

Cationic Copolymerization of 2-Chloroethyl Vinyl Ether with Styrene Derivatives

II. Temperature Dependence of Monomer Reactivity Ratios

Toshio MASUDA and Toshinobu HIGASHIMURA

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.

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ABSTRACT: Temperature dependence of monomer reactivity ratios, r_1 and r_2 , and their product $r_1 \times r_2$ were studied in the cationic copolymerization of 2-chloroethyl vinyl ether (M_1) with styrene derivatives (M_2) (*p*-methoxystyrene, *p*-methylstyrene and α -methylstyrene). Methylene chloride, toluene and benzene were used as solvents, and $\text{SnCl}_4 \cdot \text{CCl}_3\text{CO}_2\text{H}$ and $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ were used as catalysts. r_1 increased and r_2 decreased with increasing polymerization temperature in the copolymerization of M_1 with M_2 except that of M_1 with *p*-methoxystyrene. On the other hand, r_1 and r_2 hardly depended on polymerization temperature in the copolymerization between vinyl ethers or styrene derivatives. On the basis of these results, the difference in the transition state of the propagation reaction of vinyl ether and styrene derivatives was discussed. Temperature dependence of the products, $r_1 \times r_2$, was investigated and the propagating end effect was discussed in cationic copolymerization.

KEY WORDS Cationic Copolymerization/2-Chloroethyl Vinyl Ether/
p-Methylstyrene / *p*-Methoxystyrene / α -Methylstyrene / Monomer Re-
activity Ratio / Temperature Dependence / Thermodynamic Parameter

In the cationic copolymerization of 2-chloroethyl vinyl ether (CEVE) with styrene derivatives,¹ (1) the relative reactivity of both monomers depended largely on the kind of catalysts and solvents used, and (2) the product of the monomer reactivity ratios, $r_1 \times r_2$ was greater than unity in the copolymerization of CEVE with ring-substituted styrenes, although a copolymer was produced.

The differences in the activation parameters are obtained by studying temperature dependence of monomer reactivity ratios. In radical copolymerization, a linearity holds between $\log r$ and $1/T$ and the line passes near the origin.² This means that the activation entropies are equal at the addition of different monomers to the same propagating end, that is, the reaction mechanism is similar in both monomers.

Otherwise, in cationic polymerization, although few reliable data are available, plots between $1/T$ and $\log r$ do not pass the origin.³ The cationic copolymerization of CEVE with α -methylstyrene (α MS) is a typical example, in which both r_1 and r_2 become far from unity as

polymerization temperature is raised.⁴

In the present paper the temperature dependence of monomer reactivity ratios (MRR) and of their product $r_1 \times r_2$ is investigated in detail in the copolymerization of CEVE with styrene derivatives to elucidate the difference of the reaction mechanism between CEVE and styrene derivatives.

EXPERIMENTAL

Materials

p-Methoxystyrene (*p*MOS), *p*-methylstyrene (*p*MS) and *p*-chlorostyrene (*p*CS) were synthesized and purified as described before.¹ CEVE, α MS, isobutyl vinyl ether (IBVE) and styrene (ST) were commercially obtained and purified in the same manner as the monomers synthesized. Solvents (methylene chloride, toluene and benzene) and catalysts (SnCl_4 with equimolar trichloroacetic acid (TCA) as a cocatalyst and BF_3OEt_2) were purified by the usual method.

Procedures

The copolymerization was carried out as de-

scribed in a previous paper.¹ The copolymerization was carried out in $[M]_0$ (total monomer concentration) = 0.50 mol/l except the cases of ST-*p*CS and CEVE- α MS at -23°C , where $[M]_0$ (total monomer concentration) = 1.0 mol/l. Copolymer composition curves were obtained by measuring each monomer consumption by means of gas chromatography. It was confirmed that monomer consumption coincided with the yield of a methanol insoluble polymer. MRR was evaluated by the Fineman-Ross' method. The mean square errors of MRR were in the range of $\pm 5\%$.

RESULTS AND DISCUSSION

Temperature Dependence of MRR

The copolymerization of CEVE with *p*MOS was carried out with BF_3OEt_2 in toluene at -78 , -36 and 0°C . The copolymer composition curves are shown in Figure 1. The composition curves in Figure 1 exhibit S-shape and the CEVE content in copolymer increased as the temperature was raised. As the dielectric constant of toluene is almost independent of temperature, the temperature dependence observed is not based on the change in the dielectric constant of the system. The shift of the composition curves with temperature, moreover, was much larger than those in radical copolymerization of various monomers and those in cationic copolymerization of monomers,

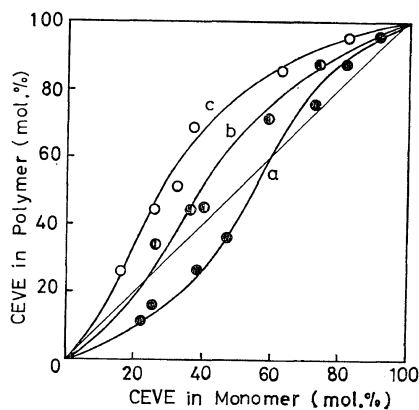


Figure 1. Composition curves for the copolymerization of CEVE with *p*MOS (BF_3OEt_2 ; toluene; $[M]_0$, 0.50 mol/l.) Temp: a (●), -78°C ; b (◐), -36°C ; c (○), 0°C .

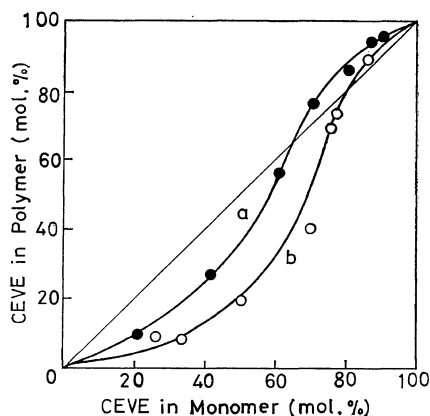


Figure 2. Composition curves for the copolymerization of CEVE with *p*MOS (BF_3OEt_2 ; methylene chloride; $[M]_0$, 0.50 mol/l.) Temp: a (●), -78°C ; b (○), 0°C .

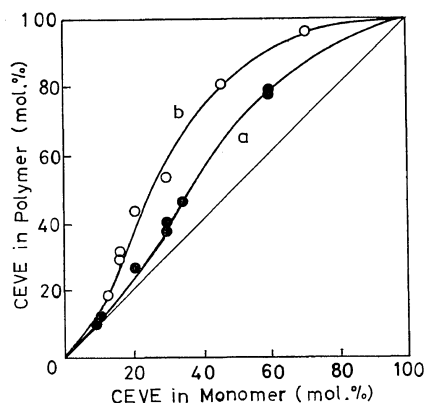


Figure 3. Composition curves for the copolymerization of CEVE with *p*MS ($\text{SnCl}_4\cdot\text{TCA}$; methylene chloride; $[M]_0$, 0.50 mol/l.) Temp: a (●), -78°C ; b (○), 0°C .

having a similar substituent. When methylene chloride was used as solvent, the shift of the composition curves was also large and in the opposite direction to the case of toluene as a solvent (Figure 2).

Figure 3 shows the composition curves in the copolymerization of CEVE with *p*MS by $\text{SnCl}_4\cdot\text{TCA}$ in methylene chloride at -78 and 0°C . A similar change in copolymer composition with temperature was observed when toluene was used as a solvent (see Table I). A characteristic of this copolymerization is that the more reactive the monomer is, the more reactive it

becomes with increasing temperature. This phenomenon cannot be explained only in terms of the difference in activation energy of the propagation reaction.

The copolymerization of CEVE with α MS was

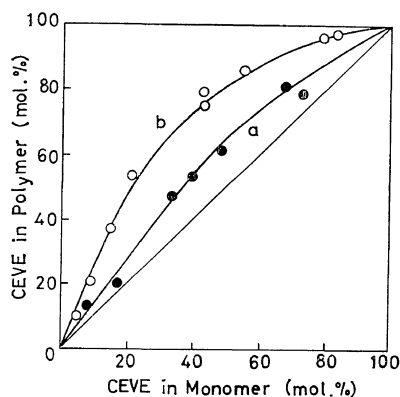


Figure 4. Composition curves for the copolymerization of CEVE with α MS (BF_3OEt_2 ; methylene chloride; $[\text{M}]_0$, 0.50 mol/l at -78°C , $[\text{M}]_0$, 1.0 mol/l at -23°C).
Temp: a (●), -78°C ; b (○), -23°C .

carried out at -23 and -78°C , considering the ceiling temperature of α MS. The CEVE content in the copolymer considerably increased by increasing the polymerization temperature in the

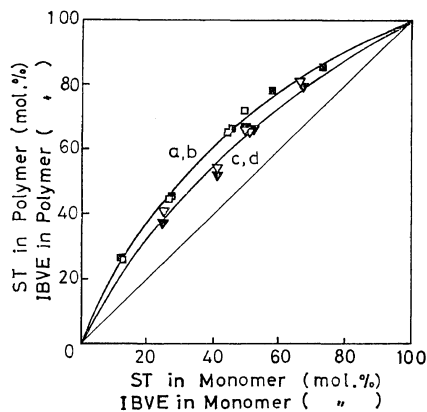


Figure 5. Composition curves for the copolymerization between homologues. ST—*p*CS ($\text{SnCl}_4 \cdot \text{TCA}$; toluene: benzene=4.0: 6.0; $[\text{M}]_0$, 1.0 mol/l), Temp: a (■), -23°C ; b (□), 30°C . IBVE—CEVE (BF_3OEt_2 ; toluene; $[\text{M}]_0$, 0.50 mol/l), Temp: c (▼), -78°C ; d (▽), 0°C .

Table I. The dependence of MRR on temperature in the cationic copolymerization of vinyl ether with styrene derivatives and of homologues

No.	Monomer pair	Catalyst	Solvent	Polymerization Temp, $^\circ\text{C}$	r_1	r_2	$r_1 \times r_2$
1	CEVE(M_1)— <i>p</i> MOS	BF_3OEt_2	PhCH_3	0	9.32	1.55	14.4
		BF_3OEt_2	PhCH_3	-36	5.06	2.36	11.9
		BF_3OEt_2	PhCH_3	-78	2.81	4.37	12.3
2	CEVE(M_1)— <i>p</i> MOS	BF_3OEt_2	CH_2Cl_2	0	1.63	9.25	15.1
		BF_3OEt_2	CH_2Cl_2	-78	3.08	4.55	14.0
3	CEVE(M_1)— <i>p</i> MOS	$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	0	1.24	12.1	15.0
		$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	-78	1.56	7.80	12.2
4	CEVE(M_1)— <i>p</i> MS	$\text{SnCl}_4 \cdot \text{TCA}$	PhCH_3	0	18.2	0.40	7.28
		$\text{SnCl}_4 \cdot \text{TCA}$	PhCH_3	-78	10.1	0.50	5.05
5	CEVE(M_1)— <i>p</i> MS	$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	0	8.00	0.88	7.02
		$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	-78	3.31	1.12	3.70
6	CEVE(M_1)— α MS	$\text{SnCl}_4 \cdot \text{TCA}$	PhCH_3	-23	5.00	0.42	2.10
		$\text{SnCl}_4 \cdot \text{TCA}$	PhCH_3	-78	3.46	0.46	1.59
7	CEVE(M_1)— α MS	BF_3OEt_2	CH_2Cl_2	-23	6.02	0.42	2.53
		BF_3OEt_2	CH_2Cl_2	-78	2.05	0.68	1.39
8	CEVE(M_1)— α MS	$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	-23	2.50	0.76	1.90
		$\text{SnCl}_4 \cdot \text{TCA}$	CH_2Cl_2	-78	1.02	1.00	1.02
9	ST(M_1)— <i>p</i> CS	$\text{SnCl}_4 \cdot \text{TCA}$	PhCH_3 : C_6H_6	30	2.82	0.43	1.21
		$\text{SnCl}_4 \cdot \text{TCA}$	=40: 60	-23	2.72	0.48	1.31
10	IBVE(M_1)—CEVE	$\text{SnCl}_4 \cdot \text{TCA}$	PhCH_3	0	2.17	0.58	1.26
		$\text{SnCl}_4 \cdot \text{TCA}$	PhCH_3	-78	2.17	0.58	1.26

copolymerization of CEVE with α MS in methylene chloride, as shown in Figure 4. The CEVE content in the copolymer increased by increasing the polymerization temperature also in toluene, though the change was not so large as in methylene chloride (See Table I). In this case, composition curves did not show S-shape at -78°C in spite of the copolymerization of monomers with very different structure; at -23°C , however, the composition curve became slightly sigmoidal.

Copolymerization between homologues was performed to compare with the above results. The results are shown in Figure 5. No difference of polymer composition was observed in the copolymerization of IBVE with CEVE by BF_3OEt_2 in toluene at -78° and 0°C . Also, there was no change in the ST-*p*CS system by $\text{SnCl}_4\cdot\text{TCA}$ in a mixed solvent (toluene:benzene (volume ratio)=40:60) at -23 and 30°C . It is concluded that in the copolymerization between homologues, copolymer composition hardly changes with temperature. It presents a striking contrast to copolymerization between monomers with different structures.

The MRR together with their product $r_1 \times r_2$ are summarized in Table I. These values were calculated on the base of the Mayo-Lewis equation, considering that MRR means directly the ratio of elementary reaction rates in propagation. This will be proper because the presence of cross-propagations were confirmed by NMR spectra of the resultant polymer as described in a previous paper.¹ The products $r_1 \times$

r_2 were larger than unity and this indicated that monomer units formed blocks of long sequences. However, from only the composition of copolymers, we cannot determine the question of whether the copolymer composition was controlled by an ultimate unit or a penultimate unit. The linearity of the Fineman-Ross plot concerned with copolymer composition held well, so that the experimental results will be discussed approximately in terms of the first Markov chain model.

In the copolymerization of CEVE (M_1) with styrene derivatives (M_2), r_1 increased and r_2 decreased by increasing the polymerization temperature in any pair of monomers by both BF_3OEt_2 and $\text{SnCl}_4\cdot\text{TCA}$ in both toluene and methylene chloride, except for the copolymerization of CEVE with *p*MOS in which r_1 decreased and r_2 increased by increasing the temperature in methylene chloride. However, it was generally observed that the difference in the reactivities of monomers becomes larger as the temperature is raised.

The temperature dependence of r_1 and r_2 in toluene was smaller than in methylene chloride in the CEVE-*p*MOS and CEVE- α MS systems. The temperature dependence was observed by both catalysts, BF_3OEt_2 and $\text{SnCl}_4\cdot\text{TCA}$.

Activation parameters were calculated from the results of Table I. They are tentatively obtained from the line connecting two values observed at two different temperatures. The values are shown in Table II. The following conclusions can be obtained from Table II: (1)

Table II. The activation parameters of MRR (from Table I)

No.	Monomer pair	Catalyst	Solvent	$\Delta H_{11}^\ddagger - \Delta H_{12}^\ddagger$	$\Delta H_{21}^\ddagger - \Delta H_{22}^\ddagger$	$\Delta S_{11}^\ddagger - \Delta S_{12}^\ddagger$	$\Delta S_{21}^\ddagger - \Delta S_{22}^\ddagger$
1	CEVE- <i>p</i> MOS	BF_3OEt_2	PhCH_3	1.9	1.6	11	4.9
2	CEVE- <i>p</i> MOS	BF_3OEt_2	CH_2Cl_2	-0.97	-1.1	-2.5	-8.3
3	CEVE- <i>p</i> MOS	$\text{SnCl}_4\cdot\text{TCA}$	CH_2Cl_2	-0.35	-0.66	-0.78	-7.3
4	CEVE- <i>p</i> MS	$\text{SnCl}_4\cdot\text{TCA}$	PhCH_3	0.09	0.34	9.0	3.1
5	CEVE- <i>p</i> MS	$\text{SnCl}_4\cdot\text{TCA}$	CH_2Cl_2	1.4	0.38	9.1	1.6
6	CEVE- α MS	$\text{SnCl}_4\cdot\text{TCA}$	PhCH_3	0.77	0.19	6.3	2.5
7	CEVE- α MS	BF_3OEt_2	CH_2Cl_2	2.1	1.0	13	5.9
8	CEVE- α MS	$\text{SnCl}_4\cdot\text{TCA}$	CH_2Cl_2	1.9	0.53	9.5	2.6
9	ST- <i>p</i> CS	$\text{SnCl}_4\cdot\text{TCA}$	$\text{PhCH}_3\text{:C}_6\text{H}_6$ =4.0:6.0	0.0	0.33	2.4	2.7
10	IBVE-CEVE	$\text{SnCl}_4\cdot\text{TCA}$	PhCH_3	0.0	0.0	1.5	1.1

Cationic Copolymerization of CEVE with Styrenes. II.

The values $(\Delta H_{i1}^\ddagger - \Delta H_{i2}^\ddagger)$ have a positive sign except the CEVE-*p*MOS-CH₂Cl₂ system. This means that vinyl ether is less reactive in terms of enthalpy, though vinyl ether is in general more reactive than styrene derivatives. (2) Both values, $(\Delta H_{i1}^\ddagger - \Delta H_{i2}^\ddagger)$ and $(\Delta S_{i1}^\ddagger - \Delta S_{i2}^\ddagger)$, in the copolymerization of CEVE with styrene derivatives especially those of $i=1$ are considerably greater than those of the copolymerization between homologues. (3) In most cases, $(\Delta S_{i1}^\ddagger - \Delta S_{i2}^\ddagger) \times T$ is larger than $(\Delta H_{i1}^\ddagger - \Delta H_{i2}^\ddagger)$ in the copolymerization of CEVE with styrene derivatives, which indicates that the copolymerizations are rather entropy-controlled reactions.

These results are followed by a deduction mentioned below, on a difference in transition states of vinyl ether and styrene derivatives. It may be assumed that the propagation reaction is subdivided into two elementary reactions.⁵



Reactions in which the total number of molecules changes are usually attended by a large entropy of activation.⁶ On the other hand, the change from π -complex into σ -complex will be accompanied with an enthalpy term rather than an entropy term. Therefore, the large entropy term will mean that the first step is

important in the above mechanism and the enthalpy term will depend predominantly on the second step. Consequently, it is concluded that vinyl ether suffers the first step more easily than styrene derivatives, but vice versa as to the second step. This inference will be supported by solvent and catalyst effects in the copolymerization of CEVE with styrene derivatives, as will be described in a subsequent paper.

The Temperature Dependence of the Product of MRR

As described in the previous section, the change in MRR with temperature suggests the difference of the transition state in addition reaction of CEVE and styrene derivatives to the carbonium ion. In the same way, it is expected that the temperature dependence of the product of MRR suggests the difference of behavior of the carbonium ion in the propagation reaction, as is shown in the following discussion.

Chūjō⁷ proposed a method for determination of the existence of the penultimate unit effect in stereospecific polymerization, which is based on the relationship between the activation free energy and polymerization temperature. The same concept will be applied to copolymerization. By plotting $\Delta\varepsilon$ vs. T in eq 1, the existence of the propagating-end effect, the difference

Table III. The products of MRR in cationic copolymerization and their temperature dependence

No.	Monomer 1	Monomer 2	Catalyst	Solvent	Polymerization temp, °C	r_1	r_2	$r_1 \times r_2$	Ref
1	IB ^a	ST	AlCl ₃ (0.5%)	CH ₃ Cl	-30	2.51 ± 0.05	1.21 ± 0.06	3.04	9
			AlCl ₃ (0.5%)	CH ₃ Cl	-90	1.66 ± 0.02	0.42 ± 0.02	0.70	9
2	IB	ST	AlCl ₃ (0.14%)	CH ₃ Cl	-30	2.36 ± 0.06	0.76 ± 0.13	1.79	9
			AlCl ₃ (0.14%)	CH ₃ Cl	-90	1.79 ± 0.02	0.24 ± 0.02	0.43	9
3	ACB ^b	<i>n</i> BVE ^c	BF ₃ OEt ₂	C ₆ H ₆	30	0.38 ± 0.04	1.30 ± 0.3	0.4-0.7	10
			BF ₃ OEt ₂	C ₆ H ₆	0	0.24 ± 0.04	4.2 ± 0.8	0.7-1.4	10
			BF ₃ OEt ₂	PhCH ₃	-20	0.14 ± 0.03	6.0 ± 1.0	0.8-1.1	10
			BF ₃ OEt ₂	PhCH ₃	-78	0.04 ± 0.02	~20	~0.8	10
4	CEVE	α MS	BF ₃ (CH ₃ CO ₂ H) ₂	(CH ₂ Cl) ₂	0	3.9 ± 0.15	0.48 ± 0.04	1.87	4
			BF ₃ (CH ₃ CO ₂ H) ₂	(CH ₂ Cl) ₂	-30	2.0 ± 0.2	0.75 ± 0.07	1.50	4
5	α MS	<i>p</i> CS	SnCl ₄	—	0	15.5 ± 1.5	0.35 ± 0.05	5.42	11
			SnCl ₄	—	-78	28 ± 2	0.12 ± 0.03	3.36	12
6	ST	<i>p</i> CS	SnCl ₄	CCl ₄	30	2.2 ± 0.3	0.35 ± 0.1	0.770	3
			SnCl ₄	CCl ₄	0	2.5 ± 0.5	0.30 ± 0.03	0.750	3
			SnCl ₄	CCl ₄	-20	2.15 ± 0.2	0.35 ± 0.05	0.753	3

^a IB, isobutene; ^b ACN, acenaphthylene; ^c *n*BVE, *n*-butyl vinyl ether.

Table IV. The activation parameters of the product of MRR in cationic copolymerization

Group	No. ^a	Monomer 1	Monomer 2	Catalyst	Solvent	ΔH , kcal/mol	ΔS , e.u.
A	1-1	CEVE	<i>p</i> MOS	BF ₃ OEt ₂	PhCH ₃	~0.27	~6.3
	1-2	CEVE	<i>p</i> MOS	BF ₃ OEt ₂	CH ₂ Cl ₂	0.11	5.8
	1-3	CEVE	<i>p</i> MOS	SnCl ₄ ·TCA	CH ₂ Cl ₂	0.32	6.5
	1-4	CEVE	<i>p</i> MS	SnCl ₄ ·TCA	PhCH ₃	0.56	5.9
	1-5	CEVE	<i>p</i> MS	SnCl ₄ ·TCA	CH ₂ Cl ₂	0.99	7.5
	1-6	CEVE	α MS	SnCl ₄ ·TCA	PhCH ₃	0.58	3.8
	1-7	CEVE	α MS	BF ₃ OEt ₂	CH ₂ Cl ₂	1.1	6.8
	1-8	CEVE	α MS	SnCl ₄ ·TCA	CH ₂ Cl ₂	1.39	6.8
	3-1	IB	ST	AlCl ₃ (0.5%)	CH ₂ Cl	2.2	11
	3-2	IB	ST	AlCl ₃ (0.14%)	CH ₃ Cl	2.1	9.9
3-3	ACN	<i>n</i> BVE	BF ₃ OEt ₂	C ₆ H ₆ or PhCH ₃	~-1.6	~-7.9	
3-4	CEVE	α MS	BF ₃ (CH ₃ CO ₂ H) ₂	(CH ₂ Cl) ₂	0.96	4.8	
3-5	α MS	<i>p</i> CS	SnCl ₄	—	~0.63	5.9	
B	1-9	ST	<i>p</i> CS	SnCl ₄ ·TCA	PhCH ₃ :C ₆ H ₆ =4.0:6.0	~-0.3	~-0.3
	1-10	IBVE	CEVE	BF ₃ OEt ₂	PhCH ₃	0	0.46
	3-6	ST	ST	SnCl ₄	CCl ₄	~0.12	~-0.20

^a Numbers refer to those of Table I and III.

of activation enthalpy and entropy based on the kind of a growing chain end, can be examined, as Furukawa also suggested.⁸

$$\Delta\varepsilon = -kT \ln(r_1 \times r_2) = \Delta H - T\Delta S \quad (1)$$

$$\text{where } \Delta H = (\Delta H_{11}^\ddagger - \Delta H_{12}^\ddagger) - (\Delta H_{21}^\ddagger - \Delta H_{22}^\ddagger) \quad (2)$$

$$\Delta S = (\Delta S_{11}^\ddagger - \Delta S_{12}^\ddagger) - (\Delta S_{21}^\ddagger - \Delta S_{22}^\ddagger) \quad (3)$$

The products of r_1 and r_2 at different temperatures are shown in Table I as to our data and in Table III as to those from other readings. In the ionic copolymerizations between homologues (Table I, No. 9, 10; Table III, No. 6), the temperature dependence of $r_1 \times r_2$ is almost negligible. On the other hand, in the ionic copolymerization of the monomers with different structures (Table I, No. 1—8; Table III, No. 1—5), the product $r_1 \times r_2$ changes significantly and gets away from unity with the rise of temperature.

ΔH and ΔS are calculated and summarised in Table IV. ST—*p*MS systems gave similar values of ΔH and ΔS (No. B-3-6 and B-1-9 in Table IV) in spite of the different experimental conditions and workers. A good agreement was also observed in the CEVE— α MS system (See No. B-3-4 and B-1-7 in Table IV).

$\Delta\varepsilon$ is, in general, independent from T in radical copolymerization. This means that the pro-

pagating-end effect at the addition of both monomers is hardly controlled by the entropy term, that is, there is no difference of activation entropy due to the kind of growing chain end.

In the cationic copolymerization between homologues, $r_1 \times r_2$ is constant and almost unified irrespective of temperature. This means that ΔH and ΔS approximately equal zero. As is seen from Table IV, both ΔH and ΔS of group B are very small. Therefore, there is no difference in reactivity of both propagating ends for monomers. This agrees with the absence of the alternating tendency in cationic copolymerization.

In the cationic copolymerizations of the monomers with different structures, ΔH and ΔS are usually different from zero (Table IV, Group A). Moreover, $T\Delta S$ is nearly equal to ΔH or is larger than ΔH in contrast to radical copolymerization. This means that the difference of reactivity of both propagating ends for monomers is controlled rather by the entropy term than by the enthalpy term. The great value of ΔS suggests the difference in the correlation between the propagating end, the gegen-ion and monomer in the transition state.

In the previous paper,¹ the results that the product $r_1 \times r_2$ was about unity in the copoly-

merization of CEVE with α MS at -78°C was explained by the similar stability of two carbonium ions formed from both monomers. It may be, however, only fortuitous that $r_1 \times r_2$ is almost unified in the copolymerization of CEVE with α MS at -78°C . For, ΔH and ΔS have considerably larger values than those of the copolymerization between homologues.

As is seen from Group A in Table IV, ΔH has a positive sign, and $T\Delta S$ has generally a larger positive value than ΔH in the copolymerization of monomers with different structures. This means that the higher the temperature, the higher the blocking tendency. The tendency is very conspicuous and consistent in all systems.

The above-mentioned difference of reactivity of both propagating ends for monomers is summarized as follows

Mechanism	Structure of monomers	ΔH	ΔS	$\Delta\varepsilon$
Radical	—	≥ 0	~ 0	≥ 0
Cationic	{ Similar	~ 0	~ 0	~ 0
	{ Dissimilar	> 0	> 0	$\cong 0$

It is concluded that vinyl ether is less reactive in terms of enthalpy and more reactive in terms of entropy than styrene derivatives; this suggests the difference between the transition state of the addition of vinyl ether and that of styrene derivatives. Further, in general, r_1 , r_2 and $r_1 \times r_2$ change remarkably with temperature in the cationic copolymerization of monomers with different structures. This means that the reaction is controlled not only by the enthalpy term but also by the entropy term, and indicates that the complex formation is not negligible and that three elements, a propagating end, a counterion and a monomer are concerned at the transition state.

The above discussion was based on the assumption that the copolymer composition was controlled by a polymer chain end, because the presence of the penultimate effect could not be confirmed. Further studies on the sequence distribution in copolymers are necessary in order to elucidate the details of the mechanism.

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