Cationic Copolymerization of 2-Chloroethyl Vinyl Ether with Styrene Derivatives. III. Solvent and Catalyst Effects on Relative Reactivity

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SUMMARY

The change in relative reactivity in the cationic copolymerization of 2-chloroethyl vinyl ether and styrene derivatives was investigated with various catalysts and solvents. p-Methoxystyrene, p-methylstyrene, and α-methylstyrene were used as styrene derivatives. The styrene content in the copolymer increased when a polar solvent and/or a strong catalyst was used. The change of relative reactivity in the copolymerization of 2-chloroethyl vinyl ether with styrene derivatives was much greater than that in the copolymerization between vinyl ethers or styrene derivatives. When nitroethane was used as a solvent, not only the polarity but also the nucleophilicity influenced the copolymer composition. The results were discussed by two energies, E^{π} and E_{rs}, which are measures of complex formation between monomer and carbonium ion, and stabilization energy in the transition state, respectively.

INTRODUCTION

In previous papers [1, 2] it was shown that monomer reactivity ratios

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(MRR) depend on the polymerization conditions in cationic polymerization of 2-chloroethyl vinyl ether (CEVE) with styrene derivatives. The remarkable change in MRR caused by polymerization conditions was often observed in anionic copolymerization; for example, copolymerization of styrene with methyl methacrylate [3] or isoprene [4]. On the other hand, in cationic copolymerization there are few examples in which MRR greatly depends on polymerization conditions, except for the styrene derivatives-isobutene system [5].

   Therefore, the cationic copolymerization of CEVE with styrene derivatives is very interesting in that it elucidates a reaction mechanism of cationic polymerization. In the present paper, the dependence of relative reactivity on polymerization conditions has been studied with various catalysts and solvents in the cationic copolymerization of CEVE with styrene derivatives. It was found that the relative reactivity of CEVE with styrene derivatives depends on the kinds of catalyst and solvent, and this result has been explained in terms of the difference in the ability of complex formation between monomer and growing carbonium ion. This interpretation is proposed for the cationic co-polymerization of styrene derivatives [6].

EXPERIMENTALS

Materials

   CEVE, isobutyl vinyl ether (IBVE), p-methoxystyrene (pMOS), p-methylstyrene (pMS), α-methylstyrene (αMS), and styrene (ST) were obtained and purified as described before [1]. Aluminum bromide of a guaranteed grade was purified by sublimation under reduced pressure. Acetyl perchlorate was prepared by a similar method to Jaacks [7]: Silver perchlorate was dried at 70°C for two hours under a vacuum. Purified methylene chloride (100 cc) and 0.010 mole of freshly distilled acetyl chloride were successively added to 0.022 mole of silver perchlorate. The mixture was stirred overnight at room temperature in the dark. The clear catalyst solution was preserved in ampoules at -20°C. The other catalysts and solvents were purified as described before [1].

Procedures

   The copolymerization procedures are the same as those described in a previous paper [1]. The relative reactivity in copolymerization was

determined by measuring the residual monomers in the reaction system by gas chromatography. Because the necessary conditions for the separation of nitroethane and CEVE by gas chromatography were not found in the re-action system using nitroethane as solvent, the relative reactivity was determined by measuring the resultant copolymer composition by its NMR spectrum.

RESULTS

The copolymerization of CEVE with styrene derivatives was carried out at -78°C in equimolar monomer ratio (total monomer concentration: 0.50 mole/1). Aluminum bromide, stannic chloride [with equimolar trichloro-acetic acid (TCA) as cocatalyst], boron fluoride etherate, and acetyl perch-lorate were used as catalysts. Toluene was used as the nonpolar solvent, and methylene chloride and nitroethane as the polar solvents.

Table 1 shows the relative reactivity of CEVE against styrene derivatives. The relative reactivity was obtained from the ratio of initial slopes in time-conversion curves of both monomers. The values in Table 1 are the averages of three or four experimental values, and the residual error was less than 10%.

In the copolymerization of CEVE with pMOS in toluene and methylene chloride, the relative reactivity of pMOS decreased in the following order of catalysts: $AlBr_3 > SnCl_4 \cdot TCA > BF_3 \cdot OEt_2 > CH_3COClO_4$. An opposite tendency, however, was observed in nitroethane solvent. When $BF_3 \cdot OEt_2$ and CH_3COClO_4 were used as catalysts, the relative reactivity of CEVE de-creased with increases in the dielectric constant of a solvent.

In the copolymerization of CEVE with pMS, the relative reactivity in toluene changed from 8.5 to >40 when CH_3COClO_4 was used instead of $AlBr_3$. The relative reactivity of the toluene–CH_3COClO_4 system as measured by gas chromatography, was confirmed by the fact that no pMS unit was observed through NMR in the copolymer obtained at low conver-sion. On the other hand, it decreased from 1.8 to 0.43 in nitroethane. The relative reactivity of CEVE decreased with an increase in the polarity of the solvent, and the large change in MRR was observed in copolymeriza-tions using $BF_3 \cdot OEt_2$ and CH_3COClO_4. It is surprising that the relative reactivity changed from >40 to 0.43, that is, by a hundred times, with a change in solvent from toluene to nitroethane, when acetyl perchlorate was used as a catalyst.

The results of the copolymerization of CEVE with αMS showed tend-encies similar to the CEVE-pMOS and CEVE-pMS systems. That is, the

Table 1. Relative Reactivity of CEVE against Styrene Derivatives in the Equimolar Copolymerization ([M]$_0$: 0.50 mole/l, $-78°C$)

Monomer	Solvent	Catalyst			
		AlBr$_3$	SnCl$_4$·TCA	BF$_3$·OEt$_2$	CH$_3$COClO$_4$
CEVE-pMOS	Toluene	0.23_7	0.33_3	0.68_7	1.7_2
	Methylene chloride	0.20_2	0.29_0	0.64_7	0.91_6
	Nitroethane	0.51_5	0.50_4	0.17_1	0.24_2
CEVE-pMS	Toluene	8.4_8	7.4_0	~27	>40
	Methylene chloride	2.1_0	2.1_0	7.0_0	9.1_0
	Nitroethane	1.7_8	1.6_3	2.9_7	0.42_9
CEVE-αMS	Toluene	2.5_7	3.1_7	4.9_9	18.0
	Methylene chloride	0.97_1	1.0_0	1.7_8	4.0_3
	Nitroethane	1.7_4	1.6_7	2.0_9	0.54_6

relative reactivity of CEVE against styrene derivatives increased greatly in toluene and methylene chloride, when CH_3COClO_4 was used as catalyst. However, the difference in MRR with the kind of catalyst was small in nitroethane. When $BF_3 \cdot OEt_2$ and CH_3COClO_4 were used as catalysts, the relative reactivity of CEVE decreased with increasing solvent polarity.

The copolymerizations of ST with pMS and of IBVE with CEVE were carried out under similar conditions in order to determine whether such large catalyst and solvent effects are observed in the copolymerization between monomers of similar structure.

Table 2. Relative Reactivity of ST against pMS in the Equimolar Copolymerization ($[M]_0$: 1.00 mole/l, 30°C)

Solvent	$AlBr_3$	$SnCl_4 \cdot TCA$	$BF_3 \cdot OEt_2$	CH_3COClO_4
Benzene	0.79_0	0.34_5	0.43_2	--
Methylene chloride	0.52_2	0.41_0	0.43_0	0.35_1
Nitroethane	0.36_8	0.38_0	0.33_9	0.38_6

Copolymerization of ST with pMS was carried out at 30°C and the total monomer concentration was 1.00 mole/1. As shown in Table 2, the relative reactivity of ST, taking that of pMS as unity, was in the range 0.34 -0.52 except for the case of the $AlBr_3$-benzene system. Tobolsky et al. reported that the styrene content became larger with a strong catalyst and in a nonpolar solvent such as $SbCl_5$-toluene system [8]. Substantially, as is seen from Table 2, the relative reactivity of ST with pMS did not vary significantly with the kind of catalyst and solvent.

Copolymerization of IVBE with CEVE was performed at -78°C and the total monomer concentration was 0.50 mole/1. As is seen from Table 3, large solvent and catalyst effects were not observed in the co-polymerization of IVBE with CEVE. The values are 2.6 and 2.7 in CH_2Cl_2-$AlBr_3$ and CH_2Cl_2-$SnCl_4 \cdot TCA$ systems. In other cases the values are 1.4 ~ 2.3. This change is much smaller than in CEVE-styrene derivative systems.

DISCUSSION

In Table 4 the changes in the relative reactivity of styrene derivatives against CEVE with different solvents and catalysts are summarized. The

Table 3. Relative Reactivity of IBVE against CEVE in the
Equimolar Copolymerization ([M]$_0$: 0.50 mole/l, $-78°C$)

Solvent	AlBr$_3$	SnCl$_4$·TCA	BF$_3$·OEt$_2$	CH$_3$COClO$_4$
Toluene	1.6$_4$	1.6$_7$	1.8$_6$	1.8$_9$
Methylene chloride	2.5$_7$	2.6$_8$	1.9$_0$	2.2$_7$
Nitroethane	1.4$_6$	1.5$_7$	1.3$_6$	1.5$_5$

Table 4. Summary of the Changes in the Relative
Reactivity of Styrene Derivatives against
CEVE in Copolymerization

No.	Fixed	Strength or polarity	Relative reactivity against CEVE		
			pMOS	pMS	αMS
a	Polar solvent	Catalyst ↑	→	→	→
b	Nonpolar solvent	Catalyst ↑	↑	↑	↑
c	Strong catalyst	Solvent ↑	⤢↘	⤳	⤢↘
d	Weak catalyst	Solvent ↑	↑	↑	↑

relative reactivity of styrene derivatives did not change significantly in a
polar solvent such as nitroethane (No. a in Table 4).

The order AlBr$_3$ > SnCl$_4$ > BF$_3$·OEt$_2$ in the catalyst activity was
observed in cationic polymerization of isobutene [9] and other monomers.
Further, the H$_0$ (Hammett acidity function) of HBF$_4$ was found to be
-16.6, while the H$_0$ of anhydrous protonic acid is from -11 to -10 [10].
Therefore, in this paper, we have settled tentatively on the following order
of catalyst activity: AlBr$_3$ > SnCl$_4$·TCA > BF$_3$·OEt$_2$ > CH$_3$COClO$_4$,
although it is well known that the order of catalytic activity of metal
halides varies with particular reactions.

As shown in No. b in Table 4, the relative reactivity of styrene derivatives
increased with the catalyst strength in a less polar solvent such as methylene
chloride and toluene. The relative reactivity of styrene derivatives increased
and then decreased with the polarity of solvent using strong catalysts such

as $AlBr_3$ and $SnCl_4 \cdot TCA$ (No. c of Table 4). It increased consistently with increases in the polarity of weak catalysts such as acetyl perchlorate (No. d of Table 4).

The authors [6] accounted for the changes of MRR in the cationic co-polymerization of styrene with p-methylstyrene [8] in terms of two quantum-mechanically calculated energies, E^{π} and E_{rs}, which, respectively, are measures of complex formation between monomer and carbonium ion, and resonance stabilization of the transition state as a result of incipient bond formation.

The above-mentioned results may also be discussed in a similar manner. The propagation reaction of cationic polymerization was assumed to divide into two elementary reactions [11]:

$$P_n^+A^- + M \underset{\longleftarrow}{\overset{K}{\longrightarrow}} (P_nM)^+A^- \xrightarrow{k} P_{n+1}^+ A^- \qquad (1)$$
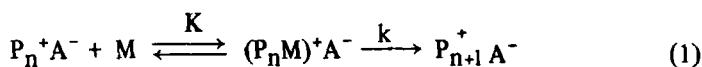
The propagation rate constant k_p can be given as in Eq. (2), supposing $K \ll 1$.

$$k_p = \frac{kK}{K[M] + 1} \simeq kK \qquad (2)$$

K and k are related to the energy terms E^{π} and E_{rs},

$$\ln K = (const)' - E^{\pi}/RT \qquad (3)$$

$$\ln k = (const)'' - E_{rs}/RT \qquad (4)$$

where E^{π} is the energy contributing to stabilization in the formation of π-complex between propagating ion and monomer, and E_{rs} is the stabilization energy accompanying bond formation between carbon r of a propagating ion and carbon s of a monomer. Accordingly, the partial activation energy due to π-electrons of propagating reaction, E^*, is related to E^{π} and E_{rs}:

$$E^* = (const) - (E^{\pi} + E_{rs}) \qquad (5)$$

E_{rs} and E^{π} are dependent on the coulomb integral, α_r, on an atom r. α_r is dominated by a charge on carbon r, so that it will vary with the distances of carbon r from a gegen-ion and from a basic solvent. This concept leads to

$$\alpha_r = \alpha - \delta\beta - \delta'\beta \qquad (6)$$

$$\delta = \text{const} \cdot \frac{Q_r e^2}{R} \qquad (7)$$

$$\delta' = \text{const} \cdot \frac{Q_r \cdot Q_N e^2}{R'} \qquad (8)$$

where α is the coulomb integral for chain end cation unperturbed by a gegen-ion or solvent; δ and δ' are measures of the influence of the electrostatic field of the gegen-ion and solvent, respectively, on the atom r; Q_r and Q_N are the net charges on the carbon r of chain end and on the nucleophilic site of a solvent, respectively, the nonperturbed systems; and R and R' are the distances between the carbon r and the gegen-ion or solvent, respectively. δ decreases as the dielectric constant of a solvent or the strength of a catalyst increases. δ' increases with the increase in the nucleophilicity of solvents. Because E_{rs} and E^π are functions of relative δ and δ' values, they can be calculated as in the previous paper [6]. E_{rs} and E^π were proved to become larger as δ decreased. Similar behavior is assumed also with regard to δ'.

The change of rate of homopolymerization to be expected is shown in Table 5. Here, toluene, methylene chloride, and nitroethane were used as

Table 5. The Dependence of δ, δ', and E* on the Kind of Solvents and Catalysts

No.	Fixed	Strength or polarity	δ	δ'	E^π, E_{rs}	E*
a	Polar solvent	Catalyst ↑	→	→	→	→
b	Nonpolar solvent	Catalyst ↑	↘	→	↗	↘
c	Strong catalyst	Solvent ↑	↘	↗	⌢	⌣↗
d	Weak catalyst	Solvent ↑	↘	↗	↗	↘

solvents; the last has not only a large dielectric constant but also a considerable nucleophilicity. As a distinct example of the influence of nucleophilicity, neither monomer was consumed in the copolymerization of CEVE with styrene derivatives in diethyl ether because of a large nucleophilicity of the solvent [12]. Such a reactivity dependence, controlled not only by solvent polarity but also by solvent nucleophilicity, is also seen in the polymerization of N-phenylethyleneimine [13].

The change of relative reactivity of CEVE against styrene derivatives will be decided by the relative importance of the change in E^π or E_{rs} with polymerization conditions in the polymerization of these monomers. As vinyl ethers have a larger solvating power than styrene derivatives [14], it is supposed that the reactivity of vinyl ethers is hardly affected by the kind of solvent and catalyst used. Therefore, the change of relative reactivities in the copolymerization of CEVE with styrene derivatives should be mainly controlled by the styrene derivatives. This means that the difference of E^π or E_{rs} (ΔE^π or ΔE_{rs}) in the copolymerization of styrene derivatives with CEVE will change similarly to that of the styrene derivatives.

On the basis of this concept, the expected and observed changes in relative reactivity are shown in Table 6. The agreement is good. For example, when a weak catalyst was used, the relative reactivity of styrene

Table 6. The Expected and Observed Dependence of Relative Reactivity of Styrene Derivatives on the Kind of Solvents and Catalysts

No.	Fixed	Strength or polarity	δ	δ'	Relative reactivity of styrene derivatives	
					Expected	Observed
a	Polar solvent	Catalyst ↑	→	→	→	→
b	Nonpolar solvent	Catalyst ↑	↘	→	↗	↗
c	Strong catalyst	Solvent ↑	↘	↗	⌢↘	*
d	Weak catalyst	Solvent ↑	↘	↗	↗	↗

*Complicated but not a large change (cf. Tables 1 and 4).

derivatives increased consistently with increasing polarity of solvent as δ decreased sharply with the solvent polarity (No. d in Table 6). When a strong catalyst was used, however, the influence of a solvent was more complex (No. c in Table 6) because the gegen-ion produced from a strong catalyst may easily dissociate. A nucleophilic solvent may easily solvate a dissociated ion and decrease the reactivity of a growing chain.

It is concluded that the rate-determining steps in the propagation reaction of vinyl ether and styrene derivatives are not the same, mainly owing to the difference in the solvating power of monomers, and that in consequence the relative reactivities of these monomers are much affected by the kind of catalyst and solvent.

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