Bull. Inst. Chem. Res., Kyoto Univ., Vol. 52, No. 2, 1974

Review

Mechanism of Cationic Copolymerization of Styrene and its Derivatives

Junji FURUKAWA*, Eiichi KOBAYASHI,** and Shunro TANIGUCHI,*

Received February 19, 1974

Cationic copolymerizations of styrene and *p*-substituted one were investigated with varied Lewis acid catalysts and solvents at different temperature. The monomer selectivity was a function of above factors, but a good linear relation holds for differences of activation energy and activation entropy for propagations of two monomers. In most cases the selectivity is entropy-controlled. In equation $\Delta H^{\ddagger}=m'\Delta S^{\ddagger}+n'$, the second term n′ seems to be a contribution to activation energy from conjugation and steric hindrance in activated complex in transition state, while the first term that from the desolvation energy in transition state and m′ is affected by the growing cation but not monomers. The desolvation energy or entropy is large for polar and bulky solvents as well as Lewis acid of high acid strength. Two growing species, *e.g.*, dissociated and non-dissociated ones, are assumed. The contribution of desolvation heat in the dissociated state is smaller for styryl cation, while larger for *p*-substituted styryl cation than that for the non-dissociated state, and this fact is interpreted by the assumption that the *p*-substituted styryl cation in dissociated state requires more close approach to the monomer in transition state, while in the non-dissociated state desolvation occurs in the vicinity of catalyst and the interaction between catalyst and monomers is an influential factor but not that between growing cation and monomers.

I. INTRODUCTION

There are a great number of reports on cationic polymerization.[1] However, the cationic polymerization is so much influenced by reaction conditions such as catalyst, co-catalyst, impurity and temperature that it is rather difficult to obtain a good reproducibility enough to discuss the mechanism. This is because that various factors affect not only propagation but also initiation and/or termination processes. The separation or evaluation of elementary processes is difficult in cationic polymerization and this fact also aggravates the difficulty of the investigation. The authors were interested in the cationic copolymerization since the composition of the copolymer is reflected only from the reactivity in propagation and, moreover, various effect of impurity on the reactivity of both monomers will be parallel to each other monomer and, as a result, a relatively good reproducibility will be obtained. Until now there had been several reports[2~7] on cationic copolymerization dealing with the effect of solvent or catalyst according to a concept of solvation of monomer and solvent to catalyst, but the scope of monomers, solvents or catalysts is not wide enough to afford a general information.

* 古川淳二，谷口俊郎: Department of Synthetic Chemistry, Kyoto University, Kyoto.
** 小林英一: Laboratory of Petroleum Chemistry, Institute for Chemical Research, Kyoto University, Uji.

This report is a summary of our works on the copolymerization of styrene and substituted styrenes with use of a catalyst of Lewis acid of various acid strength, the detail being published elsewhere. The experiments were carried out at various temperature to obtain energy and entropy of activation of copolymerization.

II. EXPERIMENTALS

Monomer such as styrene (ST), *p*-chlorostyrene (CIST), *p*-methylstyrene (MeST), or *p*-tert-butylstyrene (t-BuST) and solvent such as ethylene dichloride (EDC), nitroethane (NE) or nitrobenzene (NB) are purified according to the conventional procedure. Copolymerization was carried out in an Erlenmeyer flask covered with a butyl rubber sheet stopper. The monomer solution and the catalyst solution were injected into the flask by using a syringe through a rubber sheet stopper. After given polymerization time methanol was introduced to terminate polymerization. Polymers were obtained by precipitation with an excess amount of methanol added, followed by repeated washing with methanol and then drying under reduced pressure at room temperature. In order to eliminate the influence of the extent of polymerization, the polymerization was stopped below 10% conversion by regulating polymerization conditions such as catalyst concentration and polymerization time.

The composition of copolymers of *p*-chlorostyrene was analyzed by chlorine analysis together with occasionally adopted carbon-hydrogen analysis. The copolymers of styrene and *p*-methylstyrene or *p*-t-butylstyrene were analyzed by IR spectra by measuring the ratio of mono-substituted phenyl absorption at 760 cm^{-1} (δ_{CH}) with di-substituted phenyl one at 815 cm^{-1} (δ_{CH}). The calibration curve for polymer composition was made with mixtures of polystyrene and polymer of substituted styrene. From the relation between monomer composition and polymer one, monomer reactivity ratios, r_1 and r_2, are evaluated by Fineman-Ross method or curve-fitting one with use of computor.[8]

III. RESULT

The monomer reactivity ratio is listed in Tables I and II. Thermodynamic parameters, *i.e.*, activation energy H^* and activation entropy S^* can be obtained in a form of difference, ΔH^* and ΔS^*, in propagations of two monomers from Arrhenius equations for temperature dependence of r_1 and r_2 or that of propagation constants k_{11}, k_{12}, k_{22}, and k_{21}.

$$\log r_1 = \log \frac{k_{11}}{k_{12}} = -\frac{\Delta H_{11}^* - \Delta H_{12}^*}{RT} + \frac{\Delta S_{11}^* - \Delta S_{12}^*}{R} \quad (1)$$

and

$$\log r_2 = \log \frac{k_{22}}{k_{21}} = -\frac{\Delta H_{22}^* - \Delta H_{21}^*}{RT} + \frac{\Delta S_{22}^* - \Delta S_{21}^*}{R} \quad (2)$$

The results are listed in Tables III and IV The monomer reactivity and thermodynamic parameter are summarized as follows.

III.1. Energy-Entropy Relationship

It was found that there exists a good linear relationship between entropy difference, ΔS^* and energy one ΔH^* as shown in Fig. 1. ΔS_i^* and ΔH_i^* mean the entropy and energy

Table I. Effect of Temperature on the Copolymerization of Styrene (M_1) and *p*-Methylstyrene (M_2).

Catalyst	Polym. temp. (°C)	r_1	r_2	r_1/r_2	$r_1 \cdot r_2$
Ethylene dichloride solvent					
$SnBr_4$	−30	0.59±0.10	2.39±0.37	0.25	1.41
	60	0.38±0.20	3.50±1.09	0.11	1.33
$AlBr_3$	−30	0.59±0.03	1.09±0.08	0.54	0.64
	60	0.77±0.12	2.83±0.41	0.27	2.18
BCl_3	−30	0.53±0.01	1.42±0.03	0.37	0.75
	60	0.51±0.15	4.15±0.80	0.12	2.12
BBr_3	−30	0.64±0.05	2.20±0.15	0.29	1.41
	60	0.51±0.10	3.27±0.48	0.16	1.67
Nitrobenzene solvent					
$SnBr_4$	− 5	0.51±0.05	1.96±0.17	0.26	1.00
	80	0.47±0.05	3.12±0.22	0.15	1.47
$AlBr_3$	− 5	0.51±0.03	1.50±0.09	0.34	0.76
	80	0.63±0.10	2.50±0.35	0.25	1.57
BCl_3	− 5	0.74±0.10	2.03±0.29	0.36	1.50
	80	0.82±0.12	4.25±0.49	0.19	3.48
BBr_3	− 5	0.54±0.03	1.73±0.09	0.31	0.93
	80	0.68±0.13	3.36±0.52	0.20	2.28

Table II. Effect of Temperature on the Copolymerization of Styrene (M_1) and *p*-t-Butylstyrene (M_2).

Catalyst	Polym. temp. (°C)	r_1	r_2	r_1/r_2	$r_1 \cdot r_2$
Ethylene dichloride solvent					
$SnCl_4$	0	0.88±0.09	0.94±0.11	0.94	0.83
	57	0.58±0.05	1.17±0.07	0.50	0.68
$AlBr_3$	0	1.13±0.13	1.08±0.14	1.05	1.22
	57	0.86±0.07	1.11±0.09	0.78	0.95
BBr_3	− 9	0.74±0.07	0.61±0.07	1.21	0.45
	57	0.62±0.15	1.13±0.22	0.55	0.70
Nitrobenzene solvent					
$SnCl_4$	−10	0.85±0.02	0.35±0.02	2.43	0.30
	70	0.54±0.02	0.64±0.04	0.84	0.35
$AlBr_3$	−10	0.68±0.03	0.31±0.04	2.19	0.21
	70	0.64±0.04	0.91±0.08	0.70	0.58
BBr_3	−10	0.78±0.02	0.32±0.03	2.44	0.25
	70	0.66±0.03	0.90±0.05	0.73	0.59

Table III. Thermodynamic Parameter on the Copolymerization of Styrene (M_1) and *p*-Methylstyrene (M_2).

Catalyst	$\Delta H_{11}^* - \Delta H_{12}^*$ (kcal/mol)	$\Delta H_{21}^* - \Delta H_{22}^*$ (kcal/mol)	$\Delta S_{11}^* - \Delta S_{12}^*$ (cal/mol·deg)	$\Delta S_{21}^* - \Delta S_{22}^*$ (cal/mol·deg)
Ethylene dichloride solvent				
$SnBr_4$	−0.78	−0.68	−4.25	−4.53
$AlBr_3$	0.47	−1.7	0.68	−7.27
BCl_3	−0.07	−1.91	−1.55	−8.56
BBr_3	−0.4	−0.71	−2.54	−4.49
Nitrobenzene solvent				
$SnBr_4$	−0.21	−1.02	−2.11	−5.15
$AlBr_3$	0.43	−1.13	0.28	−5.02
BCl_3	0.23	−1.62	0.25	−7.46
BBr_3	0.51	−1.47	0.68	−6.57

Table IV. Thermodynamic Parameter on the Copolymerization of Styrene (M_1) and *p*-t-Butylstyrene (M_2).

Catalyst	$\Delta H_{11}^* - \Delta H_{12}^*$ (kcal/mol)	$\Delta H_{21}^* - \Delta H_{22}^*$ (kcal/mol)	$\Delta S_{11}^* - \Delta S_{12}^*$ (cal/mol·deg)	$\Delta S_{21}^* - \Delta S_{22}^*$ (cal/mol·deg)
Ethylene dichloride solvent				
$SnCl_4$	−1.3	−0.8	−5.1	−2.7
$AlBr_3$	−0.9	−0.1	−2.9	−0.5
BBr_3	−0.5	−1.6	−2.4	−5.1
Nitrobenzene solvent				
$SnCl_4$	−2.0	−2.7	−8.1	− 8.5
$AlBr_3$	−0.3	−4.7	−1.9	−16.2
BBr_3	−0.8	−4.6	−3.4	−15.7

difference between the reactions ii and ij, respectively, ii being the propagation reaction between i-th cation and i-th monomer and ij being the propagation reaction between i-th cation and j-th monomer. Since ΔH^* (styrene) and ΔS^* (styrene) are both negative, the energy and entropy of activation for styrene are smaller than those of substituted styrene.

$$\Delta S_i^* = S_{ii}^* - S_{ij}^* \tag{3}$$

$$\Delta H_i^* = H_{ii}^* - H_{ij}^* \tag{4}$$

In other words, styrene is energetically more reactive than substituted styrene and this fact is opposite to the apparent reactivity of monomers. The entropy term, $T\Delta S^*$, provides much larger contribution under the experimental condition, that is, the propagation is entropy-controlled, except the case of the reaction of *p*-t-butylstyrene and styrene.

Figure 1 demonstrates that activation entropy as well as activation energy are much depending upon solvents and catalysts but the linear relationship is not disturbed. The inclination and ordinate depend only upon the monomer employed. In an equation,

$$\left.\begin{aligned} &\Delta S^* = m\Delta H^* + n \\ \text{or}\quad &\Delta H^* = m'\Delta S^* + n' \end{aligned}\right\} \tag{5}$$

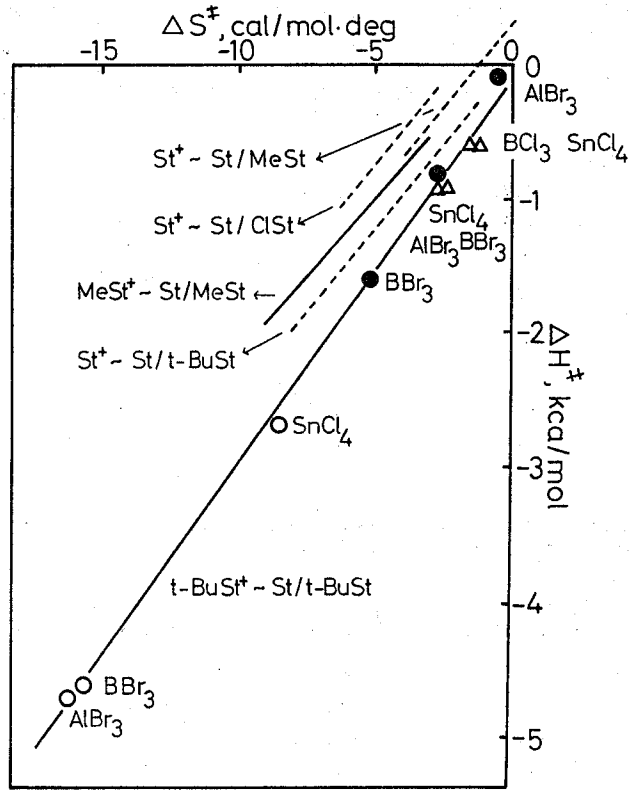

Fig. 1. Relationship between activation entropy difference and activation energy difference on the copolymerization of styrene and substituted styrene.

Solvent: ○, nitrobenzene; △, nitroethane; ●, ethylene dichloride.

the inclination m is almost constant for the attack of styryl cation (ST^+), but is smaller for that of *p*-t-butylstyryl cation (t-$BuST^+$). As a result, the attack of t-$BuST^+$ is energy-controlled and the effect is enlarged in the copolymerization in nitrobenzene; in this case, *p*-t-butylstyrene is less reactive than styrene.

III.2. Effect of Catalysts and Solvents

It was found that solvents and catalysts play an important role on the selectivity of monomers. However, the effect is very complicated and is not demonstrated as a simple function of property of solvents and catalysts. In general, polar solvent such as nitrobenzene and strong Lewis acids such as BCl_3 and BBr_3 exhibit a large effect on ΔH^* and ΔS^*, but the direction of effect is quite opposit in the case of ST^+ and t-$BuST^+$. Figure 2 illustrates a change of ΔS^* as a function of acid strength, where so-called Cook's acid strength,[9] *i.e.*, shift, $\Delta\nu_{C=O}$, of IR absorption of carbonyl group of xanthone as indicator is adopted.

In nitrobenzene, ΔS^* of t-$BuST^+$ is almost equal to that of ST^+ in the copolymerization with $SnCl_4$ but is different from each other with BBr_3: For t-$BuST^+$ ΔS^* increases with increasing acid strength, whereas for ST^+ ΔS^* decreases.

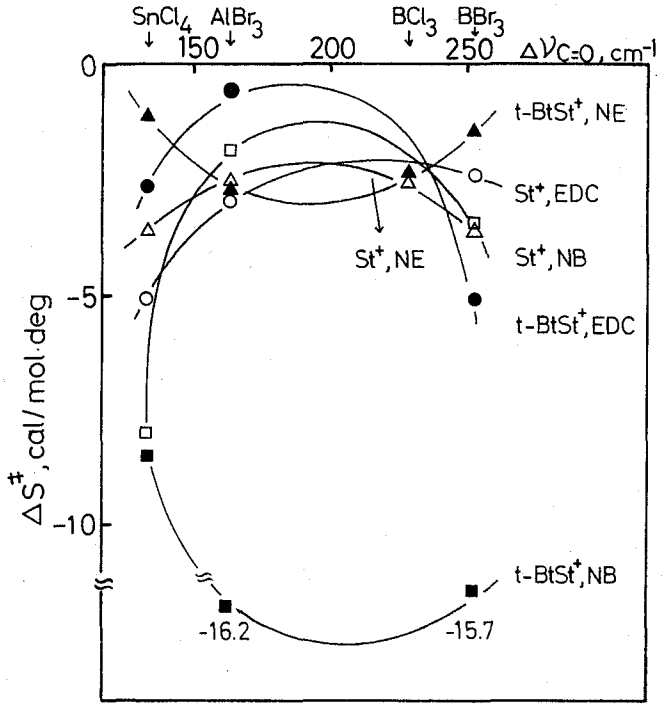

Fig. 2. Relationship between activation entropy difference and Lewis acid strength on the copolymerization of styrene and *p*-t-butylstyrene.

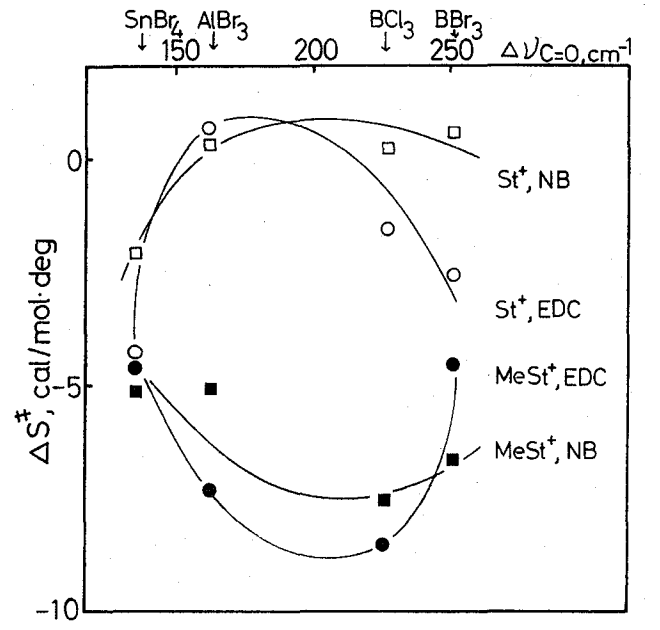

Fig. 3. Relationship between activation entropy difference and Lewis acid strength on the copolymerization of styrene and *p*-methylstyrene.

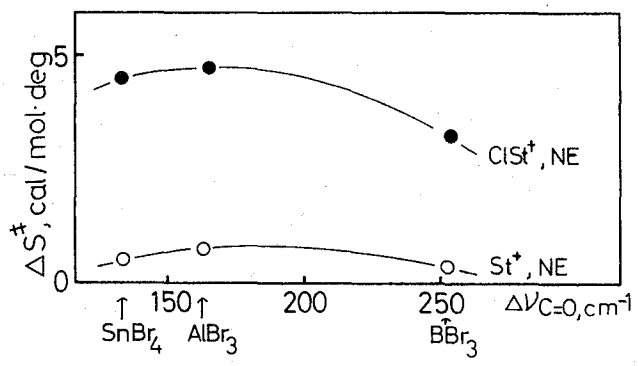

Fig. 4. Relationship between activation entropy difference and Lewis acid strength on the copolymerization of styrene and *p*-chlorostyrene.

A similar tendency is observed in the copolymerization in nitroethane (NE), although effect is not so large. Figure 3 indicates a similar tendency for the copolymerization of styrene and *p*-methylstyrene. The copolymerization of styrene and *p*-chlorostyrene does not show a simple tendency (Fig. 4) and does not afford a simple linear relationship between ΔS^* and ΔH^*.

IV. DISCUSSION

The effect of catalyst is very complicate but a tendency that strong acids affect more enormously the selectivity than weak ones and a fact that this tendency is enlarged in polar solvent suggest the existence of two different states of activation. For example, the concept of dissociated state and non-dissociated state is convenient to understand the effect of acid strength and polar nature of solvent. The growing polymer cation may be solvated both in non-dissociated and dissociated state. Even in polymerization with strong Lewis acid the growing cation does not exist as a free cation but as a solvated one, because ΔS^* for strong acid is not the same in different solvents. And also the growing species in the non-dissociated state is also combined with solvents, because ΔS^* for weak acid is also different in different solvents.

It is noticed that the effect of growing species is quite opposit for the styryl cation and

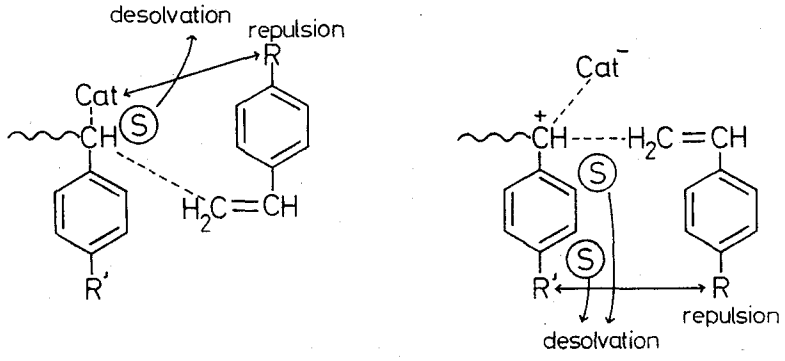

Fig. 5. Schematic diagram of solvation and desolvation at transition state.

substituted styryl cation in polar solvent and strong acid. The fact that the monomer selection is entropy-controlled and the ΔH^* is as small as several kilocalories indicates that the process is a desolvation-controlled phenomenon; the solvated growing cationic species may be desolvated in the transition state and requires the desolvation energy but obtains the entropy of liberated solvent. The solvation of the growing species as well as the desolvation in the transition state is different for the case of non-dissociated and dissociated states. In the latter case, the catalyst anion is appart from the growing cation, and the solvent may be located in the vicinity of conjugated growing cation, whereas in the former case the charge is localized in ion-pair and the solvent may be linked with ion-pair as illustrated in Fig. 5.

According to this scheme it is understandable that in the non-dissociated form the interaction between the catalyst and the substituent R of monomers may be more influential than that between the monomer substituent R and the polymer substituent R′, whereas in the dissociated form the R-R′ interaction is influential on the removal of solvent located in the vicinity of the substituent R′. Furthermore, the latter effect is more significant for the bulky substituent R′ than hydrogen, *i.e.,* R′=H or in other words the tert-butyl group in the growing polymer cation is more influential than the non-substituted styryl cation, where R′ is H. The interaction increases in the following order.

$$R'-R>Cat-R>H-R$$

The above relation is demonstrated roughly by the following equation.

$$\Delta H^*=h_s\{a(1-x)+bx\}=h_s\{a+(b-a)x\} \quad (6)$$

and

$$\Delta S^*=s_s\{a'(1-x)+b'x\} \quad (7)$$

The contribution of the desolvation to the activation energy or entropy difference, ΔH^* or ΔS^*, consists of two terms, a(1-x) arising from the non-dissociated form and bx from the dissociated form, where a and b are the contributions from the former and the latter, respectively.

Here, x is a degree of dissociation and may run parallel to the acid strength of Lewis acid. The heat of solvation h_s is characteristic of solvents depending not only on the solubility parameter but also bulkiness of solvent molecules, because a polar and bulky solvent such as nitrobenzene has a large effect but non-bulky nitroethane and less polar ethylene dichloride do not. The factors a and b may be correlated with the degree of conjugation of styryl and substituted styryl cations and their monomers as well as their bulkiness. Equation (6) affords a relation illustrated schematically in Fig. 6, where $a > b$ for the styryl cation whereas $a<b'$ for the substituted styryl cation.

Finally, the energy-entropy relation is discussed in terms of the desolvation. The Eq. (5) suggests also a linear relationship between energy H^* and entropy S^* for the activation in each propagation process, *i.e.,*

$$H_{11}^*=m'S_{11}^*+(H_{11})_0^* \quad (8)$$

and

$$H_{12}^*=m'S_{12}^*+(H_{12})_0^* \quad (9)$$

Here, $(H_{11})_0^*$ and $(H_{12})_0^*$ are the difference when $(S_{11}^*-S_{12}^*)$ are zero or the difference in the activation energy of non-desolvation processes such as conjugation energy in the

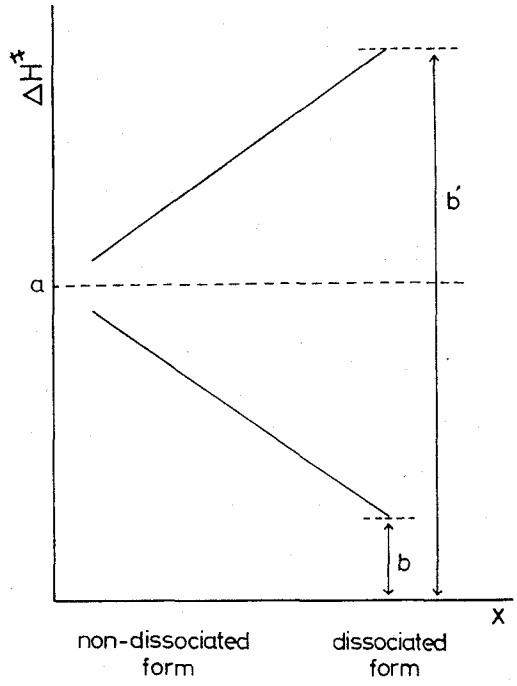

Fig. 6. Schematic expression of equation (6).

transition state. Indeed, the experimental data show the following order concerning the cation/monomer attack, which is agreed with the result from the organic theory.

$$H_0^*(\text{t-BuST}^+/\text{t-BuST}) - H_0^*(\text{t-BuST}^+/\text{ST}) > 0$$
$$H_0^*(\text{ST}^+/\text{t-BuST}) - H_0^*(\text{ST}^+/\text{ST}) \cong 0$$
$$H_0^*(\text{MeST}^+/\text{MeST}) - H_0^*(\text{MeST}^+/\text{ST}) < 0$$
$$H_0^*(\text{ST}^+/\text{CIST}) - H_0^*(\text{ST}^+/\text{ST}) \ll 0$$

The coefficient m′ is the desolvation heat per unit desolvation entropy. Compairing Eqs. (5) and (6) the energy-entropy linear relation for the non-dissociated state is the same as that for the dissociated state, because Eq. (5) involves the degree of dissociation which is a function of catalyst and solvent, but the coefficient m′ of Eq. (5) is independent of catalyst and solvent. The coefficient m′ is also not significantly affected by the kind of monomers in the case when the growing species is styryl cation, but t-BuST$^+$ and MeST$^+$ cations indicate large values. This fact may be interpreted by the assumption that t-BuST$^+$ or MeST$^+$ cation may possess larger steric hindrance or require more close approach of the cation to monomers due to higher conjugation of the activated cation-monomer complex in the transition state. The close approach may facilitate to squeeze out the more tightly linked solvent and require larger desolvation heat.

V. CONCLUSION

It was found that *p*-methyl and *p*-methoxystyrene are more reactive than styrene itself, but the energy of activation of the former is larger than that of the latter. Substituted styryl cations possess more conjugated form in transition state and more closely approaches

to monomers in the transition state. Consequently, they require larger desolvation energy but give larger entropy of solvent liberation. As a result, substituted styrenes and their cations possess higher reactivity in copolymerization. The effect of solvents and catalysts is ascribed not only to the contribution of desolvation but also to that of dissociation of the growing species.

REFERENCES

(1) "The Chemistry of Cationic Polymerization," Edited by P. H. Plesch, Pergamon Press, Oxford (1963).
(2) C. G. Overberger and V. G. Kamath, *J. Amer. Chem. Soc.*, **81**, 2910, (1959).
(3) C. G. Overberger and V. G. Kamath, *ibid.*, **85**, 446 (1963).
(4) C. S. Marvel and J. F. Dunphy, *J. Org. Chem.*, **25**, 2209 (1960).
(5) Y. Imanishi, T. Higashimura, and S. Okamura, *J. Polymer Sci. A*, **3**, 2455 (1965).
(6) N. Kanoh, K. Ikeda, A. Gotoh, T. Higashimura, and S. Okamura, *Makromol. Chem.*, **86**, 200 (1965).
(7) T. Masuda, T. Higashimura, and S. Okamura, *Polymer J.*, **1**, 19 (1970).
(8) A. I. Ezrielev, E. L. Brokhima, and E. S. Roskin, *Vysokomol. Soed.*, **11**, 1670 (1969).
(9) D. Cook, *Can. J. Chem.*, **41**, 522 (1963).