Ring-Opening Polymerization of Epichlorohydrin and Its Copolymerization With Other Alkylene Oxides by Quaternary Catalyst System

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ABSTRACT: An effective quaternary catalyst consisting of trialkyl aluminum, phosphoric acid, electron donor, and water for ring-opening polymerization of epichlorohydrin (ECH), as well as its copolymerization with ethylene oxide (EO), propylene oxide (PO), and allyl glycidyl ether (AGE) to obtain elastomers, were studied. We investigated the optimum composition for the quaternary catalyst; the character of the catalyst; the reactivity of the four alkylene oxides during homopolymerization and copolymerization; the behavior of ECH, EO, and PO during terpolymerization; and glass transition temperatures of the copolymer and terpolymers. The results showed that the nitrogen-containing electron donors are suitable as the third component, whereas oxygen-containing electron donors are not. Water as the fourth component can increase the molecular weight of the homopolymer and copolymers of ECH. According to the polymerizability of tetrahydrofuran with the quaternary catalyst and the reactivity ratios of the four alkylene oxides, the quaternary catalyst was assumed to be of a coordinated anionic type. The reactivity ratios for these four alkylene oxides were determined to be EO > PO > AGE > ECH. They were verified by terpolymerization of ECH, EO, and PO. The glass transition temperature of the terpolymer exhibits a minimum value at nearly 3:1 molar ratio of PO to EO, when the molar ratio of ECH used is constant at the beginning of terpolymerization. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2446–2454, 2001

Key words: ring-opening polymerization, epichlorohydrin, catalyst, elastomer

INTRODUCTION

The importance of the ring-opening polymerization of alkylene oxides has been recognized from the early days of the science of macromolecules, and catalysts for the ring-opening polymerization of alkylene oxides have been studied for many years. Homopolymers and copolymers of epichlorohydrin (ECH) or propylene oxide (PO) have been developed as oil-resistant, thermal aging-resistant, and ozone-resistant elastomers since 1960.

Vandenberg[1,2] first reported that the combination of trialkyl aluminum, water, and ether or acetyl acetone is a favorable catalyst for the polymerization of epichlorohydrin (ECH) and several other alkylene oxides to produce high-molecular-weight amorphous polymers. He suggested that the active centers of the catalyst are the hydrolyzed product of trialkyl aluminum, R_2Al–O–AlR_2 and $(R_2$Al–O$)_n$. Araki[3] synthesized a product from reaction of LiOAl$(C_2H_5)_2$ with $(C_2H_5)_2$AlCl and showed that the synthesized product was as ac-

tive as the hydrolyzed product of trialkyl aluminum in the polymerization of ECH. Ossefort et al.[4] studied the copolymerization of ECH with EO, PO, and allyl glycidyl ether (AGE) using the Vandenberg catalyst and indicated that the low temperature properties of the four component copolymers are better than those of the ECH–EO copolymers, but with lower conversion.

In addition to Vandenberg's catalyst, other kinds of catalysts have been found for the ring-opening polymerization of ECH, such as organo-Al–Zn catalyst, other metallorganic catalysts, organo-Al–porphyrin catalyst, rare earth metallic catalyst, and organo-Al–P catalyst. Hsieh[5] found that by means of a trialkyl aluminum–zinc acetylacetonate–water catalyst, ECH or propylene oxide (PO) can be polymerized or copolymerized to elastomers, and that the efficiency of the catalyst is high. Hsieh[5] also studied the terpolymerization of ECH, EO, and AGE using trialkyl aluminum–zinc acetylacetonate–water catalyst and reported the properties of the elastomeric product. Kuntz and Kroll[6] used dialkyl aluminum acetylacetonate–water–diethyl zinc as the catalyst in the polymerization of ECH and considered the active center to be composed of Zn–O–Al. Kuntz[7] investigated the relationship between conversion and monomer composition during terpolymerization of ECH, PO, and AGE using dialkyl aluminum acetyl acetonate–water–diethyl zinc catalyst. Lamot[8] used $(PhCH_2CH_2)_2Ca$ as a catalyst for the polymerization of ECH and obtained the polymer with molecular weight of 10^5 and yield of 46.5–82.4%. Nomura et al.[9] employed arylantimony as a catalyst for polymerizing ECH. Contrera et al.[10] found that diphenyl zinc alone can be used as a catalyst for ECH polymerization. Inuoe et al.[11] carried out the polymerization of ECH with (tetraphenylporphinato) aluminum chloride as a catalyst, which yielded the polymer with narrow molecular-weight distribution, but with lower molecular weight. Huang et al.[12] reported that amorphous polymers of ECH with a molecular weight of 10^4–10^5 were prepared by ring-opening polymerization using a propylene oxide–$FeCl_3$ complex, $AlEt_2Cl$, and an aluminum porphyrin catalyst.

Wu and Shen[13] studied the polymerization of ECH using acetylacetonate of rare earth elements combined with i-Bu_3Al and water as the catalyst and found that Nd was a good rare earth element to be used as a component of the catalyst, yielding a polymer of high molecular weight and low crystallinity. Shen et al.[14] carried out the ring-opening polymerization of ECH using rare-earth catalyst comprising a complex of chitosan with neodymium , i-Bu_3Al and methyl benzoate and indicated that the polymer obtained has a low crystallinity and a high molecular weight.

Li and Wang and colleagues[15] used lanthanide (Y or Eu)–alkylaluminum bimetallic complex as a single component to polymerize ECH. Kida et al.[16] reported that a ternary catalyst consisting of trialkyl aluminum, 100% phosphoric acid, and Lewis base displayed higher activity in the polymerization of ECH or PO. We[17,18] studied a more effective quaternary catalyst system, consisting of alkyl aluminum, phosphoric acid, a nitrogen-containing electron donor, and water in the polymerization of ECH, as well as its copolymerization with ethylene oxide (EO). The quaternary catalyst is highly effective, as the amount of triisobutyl aluminum used in homopolymerization is only 1% (w/w) based on ECH, and that used in copolymerization is only 2% based on (ECH+EO), with the conversion over 95% at 70°C for 4 h, and the products obtained exhibit very good properties of elastomer., whereas the amount of triisobutyl aluminum used in the Vandenberg catalyst is 6% and 8%, respectively.

This article discusses further study of (1) the optimum composition of the highly efficient quaternary catalyst, which consists of aluminum, phosphoric acid, electron donor, and water; (2) the reactivity of four alkylene oxides during homopolymerization and copolymerization, using the quaternary catalyst and behavior of ECH, EO, and PO during terpolymerization; and (3) glass transition temperatures of the terpolymers obtained by this quaternary catalyst. The objective is to characterize the quaternary catalyst with respect to the possible structure of active center, reactivity ratios of ECH with other alkylene oxides and type or nature of the polymerization, using this quaternary catalyst, as well as to obtain an optimum composition of the terpolymer for use as an elastomer for low-temperature purposes.

EXPERIMENTAL

Materials

Triisobutyl aluminum was purchased as a 25% hydrocarbon solution. In this study, 85% phosphoric acid of analytic reagent grade was used as a mixture containing 1:1 molar ratio of H_3PO_4 to

water. Epichlorohydrin (ECH) of commercial grade was purified by distillation and stored over a 4A molecular sieve. Allylglycidyl ether (AGE) was prepared from epichlorohydrin and allyl alcohol using boron trifluoride etherate as the catalyst, followed by reaction with 50% NaOH, and purified by distillation under reduced pressure and stored over a 4A molecular sieve. Propylene oxide (PO), ethylene oxide (EO), and tetrahydrofuran (THF) of commercial grade were purified by storing over potassium hydroxide (KOH) overnight and by distillation. The distillate was stored over a 4-A molecular sieve. Toluene of CP grade was used directly after storing over a 4A molecular sieve.

Preparation of Quaternary Catalyst

The quaternary catalyst was prepared in a dried flask under purified nitrogen atmosphere. Triisobutyl aluminum was diluted to 5% concentration by adding to toluene via syringe. Then ethyl ether solution of 85% phosphoric acid at about 5% concentration was added dropwise to the diluted triisobutyl aluminum solution at room temperature according to the molar ration of H_3PO_4/i-Bu_3Al = 0.25. Finally, nitrogen-containing electron donor was added by syringe according to the molar ratio of electron donor/i-Bu_3Al = 0.15. The resulting catalyst solution was apparently homogeneous when prepared in this order .

Polymerization

Polymerization was carried out in dried bottles under purified nitrogen; 15 g monomer and 100 mL toluene were added first; then the catalyst solution prepared as described above, containing 1% triisobutyl aluminum/ECH was added into the polymerization bottle during stirring with a magnetic stirrer. The polymerization was carried out at 70°C for 4 h and then stopped by adding excess petroleum ether containing 0.1% antioxidant 264(2,6-di-t-butyl-4-methylphenol). The precipitated polymer was separated and washed with petroleum ether. The washed polymer was dried in vacuum oven at 60°C. When propylene oxide was used as a comonomer, the polymerization was stopped by adding toluene containing antioxidant 264; and the mixture was evaporated to remove the solvent and unreacted monomer. The inherent viscosity of polymer of ECH or its copolymer was measured in cyclohexanone solution at a 0.1-g/dL concentration at 50°C.

Determination of Reactivity Ratios

Various feed compositions for each of the comonomer pairs were prepared and polymerized in toluene solution in the presence of the quaternary catalyst to less than 10% conversion. Mole fractions of ECH units in the copolymers were calculated from the chlorine content of the copolymers, which was determined by an oxygen combustion procedure; the contents of oxypropylene units and oxyethylene units were determined by 60-MHz ^{1}H-nuclear magnetic resonance (NMR) spectrometry, using benzene as the solvent and tetramethylsilane (TMS) as the internal reference. The NMR spectra show peaks at $\delta_{1.05-1.15}$ due to protons in CH_3 group and at $\delta_{3.41-3.57}$ due to protons in CH_2 and CH groups. The weight percentage of oxypropylene unit (W_{PO}) can be calculated from area of the two peaks and weight percentage of chlorine content (W_{Cl}) according to the following equation:

$$A_{(1.05-1.15)}/A_{(3.41-3.57)}$$
$$= 5.16 W_{PO}/(908 - 9.58 W_{Cl} - 3.92 W_{PO})$$

The weight percentage of oxyethylene units can be calculated by difference.

Determination of Glass Transition Temperature

The glass transition temperatures of the copolymers and terpolymers were determined by differential scanning calorimetry (DSC) curves using a Perkin–Elmer DSC-2 apparatus with a heating rate of 2°C/min and a sample weight of ~5 mg.

RESULTS AND DISCUSSION

Study of the Components of the Quaternary Catalyst

Table I shows that the activity of the quaternary catalyst is rather low without the addition of an electron donor and that nitrogen-containing electron donors can evidently promote the activity of the catalyst, but oxygen-containing electron donors cannot. This is probably because of the weak ability in complex formation between aluminum and an oxygen-containing electron donor. A complex formation is necessary for forming active sites. Tertiary amines, thiazoles, and thiurams are all suitable as the third catalyst component. Compounds such as amide, imide, and nitroben-

Table I   Effect of Various Compounds as the Third Component of the Catalyst on Homopolymerization of Epichlorohydrin and Copolymerization of Epichlorohydrin With Ethylene Oxide

Name of Compound	Compound/i-Bu$_3$Al (Molar Ratio)	Conversion (%)	
		Homopolym[a]	Copolym[b]
—	0	35	28
Tetrahydrofuran	0.15	29	—
Cyclohexanone	0.15	33	—
Dimethylformamide	0.15	28	—
Caprolactam	0.15	33	—
Succinimide	0.15	31	—
Nitrobenzene	0.15	—	13
Benzothiazole sulfenamide	0.20	98	—
Tetramethyl thiuram disulfide	0.15	76	93
Ethylene thiourea	0.15	48	—
Pyridine	0.10	99	93
Triethylamine	0.20	99	—
N,N-Dimethylaniline	0.15	97	—
N,N-Dimethylaniline	0.20	—	99
Isoquinoline	0.15	84	100
Aniline	0.20	57	35
N-Phenyl-β-naphthylamine	0.20	40	—
N-Phenyl-β-naphthylamine	0.15	—	29

[a] Conditions of homopolymerization: i-Bu$_3$Al/monomer = 1.0 wt %, 70°C 4 h, 15 g monomer/dl toluene.
[b] Conditions of copolymerization: i-Bu$_3$Al/monomers = 2.0 wt %, 90°C 4 h, 20-g monomers/dL toluene. Ethylene oxide/epichlorohydrin (EO/ECH) = 1 : 1 molar ratio.

zene do not promote the activity of catalyst. This may be interpreted as the result of delocalization of the lone electron pair in the amide group or the nitro group. Thus it is impossible for these nitrogen atoms to complex efficiently with an aluminum atom to form the active site of the catalyst. Primary or secondary amine has almost no beneficial effect on catalyst activity, owing to the presence of active hydrogen atom in the amine which reacts with the alkyl on aluminum forming an inactive substance.

Phosphoric acid is used as the second component of the catalyst. Without it the activity is quite low. Table II shows that there is no polymer yield when tributyl phosphate is used instead of phosphoric acid. Thus, the active hydrogen atoms in phosphoric acid are necessary for reaction with aluminum and then complexing with the nitrogen-containing electron donor to form the active sites. If aniline containing active hydrogen atoms is used in combination with tributyl phosphate and trialkyl aluminum, the polymerization of ECH cannot be induced. Therefore, Al–O–P bond formed by the reaction of active hydrogen atoms in phosphoric acid with trialkyl aluminum is necessary for the active site of the quaternary cata-

Table II   Effect on Polymerization of Epichlorohydrin by Change of the Second Component of the Catalyst

Catalyst	Composition of Catalyst (Molar Ratio)	Conversion (%)
i-Bu$_3$Al—H$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$—H$_2$O	1 : 0.25 : 0.15 : 0.25	97
i-Bu$_3$Al—H$_2$O—C$_6$H$_5$N(CH$_3$)$_2$	1 : 0.50 : 0.15	4
i-Bu$_3$Al—(C$_4$H$_9$)$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$	1 : 0.30 : 0.15	0
i-Bu$_3$Al—(C$_4$H$_9$)$_3$PO$_4$—C$_6$H$_5$NH$_2$	1 : 0.30 : 0.15	0

Table III   Effect of Water as Catalyst Component on Homopolymerization of Epichlorohydrin and Copolymerization of Epichlorohydrin With Ethylene Oxide

Catalyst	Composition (Molar Ratio)	Conversion		η_i
		Homopolym[a]	Copolym	
i-Bu$_3$Al—H$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$	1 : 0.30 : 0.10	89		1.46
i-Bu$_3$Al—H$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$	1 : 0.30 : 0.15	96		1.75
i-Bu$_3$Al—H$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$—H$_2$O	1 : 0.25 : 0.10 : 0.25	95		1.85
i-Bu$_3$Al—H$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$—H$_2$O	1 : 0.25 : 0.15 : 0.25	99		2.32
i-Bu$_3$Al—H$_3$PO$_4$—C$_5$H$_5$N	1 : 0.30 : 0.10	97		1.25
i-Bu$_3$Al—H$_3$PO$_4$—C$_5$H$_5$N—H$_2$O	1 : 0.25 : 0.10 : 0.25	90		1.55
i-Bu$_3$Al—H$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$	1 : 0.30 : 0.15		98	1.48
i-Bu$_3$Al—H$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$	1 : 0.30 : 0.25		99	1.25
i-Bu$_3$Al—H$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$	1 : 0.30 : 0.30		54	0.66
i-Bu$_3$Al—H$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$—H$_2$O	1 : 0.25 : 0.15 : 0.25		99	1.80
i-Bu$_3$Al—H$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$—H$_2$O	1 : 0.25 : 0.25 : 0.25		98	1.65
i-Bu$_3$Al—H$_3$PO$_4$—C$_6$H$_5$N(CH$_3$)$_2$—H$_2$O	1 : 0.25 : 0.30 : 0.25		99	1.76

[a] Conditions of homopolymerization: i-Bu$_3$Al/monomer = 0.8% wt %, 70°C 4 h, 15-g monomer/dL toluene.
[b] Conditions of copolymerization: i-Bu$_3$Al/monomers = 1.75 wt %, 90°C, 4 h, 20-g monomers/dL toluene, ethylene oxide/epichlorohydrin (EO/ECH) = 1 : 1 (molar ratio).

lyst. Al–N bond, formed by reaction of aniline with trialkyl aluminum, has no such effect.

Table III indicates the function of water as the fourth component of catalyst. The molecular weight of the polymer is represented by the inherent viscosity. It can be seen that water can enhance the molecular weight of the polymer either in homopolymerization of ECH or in copolymerization of ECH with EO.

The catalyst is apparently homogeneous and more effective when prepared in the right order, i.e., adding ether solution of 85% phosphoric acid, in which the molar ratio of water to H$_3$PO$_4$ is about 1:1, to a toluene solution of triisobutyl aluminum, followed by addition of nitrogen-containing electron donor. The catalyst appears to be inhomogeneous and less effective when prepared in other sequences.

The effect of molar ratio of the third component to triisobutyl aluminum on homopolymerization of ECH, using pyridine as the third component with molar ratio of phosphoric acid to triisobutyl aluminum at 0.25, is shown in Figure 1. When increasing the molar ratio of pyridine to triisobutyl aluminum, the polymer yield and inherent viscosity of the polymer reach a maximum value; thereafter, both the conversion and the inherent viscosity decrease. The optimum range of electron donor/triisobutyl aluminum is situated at molar ratio of 0.1–0.15.

Figure 2 shows the effect of molar ratio of *N,N*-dimethyl aniline as the third component of cata-

lyst to trisobutyl aluminum on terpolymerization of EO, PO, and ECH with molar ratio of phosphoric acid to triisobutyl aluminum at 0.25. The optimum molar ratio of the electron donor to triisobutyl aluminum appears at 0.15–0.20.

The effect of molar ratio of phosphoric acid to triisobutyl aluminum in the copolymerization of ECH and EO is shown in Figure 3. The optimum value occurs at ~0.25. Since the molar ratio of water to triisobutyl aluminum is the same as that
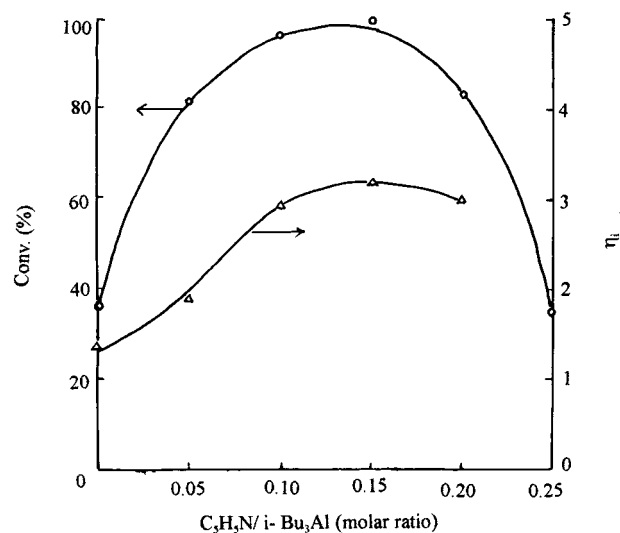

Figure 1   Effect of molar ratio of pyridine to triisobutyl aluminum on homopolymerization of epichlorohydrin (H$_3$PO$_4$/i-Bu$_3$Al = 0.25 molar ratio).
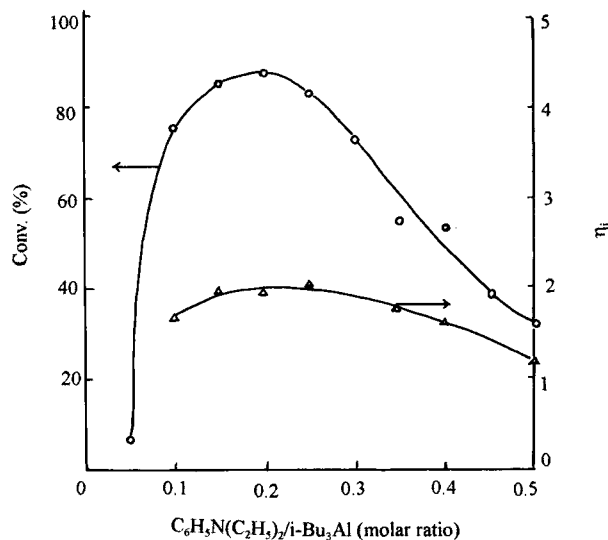
Figure 2 Effect of molar ratio of dimethylaniline to triisobutyl aluminum on terpolymerization of epichlorohydrin (ECH), ethylene oxide (EO), and propylene oxide (PO) (H_3PO_4/i -Bu_3Al = 0.25 molar ratio).

of phosphoric acid to triisobutyl aluminum, the optimum ratio of the former is also 0.25.

In summary, the most favorable composition of the catalyst is triisobutyl aluminum: phosphoric acid: nitrogen-containing electron donor: water = 1: 0.25: 0.15–0.20: 0.25 or = 4: 1: 0.6−0.8 :1.

Character of the Quaternary Catalyst

According to the most favorable composition of the catalyst the active site is presumed to be composed of:

$$R_2Al{-}O{-}\overset{\overset{\textstyle O}{\|}}{\underset{\underset{\textstyle O{-}AlR_2}{|}}{P}}{-}O{-}Al{-}O{-}AlR_2$$
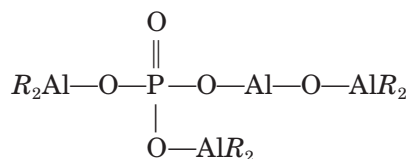
which is complexed with the nitrogen-containing electron donor compound. The presence of P–O–Al–O–Al bond in the active site may enhance the propagation reaction and reduce the chain transfer or termination reaction, thus increasing the molecular weight of the polymer.

In order to recognize the character of the quaternary catalyst system, the polymerization of tetrahydrofuran (THF) and the reactivity ratios of different alkylene oxides in copolymerization using this catalyst have been studied. Polymerization of THF was carried out at 0°C for 24 h

with ECH as polymerization promoter in molar ratio of 1:1 to triisobutyl aluminum. It is shown in Table IV that i-Bu_3Al–H_3PO_4–H_2O catalyst can induce the polymerization of THF, whereas the quaternary catalyst system shows no polymerization activity on THF. According to Meerwein et al.,[19] THF can only be polymerized by a cationic mechanism, and so polymerization by the quaternary catalyst system cannot be a cationic mechanism.

It is of interest to note that when the polymerization of ECH by the quaternary catalyst was finished, it can continue after further addition of ECH, but the molecular weight of the polymer cannot increase further, as shown in Table V. This implies that the polymerization is not of a living type without chain transfer but of an immortal type with chain transfer process.

Reactivity of Four Alkylene Oxides During Homopolymerization and Copolymerization

The reactivity ratios for different monomer pairs between ECH, EO, PO, and AGE in copolymerization under the action of this catalyst were determined by the Fineman–Ross[19] procedure, as shown in Table VI. From the reactivity ratios for EO and ECH ($r_1 > 1$, $r_2 = 0.03$), it can be recognized that at the beginning of the copolymerization the EO ended sites combine more rapidly
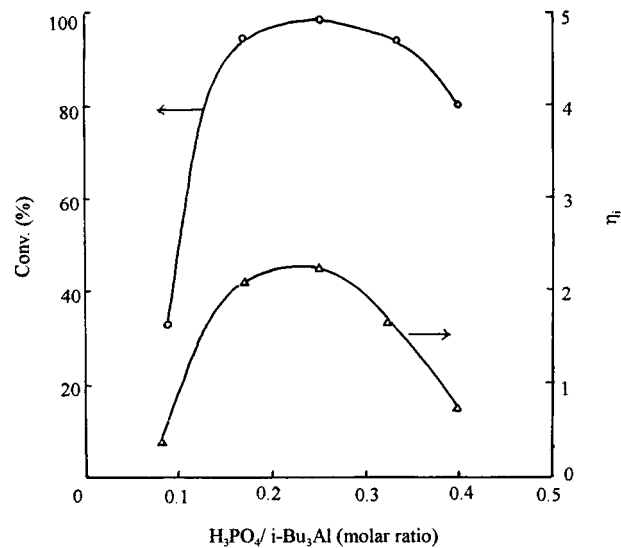

Figure 3 Effect of molar ratio of phosphoric acid to triisobutyl aluminum on copolymerization of epichlorohydrin (ECH) and ethylene oxide (EO) [DMA/H_3PO_4 = 0.15, EO/ECH = 32.3/67.7 (wt)].

Table IV   Polymerizability of Tetrahydrofuran

Catalyst	Composition (Molar Ratio)	Conversion (%)
i-Bu$_3$Al—H$_3$PO$_4$—tetramethyl thiuram disulfide—H$_2$O	1 : 0.25 : 0.15 : 0.25	0[a]
i-Bu$_3$Al—H$_3$PO$_4$—H$_2$O	1 : 0.25 : 0.25	32

[a] A small amount of polymer resulted from the promotor epichlorohydrin.

with EO than with ECH, whereas the probability of combination of ECH ended sites with ECH is small in comparison with EO. It is more likely that the formation of long sequence of oxyethylene units occurs in the copolymer. Copolymerization between PO and ECH is analogous to that of EO and ECH, but the probability of linking several oxypropylene units together in copolymer is less than that of oxyethylene according to the values of reactivity ratios. In a comparison of these copolymerization data with the data obtained by Hsieh,[5] Kuntz,[7] and Ishide,[21] this quaternary system contrasts that of the ferric chloride–PO system,[21] which belongs to a cationic mechanism, but similar to those of the other systems which were assumed to be of coordinated anionic type.

With regard to the reactivity ratios for AGE–ECH and EO–PO pairs r_1 is not very different from r_2 and the reactivity ratio product is not so far from unity as in the EO–ECH case (Table VI), so it is more likely that these monomer pairs copolymerized more randomly, although AGE or EO appears to be copolymerized slightly more easily. If $1/r_2$ is used in comparing the ability of copolymerization of the monomers, the monomer reactivity decreases in the sequence: EO > PO > AGE > ECH. This is different from the ability of homopolymerization, which decreases in another order: EO > PO > ECH > AGE. (Fig. 4). The size of substituent increases as: EO > PO < ECH < AGE, and the basicity of the monomer decreases as: PO = AGE > EO > ECH. Most likely, steric hindrance plays a primary role during homopolymerization, whereas both polarity and steric hindrance influence the monomer reactivity during copolymerization.

Behavior of ECH, EO, and PO During Terpolymerization

Because a terpolymer containing ECH, PO, and EO is suitable for use as an oil-resistant elastomer for low-temperature purposes, the terpolymerization of ECH, EO, and PO in equal moles by this quaternary catalyst system has been studied and the variation of terpolymer composition as a function of conversion in batch polymerization has been followed. Figure 5 shows that at the beginning of the terpolymerization oxyethylene units and oxypropylene units are richer in the terpolymer. This indicates that EO copolymerizes more rapidly, PO the second, and ECH the slowest. This finding also confirms the reactivity ratio values for these three monomers described above, which shows that EO is the most active monomer. With increased conversion, the relative amount of ECH units increases gradually, while that of oxyethylene and oxypropylene units decreases correspondingly. It is evident that as the concentration of EO and PO decrease, the amount of ECH polymerized increases until the composition of terpolymer reaches the original molar proportion of monomer mixture (1:1:1).

Table V   Effect of Complementary Addition of Monomer on Polymerization of Epichlorohydrin

No. of ECH Addition	Wt. of Monomer (g)	Polym. Time (h)	Total Conversion (%)	η_{1i} (dl/g)
1	3	3	93.3	2.17
2	3 + 3	3 + 3	94.2	2.18
3	3 + 3 + 3	3 + 3 + 3	96.1	2.13

Conditions of polymerization at the outset: 70°C, ECH/toluene = 10 g/dL, i-Bu$_3$Al/ECH = 2.5 wt %, i-Bu$_3$Al : H$_3$PO$_4$: C$_6$H$_5$N(CH$_3$)$_2$: H$_2$O = 1.0 : 0.25 : 0.15 : 0.25 (molar ratio).

Table VI   Reactivity Ratios for Different Monomer Pairs

Monomer Pairs	r_1	r_2	$1/r_2$
EO–ECH	6.55 ± 0.15	0.03 ± 0.02	33.3
PO–ECH	2.75 ± 0.30	0.11 ± 0.03	9.1
AGE–ECH	1.42 ± 0.16	0.49 ± 0.06	2.0
PO–EO	0.32 ± 0.02	2.15 ± 0.12	—

EO, ethylene oxide; ECH, epichlorohydrin; PO, propylene oxide; AGE, allyl glycidyl ether.

Glass Transition Temperatures of the Copolymers and Terpolymers of ECH

In order to choose the optimum composition of the terpolymer for low-temperature purposes, the glass transition temperature of the terpolymers was measured. It varies with the starting composition of the monomer mixture under terpolymerization. When the molar ratio of the epichlorohydrin in the mixture is kept constant, the glass transition temperature of the terpolymer exhibits a minimum value as the molar ratio of PO increase (Fig. 6). If the molar ratio of ECH to monomer mixture is 1:2, the minimum glass transition temperature of the terpolymer formed occurs at a PO-to-EO molar ratio of 3:1. If the molar ratio of ECH to the monomer mixture is 1:3, the mini-
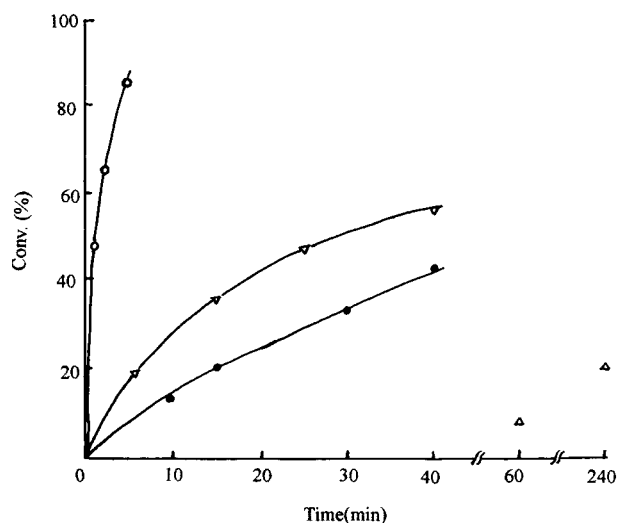

Figure 5   Variation of composition of terpolymer with conversion. ○, ethylene oxide (EO); △, propylene oxide (PO); ●, and epichlorohydrin (ECH).

mum glass transition temperature of the terpolymer also occurs at nearly 3:1 molar ratio of PO to EO. It is evident that the glass transition temperature of the terpolymer at suitable proportion of monomers may be lower than that of copolymer. This may be due to a more random distribution of different monomer units in terpolymer which causes the lowering of glass transition temperature. However, the terpolymer shows only one glass transition temperature between those for

Figure 4   Comparison of the rates of homopolymerization of different alkylene oxides. ○, EO (Al/EO = 0.28 mol %); ▽, PO (Al/PO = 0.4 mol %); ●, ECH (Al/ECH = 0.4 mol %); △, AGE (Al/AGE = 1.44 mol %). EO, ethylene oxide; PO, propylene oxide; ECH, epichlorohydrin; AGE, allyl glycidyl ether.
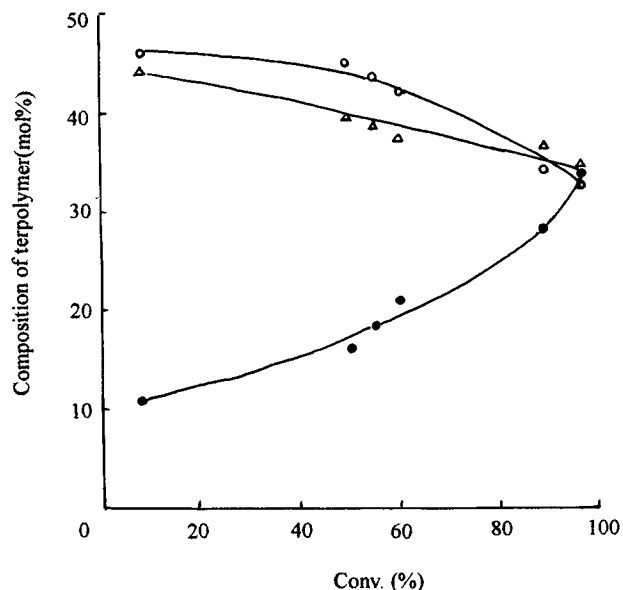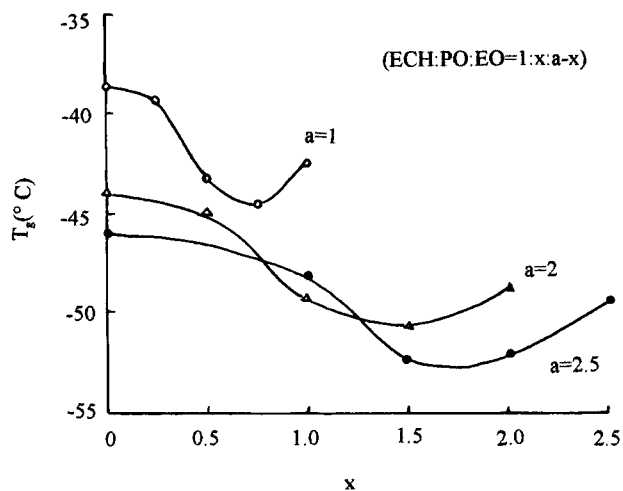

Figure 6   Change of glass transition temperature of the terpolymer with the starting composition of the monomer mixture (ECH:PO:EO) = 1:x:a-x.

the pure homopolymers, indicating that terpolymerization has indeed occurred.

CONCLUSIONS

The quaternary catalyst is highly effective for ring-opening polymerization of alkylene oxides. Tertiary amines, thiazole and thiurams, which contain electron-donating nitrogen atoms, are an efficient third catalyst component, whereas oxygen-containing donors are not. Water as the fourth component can enhance the molecular weight of the homopolymer or copolymer of ECH.

When prepared in the right order, the quaternary catalyst displays high activity. The optimum ratio of the four components triisobutyl aluminum : phosphoric acid : nitrogen-containing electron donor : water is 1:0.25:0.15–0.20:0.25 or 4: 1:0.6–0.8:1. According to the polymerizability of tetrahydrofuran by the quaternary catalyst and the reactivity ratios of different alkylene oxides, the quaternary catalyst was presumed to be of a coordinated anionic type. When the polymerization of ECH was finished, it can continue further when additional monomer was added, but the molecular weight of the polymer obtained remains constant.

According to the reactivity ratios determined, the monomer reactivity in the copolymerization decreases in the order EO > PO > AGE > ECH, whereas the reactivity of the monomer in the homopolymerization decreases in another order EO > PO > ECH > AGE.

During the terpolymerization of ECH, PO, and EO, the reactivity of the monomers was found to decrease in the order EO > PO > ECH, which agrees with the reactivity ratios determined for these monomers. When the molar ratio of ECH used in the terpolymerization is kept constant, the glass transition temperature of the terpolymer exhibits a minimum value at nearly 3:1 molar ratio of PO to EO. The composition of the terpolymer with the lowest glass transition temperature can be used as the optimum composition of the elastomer for low-temperature purposes.

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