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Alternating copolymerization of isobutylene and acrylic ester with alkylboron halide

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It was found that alkylboron halide, such as ethylboron dichloride and diethylboron chloride, was a highly active catalyst for the alternating copolymerization of isobutylene and acrylic ester. The alternating sequential structure of the resulting copolymers was proved by analysis of n.m.r. spectra. The Lewis acidity of the catalyst, the molar ratio of catalyst to acrylic ester and the molar ratio of isobutylene to acrylic ester played important roles in determining the regularity of the alternating sequence. Copolymer molecular weight had an intimate correlation with the Lewis acidity of the catalyst. The polymerization rate was maximum at about −50°C and decreased rapidly above 0°C. The present copolymerization proceeded via a complexed radical mechanism. The cocatalytic effect of oxygen was remarkable and the molecular weight controlling effect of mercaptan was notable. Alkylboron halide has various advantages compared with alkylaluminium halide.

(Keywords: isobutylene; acrylic ester; alternating copolymerization)

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 form alternating copolymers, but is difficult to copolymerize with acrylic ester (AE) or acrylonitrile. In radical copolymerization of IB and AE, the resulting polymers contain at most 20–30 mol% of IB and have low molecular weights because of the degradative chain transfer of IB[1–3].

The effects of metal halides on vinyl polymerization were studied and it was shown that the reactivity of a monomer can be varied by complexing it with metal halides[4–6]. Subsequently, Hirooka and co-workers[7–13] 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, which have low *e* values, in the presence of alkylaluminium halide to give 1:1 alternating copolymers, and they synthesized numerous novel alternating copolymers. That is, via the complexed copolymerization catalysed with alkylaluminium halide, it is possible to obtain a copolymer of IB and AE which contains 50 mol% of IB and has a high molecular weight.

On the other hand, it has also been shown that various trialkylborons (BR_3) initiate vinyl polymerization[14–16]. These reports suggested that the initiation and propagation stages of the polymerization with BR_3 proceed via a free-radical mechanism. Compared with BR_3 or alkylaluminium halide, instances of the use of alkylboron halide as a polymerization catalyst are rare[17–19]. Furukawa *et al.*[17] showed that dibutylboron bromide or dibutylboron chloride catalyses the polymerization of vinyl monomers and found that oxygen (O_2) and oxygen compounds act as cocatalysts, similar to the case of BR_3. Thus alkylboron halide has been considered to be the same kind of initiator as BR_3 – a simple, low-temperature free-radical initiatior – and, to our knowledge, there are no reports that an alternating copolymer of IB and AE can be obtained with alkylboron halide.

However, we have found that alkylboron halide catalyses the alternating copolymerization of IB and AE with a much higher activity than alkylaluminium halide. The present paper describes the characteristics of the alternating copolymerization.

EXPERIMENTAL

Materials

IB was a pure grade (purity > 99.0%) obtained from Phillips Ltd, and was used after drying over 3 Å molecular sieves. AEs, obtained from Toa Gosei Chemical Ltd, were distilled and dried over 4 Å molecular sieves. Toluene, chlorobenzene and benzene, commercial G. R. grade samples obtained from Nakarai Chemical Ltd, were used after drying over 4 Å molecular sieves.

Triethylboron (BEt_3), triethylaluminium ($AlEt_3$) and ethylaluminium sesquichloride ($AlEt_{1.5}Cl_{1.5}$) were obtained from Ethyl Corporation Ltd. Boron trichloride (BCl_3) was obtained from Matheson Ltd. Ethylboron dichloride ($BEtCl_2$) was synthesized using the method of

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Table 1 Copolymerization of isobutylene (IB) and acrylic ester (AE) catalysed with alkylboron halide[a]

Run no.	Catalyst (mmol)	Monomer IB (mmol)	Monomer AE[b] (mmol)	Polymerization Time (h)	Polymerization Yield (g)	Polymer Elemental analyses (wt%) C	H		Polymer AE in polymer (mol %)	Polymer Conversion on AE (%)	Polymer $[\eta]$ (dl g^{-1})
1	BCl_3	2	100	MA 20	3	0	–	–	–	0	–
2	$BEtCl_2$	2	100	MA 20	3	2.87	67.41	9.90	50.7	100	5.81
3	$BEtCl_2$	0.2	100	EA 20	7	2.98	69.14	10.93	50.4	95.5	5.25
4	$BEtCl_2$ + BEt_2Cl	1 + 1	100	MA 20	3	2.85	67.21	10.52	51.3	100	4.50
5	BEt_2Cl	2	100	MA 20	3	2.68	66.88	10.56	52.6	94.4	3.03
6	BEt_3	2	100	MA 20	3	0	–	–	–	0	–
7	$BEtCl_2$	2	100	–	3	0	–	–	–	–	–
8[c]	$BEtCl_2$	2	–	MA 40	3	3.01	55.98	7.16	100	85.0	4.45
9	$AlEt_{1.5}Cl_{1.5}$	2	100	MA 20	3	0	–	–	–	0	–

[a] Polymerization conditions: reaction at −20°C under N_2 atmosphere; reaction vessel, a glass tube
[b] MA, methyl acrylate; EA, ethyl acrylate
[c] Reaction at −60°C

Willcockson[20]:

$$3BCl_3 + AlEt_3 \xrightarrow[C_6H_5Cl]{} 3BEtCl_2 + AlCl_3$$

Diethylboron chloride (BEt_2Cl) was synthesized following the method of Buls *et al.*[21]:

$$2BEt_3 + BCl_3 \longrightarrow 3BEt_2Cl$$

Polymerization

Polymerizations were conducted under a nitrogen (N_2) atmosphere or an O_2–N_2 mixed gas flow. The copolymerization of IB and ethyl acrylate (EA) with $BEtCl_2$ catalyst, under an O_2–N_2 mixed gas flow, is now described as an example.

A glass flask equipped with a stirrer, a thermometer, a gas inlet and a gas outlet was evacuated and flushed with N_2. Then toluene and EA were introduced into the flask under the atmosphere of an O_2–N_2 mixed gas containing 0.25 vol% of O_2, and the flask was cooled to −20°C. IB was liquefied, by cooling with dry ice/methanol, into a graduated glass tube which had been repeatedly evacuated and flushed with N_2 beforehand. This IB was introduced into the flask by N_2 pressure. The reaction system was then adjusted to a fixed polymerization temperature and the addition of $BEtCl_2$ initiated the polymerization. Stirring was continued during the polymerization and flow of the O_2–N_2 mixed gas was maintained through the vapour part of the flask at an appointed velocity. As the polymerization proceeded, the reaction system became viscous and yet remained colourless, transparent and homogeneous. Samplings were done at appropriate intervals. The degree of conversion was determined from the polymer yield. After a prescribed polymerization time, the polymer solution was poured into an excess of methanol and a white polymer was coagulated. The solid product was washed with methanol and weighed after drying *in vacuo*. Polymer samples for analysis were purified by dissolving in benzene and reprecipitating into methanol.

Measurements

Intrinsic viscosities ($[\eta]$) were measured in benzene at 30°C using Ubbelohde viscometers. N.m.r. spectra were taken on a 100 MHz s^{-1} high-resolution n.m.r. spectrometer (model JNM 4H-100, Japan Electron Optics Laboratory Inc.) at 150°C in *o*-dichlorobenzene as ~ 4% (w/v) solutions. Hexamethyldisiloxane was used as internal standard.

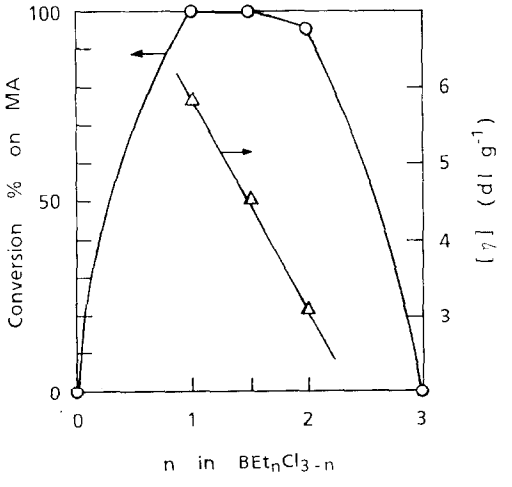


Figure 1 Copolymerization of IB and MA catalysed with ethylboron chlorides (BEt_nCl_{3-n}). Conditions: IB, 100 mmol; MA, 20 mmol; BEt_nCl_{3-n}, 2 mmol; reaction at −20°C for 3 h under N_2 atmosphere; reaction vessel, a glass tube

RESULTS

Synthesis of alternating copolymers

Table 1 shows the results of the copolymerization of IB and AE with several alkylboron halides. IB did not homopolymerize with $BEtCl_2$ (run 7) but methyl acrylate (MA) homopolymerized under a low $BEtCl_2$ concentration (run 8). However, when IB and AE coexisted, the copolymer of IB and AE was produced selectively. Even when the molar ratio of $BEtCl_2$ to EA was as low as 0.01, it had a high polymerization activity (run 3). BEt_2Cl (run 5) had also a fairly high activity but was inferior to $BEtCl_2$. Both BEt_3 (run 6) and BCl_3 (run 1) had no activity. This was the same tendency as found by Hirooka *et al.*[7] during the copolymerization of propylene and acrylonitrile with alkylaluminium halide. $AlEt_{1.5}Cl_{1.5}$ had no activity at all under these polymerization conditions (run 9). A 1 : 1 mixture of $BEtCl_2$ and

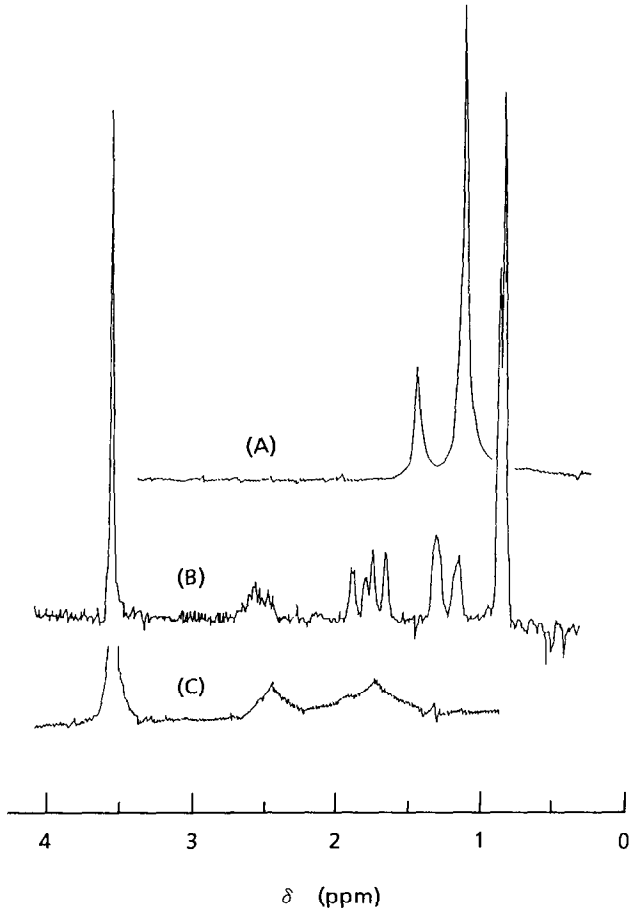


Figure 2 ^{1}H n.m.r. spectra of (A) polyisobutylene, (B) IB–MA copolymer (catalyst, $BEtCl_2$; MA, 51.1 mol% (elemental analyses); $[\eta]$, 3.22 dl g^{-1}) and (C) poly(methyl acrylate)

BEt_2Cl, which corresponds to $AlEt_{1.5}Cl_{1.5}$, had also a high activity (run 4) – the compound ethylboron sesquichloride ($BEt_{1.5}Cl_{1.5}$) does not exist. All the copolymers produced comprised equimolar amounts of IB and AE, based on the results of elemental analyses.

Figure 1 shows the effect of the variation of n in ethylboron chlorides (BEt_nCl_{3-n}) on the copolymerization of IB and MA. Both BCl_3 (no alkyl group) and BEt_3 (no chlorine atom) were ineffective as mentioned above, and compounds containing both alkyl group and chlorine atom in the molecule were highly effective. The molecular weight increased in the order BEt_2Cl< 1 : 1 mixture of BEt_2Cl and $BEtCl_2$ < $BEtCl_2$, in proportion to the Lewis acidity of the boron compounds. The copolymer composition was constant, *i.e.* 1 : 1, and the molecular weight was also almost constant throughout the polymerization despite the conversion.

Evidence of alternating sequences

Analysis of the sequential structure and stereoregularity of the copolymer of IB and AE was almost impossible by means of ^{1}H n.m.r. measurement at room temperature, but, when measured at a high temperature of 150°C, remarkably clear spectra were obtained which could be analysed reliably. *Figure 2* shows the ^{1}H n.m.r. spectrum of the copolymer of IB and MA synthesized with $BEtCl_2$. The composition of the copolymer, which was calculated from the area ratio of the CH_3 peak of IB to the CH_3 peak of MA, coincided with the result of elemental analysis (*Table 2*).

Table 2 Composition of copolymer of IB and MA

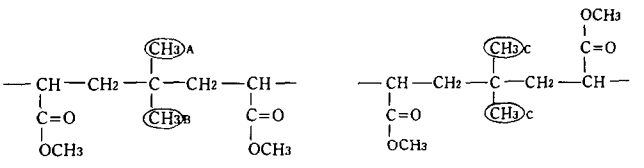
	Composition (mol%)	
Analysis	IB	MA
N.m.r.	50.7	49.3
Elemental	48.9	51.1

CH_3 peak of IB. The copolymer provided a sharp triplet at 0.85 ppm (δ value), corresponding to the CH_3 peak of the IB. In IB homopolymer, this peak appeared at 1.11 ppm. Judging from the reappearance of the spectrum, the new peak at 0.85 ppm was obviously one that could be ascribed to the copolymerization. Moreover, the peak at 1.11 ppm did not exist in the copolymer. The high magnetic field shift in the copolymer was ascribed to the magnetic anisotropy effect of the C=O in MA units adjacent to IB units. Theoretically, this effect is inversely proportional to cube of distance, so the contribution of distant C=O groups will be negligible. Therefore it was permitted to conclude that the IB–IB sequence does not exist in the copolymer.

CH_2 peak. In IB homopolymer the CH_2 peak appeared at 1.40 ppm as a sharp singlet and in MA homopolymer it appeared at 1.5 to 2.0 ppm as a broad peak, but in the copolymer the peak at 1.40 ppm did not exist and six relatively sharp peaks were observed from 1.1 to 1.9 ppm. Therefore the possibility of IB–IB sequences is very small. Conversely, if the sequence MA–MA exists, the protons that are able to undergo spin coupling increase in number and so the peak between 1.5 and 2.0 ppm is expected to be broad. That these peaks were actually very sharp led to the consideration that IB units, which have no CH proton, must exist next to MA units. Thus we can conclude that the copolymer has an alternating sequential structure.

CH peak. The sample that had been concluded to be an alternating copolymer also had a broad CH peak, and therefore the possibility of head–head bonding was denied.

Stereoregularity. Turning again to the CH_3 peak of the IB unit, this appeared as a triplet. It was clear that this reflected the stereoregularity of the copolymer (MA unit). The assignment of the CH_3 peak of IB units was considered as follows.



As mentioned already, only the magnetic anisotropy effect of the nearest C=O group was considered as the cause of the shift of the CH_3 peak of IB. Therefore $(CH_3)_B$, which was supposed to be nearest to C=O groups, was assigned to the peak on the high magnetic field site and $(CH_3)_A$, the one furthest away, was

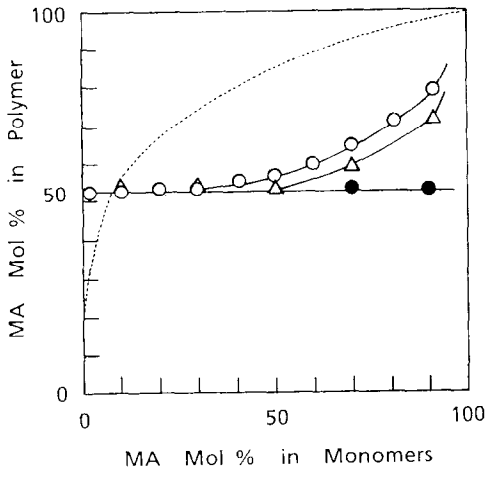


Figure 3 Monomer–polymer composition diagrams in the copolymerization of IB and MA. Conditions: under N_2 atmosphere; reaction vessel, a glass tube; ○, $BEtCl_2/MA = 0.02$ (molar ratio), −20°C; △, $AlEt_{1.5}Cl_{1.5}/MA = 0.1$ (molar ratio), 0°C; ●, $AlEt_{1.5}Cl_{1.5}/MA = 0.9$ (molar ratio), 0°C; (- - - -), curve predicted from Q, e values

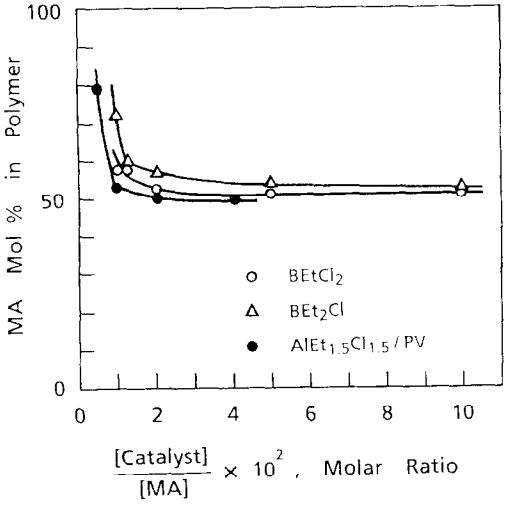


Figure 4 Effect of catalyst concentration on the copolymerization of IB and MA. Conditions for BEt_nCl_{3-n} catalyst: IB, 160 mmol; MA, 80 mmol; reaction at −20°C for 3 h under N_2 atmosphere; reaction vessel, a glass tube. Conditions for $AlEt_{1.5}Cl_{1.5}$/ t-butyl peroxy pivalate (PV) catalyst: IB, 100 mmol; MA, 50 mmol; $PV/AlEt_{1.5}Cl_{1.5} = 2/1$ (molar ratio); reaction at 0°C for 3 h under N_2 atmosphere; reaction vessel, a glass tube

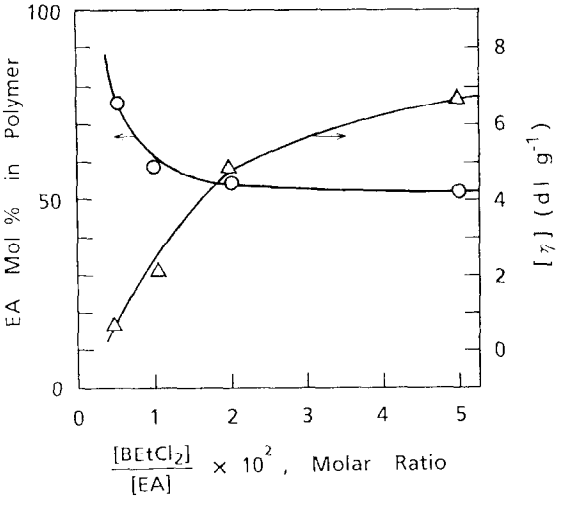


Figure 5 Effect of ethylboron dichloride concentration on the copolymerization of IB and EA. Conditions: IB, 160 mmol. EA, 80 mmol; reaction at −20°C for 3 h under N_2 atmosphere; reaction vessel, a glass tube

assigned to the peak on the low magnetic field site. The strength of $(CH_3)_A$ and $(CH_3)_B$ peaks was about equal and the $(CH_3)_C$ peak was the strongest, so the stereoregularity was considered to be nearly random. In the copolymerization of styrene and methyl methacrylate[22,23], highly coheterotactic alternating copolymers were obtained by using excess BCl_3 under photoirradiation at below −60°C.

Kuntz *et al.*[24] analysed in detail the sequential structure of the alternating copolymer of IB and MA, synthesized with an $AlEt_{1.5}Cl_{1.5}$/peroxide catalyst system, on the basis of ^1H and ^{13}C n.m.r. spectra. The ^1H n.m.r. spectrum of the present copolymer synthesized with $BEtCl_2$ closely resembles that of the copolymer synthesized with $AlEt_{1.5}Cl_{1.5}$/peroxide.

Effects of various factors

Monomer composition and catalyst concentration. The composition of the copolymers at various monomer feed ratios was examined for the copolymerization of IB and MA catalysed with $BEtCl_2$. The results are shown in *Figure 3*. All polymerizations were stopped below 5% conversion. When the IB concentration ([IB]) was higher than the MA concentration ([MA]), the resulting polymers always had a nearly equimolar composition independent of the molar ratio at feed, even if the molar ratio of $BEtCl_2$ to MA was as low as 0.02 (the copolymer composition was also influenced by $BEtCl_2$ concentration, as will be explained later). But, when [IB] < [MA], the content of MA in the polymer increased as [MA] increased. This might be related to the fact that MA homopolymerized with $BEtCl_2$. In the case of $AlEt_{1.5}Cl_{1.5}$, when its molar ratio to MA was as high as 0.9, 1 : 1 copolymers were produced even when [IB] < [MA]. That is, MA complexed with $AlEt_{1.5}Cl_{1.5}$ did not homopolymerize, but when its molar ratio to MA was as low as 0.1, the regulation of alternation became weak and MA-rich copolymers were produced for [IB] < [MA][24,25]. $BEtCl_2$, differing from $AlEt_{1.5}Cl_{1.5}$, was too active to perform the copolymerization if its molar ratio to MA was close to 1. Free-radical copolymerization of IB and MA in wide feed molar ratios was difficult, therefore monomer reactivity ratios, $r_1(MA) = 4.99$ and $r_2(IB) = 0.018$, were calculated from Q, e values[26] designated by Alfrey and Price. The composition curve is dotted in *Figure 3*. The present copolymerization clearly differs from conventional radical copolymerization.

Figures 4 and *5* show the effects of catalyst concentration ([Cat]) on the copolymerization of IB and AEs. The AE content in the monomers was 33 mol%. When the molar ratio of BEt_nCl_{3-n} ($n = 1, 2$) to MA was higher than a certain value, the composition of the resulting copolymers was always 1 : 1 of IB and MA (*Figure 4*), but as this ratio decreased the regulation of alternation became weak and the MA content tended to increase. BEt_2Cl had a weaker regulative ability than $BEtCl_2$, and $AlEt_{1.5}Cl_{1.5}$ had a stronger regulative ability than

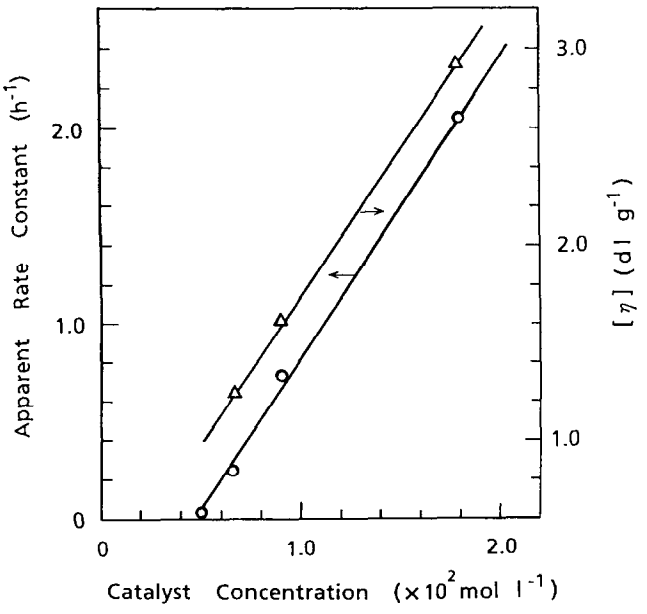


Figure 6 Effect of catalyst concentration on the copolymerization of IB and EA. Conditions: catalyst, $BEtCl_2/BEt_2Cl = 1/1$ (molar ratio); IB, 0.93 mol l^{-1}; EA, 0.38 mol l^{-1}; solvent, toluene (total liquid volume, 450 ml); reaction at −20°C under 20 cm^3 min^{-1} of O_2–N_2 mixed gas (O_2, 0.25%) flow; reaction vessel, a glass flask

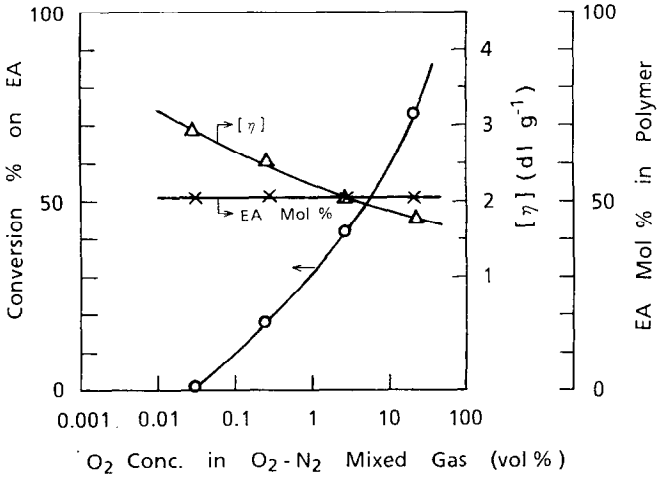


Figure 7 Effect of oxygen concentration on the copolymerization of IB and EA. Conditions: IB, 0.93 mol l^{-1}; EA, 0.38 mol l^{-1}; catalyst, $BEtCl_2/BEt_2Cl = 0.44/0.44 \times 10^{-2}$ mol l^{-1}; solvent, toluene (total liquid volume, 450 ml); reaction at −20°C for 15 min; 20 cm^3 min^{-1} of O_2–N_2 mixed gas was flowed through the vapour part of the reaction flask

$BEtCl_2$. The molecular weight increased as $[BEtCl_2]$ increased (*Figure 5*). In the case of $BEtCl_2$, when the AE content in the monomers was < 50 mol% and the $BEtCl_2$/AE molar ratio was > 0.02, 1 : 1 alternating copolymers were always obtained.

Figure 6 shows the effect of [Cat] (a 1 : 1 mixture of $BEtCl_2$ and BEt_2Cl) on the copolymerization of IB and EA. The apparent rate constant, obtained from the gradient of the first-order plot to EA concentration ([EA]), was proportional to [Cat]. It is noticeable that the straight line did not pass through the origin, i.e. it is a characteristic of the present copolymerization that reaction does not occur at all below a constant [Cat].

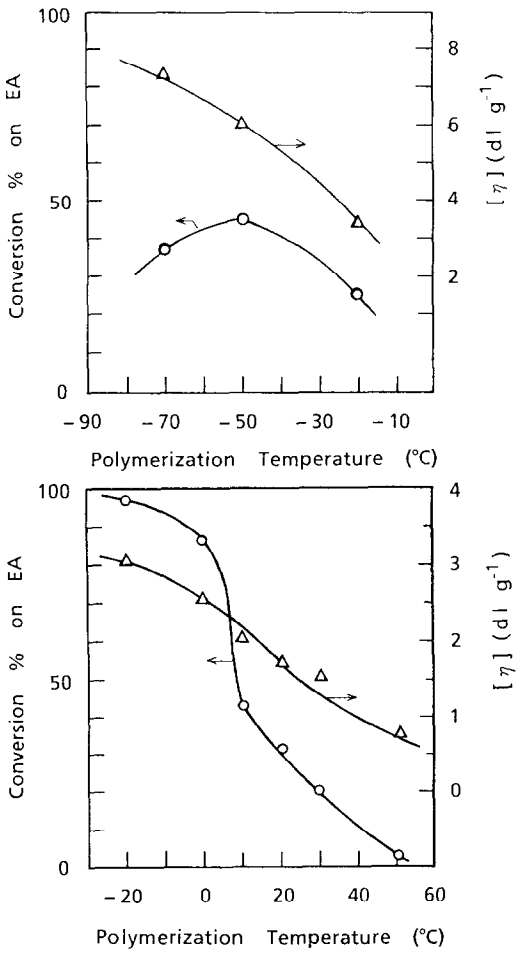


Figure 8 Effect of temperature on the copolymerization of IB and EA. (a) Conditions: IB, 210 mmol; EA, 200 mmol; $BEtCl_2$, 4 mmol; toluene, 300 ml; reaction for 3 h under N_2 atmosphere; reaction vessel, a glass flask. (b) Conditions: IB, 400 mmol; EA, 200 mmol; $BEtCl_2$, 2.0 mmol; O_2, 0.5 mmol (O_2–N_2 mixed gas); reaction for 1.5 h; reaction vessel, a 200 ml glass autoclave (closed system)

Oxygen concentration. The effect of O_2 was studied at various concentrations (*Figure 7*). O_2 was flowed through the vapour part of the reaction flask as an O_2–N_2 mixed gas while the liquid part was being stirred. The cocatalytic effect of O_2 was notable and the polymerization rate increased with O_2 concentration ($[O_2]$). The alternating regularity of the copolymers was still maintained even when the rate became fast by the addition of O_2. The molecular weight of the copolymers decreased as $[O_2]$ increased.

Polymerization temperature. The effect of temperature on the copolymerization of IB and EA is shown in *Figures 8a* and *b*. The polymerization rate was maximum at around −50°C, dropping suddenly above 0°C. The molecular weight increased monotonically with decreasing temperature. In the case of $AlEtCl_2$ catalyst[25], the polymerization rate was maximum at +50°C and the molecular weight was maximum at 0°C.

Monomer concentration. *Figure 9* shows the effect of [IB] on the copolymerization of IB and EA. The apparent rate constant, obtained from the gradient of the first-order plot to [EA], increased linearly with [IB] until a certain concentration was reached, above which the

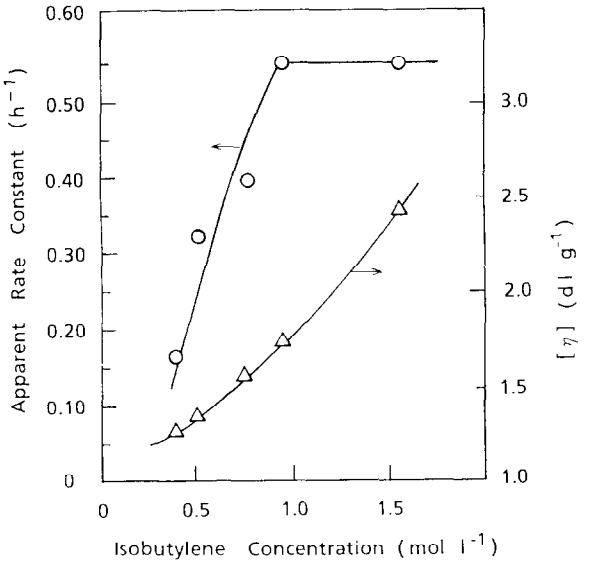


Figure 9 Effect of IB concentration on the copolymerization of IB and EA. Conditions: EA, 0.38 mol l^{-1}; catalyst, $BEtCl_2/BEt_2Cl = 0.44/0.44 \times 10^{-2}$ mol l^{-1}; solvent, toluene (total liquid volume, 450 ml); reaction at −20°C under 20 cm^3 min^{-1} of O_2–N_2 mixed gas (O_2, 0.25%) flow; reaction vessel, a glass flask

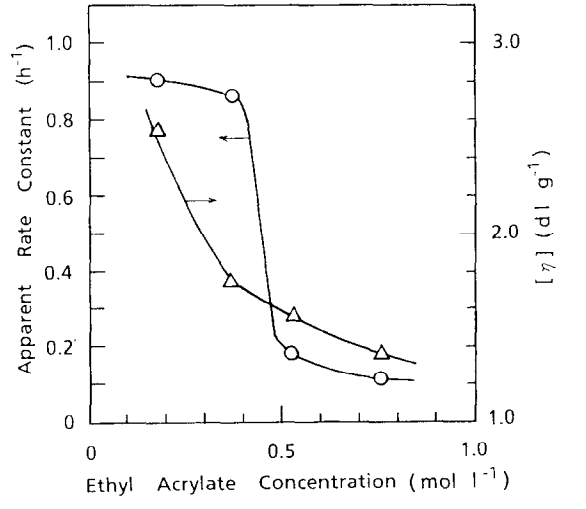


Figure 10 Effect of EA concentration on the copolymerization of IB and EA. Conditions: IB, 0.93 mol l^{-1}; catalyst, $BEtCl_2/BEt_2Cl = 0.44/0.44 \times 10^{-2}$ mol l^{-1}; solvent, toluene (total liquid volume, 450 ml); reaction at −20°C under 20 cm^3 min^{-1} of O_2–N_2 mixed gas (O_2, 0.25%) flow; reaction vessel, a glass flask

rate remained constant. The molecular weight increased with [IB].

Figure 10 shows the effect of [EA] on the copolymerization of IB and EA. The apparent rate constant, obtained from the gradient of the first-order plot to [EA], was not first-order with respect to [EA] and increased as [EA] decreased, reaching a constant rate below a certain concentration. The molecular weight of the copolymer also increased with decreasing [EA]. At low [EA] the produced polymers were all alternating copolymers comprising equimolar amounts of IB and EA.

Mercaptan. The experimental results presented so far suggest that the current alternating copolymerization of IB and AE proceeds via a radical mechanism. If

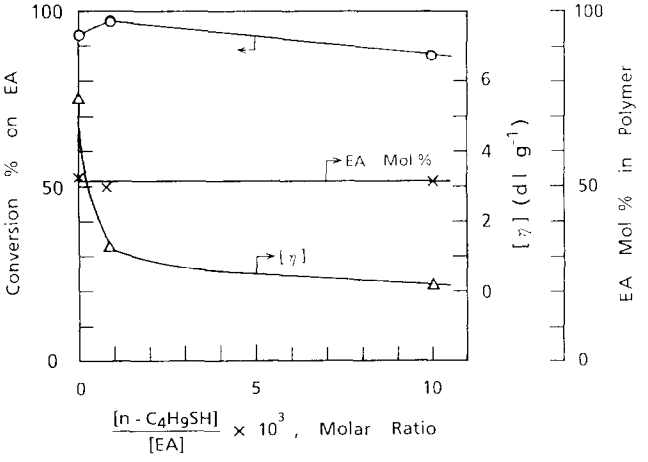


Figure 11 Effect of mercaptan concentration on the copolymerization of IB and EA. Conditions: IB, 800 mmol; EA, 160 mmol; $BEtCl_2$, 3.2 mmol; reaction at −20°C for 3 h under N_2 atmosphere; reaction vessel, a glass flask

this is the case then mercaptan should have a chain transfer effect. Actually, a suitable quantity of n-butyl mercaptan had a remarkable effect in lowering the molecular weight without decreasing the polymerization rate (*Figure 11*). This proved the radical nature of the polymer end. Despite the addition of mercaptan, the composition of the copolymers was preserved at 1 : 1.

DISCUSSION

Copolymerization mechanism

The mechanism of the present alternating copolymerization with alkylboron halide has several points in common with that of copolymerization with alkylaluminium halide, as investigated by Hirooka[10].

Initiation reaction. It is known that BR_3 or alkylboron halide initiates vinyl polymerization by reacting with the trace of coexisting oxygen[17,18]. In the case of BR_3, trialkylboron peroxide was detected as a reaction product but, as this is unable to initiate polymerization by itself, a redox mechanism with BR_3 was therefore proposed. The most probable initiation mechanism is considered to be[27,28]:

$$BR_3 + O_2 \xrightarrow{k_o} R_2BOOR \quad (1)$$

$$R_2BOOR + BR_3 \xrightarrow{k_r} BR_3 + R_2BO\cdot + RO\cdot \quad (2)$$

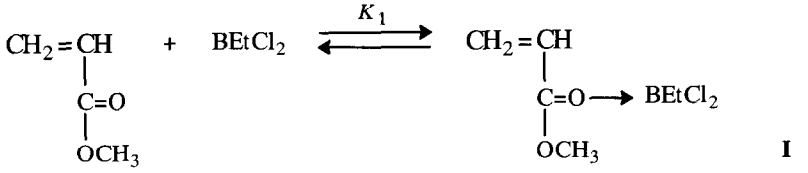
In the present alternating copolymerization of IB and MA with $BEtCl_2$, production of the initiating radical is considered to proceed as follows:

$$BEtCl_2 + O_2 \xrightarrow{k_o} Cl_2BOOEt \quad (3)$$

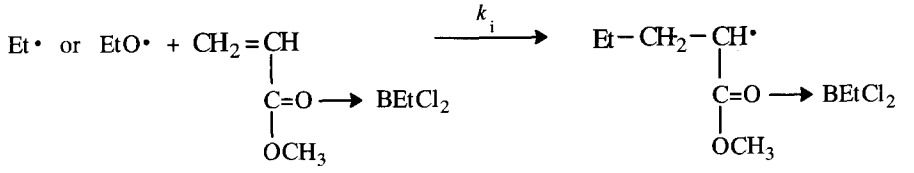
$$Cl_2BOOEt + BEtCl_2 \xrightarrow{k_r} Cl_2BOBCl_2 + EtO\cdot + Et\cdot \quad (4)$$

When the radical produced in (4) attacks the MA→$BEtCl_2$ complex (**I**) produced in (5), copolymeriza

tion starts (equation (6)):



(5)



(6)

Boron–carbon bonds will be more reactive to O_2 than aluminium–carbon bonds because of the difference between the electronegativities of the metals. As the temperature decreases, the rate of formation of the initiating radical by the reaction between catalyst and O_2 becomes slow, resulting in lowering of the polymerization rate (*Figure 8a*). Conversely, as the temperature increases, the equilibrium (5) inclines towards the left side and the concentration of charge transfer complex ([**I**]) becomes low; as a result it is difficult to carry out the polymerization above +50°C (*Figure 8b*).

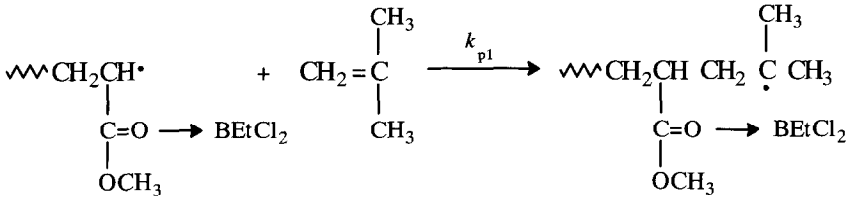
When $[O_2]$ is high, Cl_2BOOEt in equation (4) is more highly oxidized and becomes inactive[17,28]:

$$Cl_2BOOEt + O_2 \longrightarrow \text{inactive species} \qquad (4a)$$

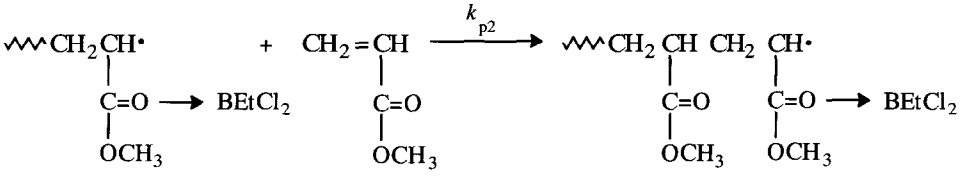
That is, if too much O_2 is supplied to the catalyst, the catalyst is consumed during the polymerization and deactivated (*Figure 12*). When $[O_2]$ was below a certain value, the initiating radical was hardly produced and the polymerization rate was very slow (*Figure 7*). The molecular weight decreased in proportion to $[O_2]$, but the alternating regularity was still maintained. These phenomena show that O_2 is effective mainly in the initiation and termination stages, and takes little part in the propagation stage. The reaction between catalyst and O_2 occurs in the liquid phase, and $[O_2]$ in the liquid phase is dependent on the amount of O_2–N_2 gas flowing through the vapour part of the reaction flask and the stirring speed. Therefore, for a more strict analysis of the mechanism, it would be necessary to determine $[O_2]$ in the liquid phase quantitatively.

Alkylboron halide, such as $BEtCl_2$ and BEt_2Cl, was an active catalyst for the present alternating copolymerization, but BEt_3 and BCl_3 were not active at all (*Table 1* and *Figure 1*). BEt_3 has a weak Lewis acidity and is difficult to complex with AE, therefore the intermediate complex **I** in (5) will not be formed. On the other hand, BCl_3 is able to complex with AE but the source of radical generation, i.e. B–Et bonding in equations (3) and (4), does not exist.

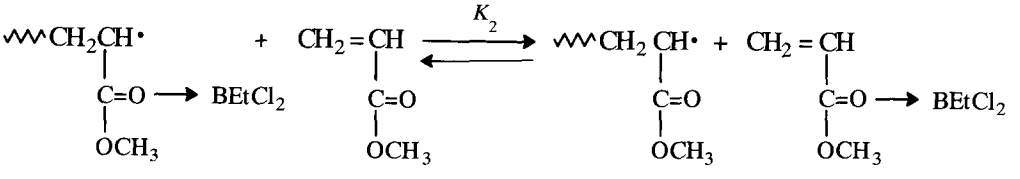
Propagation reaction. The reactions after (6) are considered to continue as follows:



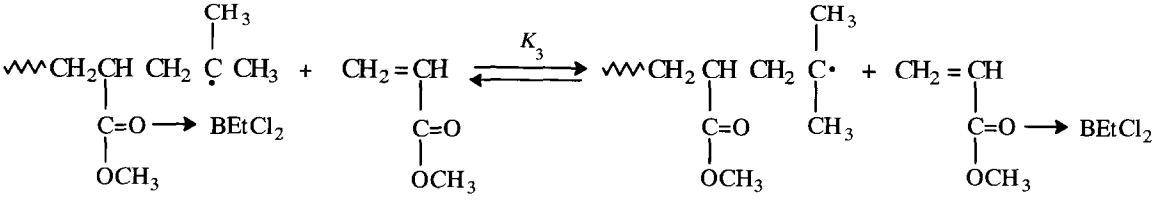
(7)



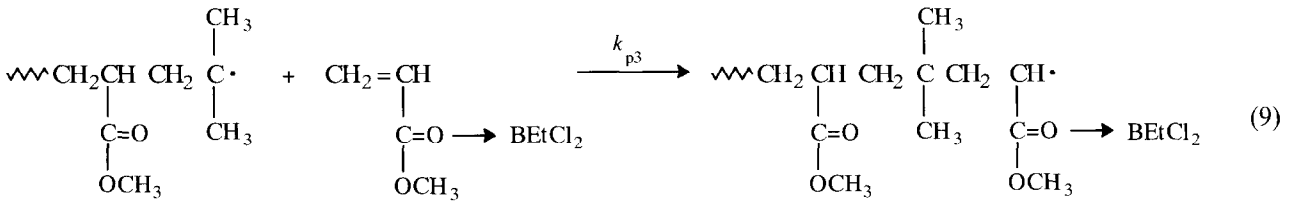
(7a)



(7b)



(8)



(9)

The complexed MA-terminated radical is more reactive towards electron-rich IB than towards electron-deficient complexed MA or free MA (equations (7)). Moreover, the electron-rich IB-terminated radical is more reactive towards the most electron-deficient complexed MA than towards IB or free MA (equation (9)). Therefore, in the presence of an excess of IB to MA and under a relatively high [Cat], the alternating copolymerization predominated and the produced copolymers contained essentially equimolar amounts of IB and MA. But when [Cat] was low, especially when the molar ratio of IB to AE was < 1, the regulation of alternation was disturbed and AE-rich polymers were produced (*Figures 3–5*). In the equilibrium of (5), at a low $BEtCl_2$ concentration, [I] is low and the equilibrium is inclined towards the left side. Therefore the concentration of uncomplexed free MA increases and (7a) contributes at the same time as (7) though $k_{p1} > k_{p2}$. That is, the incorporation of IB by the alternating copolymerization is competitive with the homopolymerization of free MA (not complexed MA) and the resulting polymers became MA-rich.

Logothetis and McKenna[29,30] copolymerized propylene or ethylene with AE by means of a boron trifluoride/azobisisobutyronitrile catalyst system. When the molar ratio of AE to olefin at the initial feed was > 1, the produced copolymers contained > 50 mol% of AE. They explained the copolymer composition by the competitive reaction between the alternating copolymerization and the homopolymerization of complexed AE (not free AE). On the other hand, Hirai *et al.*[22] copolymerized styrene (ST) and methyl methacrylate (MMA) with BCl_3 or $BEtCl_2$ under photoirradiation and found that 1 : 1 alternating copolymers were produced in wide feed molar ratios (MMA/ST = 2/8–8/2) even at a low boron concentration (1/100 mol to MMA). Methyl methacrylate and styrene might hardly homopolymerize under these conditions.

As for AE concentration, the polymerization rate and molecular weight both decreased as [AE] increased (*Figure 10*). These phenomena were contrary to first-order kinetics and the characteristic of the present alternating copolymerization. When [AE] increases, the active species of the growing complexed radical is weakened according to the equilibrium of (7b), as a result the propagation reaction is suppressed and the chain transfer reaction is accelerated.

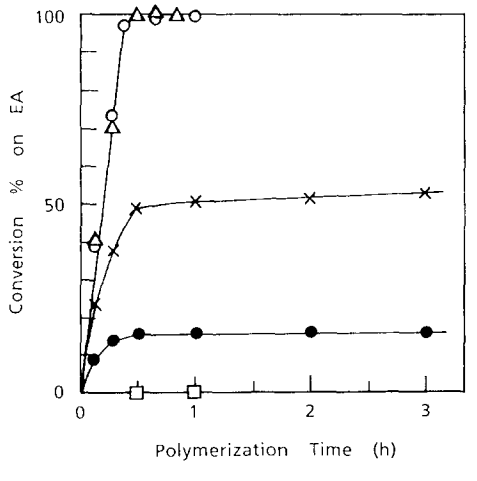


Figure 12 Relationship between oxygen concentration and catalyst concentration in the copolymerization of IB and EA. Conditions: IB, 0.93 mol l^{-1}; EA, 0.38 mol l^{-1}; solvent, toluene (total liquid volume, 450 mol); reaction at −20°C under 20 cm^3 min^{-1} of O_2–N_2 mixed gas (O_2, 20.9%) flow; reaction vessel, a glass flask. [Cat] ($\times 10^{-3}$ mol l^{-1}): ○, 8.9; △, 7.6; ×, 6.7; ●, 5.8; □, 3.8

Comparison of boron with aluminium

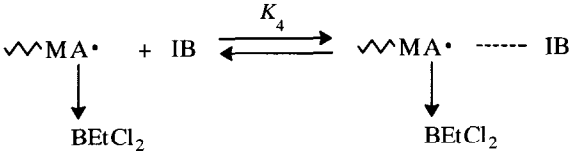
In complexed copolymerization the Lewis acidity of the catalyst plays a key role. The acidity of the coordinated metal controls the possibility of the propagation reaction, therefore there must exist an optimum acidity for the catalyst. At the same time there must also exist an optimum polarity of the conjugated vinyl monomers. Furukawa *et al.*[31] found that an optimum acidity existed in alkylaluminium halides for the alternating copolymerization of butadiene and acrylonitrile with alkylaluminium halide/vanadium compound catalyst systems.

Among ethylboron chlorides (BEt_nCl_{3-n}), $BEt_{1.5}Cl_{1.5}$ (an equimolar mixture of $BEtCl_2$ and BEt_2Cl) had maximum activity (*Figure 1*). From the point of view of propagation rate, a strong Lewis acidity is desirable (equations (7) and (9)), but for recycling of the catalyst, a weak Lewis acidity is required (equation (8)). According to the balance of these two factors, $BEt_{1.5}Cl_{1.5}$ would have maximum activity. In the alternating copolymerization of IB and AE with $AlEt_{1.5}Cl_{1.5}$, a large quantity of catalyst was needed. $AlEt_{1.5}Cl_{1.5}$ still complexes with AE even when it is incorporated into the copolymer and the recycling reaction (8) is difficult. On the other hand, in the present copolymerization, alkylboron halide dissociates and recycles after MA → BEt_nCl_{3-n} complex is copolymerized and incorporated into the polymer. Recycling of the alkylboron halide will occur because of the stronger bonding force of BEt_nCl_{3-n} ← MA (monomer) than of BEt_nCl_{3-n} ← MA (polymer)[25].

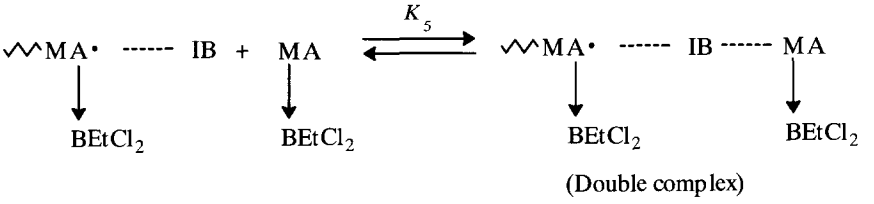
The alternating regularity of the copolymer was proportional to the Lewis acidity of the catalyst. The regulative ability of alternation was in the order $AlEt_{1.5}Cl_{1.5} > BEtCl_2 > BEt_2Cl$ (*Figure 4*). As the Lewis acidity becomes stronger, the electron density of the complexed MA radical at the growing end and the olefinic electron density of the complexed MA monomer decrease, so that the interactions with IB (equation (7)) and the IB radical (equation (9)) become stronger. This may be the reason for the elevated alternating regularity.

The molecular weight was also proportional to the Lewis acidity of the catalyst (*Figure 1*). With increasing

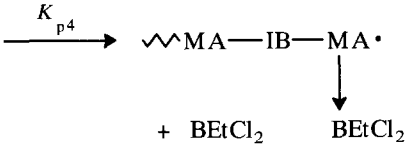
Lewis acidity the propagation rate becomes faster and the chain transfer rate becomes slower because of stabilization of the terminal radical (equations (7) and (9)). Hirooka[10] proposed a 'complexed radical mechanism' as the propagation mechanism of the alternating copolymerication of styrene and MA. Following this 'complexed radical mechanism', (7) and (9) may be rewritten as follows:



(10)



(11)



(12)

It is difficult to polymerize IB via radical polymerization because of the degradative chain transfer through the allyl resonance. But in alternating copolymerization – either complexed or conventional – copolymers of IB are obtained in fairly good yields and in high molecular weights. In the present alternating copolymerization, the restrained degradative chain transfer of IB is explained by equations (10)–(12).

There exists a 'sesqui' type in alkylaluminium halide, but not in alkylboron halide. The equimolar mixture of $AlEt_3$ and $AlCl_3$ easily forms $Al_2Et_3Cl_3$, even at room temperature. In the case of boron, the mixture of BEt_3 and BCl_3 does not show any change at room temperature, the exchange reaction occurring at about 200°C to produce $BEtCl_2$ and BEt_2Cl[21] – but a sesqui type '$B_2Et_3Cl_3$' does not form. Moreover, trialkylaluminium reacts readily with water but BR_3 is not decomposed with water, and alklyboron halide is more sensitive to O_2 than alkylaluminium halide as mentioned before. In the alternating copolymerization of IB and AE, the viscosity of the polymerization solution catalysed with alkylaluminium halide was much higher than that of the solution catalysed with alkylboron halide. In general, a lower viscosity polymerization solution is desirable for a production process. Alkylaluminium halide might partially complex with carbonyl groups of different polymer chains and pseudo-crosslink them. This pseudo-crosslinking disappears upon the addition of a little methanol and the viscosity of the polymerization solution is reduced.

These various differences between organoaluminium and organoboron compounds may be ascribed to the differences between the Lewis acidity, electronegativity and p-orbital size of both metals. There are many similarities between alkylboron halide and alkylaluminium halide as catalyst, but in the following points alkylboron halide is superior to alkylaluminium halide:

1. the catalytic efficiency is much higher;
2. a high molecular weight polymer is obtained in a high yield;
3. the copolymerization is easily controlled by O_2 in terms of both rate and molecular weight;
4. the viscosity of the polymerization solution is low, i.e. there is no pseudo-crosslinking; and
5. elimination of the catalyst is easy – there is no colouring of the copolymer.

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