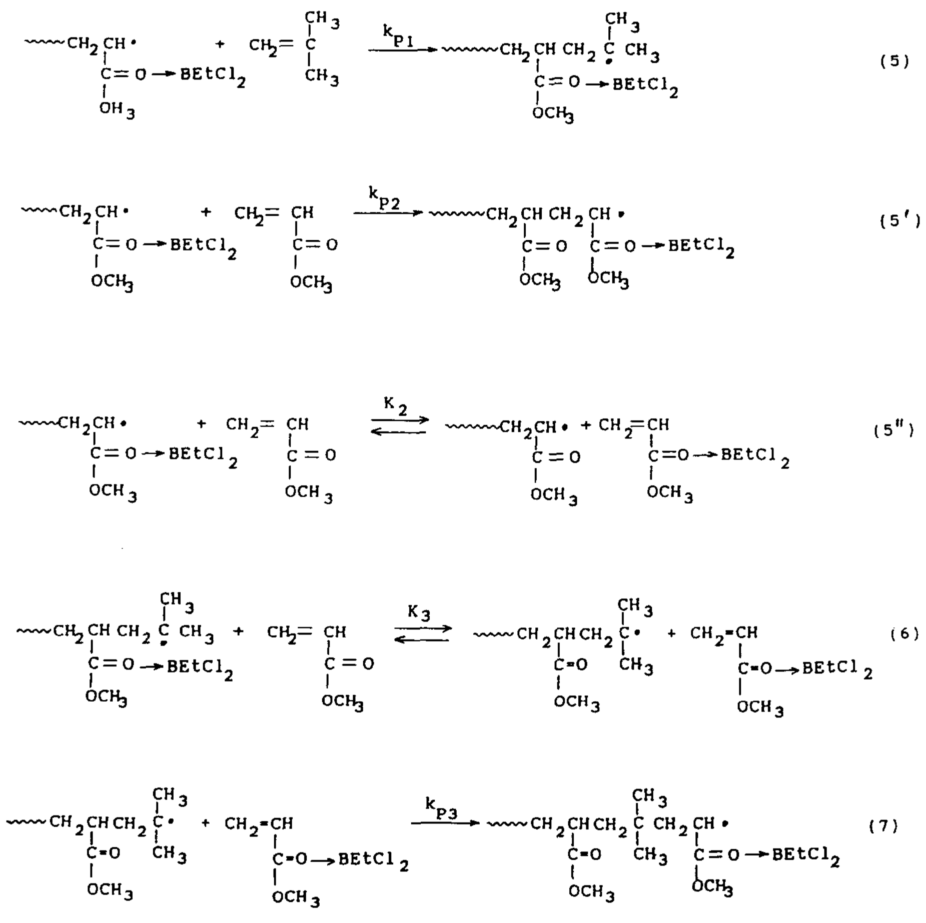
**Scheme 3**

the other hand, in the ternary system it was relatively low in the early stage and increased in the course of polymerization. Judging from the above result, in the case of batch polymerization, ACL-rich terpolymer seemed to be formed in the early stage and ACL-poor terpolymer in the latter period.

The mechanism of the alternating copolymerization of IB and MA with $BEtCl_2$ has already been proposed[1]. In the polymerization system, the initiator is likely produced by the reaction of $BEtCl_2$ and coexisting $O_2$ (equations (1) and (2) in *Scheme 1*). And when the radical produced in equation (2) attacks the MA → $BEtCl_2$ complex **[I]** in equation (3), the polymerization starts (equation (4)). The propagation reaction after equation (4) is considered to continue as shown in *Scheme 2*.

When ACL coexists equation (3′) is established at the same time as equation (3). The $Q$ and $e$ values[5] of ACL ($Q = 1.82$, $e = 1.92$) are much larger than those of MA ($Q = 0.45$, $e = 0.64$), so the charge-transfer complex **[I′]** (*Scheme 3*) is preferentially formed rather than the complex **[I]**, i.e. $K_1' > K_1$. Therefore, in the early stage of the terpolymerization ACL polymerized selectively. But the conversion of ACL in IB–ACL copolymerization was lower than that of MA in IB–MA copolymerization and the molecular weight of IB–ACL copolymer was lower than that of IB–MA copolymer (*Table 1*).

When ACL coexists, the propagation reaction of equation $(5''')$ exists at the same time as equation (5). The stability of the ACL-terminated growing radical (*Scheme 3*) may be higher than that of the MA-terminated



**Scheme 2**

**Table 2** Synthesis of the homogeneous terpolymer of isobutylene (IB), methyl acrylate (MA) and acryloyl chloride (ACL)[a]

| Polymerization | | | |
|---|---|---|---|
| Time (h) | Conversion (%) MA | Conversion (%) ACL | Polymer $[\eta]$ (dl g$^{-1}$) |
| 1 | 99.9 | 100 | 1.72 |
| 2 | 100 | 99.7 | |
| 3 | 100 | 95.1 | 1.68 |
| 4 | 99.9 | 100 | |
| 5 | 100 | 100 | 1.75 |

[a] Conditions: IB, 800 mmol; MA, 360 mmol; ACL, 40 mmol; BEtCl$_2$/BEt$_2$Cl, 8/8 mmol; toluene, 240 ml; temp., $-20$°C; order of addition, toluene → IB → BEtCl$_2$ → BEt$_2$Cl → the mixture of MA and ACL was added continuously in 4 h; 20 cm$^3$ min$^{-1}$ of O$_2$–N$_2$ mixed gas (O$_2$ 2.5%) was flowed through the vapour part of the flask; vessel, a glass flask

growing radical, i.e. $k'_{\mathrm{p1}}$ is smaller than $k_{\mathrm{p1}}$, and the possibility of chain-transfer reaction is higher in ACL. As another reason for the slower polymerization rate in ACL, the bonding force of the complex of ACL and BEtCl$_2$ may be so strong that BEtCl$_2$ will be hard to dissociate and recycle even after incorporation into the polymer (equation (6)).

The synthesis of the homogeneous terpolymer in which ACL was uniformly distributed was tried by adding the mixture of MA and ACL continuously. The results are shown in *Table 2*. The molar ratio of IB/MA/ACL/catalyst at the final point of the addition was 50/22.5/2.5/1. The mixture of MA and ACL was added in 4 h. As seen in the table the conversions of both MA and ACL were almost 100% at every point of the polymerization and the intrinsic viscosity was also constant through the polymerization. The produced terpolymer was considered to have a relatively homogeneous distribution of ACL.

It was undoubted that IB–ACL copolymer was not a blend of both homopolymers because IB did not homopolymerize with alkylboron halide. The terpolymer was also surely not a blend of IB–MA copolymer and IB–ACL copolymer from the following experiments. As shown in *Table 3* the AILM (**I**) was almost perfectly insoluble in methanol except for a little low-molecular-weight component. On the other hand the reaction product with monoethanolamine (**II**) (this will be described in detail in the later section on 'Polymer reactions') was nearly completely soluble in methanol except for a small amount of high-molecular-weight component. As another experiment, when the reaction mixture of AILM and monoethanolamine was poured into water, little water-soluble polymer was obtained and a water-insoluble polymer which contained monoethanolamine unit in an adequate amount (from the elemental analysis) was obtained—in this connection, IB–ACL copolymer which contains 50 mol% of ACL is water-soluble.

*Terpolymerization of isobutylene, acrylic ester and maleic anhydride.* MAH has two electron-attractive carbonyl groups in the conjugated position with the olefinic double bond and the electron density[5] of the olefinic double bond is rather lower ($Q = 0.86$, $e = 3.69$) than MA ($Q = 0.45$, $e = 0.64$), so it forms a charge-transfer complex with IB even in the absence of alkylboron halide and copolymerizes alternatingly by conventional radical polymerization. The present alternating copolymerization of IB and AE catalysed by alkylboron halide is considered to proceed via a radical mechanism[1], so MAH was expected to be incorporated into the alternating copolymers of IB and AE in a high yield.

**Table 3** Solubility in methanol of the reaction product (**II**) of AILM (**I**) and monoethanolamine[a]

$$\underset{(\mathrm{I})}{\mathrm{P{\sim}COCl}} + \mathrm{H_2NC_2H_4OH} \longrightarrow \underset{(\mathrm{II})}{\mathrm{P{\sim}CONHC_2H_4OH}} + \mathrm{HCl}$$

| | Methanol-soluble | | Methanol-insoluble | |
|---|---|---|---|---|
| Polymer | Amount (%) | $[\eta]$ (dl g$^{-1}$) | Amount (%) | $[\eta]$ (dl g$^{-1}$) |
| **I** | 4.6 | | 95.4 | 0.52[b] |
| **II** | 91.6 | 0.28[b] | 8.4 | 1.38[c] |

[a] AILM: IB–MA–ACL; molar composition, 49.1/45.7/5.2. Reaction conditions: H$_2$NC$_2$H$_4$OH/COCl molar ratio, 10; temp., 24°C; time, 30 min; solvent, toluene

[b] Solvent, toluene

[c] Solvent, tetrahydrofuran

The terpolymerization of IB, MA and MAH was conducted in ethylene dichloride solvent under an O$_2$–N$_2$ mixed gas flow. The molar ratio of IB/MA/MAH/catalyst in the feed was 33/8.3/8.3/1 and the catalyst was a 1 : 1 mixture of BEtCl$_2$ and BEt$_2$Cl. The time conversions of MA and MAH are shown in *Figure 3*. In the same manner as the terpolymerization of IB, MA and ACL, the reactivity of MAH was higher than MA but the difference was not so much as for ACL. As mentioned above MAH has high $Q$ and $e$ values, so it preferentially formed the charge-transfer complex with catalyst (equation (3)) rather than MA and its propagation rate (equations (5) and (7)) was faster than MA. The produced polymers always comprised about 50 mol% of IB and about 50 mol% of the sum of MA and MAH.

The synthesis of the homogeneous terpolymer in

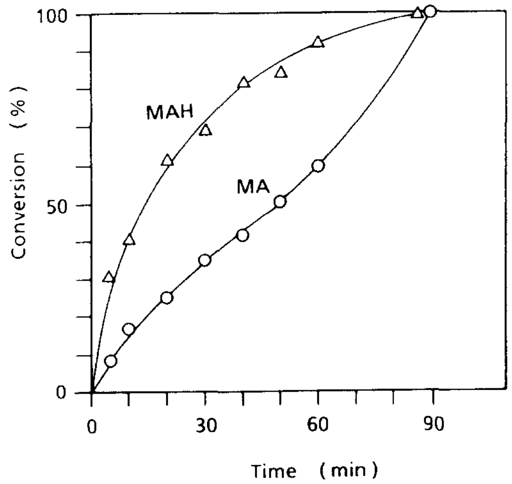


**Figure 3** Time conversion of the terpolymerization of isobutylene (IB), methyl acrylate (MA) and maleic anhydride (MAH). Conditions: IB, 500 mmol; MA, 125 mmol; MAH, 125 mmol; BEtCl$_2$/BEt$_2$Cl, 7.5/7.5 mmol; solvent, ethylene dichloride (EDC) (total liquid volume 330 ml); temp., 0°C; order of addition, EDC → IB → MA → MAH/EDC → BEtCl$_2$ → BEt$_2$Cl; 12.5 cm$^3$ min$^{-1}$ of O$_2$–N$_2$ mixed gas was flowed through the liquid phase of the flask; vessel, a glass flask

**Table 4** Terpolymerization of isobutylene (IB), methyl acrylate (MA) and maleic anhydride (MAH)[a]

| | Monomer | | | | | Polymerization | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Conversion (%) | | | |
| Run No. | MA (mol) | MAH (mol) | ACL (mol) | n-Dodecyl mercaptan (mmol) | Catalyst $BEtCl_2$ (mmol) | Temp. (°C) | MA | MAH | ACL | Polymer $[\eta]$ ($dl\,g^{-1}$) |
| 1 | 1.8 | 0.2 | – | – | 40 | −20 | 100 | 100 | – | 2.28 |
| 2[b] | 1.8 | 0.2 | – | 4 | 80 | −20 | 99.6 | 100 | – | 0.45 |
| 3 | 1.8 | 0.2 | – | – | 80 | +20 | 100 | 100 | – | 1.12 |
| 4[c] | 1.0 | 1.0 | – | 12 | 120 | 0 | 92.6 | 100 | – | 0.36 |
| 5 | 1.8 | 0.2 | 0.04 | 3 | 80 | −20 | 100 | 100 | 100 | 0.63 |

[a] Conditions: IB, 4.0 mol; toluene, 1.33 litre; order of addition, toluene → IB → $BEtCl_2$ → the mixture of MA and MAH was added continuously in 3 h; time, 5 h; 500 $cm^3\,min^{-1}$ of $O_2$–$N_2$ mixed gas ($O_2$ 1.9%) was flowed through the vapour part of the flask; vessel, a glass flask

[b] MAH was used without purification

[c] Solvent, ethylene dichloride 0.81 litre

which MAH was uniformly distributed was tried by adding the mixture of MA and MAH continuously. Several examples of the terpolymerization are shown in *Table 4*. When the terpolymer contained MAH in a fairly large extent, it was hard to dissolve in toluene and in such cases ethylene dichloride was desirable for the solvent (run No. 4). As seen in *Figure 4* the glass transition temperature of the terpolymers of IB, MA and MAH increased according to the content of MAH and the hardness of the cast film was controlled by the content of MAH. The stiffness of polymer chains would be elevated by the incorporation of acid anhydride ring.

### *Polymer reactions of the reactive copolymers*

Acid chloride and acid anhydride groups are very reactive and chemical reactions between acid chloride or acid anhydride group and other functional groups are well known in monomers. Therefore those chemical reactions were applied to AILM and AIHM. In a polymer reaction the compatibility between polymer, reactant and solvent is very important. AILM and AIHM contain about 50 mol% of polar acrylic monomers, so good compatibility with polar compounds for polymer reactions was expected. AILM and AIHM were usually polymerized in toluene solvent, and therefore the polymerization solution was used as it was for polymer reactions. AILM is very reactive but its toluene solution has long-time stability if it is isolated from moisture.

By the polymer reactions based on AILM and AIHM, various functional copolymers of IB and AE were synthesized which contained carboxyl group, amide group, hydroxyl group, nitrile group, epoxy group and so forth on the pendant of the polymer chains. They are summarized in *Tables 5* and *6*. The progress of reaction was measured by i.r. spectra.

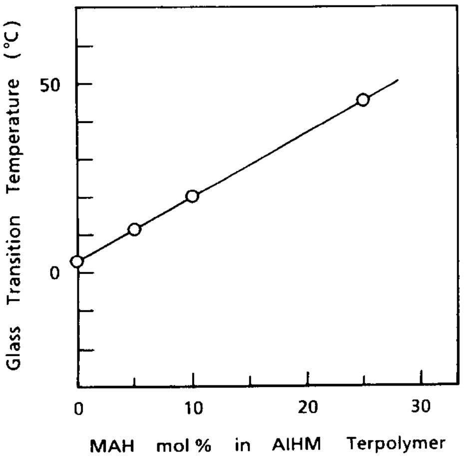


**Figure 4** Glass transition temperature ($T_g$) of the terpolymers of isobutylene, methyl acrylate and maleic anhydride (MAH)

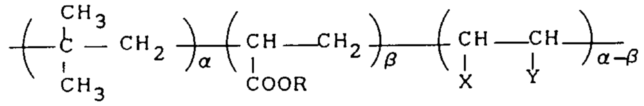
### *Introduction of functional groups by polymer reactions based on AILM*

These reactions are summarized in *Table 5*.

*Hydrolysis reaction.* Water (40 times equivalents per ACL) hardly dissolves in toluene, so the addition of a hydrophilic solvent such as tetrahydrofuran (the same weight as the toluene solution of AILM) was useful for accelerating the reaction rate. The reaction was completed after refluxing (70°C) for 9 h.

*Amidation reaction.* If an excess of aqueous ammonia (28%) was added to the toluene solution of AILM at room temperature, the amidation reaction proceeded easily. Primary and secondary amines also reacted with AILM in the same manner as aqueous ammonia to give amide polymers. Bifunctional amines such as ethylenediamine and hexamethylenediamine also rapidly reacted with AILM to give crosslinked polymers in this case. The mixing of monoethanolamine or aminopropionitrile (10 times equivalents per ACL respectively) with the toluene solution of AILM at room temperature gave amide products quantitatively without crosslinking. The acid chloride group is much more reactive to the amino

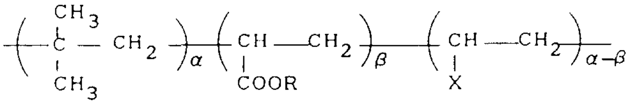
**Table 5** Derivatives of AILM. Product:



$$\left(\underset{CH_3}{\overset{CH_3}{C}}-CH_2\right)_{\alpha}\left(\underset{COOR}{CH}-CH_2\right)_{\beta}\left(\underset{X}{CH}-\underset{Y}{CH}\right)_{\alpha-\beta}$$

| Reaction | Reactant | Product, X |
|---|---|---|
| Hydrolysis | $H_2O$ | COOH |
| Amidation | $NH_3$<br>$H_2N(CH_2)_2OH$<br>$H_2N(CH_2)_2CN$ | $CONH_2$<br>$CONH(CH_2)_2OH$<br>$CONH(CH_2)_2CN$ |
| Esterification | R′OH<br>$HOCH_2\underset{\diagdown O \diagup}{CH-CH_2}$<br>$HO(CH_2)_2CN$ | COOR′<br>$COOCH_2\underset{\diagdown O \diagup}{CH-CH_2}$<br>$COO(CH_2)_2CN$ |

**Table 6** Derivatives of AIHM. Product:



$$\left(\underset{CH_3}{\overset{CH_3}{C}}-CH_2\right)_{\alpha}\left(\underset{COOR}{CH}-CH_2\right)_{\beta}\left(\underset{X}{CH}-CH_2\right)_{\alpha-\beta}$$

| | Reactant | | Product | |
|---|---|---|---|---|
| Reaction | 1 | 2 | X | Y |
| Hydrolysis | NaOH | HCl | COOH | COOH |
| Amidation | $NH_3$<br>$H_2N(CH_2)_2OH$ | <br>HCl | $CONH_2$<br>$CONH(CH_2)_2OH$ | $COO^-NH_4^+$<br>COOH |
| Esterification | NaOH | $\underbrace{H_2C{-}CH}_{O}CH_2Cl$ | COOH | $COOCH_2\underbrace{CH{-}CH_2}_{O}$ |

group than to the hydroxyl group, so under the condition of excess monoethanolamine the reaction between acid chloride and hydroxyl groups was repressed.

*Esterification reaction.* The reaction of AILM with alcohol (20 times equivalents per ACL) was slower than with amine at room temperature, but elevated temperature (60–80°C) accelerated the esterification reaction. Bifunctional monomers such as glycidol and ethylene cyanohydrin reacted at the hydroxyl group and gave gel-free polymers having epoxy group or nitrile group on the pendant of the polymer chains. The epoxy group was cured with polyamine.

### *Introduction of functional groups by polymer reactions based on AIHM*

These reactions are summarized in *Table 6*.

*Hydrolysis reaction.* The acid anhydride group was easily ring-cleaved with sodium hydroxide (1.3 times equivalents per MAH) at room temperature. If the cleaved salt was acidified with hydrogen chloride, a polymer having two adjacent carboxyl groups was obtained.

*Amidation reaction.* The acid anhydride group was easily ring-cleaved with ammonia at room temperature. When AIHM contained MAH in fairly high extent (15–25 mol%), it was obtained as an aqueous solution by the ring-cleavage reaction of the solid polymer with an excess of ammonia or sodium hydroxide. The produced aqueous solution was homogeneous and slightly turbid white but gave a transparent film after casting. Monoethanolamine also easily reacted with the acid anhydride group at room temperature and gave a polymer having adjacent hydroxyl and carboxyl groups.

*Esterification reaction.* First the acid anhydride group was cleaved with sodium hydroxide and then the reaction product was further reacted with epichlorohydrin. As a result the epoxy group was introduced on the pendant of the polymer chains. If the molar ratio of sodium hydroxide to acid anhydride group was 1, the produced polymer had adjacent epoxy and carboxyl groups. If the molar ratio was 2, the produced polymer had two adjacent epoxy groups.

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