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Alternating copolymers of isobutylene and acrylic ester by complexed copolymerization

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Alternating copolymers of isobutylene and acrylic ester (designated as 'AIM' copolymers) were synthesized by complexed copolymerization in the presence of alkylboron halide. Various characteristic properties of the AIM copolymers were revealed. AIM copolymers showed singular properties which could not be expected from those of the corresponding homopolymers. The glass transition temperature, thermal decomposition temperature and tensile strength of AIM copolymers were greater than those of both homopolymers, i.e. additivity was not established. The solubility parameter and refractive index of AIM copolymers showed slightly smaller values than the additive ones of both homopolymers. The hydrolysis resistance of AIM copolymers was excellent compared with that of the corresponding poly(acrylic ester)s.

(Keywords: isobutylene; acrylic ester; alternating copolymer)

INTRODUCTION

It is well known that isobutylene (IB) copolymerizes with monomers having high *e* values (designated by Alfrey and Price), such as maleic anhydride, to produce alternating copolymers, but is difficult to copolymerize with acrylic ester (AE) and acrylonitrile. In radical copolymerization of IB and AE, the resulting copolymers contain at most 20–30 mol% of IB and have low molecular weights because of the degradative chain transfer of IB[1–3].

Hirooka and co-workers[4–10] discovered that conjugated vinyl monomers (B group monomers) such as acrylonitrile and AE, which have a nitrile or carbonyl group in the conjugated position, react spontaneously with donor monomers (A group monomers) such as propylene, styrene and IB, in the presence of alkylaluminium halide to give 1 : 1 alternating copolymers. That is, by the complexed copolymerization catalysed with alkylaluminium halide, it is possible to obtain an alternating copolymer of IB and AE which contains 50 mol% of IB and has a high molecular weight. Recently, the present authors found that alkylboron halide has a much higher catalytic activity than alkylaluminium halide and synthesized various alternating copolymers of IB and AE[11].

There have been few studies on how the nature of copolymers is affected by their sequential structure. This is because, in the past, the sequential structure of most copolymers could not be controlled at will. Furukawa and co-workers[12,13] indicated that the alternating copolymer of butadiene and acrylonitrile was superior in various properties to the corresponding 1 : 1 random copolymer. Yabumoto *et al.*[14] noticed that the 1 : 1 copolymer of styrene and acrylonitrile obtained in the presence of zinc chloride had a higher glass transition temperature (T_g) than that of the corresponding 1 : 1 random copolymer synthesized by radical copolymerization. Moreover, the former had hardly any colour due to the substantial absence of acrylonitrile–acrylonitrile sequences. Hirooka *et al.*[9] found that thermal decomposition of the alternating copolymer of styrene and acrylonitrile synthesized with alkylaluminium halide occurred at a temperature ~ 10°C higher than that of the corresponding 1 : 1 random copolymer.

Thus it is very interesting to study how the properties of a copolymer are affected by the sequential structure. There are detailed reports in the literature about the combinations styrene–(meth)acrylic ester[5–10,15,16], propylene–AE[5,6,8,17–19] and ethylene–AE[5,6,8,17,18,20,21], but few reports about the combination IB–AE[9,22,23] related to both synthesis and properties. In a previous paper[11] we reported both the new catalyst affording alternating copolymers of IB and AE, and the characteristics of the alternating copolymerization. The alternating copolymers of IB and AE are novel polymers which we designate as 'AIM' copolymers, where 'A' means AE, 'I' means IB and 'M' means methylene linkage. The present paper describes the various characteristic properties of AIM copolymers.

EXPERIMENTAL

Synthesis of alternating copolymers

The alternating copolymers of IB and AE were synthesized via complexed copolymerization catalysed with alkylboron halide. Details are given in the previous paper[11].

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Table 1 Basic properties of AIM copolymers

Polymer[a]	Acrylic ester in polymer (mol %)	$[\eta]$ ($dl\,g^{-1}$)	T_g (°C)	T_d (°C)	n_D^{20}	d^{23} ($g\,cm^{-3}$)	Tensile tests: Strength ($kg\,cm^{-2}$)	Tensile tests: Elongation at break (%)
IB–MA	51.1	3.22	7	387	1.488	1.054	21	780
IB–EA	52.8	3.97	−12	365	1.480	1.020	14	1010
IB–BA	52.3	5.04	28	378	1.479	0.992	4	> 3000
IB–EHA	54.7	3.84	−42	380	1.473	0.951	1	> 3000
PMA	100	1.56	0.5	343	1.467	1.221	18	660
PEA	100	2.55	−21.5	337	1.465	1.133	3	> 3000
PBA	100	2.35	−54	360	1.463	1.064	1	> 3000
PEHA	100	1.21	−64	358	–	–	–	–
PIB	0	2.48	−73	363	1.508	0.917	1.5	> 3000

[a] IB, isobutylene; MA, methyl acrylate; EA, ethyl acrylate; BA, n-butyl acrylate; EHA, 2-ethylhexyl acrylate; PMA, poly(methyl acrylate); PEA, poly(ethyl acrylate); PBA, poly(n-butyl acrylate); PEHA, poly(2-ethylhexyl acrylate); PIB, polyisobutylene

Measurements

Intrinsic viscosities ($[\eta]$) were measured in benzene at 30°C using Ubbelohde viscometers. T_gs were measured using a differential scanning calorimeter (model 1800, Rigakudenki Co., Ltd). Thermal decomposition temperatures (T_ds) were determined in nitrogen atmosphere using a DT10 type differential thermal analyser (Shimazu Seisakusho Ltd). Refractive indices (n_D^{20}) were measured using an Abbe Refractometer (Shimazu Seisakusho Ltd). Densities (d^{23}) were obtained by a buoyancy method. Tensile tests were carried out according to Japan Industrial Standard K-6301-1-1962 at 23°C, using an Autograph 100A instrument (Shimazu Seisakusho Ltd).

RESULTS AND DISCUSSION

The basic properties of AIM copolymers are summarized in *Table 1*, including those of the corresponding homopolymers.

Glass transition temperature

The T_g of a copolymer is affected by the combination of monomers rather than by the properties of individual monomers. Generally, there are three types of curve in the relationship between T_g and copolymer composition, i.e. concave, linear and convex. The T_g of AIM copolymers was higher than that of both homopolymers, i.e. the correlation curve corresponded to a convex type (*Figure 1*). T_g is closely related to the rotational motion around carbon–carbon bonds in the polymer backbone, i.e. micro-Brownian motion. The convex correlation curve of AIM copolymers can be attributed to the steric interaction between alternating methyl groups of IB and ester groups of AE restricting the motion of the polymer backbone. On the other hand, in the alternating copolymer of ethylene and ethyl acrylate[20,21], the T_g of the copolymer (−25°C) was lower than that of poly(ethyl acrylate) (−22°C). In this case, the mobility of the poly(ethyl acrylate) backbone might be raised by the incorporation of ethylene between two ethyl acrylates.

Uematsu and Honda[24] investigated the correlation between T_g and copolymer composition and indicated the importance of the chain stiffness energy of sequential segments. The T_g of an alternating copolymer is not always in agreement with that of the corresponding 1 : 1 random copolymer and the sequential distribution of a copolymer seems to affect T_g. Hirooka and Kato[10] investigated further the correlation between T_g and copolymer composition, on the basis of the equation presented by Uematsu and Honda, and deduced the relative equation between the T_g of an alternating copolymer and that of the corresponding 1 : 1 random copolymer. According to their theory, in the case of a convex type T_g–copolymer composition curve, the T_g of an alternating copolymer is higher than that of the corresponding 1 : 1 random copolymer. So, if a 1 : 1 random copolymer of IB and AE is synthesized, its T_g will be lower than that of the corresponding AIM copolymer.

Figure 2 shows the relationship between T_g and polarity in several alternating copolymers of olefin and AE. The data for ethylene and propylene were obtained by Logothetis and McKenna[17–21]. For the four polymer types, i.e. IB–AE, propylene (P)–AE, ethylene (E)–AE alternating copolymers and poly(acrylic ester) (PAE),

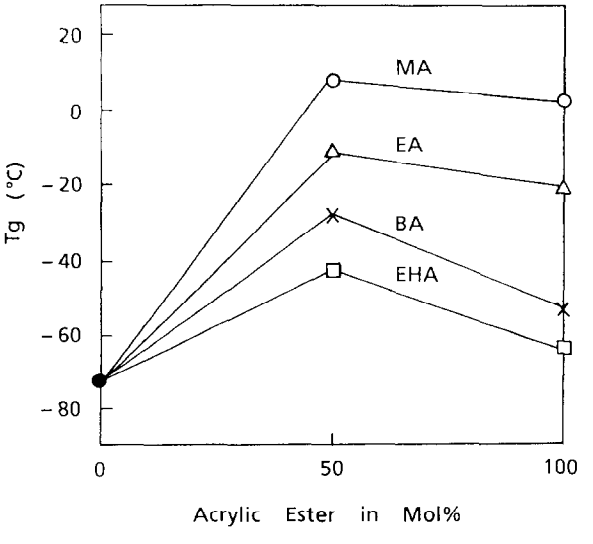


Figure 1 T_g of AIM copolymers. MA, methyl acrylate; EA, ethyl acrylate; BA, n-butyl acrylate; EHA, 2-ethylhexyl acrylate

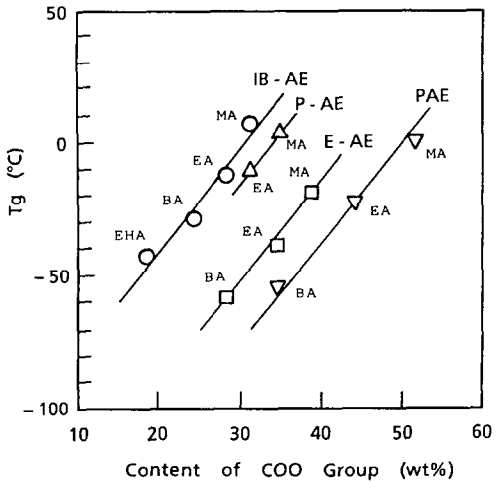
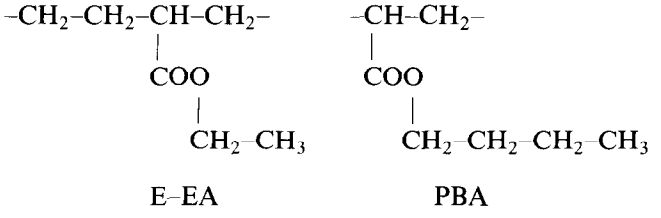


Figure 2 Relationship between T_g and content of ester group in the alternating copolymers of olefin and acrylic ester. IB, isobutylene; P, propylene; E, ethylene; AE, acrylic ester; PAE, poly(acrylic ester); MA, methyl acrylate; EA, ethyl acrylate; BA, n-butyl acrylate; EHA, 2-ethylhexyl acrylate

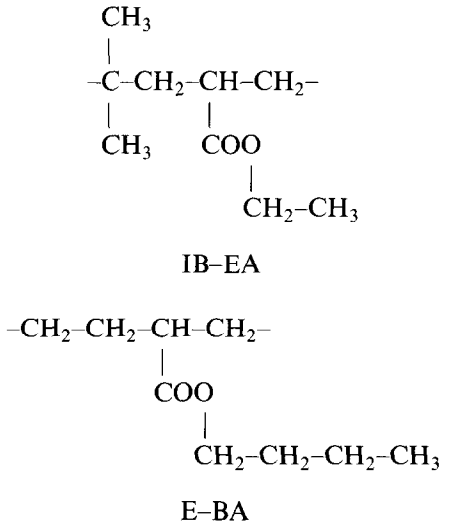
the relationship between T_g and ester group content was linear and individual lines were parallel to each other. At the same content of ester group, T_g increased in the order IB–AE > P–AE > E–AE > PAE.

Hatakeyama and Kanetsuna[25] investigated the effect of hydrogen bonding on the structure of an amorphous glassy polymer and confirmed that increased hydrogen bonding results in a rise of T_g. All polymers in *Figure 2* are amorphous, and intra- and intermolecular interactions by the polar effect increase with the content of ester group. The polar effect may be one reason why the T_g increases with increasing ester group content. On the other hand, increasing the content of ester groups means that the alkyl group length of the ester residue becomes shorter. The plasticizing effect of branched chains is proportional to their length in a certain range. The branched chain effect may explain why the T_g decreases in inverse proportion to the ester group content.

The ester group contents of E–ethyl acrylate (EA) alternating copolymer and poly(n-butyl acrylate) (PBA) are identical, as are those of IB–EA and E–n-butyl acrylate (BA). But the T_g of the former was higher than that of the latter in both cases. Comparing E–EA alternating copolymer and PBA



the hydrocarbon component seems to have a greater effect in raising the chain stiffness energy when it is in the polymer backbone than when it is in the branched chain. Conversely, when the hydrocarbon component exists in the branched chain of a polymer, packing of polymer molecules becomes looser and rotational motion around the polymer backbone will occur more easily. Comparing IB–EA and E–BA alternating copolymers



the much higher T_g of the former than the latter will be derived from the steric hindrance effect of IB adding to the branched chain effect mentioned above.

Thermal decomposition temperature

The T_d of AIM copolymers was higher than that of both polyisobutylene (PIB) and PAE (*Figure 3*). The thermal decomposition of a polymer is closely related to the bonding energy of atoms composing the polymer molecule. Lancaster *et al.*[26] noticed that the presence of branched chains has a detrimental effect on the thermal stability of a polymer. That is, the T_d of PIB (363°C) is lower than that of polypropylene (387°C), which has less branched chain than PIB. In the copolymer of IB and AE, when the AE content increases, the number of branched chains decreases, so T_d should rise. On the other hand, it is well known that the bonding force of tertiary carbon and hydrogen is relatively weak. That is, T_d of poly(methyl acrylate) (343°C) is lower than that of polyethylene (406°C), which has no tertiary carbon. When the AE content decreases the number of

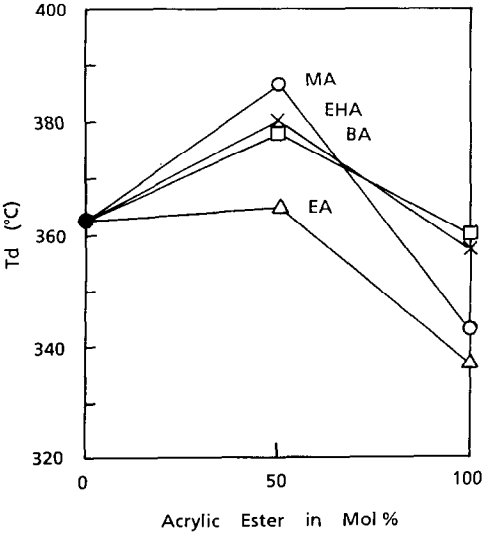


Figure 3 T_d of AIM copolymers. MA, methyl acrylate; EA, ethyl acrylate; BA, n-butyl acrylate; EHA, 2-ethylhexyl acrylate

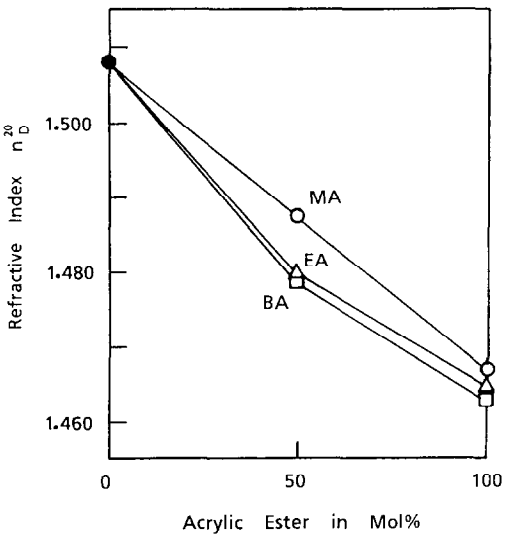


Figure 4 Refractive index of AIM copolymers. MA, methyl acrylate; EA, ethyl acrylate; BA, n-butyl acrylate

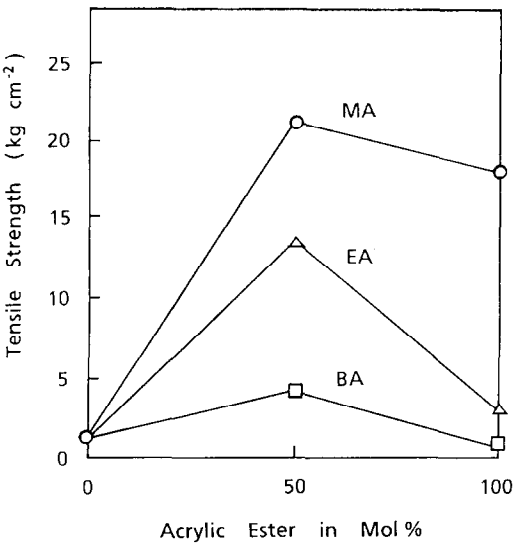


Figure 6 Tensile strength of AIM copolymers. MA, methyl acrylate; EA, ethyl acrylate; BA, n-butyl acrylate

tertiary carbons decreases, so T_d should rise. According to the overlapping of these two factors the T_d of AIM copolymers should be higher than that of both homopolymers.

Hirooka *et al.*[9] compared the alternating copolymer of styrene and acrylonitrile with the corresponding 1 : 1 random copolymer and found that the T_d of the alternating copolymer was about 10°C higher than that of the random copolymer. It would be very interesting to compare the T_d of AIM copolymers with that of the corresponding 1 : 1 random copolymers.

Refractive index

The refractive index of AIM copolymers was slightly smaller than the additive value of both homopolymers (*Figure 4*). This might be because the alternating regular sequential structure of IB and AE increased the bulkiness of the polymer chain and reduced the packing of polymer molecules.

Tensile properties

Figure 5 shows the stress–strain curves of AIM copolymers and *Figure 6* indicates the unexpectedly high green strength of AIM copolymers compared with the corresponding homopolymers. These results can be attributed to enhancement of the chain stiffness by the alternating regular sequential structure, in the same manner as for T_g. Judging from the stress–strain curve and T_g, the alternating copolymer of IB and methyl acrylate has properties intermediate between those of a rubber and a plastic, while alternating copolymers of IB and EA and IB and BA both have rubber-like properties.

Solubility parameter

The solubility parameter of AIM copolymers was obtained by Small's group contribution method[27]:

$$\delta = \frac{\Sigma F_i}{V} = \frac{\rho \Sigma F_i}{M}$$

where F_i is the molar attraction constant of component i composing the molecule, V is the molar volume, ρ is density and M is molecular weight. The results are shown in *Figure 7*.

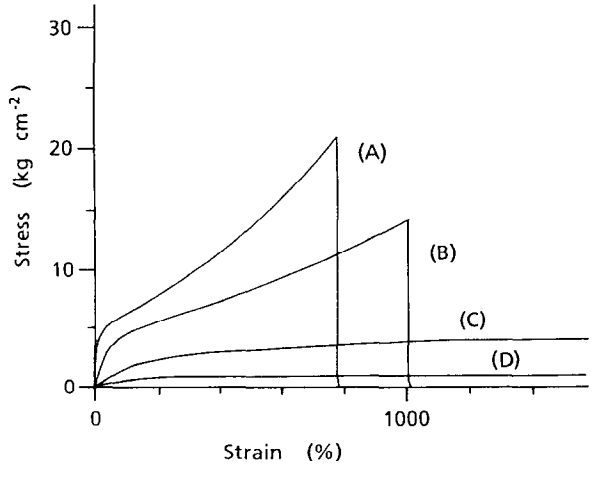


Figure 5 Stress–strain curves of AIM copolymers: (A) isobutylene–methyl acrylate, (B) isobutylene–ethyl acrylate, (C) isobutylene–n-butyl acrylate, (D) isobutylene–2-ethylhexyl acrylate

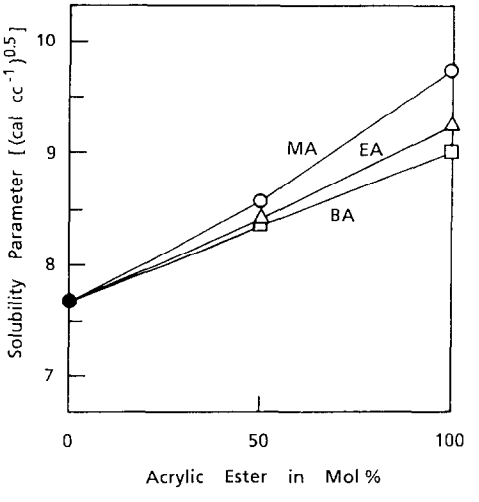


Figure 7 Solubility parameter of AIM copolymers by Small's method. MA, methyl acrylate; EA, ethyl acrylate; BA, n-butyl acrylate

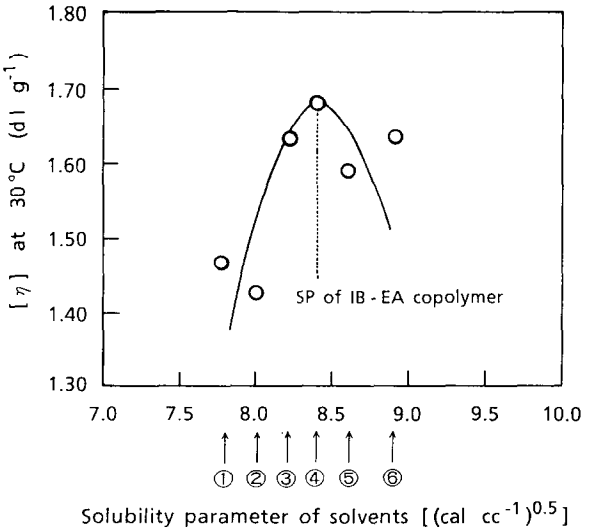


Figure 8 Solubility parameter of the alternating copolymer of isobutylene and ethyl acrylate by the intrinsic viscosity method. Solvents: 1, 2-ethylhexyl acrylate; 2, isopropyl isobutylate; 3, ethyl benzoate; 4, benzonitrile; 5, ethyl acrylate; 6, methyl acrylate

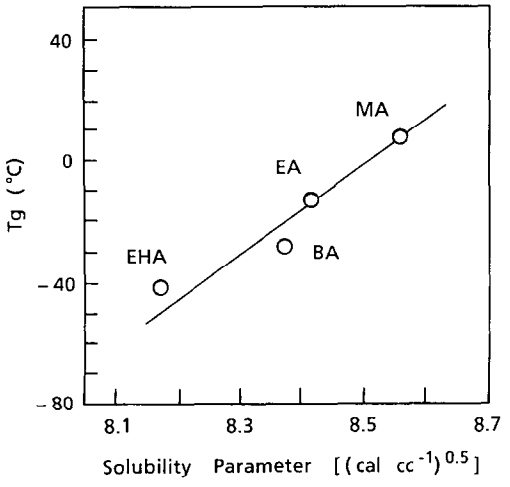


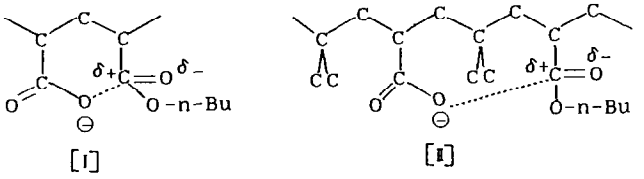
Figure 9 Relationship between T_g and solubility parameter in AIM copolymers. MA, methyl acrylate; EA, ethyl acrylate; BA, n-butyl acrylate; EHA, 2-ethylhexyl acrylate

It is known that polymer solutions exhibit a maximum value of intrinsic viscosity when the solubility parameter of the solvent is close to that of the polymer. The solubility parameter of the alternating copolymer of IB and EA obtained by the intrinsic viscosity method is shown in *Figure 8*. The value, 8.4, agreed well with that (8.41) obtained by Small's method, although there was concern about the dispersion of the data. The solubility parameter of AIM copolymers was slightly lower than the value on the additive line of both homopolymers (*Figure 7*). The alternating regular sequential structure of IB and AE increases the bulkiness of the polymer chain, loosens the packing of polymer molecules and hence increases the molar volume, and may explain why the values are lowered from the additive line. AIM copolymers have both non-polar and polar natures, so good compatibility with both non-polar and polar polymers are expected. The relationship between T_g and solubility parameter of AIM copolymers is shown in *Figure 9*. Solubility parameter is related to the polarity and bulkiness of a polymer, as is T_g (*Figure 2*), so the correlation in *Figure 9* seems to be reasonable.

Hydrolysis resistance

The hydrolysis resistance of an AIM copolymer (IB–BA) was studied and compared with that of the corresponding PAE (PBA). Details of the method are given in *Table 2*. The concentration of ester groups in both polymers was identical. The hydrolysis reaction was conducted using potassium hydroxide, at 50°C, in a mixed solvent of benzene, n-butanol and water.

From the results, shown in *Figure 10*, it is apparent that the AIM copolymer is much more resistant to hydrolysis than the corresponding PAE. The early rate of hydrolysis of the alternating copolymer of IB and BA was 0.102×10^{-3} mol l^{-1} h^{-1}, compared with 3.61×10^{-3} mol l^{-1} h^{-1} for PBA, the former being 1/35 of the latter. Smets and Humbeeck[28] indicated that the hydrolysis of ester groups in PAE is self-catalytic, owing to the presence of adjacent, previously hydrolysed, carboxylate ions. That is, the hydrolysis occurs in an unzipping reaction in **I**.



[I] [II]

In the present alternating copolymer, IB exists between two AEs as in **II**, so the hydrolysis was not accelerated so much intramolecularly by the adjacent carboxylate ions.

Table 2 Hydrolysis resistance[a] of AIM copolymer

Polymer	BA in polymer (mol%)	$[\eta]$ (dl g^{-1})	Amount of sample (g)	Concentration of ester groups (mol l^{-1})	KOH (mol l^{-1})	H_2O (mol l^{-1})	Benzene/n-Butanol (1/1 vol ratio) (ml)
IB–BA	54.3	3.66	0.9905	0.0269	0.0370	0.555	200
PBA	100	3.98	0.7257	0.0283	0.0379	0.555	200

[a] Reaction scheme: PCOO–n-Bu + KOH→PCOOK + n-BuOH, where P = polymer residue. Method: (1) polymer was dissolved in benzene/n-butanol mixed solvent and KOH (aq) was added; (2) reaction was carried out in a flask equipped with a reflux condenser under stirring at 50°C; (3) after various times, 20 ml of reaction solution was sampled and diluted with 50 ml acetone, 10 ml water. To this, phenolphthalein was added and the amount of reacted ester was obtained by titrating the amount of unreacted KOH with 0.1 N HCl (aq)

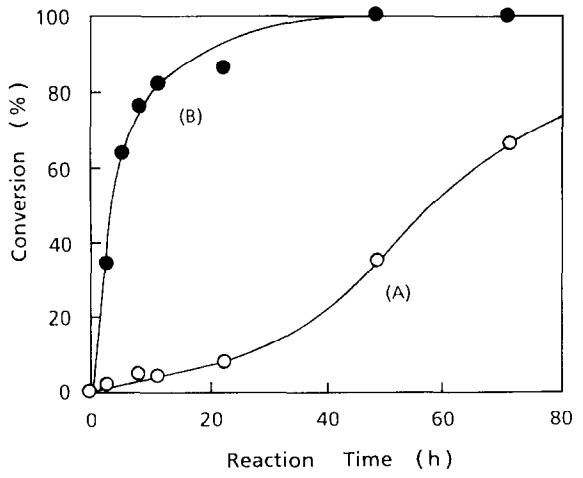


Figure 10 Hydrolysis resistance of (A) alternating copolymer of isobutylene and n-butyl acrylate and (B) poly(n-butyl acrylate)

CONCLUSIONS

Alternating copolymers of IB and AE have been synthesized by complexed copolymerization in the presence of alkylboron halide.

Various characteristic properties of these AIM copolymers have been revealed. AIM copolymers showed singular properties which could not be expected from those of the corresponding homopolymers. These phenomena seem to arise from the alternating regular sequential structure of the copolymers. In particular, they seem to be caused by the chain stiffening effect, the complete separation of ester groups by IB units and the uniform distribution of polar ester groups.

The T_g, T_d and tensile strength of AIM copolymers were higher than those of both homopolymers, i.e. additivity was not established. The solubility parameter and refractive index of AIM copolymers showed values slightly smaller than the additive ones of both homopolymers. Compared with the corresponding PAE, the hydrolysis resistance of AIM copolymer was excellent.

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