From the Department of Polymer Chemistry, Faculty of Engineering, Kyoto University,
Kyoto, Japan

Rate Constant of Propagation Reaction in Stationary State of Cationic Polymerization

Part V[1]. Copolymerization

By N. Kanoh, A. Gotoh, T. Higashimura, and S. Okamura

(Eingegangen am 13. November 1962)

SUMMARY:

In order to determine the relationship between the relative reactivity of the monomer and that of its propagating species the propagation rate constant of the cationic copolymerization was measured. The relative reactivity of the monomer was found in the following order:
for styrene derivative: p-methoxystyrene > p-methylstyrene > styrene > p-chlorostyrene;
for alkyl vinyl ether: isobutyl vinyl ether > 2-chloroethyl vinyl ether.

On the other hand, the order of the relative reactivity of the propagating species ending in the styrene derivative and the alkyl vinyl ether was as follows:
for styrene derivative: p-methoxystyrene > p-methylstyrene > styrene > p-chlorostyrene;
for alkyl vinyl ether: 2-chloroethyl vinyl ether > isobutyl vinyl ether.

ZUSAMMENFASSUNG:

Die Geschwindigkeitskonstante der Wachstumsreaktion bei der kationischen Polymerisation wurde bestimmt, um eine Beziehung aufzustellen zwischen der relativen Reaktivität des Monomeren und dessen aktiver, ionisch wachsender Kette. Für die relative Reaktivität der Monomeren wurde die folgende Reihenfolge gefunden:
Substituierte Styrole: p-Methoxystyrol > p-Methylstyrol > Styrol > p-Chlorstyrol;
Alkylvinyläther: i-Butylvinyläther > 2-Chloräthylvinyläther.

Demgegenüber war die Reihenfolge der relativen Reaktivität der wachsenden Kette mit Styrol bzw. Alkylvinyläther als letztem Baustein wie folgt:
Substituierte Styrole: p-Methoxystyrol > p-Methylstyrol > Styrol > p-Chlorstyrol;
Alkylvinyläther: 2-Chloräthylvinyläther > i-Butylvinyläther.

1. *Introduction*

In the propagation reaction of radical polymerization, it was already recognized both experimentally[2] and theoretically[3] that the more reactive the monomer is the less reactive is its radical. But in the propagation reaction of cationic polymerization the relationship between the reactivity of the monomer and of the propagating species ending in the monomer is expected to be more complicated because the effect of the electrostatic interaction between the propagating species and the attacking monomer may take an important part in the propagation reaction in this case. One of the most direct research methods in this respect may be to determine the cross propagation constant (k_{12}, k_{21}).

According to the definition of the monomer reactivity ratio

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}} \tag{1}$$

where k_{11} or k_{22} is the propagation constant in the polymerization of M_1 or M_2 respectively. The method to measure them was already presented by us[4]. k_{12} or k_{21} can be calculated together with the values of the monomer reactivity ratios (r_1, r_2). From the amount of the cross propagation constant the order of the reactivities of the monomers and also of the propagating species ending in these monomers can be determined.

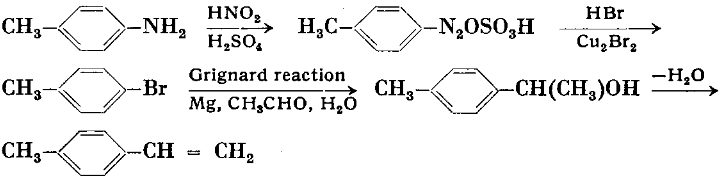
In this paper we used *p*-methoxystyrene, *p*-methylstyrene, styrene and *p*-chlorostyrene as styrene derivatives; isobutyl vinyl ether and 2-chloroethyl vinyl ether as alkyl vinyl ethers. They were polymerized in ethylene chloride by using iodine as initiator.

2. *Experimental and Results*

2.1 *Materials and Procedures*

Materials

p-Methoxystyrene was prepared by QUELET's method, about which we have already reported[4]. *p*-Methylstyrene was prepared by the following reaction.



d = 0.891 (30°C.); $n_D^{21} = 1.541_2$ [$n_D^{25} = 1.539_5$][5]; BP = 68.5°C. (9.5 mm. Hg) [82–83°C. (27 mm. Hg)][5].

C_9H_{10} (118.2) Calcd. C 91.53 H 8.47
Found C 91.44 H 8.56

p-Chlorostyrene was prepared by a similar way as *p*-methylstyrene.

d = 1.084 (30°C.) [1.090 (20°C.)][6]; $n_D^{30} = 1.560_4$ [1.565_8 (20°C.)][6]; BP = 71–72°C. (11 mm. Hg) [53–54°C. (3 mm. Hg)][6].

These styrene derivatives were purified and dehydrated by similar methods as styrene and distilled *in vacuo* repeatedly before use. About other materials used we have already reported in the proceeding papers[4].

Procedures

The propagation rate constant was measured by an iodometry method. The procedure has already been indicated in detail[4]. The chemical composition of the copolymer obtained was determined by elementary analysis or with infrared spectrometry. Polymerizations were carried out at 30 °C. using iodine as initiator in ethylene chloride.

2.2 *Propagation rate constants (k_p) of the styrene derivatives*

The method for determining the propagation rate constant was reported in the proceeding papers, so we will denote only the experimental results.

Table 1. Rates of Polymerization and Propagation Constants
(initiator: iodine; solvent: ethylene chloride; 30 °C.)

No.	[M] (mole/l.)	$[I_2]_{total}$ (mmole/l.)	$R_p \cdot 10^3$ (mole/l.min.)	[M*] (mmole/l.)	k_p (l./mole·min.)
a) *p*-methylstyrene					
1	0.50	20.1	6.93	2.9	4.6
2	0.50	24.2	10.8	4.0	5.4
3	0.50	28.2	15.9	5.2	6.1
4	0.50	32.2	21.8	6.8	6.4
5	0.50	36.2	25.9	8.3	6.2
6	1.00	28.2	13.5	–	–
7	0.75	28.2	15.1	–	–
8	0.50	28.2	16.3	–	–
9	0.25	28.2	8.33	–	–
10	0.16	28.2	5.40	–	–
b) *p*-chlorostyrene					
1	0.52	159	1.25	36	0.067
2	0.52	159	1.40	36	0.075

a) *p*-Methylstyrene

The time-conversion curves of the polymerization of *p*-methylstyrene obtained by using a PEPPER type dilatometer are shown in Fig. 1. The rates of polymerization (Rp) calculated from their initial slopes are summarized in Table 1. There is a fairly definite value of monomer concentration ([M] $\simeq$ 0.5 mole/l.), at which the rate of polymerization reaches a maximum value. It may be said that the dielectric constant of the polymerizing solution decreases as the monomer concentration increases and so the rate of polymerization decreases at last. The stationary concentration of the propagating species ([M*]) in the polymerizing solution was measured by iodometry. Then k_p values were calculated and summarized in Table 1.

Tabl 2. Propagation Rate Constants (k_p) of Vinyl Monomers in the Polymerization Initiated by Iodine in Ethylene Chloride (at 30°C.)

Monomer	k_p (l./mole·min.)
p-chlorostyrene	0.071
styrene	0.22
p-methylstyrene	5.7
p-methoxystyrene	350*)
2-chloroethyl vinyl ether	290
isobutyl vinyl ether	390

*) We could not yet determine a definite value of this system.

b) Other styrene derivatives

Iodine is a rather weak initiator of cationic polymerization, but it was proved that such less reactive monomer as *p*-chlorostyrene could be polymerized by iodine and a white powder polymer was obtained quantitatively. The rate of polymerization and the stationary concentration of the propagating species were measured also in this system and k_p was calculated. Results are shown in Table 1. k_p-values of other monomers on the polymerization initiated by iodine in ethylene chloride were already measured4) and summarized in Table 2 together with the results obtained here.

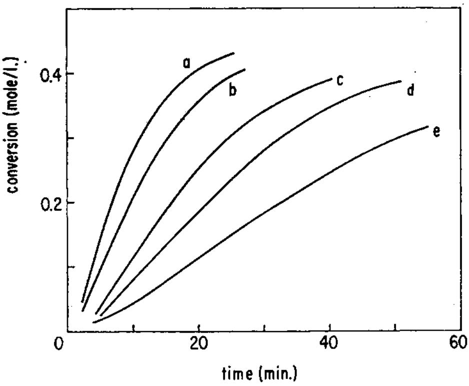


Fig. 1

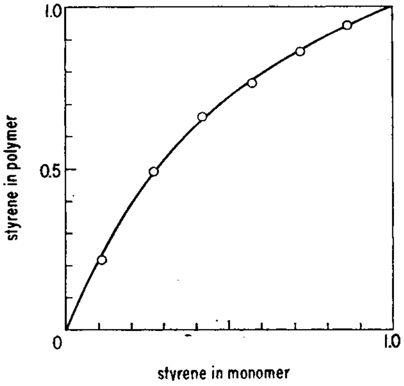


Fig. 2

Fig. 1. Time-Conversion Curves. (*p*-methylstyrene-iodine-ethylene chloride system) [M] = 0.5 mole/l.

a) $[I_2]$ = 36.2 mmole/l.; b) 32.2; c) 28.2; d) 24.2; e) 20.1

Fig. 2. Copolymer Composition Curve between *p*-Chlorostyrene and Styrene (initiator: iodine; solvent: ethylene chloride)

2.3 *Copolymerization*

a) *p*-Chlorostyrene with styrene

The chlorine contents of the copolymer were measured by elementary analysis in order to calculate the copolymer composition. In this system, the polymerization was stopped below 10% conversion. The results are shown in Table 3 and Fig. 2.

b) *p*-Chlorostyrene with *p*-methylstyrene

The copolymer composition was determined by measuring the chlorine content of the copolymer obtained (Table 4). In this system and also in the following system, the conversions being rather high, monomer reactivity ratios were calculated by using the integral form of the copolymer composition equation developed by MAYO and LEWIS[7].

Table 3. The Copolymer Composition between *p*-Chlorostyrene and Styrene **)

No.	Styrene in monomer (mole fraction)	Chlorine content in copolymer (Wt.-%)	Styrene in copolymer (mole fraction)
1	1.00	1.49	0.96*)
2	0.86	2.01	0.94
3	0.72	4.53	0.86
4	0.57	7.67	0.76
5	0.42	10.30	0.66
6	0.27	14.79	0.49
7	0.11	21.02	0.22
8	0.00	25.26	0.02

*) This error may be caused from the iodine fraction which add to the chain end in the process of initiation reaction. Considering the large atomic weight of iodine this discrepancy may be neglegible.

**) In every copolymerization the total monomer concentration is 10 vol.-%.

Table 4. The Copolymer Composition between *p*-Chlorostyrene and *p*-Methylstyrene

No.	*p*-Chlorostyrene in monomer (mole fraction)	Conversion (Wt.-%)	Chlorine content in copolymer (Wt.-%)	*p*-Chlorostyrene in copolymer (mole fraction)
1	0.21	46.0	2.19	0.0736
2	0.36	37.1	2.98	0.101
3	0.51	25.8	4.81	0.165
4	0.66	13.8	6.87	0.283
5	0.81	8.9	10.76	0.381

c) Styrene with *p*-methylstyrene

Copolymer compositions were measured with the aid of infrared spectrometry. The sharp bands in the infrared spectrum of the copolymer at 2900 cm^{-1} and 820 cm^{-1} respectively correspond to the methylene group and aromatic *p*-disubstitution respectively. The infrared spectra of the polymers mixed in known ratios of polystyrene and poly-*p*-methylstyrene were measured and the relationship between the copolymer composition and (D_{820}/D_{2900})-value was preliminarily obtained and proved to be linear. The copolymer composition was calculated from the ratio between the optical densities (D_{820}/D_{2900}) of the peaks (Table 5).

d) *p*-Methylstyrene with *p*-methoxystyrene

The copolymer composition was calculated from the ratio between the optical density of the infrared band at ca. 1250 cm^{-1} (corresponds to aryl ether) and that of the band at 2900 cm^{-1} (methylene group). The conversions were all below 10%. The results are shown in Tab. 6.

Table 5. The Copolymer Composition between Styrene and *p*-Methylstyrene

No.	Styrene in monomer (mole fraction)	Conversion (Wt.-%)	D_{820}/D_{2900}	Styrene in copolymer (mole fraction)
1	0.23	34.4	1.28	0.025
2	0.38	25.2	1.13	0.139
3	0.54	21.2	0.989	0.248
4	0.68	14.9	0.866	0.343
5	0.83	10.0	0.614	0.530

Table 6. The Copolymer Composition between *p*-Methylstyrene and *p*-Methoxystyrene

No.	*p*-Methoxystyrene in monomer (mole fraction)	D_{1250}/D_{2900}	*p*-Methoxystyrene in copolymer (mole fraction)
1	0.20	2.11	0.477
2	0.35	3.09	0.686
3	0.50	3.75	0.847
4	0.65	3.84	0.869
5	0.80	3.99	0.900

e) 2-Chloroethyl vinyl ether with styrene, *p*-methylstyrene or *p*-methoxystyrene

The copolymer composition was calculated from the chlorine content of the copolymer obtained. In each case the conversion was below 10%. Results are summarized in Fig. 3.

When an alkyl vinyl ether was copolymerized with another alkyl vinyl ether or when a styrene derivative was copolymerized with another styrene derivative, the copolymer composition curve was monotonous and the product of r_1 and r_2 was almost unity in every case. But when 2-chloroethyl vinyl ether was copolymerized with the styrene derivative,

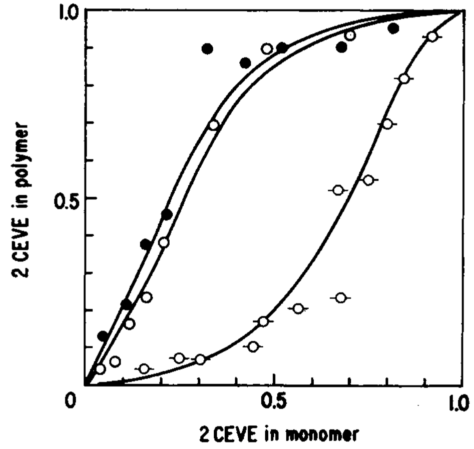


Fig. 3. Copolymer Composition Curves between Styrene Derivatives and 2-Chloroethyl Vinyl Ether
(initiator: iodine; solvent: ethylene chloride)
●: styrene; ○: *p*-methylstyrene; -○-: *p*-methoxystyrene

the copolymer composition curve was sigmoid and both r_1 and r_2 were larger than unity. The sigmoid shape of the composition curve was also obtained when carbon tetrachloride was used as solvent instead of ethylene chloride in this copolymerization system. This means that the styrene derivative or the alkyl vinyl ether has the tendency to propagate to the active species ending in the styrene derivative or alkyl vinyl ether respectively.

Monomer reactivity ratios obtained here are summarized in Table 7.

Table 7. Monomer Reactivity Ratios
(initiator: iodine; solvent: ethylene chloride; 30°C.)

M_1	M_2	r_1	r_2
p-Chlorostyrene	Styrene	0.45	2.5
p-Chlorostyrene	*p*-Methylstyrene	0.19	6.5
Styrene	*p*-Methylstyrene	0.20	4.2
p-Methylstyrene	*p*-Methoxystyrene	0.30	4.3
Styrene	2-Chloroethyl vinyl ether	3	36
p-Methylstyrene	2-Chloroethyl vinyl ether	5	45
p-Methoxystyrene	2-Chloroethyl vinyl ether	11	2
Isobutyl vinyl ether	2-Chloroethyl vinyl ether	2.0	0.5[4]

2.4 *Cross-propagation constant*

From the monomer reactivity ratios and the propagation constants shown in Table 7 and Table 2 respectively, the cross propagation constants (k_{12}, k_{21}) can be calculated using Eq. 1; they are summarized in Table 8.

Table 8. Rate Constant of the Cross Propagation Reaction (l./mole·min.)

Propagating species \ Monomer	p-Chloro-styrene	Styrene	p-Methyl-styrene	p-Meth-oxy-styrene	2-Chloro-ethyl vinyl ether	Isobutyl vinyl ether
p-Chlorostyrene	0.071	0.16	0.37			
Styrene	0.088	0.22	1.1		0.073	
p-Methylstyrene	0.88	1.4	5.7	19	1.1	
p-Methoxystyrene			82	350	32	
2-Chloroethyl vinyl ether		8.1	6.4	145	290	580
Isobutyl vinyl ether					195	390

3. *Discussion*

The relative reactivity of the monomer or that of the propagating species can be judged from Table 8. Independent of the kind of the propagating species which the monomer should attack, the relative reactivity of monomer was in the following order:

for styrene derivatives: p-methoxystyrene > p-methylstyrene > styrene > p-chlorostyrene;
for alkyl vinyl ethers: isobutyl vinyl ether > 2-chloroethyl vinyl ether.

This order of the relative reactivity of the monomer is the same as expected in terms of the e-value of the monomer.

On the other hand, the relative reactivity of the propagating species ending in the styrene derivative or in the alkyl vinyl ether is as follows:

for styrene derivative: p-methoxystyrene > p-methylstyrene > styrene > p-chlorostyrene;
for alkyl vinyl ether: 2-chloroethyl vinyl ether > isobutyl vinyl ether.

For the styrene derivatives the order of the relative reactivity of the monomer is the same as that of its propagating species, but for the alkyl vinyl ether the order of the relative reactivity of the monomer is reverse to that of its propagating species.

It was prospected by us that not only in radical but also in cationic or anionic polymerizations as the monomer is less reactive in each polymerization, its radical, carbonium ion or carbanion may be more reactive, that is to say, they may form a covalent bond more easily with the β-carbon atom of the attacking monomer[8]. In fact, between the relative reactivity of the alkyl vinyl ether monomers and that of their propagating species the relationship agreed with the theoretically expected. But with respect to styrene derivatives the order of the relative reactivity of the propagating species obtained here is reverse to that derived theoretically. This means that there may be another rate determining step than the formation of the covalent bond between the carbonium ion and the β-carbon atom of the attacking monomer in the process of the propagation reaction of the cationic polymerization. Thus, the styrene derivative and the alkyl vinyl ether was proved to display a different type of behaviour, and it was curious enough that the sigmoid shape of the copolymer composition curve was obtained when they were copolymerized.

These results will be discussed in following papers[9].

---

[1] Part IV. N. KANOH, T. HIGASHIMURA, and S. OKAMURA, Makromolekulare Chem. **56** (1962) 65.

[2] M. S. MATHESON, E. E. AUER, E. B. BEVILACQUA, and E. J. HART, J. Amer. chem. Soc. **71** (1949) 497, 2610.

[3] a) S. OKAMURA, K. KATAGIRI, and T. YONEZAWA, J. Polymer Sci. **42** (1960) 535; b) T. YONEZAWA, T. HIGASHIMURA, K. KATAGIRI, S. OKAMURA, and K. FUKUI, Chem. High Polymers Japan **14** (1957) 46.

[4] S. OKAMURA, N. KANOH, and T. HIGASHIMURA, Makromolekulare Chem. **47** (1961) 19, 47; N. KANOH, T. HIGASHIMURA, and S. OKAMURA, Chem. High Polymers Japan **19** (1962) 181.

[5] C. G. OVERBERGER, L. H. AROND, D. TANNER, J. J. TAYLOR, and T. ALFREY Jr., J. Amer. chem. Soc. **74** (1952) 4848.

[6] L. A. BROOKS, J. Amer. chem. Soc. **66** (1944) 1295.

[7] F. R. MAYO and F. M. LEWIS, J. Amer. chem. Soc. **66** (1944) 1594.

[8] T. HIGASHIMURA, Y. IMANISHI, T. YONEZAWA, K. FUKUI, and S. OKAMURA, Polymer [London] **3** (1962) 167.

[9] N. KANOH, A. GOTOH, T. HIGASHIMURA, and S. OKAMURA, Makromolekulare Chem. **63** (1963) 115.