BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 543—547 (1968)

High Pressure Copolymerization of Styrene and Vinyl Acetate with Vinyl Chloride

Tatsuya IMOTO and Yoshiaki OGO
Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka

and Hideo NAKAMOTO
Mitsubishi Rayon Co., Ltd., Misono-cho, Otake-shi, Hiroshima

(Received July 3, 1967)

The radical copolymerization of vinyl chloride and styrene, and that of vinyl chloride and vinyl acetate, were investigated in an acetone solution at 50°C under high pressures of up to 3000 kg/cm^2. The monomer reactivity ratios of these copolymers were not affected by the pressure, while their molecular weights and overall rates of copolymerization increased with the pressure. The increments of the four rate constants of the growing chain of copolymerization (k_{11}, k_{12}, k_{21}, and k_{22}) with the pressure are all of the same order. In such a case, ΔV^*_{11} is ΔV^*_{12}, and ΔV^*_{22} is ΔV^*_{21} (ΔV^*_{ij} is the activation volume in which the i radical reacted with the j monomer). The conclusion drawn from our previous works, that the monomer reactivity ratios of the copolymerization between nonconjugated monomers are independent of the pressure was supported by the experimental results of this report.

Radical copolymerization under high pressures has been studied by several groups of workers in recent years, but the great majority of works on high-pressure copolymerization have dealt with the effect of the pressure on the monomer reactivity ratio in the copolymerization system.

In the copolymerization processes, there are four possible ways in which a monomer can add:

$$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1\cdot$$

$$M_1\cdot + M_2 \xrightarrow{k_{12}} M_2\cdot$$

$$M_2\cdot + M_1 \xrightarrow{k_{21}} M_1\cdot$$

$$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2\cdot$$

where $M_1\cdot$ and $M_2\cdot$ represent chains ending in the M_1 and M_2 monomer units respectively, and where the parameters, $r_1=k_{11}/k_{12}$ and $r_2=k_{22}/k_{21}$, are defined as monomer reactivity ratios.

Zutty and Burkhart[1] investigated the copolymerizations of styrene and acrylonitrile, and of methyl methacrylate and acrylonitrile, under high pressures of up to 1000 kg/cm^2; they reported that their individual monomer reactivity ratios increase with the pressure.

On the other hand, the monomer reactivity ratios in the styrene - vinyl acetate and styrene - n-butyl vinylether systems were found in our previous experiment[2] not to change with the pressure.

Many investigations of high-pressure radical copolymerization have been undertaken in order to explain these disagreements. We investigated a series of copolymerizations under high pressure[3-8]; the most reasonable conclusion to be drawn from the available results was that the reactivity ratios of the copolymerization of the nonconjugated vinyl monomer with styrene did not vary with the pressure.

However, the vinyl acetate and n-butyl vinylether used in our previous work are monomers with the lowest reactivity of all the vinyl compounds. Therefore, the constancy of the reactivity ratios in copolymerizations under high pressure may be attributed to their original reactivities. The present investigation was undertaken to determine their effect by means of the copolymerization of vinyl chloride (VC) with a considerable reactivity among various conjugated monomers and styrene (St) or vinyl acetate (VAc).

Experimental

Styrene and vinyl acetate were distilled under a vacuum just before use. Benzoylperoxide (BPO), used as initiator, was purified by precipitating it from a chloroform solution into methanol, dried *in vacuo* at

---

[1] N. L. Zutty and R. D. Burkhart, *J. Polymer Sci.*, **57**, 793 (1962).

[2] T. Imoto and H. Asai, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 152 (1964).

[3] T. Imoto and H. Asai, *ibid.*, **84**, 871 (1963).

[4] T. Imoto and H. Asai, *ibid.*, **85**, 155 (1964).

[5] T. Imoto and H. Asai, *ibid.*, **85**, 247 (1964).

[6] T. Imoto and H. Asai, *ibid.*, **85**, 252 (1964).

[7] T. Imoto and H. Asai, *ibid.*, **85**, 312 (1964).

[8] T. Imoto and H. Asai, *ibid.*, **85**, 347 (1964).

room temperature, and stored in the dark. Vinyl chloride was purified with sodium hydroxide and dried with calcium chloride.

The acetone used as a solvent, the BPO, and the distilled vinyl monomer were placed in a polyethyrene tube with a capacity of 15 *ml*, and the tube was immersed in dry ice - methanol bath at −40°C. Purified gaseous vinyl chloride was introduced and liquified in the tube. Then the tube was immediately immersed in a high-pressure autoclave at 50°C.

The copolymer mixture thus obtained was precipitated into a large amount of methanol as a precipitant, dried completely *in vacuo* at room temperature, and its polymerization yield determined.

The compositions of the copolymers were calculated from the chloride contents as measured by Schöniger's flask-combustion method; then the reactivity ratios were evaluated by the Fineman-Ross method,[9] in which the $F=[M_1]/[M_2]$ and $f=d[M_1]/d[M_2]$ terms are connected by the following equation:

$$\frac{F}{f}(f-1)=r_1\frac{F^2}{f}-r_2 \qquad (1)$$

where $[M_1]$ and $[M_2]$ are the respective concentrations of the two monomers. Plotting the values of $F/f(f-1)$ *versus* F^2/f, r_1 and r_2 can be evaluated from, respectively, the slope and intercept of the straight line expressed by Eq. (1).

The pressure of the reaction system was measured by pressure guages (Bourdon tube and/or strain guage) directly connected to autoclaves.

Results and Discussion

Pressure Dependence of Monomer Reactivity Ratios. The experimental data for the St-VC and VC-VA systems are summarized in Tables 1 and 2. The monomer-polymer composition curves obtained at a 5% total conversion,

Table 1. St-VC copolymerization in each pressure at 50°C

Pressure kg/cm²	St in monomer mol%	Polymerization hr	Conversion wt%	Chlorine content %	St in polymer mol%
1	12.0	64.0	5.30	10.00	82.40
	35.6	24.0	7.71	2.34	95.88
	52.1	16.5	9.78	1.73	95.96
	55.71	24.0	11.50	1.41	97.60
	60.8	20.0	9.20	1.40	97.54
	73.3	6.2	4.28	0.70	98.77
1000	9.0	45.0	7.20	17.10	69.90
	41.3	28.9	1.65	2.24	95.35
	46.0	23.0	10.60	2.50	95.60
	51.0	2.8	1.90	1.56	96.26
	63.5	3.5	1.95	1.16	97.96
	66.0	5.7	3.12	1.18	97.92
	75.7	—	—	0.68	98.80
3000	16.0	16.0	8.61	9.90	82.60
	27.3	3.5	3.88	4.57	91.95
	40.0	4.0	7.50	2.73	96.05
	50.7	3.0	4.76	2.34	95.87
	57.0	2.7	8.63	1.69	97.03
	66.0	2.0	4.78	1.13	98.01
	82.0	2.0	6.22	0.83	98.54

Table 2. VC-VA copolymerization in each pressure at 50°C

Pressure kg/cm²	VC in monomer mol%	Polymerization hr	Conversion wt%	Chlorine content %	VC in polymer mol%
1	34.0	3.5	4.3	27.0	47.6
	45.0	3.5	6.1	34.1	60.2
	56.0	3.5	3.4	40.3	71.0
	88.0	2.0	3.0	52.4	92.3
1000	52.0	3.5	25.0	37.6	66.3
	68.0	3.5	23.2	45.3	79.8
	77.0	1.5	6.7	48.6	85.6

---

[9] M. Finemann and S. D. Ross, *J. Polymer Sci.*, **5**, 269 (1950).

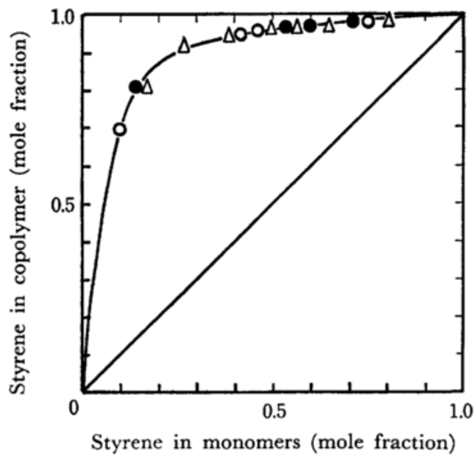

Fig. 1. Copolymer composition curve for St-VC system (50°C).
-△-: 3000 kg/cm^2, -○-: 1000 kg/cm^2
-●-: 1 kg/cm^2

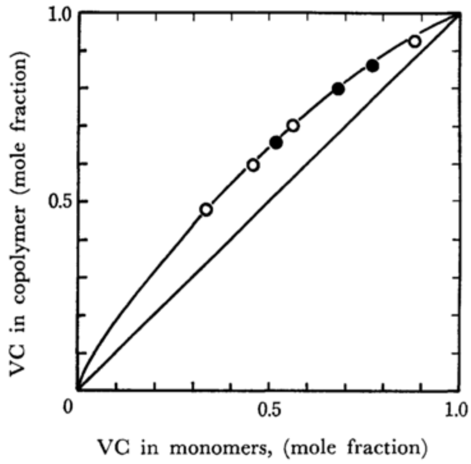

Fig. 2. Copolymer composition curve for VC-VA system.
-○-: 1000 kg/cm^2, -●-: 1 kg/cm^2

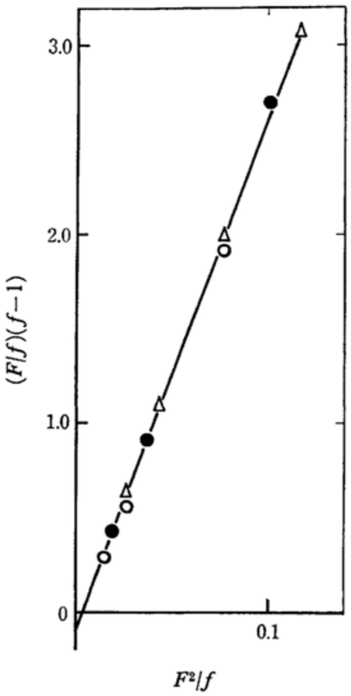

Fig. 3. Finemann-Ross plots for St-VC system.
-△-: 3000 kg/cm^2, -○-: 1000 kg/cm^2,
-●-: 1 kg/cm^2

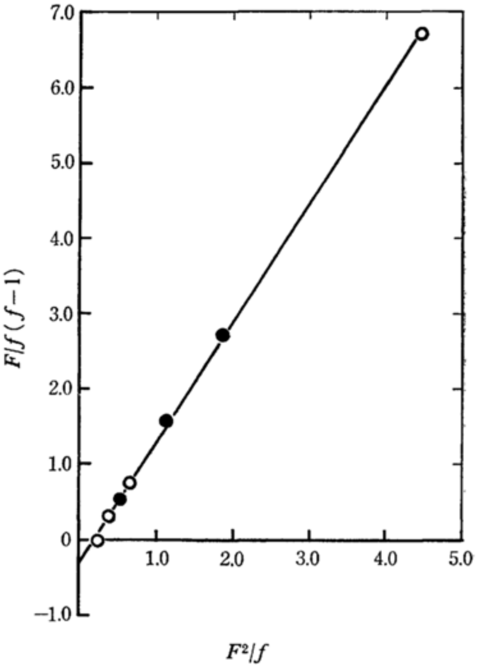

Fig. 4. Finemann-Ross plots for VC-VA system.
-○-: 1000 kg/cm^2, -●- 1 kg/cm^2

regardless of the reaction period under each pressure for the two systems, are shown in Figs. 1 and 2. In addition, the plots obtained by the Fineman-Ross method are illustrated in Figs. 3 and 4.

As Figs. 1 and 2 show, the copolymer compositions under high pressures form the same line as that of the atmosphere, within the limits of experimental error. The fact suggests that the copolymer compositions are quite independent of the pressure for the St-VC and VC-VA systems; that is the monomer reactivity ratios are not affected by the pressure.

The values of r_1 and r_2 evaluated from the slope and the intercept in Figs. 3 and 4 are summarized in Table 3. The values agree with those obtained by other workers[10,11] and show that the styrene monomer has a much greater tendency than does

---

[10] E. Ham, E. C. Chapin and R. G. Fordyce, *J. Am. Chem. Soc.*, **70**, 538 (1948).

[11] F. R. Mayo, C. Walling, F. M. Lewis and W. F. Hulse, *ibid.*, **70**, 1523 (1948).

vinyl chloride to add either to a styrene-free radical or to a vinyl chloride-free radical.

The results of the studies of the high-pressure copolymerization of the St-VC system lend some support to our previous conclusion about the pressure effect on copolymerization. Moreover, the conclusion may be extended as follows by considering the above findings regarding the VC-VA system: "The reactivity ratios of the copolymerization between nonconjugated monomers are also independent of the pressure. Therefore, the pressure affects only the copolymerization of a pair of conjugated monomer."

The effect of the pressure on the rate of chemical reactions can be related to the volume change from reactants to the transition state with Van't Hoff's expression:

$$\left(\frac{\mathrm{d}\ln k}{\mathrm{d}P}\right)_T = -\frac{\Delta V^*}{\boldsymbol{R}T} \tag{2}$$

where ΔV^* is an activation volume.

Assuming that ΔV^* does not vary with the pressure, Eq. (2) leads to:

$$\ln\frac{(k)_P}{(k)_1} = -\frac{\Delta V^*}{\boldsymbol{R}T}(P-1) \fallingdotseq -\frac{\Delta V^*}{\boldsymbol{R}T}P \tag{3}$$

where $(k)_P$ and $(k)_1$ are the rate constants at P kg/cm^2 and atmosphere respectively.

By substituting r_1 and r_2 into Eq. (3), the following equations are obtained:

$$\ln\frac{(r_1)_P}{(r_1)_1} = \frac{\Delta V^*_{11} - \Delta V^*_{12}}{\boldsymbol{R}T}P \tag{4}$$

$$\ln\frac{(r_2)_P}{(r_1)_1} = \frac{\Delta V^*_{22} - \Delta V^*_{21}}{\boldsymbol{R}T}P \tag{5}$$

where $(r)_P$ and $(r)_1$ are the reactivity ratios at P kg/cm^2 and atmosphere respectively. ΔV^*_{ij} is the activation volume for the addition of the j monomer to a chain ending in the i radical.

The constancy of the reactivity ratios with the pressure leads to $\Delta V^*_{11}=\Delta V^*_{12}$ and $\Delta V^*_{22}=\Delta V^*_{21}$. This fact indicates that the two rate constants, k_{11} and k_{12}, similarly increase with the pressure.

In the case of styrene, since ΔV^*_{11} has been known to be -11.5 cc/mol from the data of Nicholson and Norrish,[12] the activation volume of the propagation reaction between the styryl radical and the vinyl chloride molecule, ΔV^*_{12}, may be -11 cc/mol.

Effect of Pressure on the Overall Copolymerization Rates in the St-VC System. The overall copolymerization rates in each pressure are shown in Fig. 5. St and VC are not easy to copolymerize and require a long time to produce VC-rich compositions (see Table 1).

The overall copolymerization rates are markedly accelerated by the pressure and become larger with an increase in the initial styrene mole fraction. This behavior is related to the activation volumes of styrene and vinyl chloride in homopolymerizations. The overall copolymerization rates at each pressure with 50 mol percent of styrene are illustrated in Table 4.

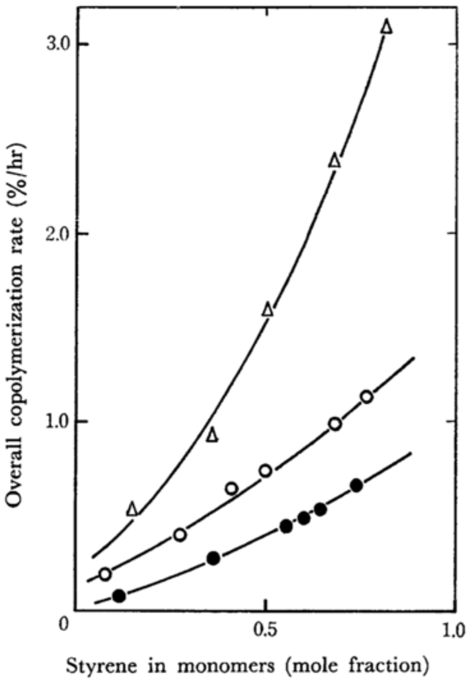

Fig. 5. Effect of pressure on the overall copolymerization rates for St-VC system (50°C).
-△-: 3000 kg/cm^2, -○-: 1000 kg/cm^2,
-●-: 1 kg/cm^2

TABLE 3. THE MONOMER REACTIVITY RATIOS FOR THE SYSTEM OF St-VC AND VC-VA

System	r_1	r_2
St-VC	28	0.08
Ham *et al.*[10]	34	0.077
VC-VA	1.60	0.30
Mayo *et al.*[11]	1.68±0.08	0.23±0.02

TABLE 4. THE OVERALL COPOLYMERIZATION RATES IN EACH PRESSURE AT 0.5 mol%

Pressure kg/cm^2	Rate %/hr	Ratio of rates $(R)_p/(R)_1$
1	0.4	—
1000	0.8	2.0
3000	1.6	4.0

According to the transition-state theory, the following relation is given;

$$k_{11} = \boldsymbol{k}T/\boldsymbol{h}\exp(\Delta S_{11}^*/\boldsymbol{R})\exp(-\Delta H_{11}^*/\boldsymbol{R}T) \tag{6}$$

where $\boldsymbol{k}$ is Boltzman's constant, $\boldsymbol{h}$ is Planck's

---

[12] A. E. Nicholson and R. G. W. Norrish, *Discussions Faraday Soc.*, **22**, 97, 104 (1956).

constant, ΔS^* is the activation entropy, and ΔH^* is the activation enthalpy. By substituting $r_1=k_{11}/k_{12}$ for Eq. (6), we have:

$$r_1 = \exp[(\Delta S_{11}{}^* - \Delta S_{12}{}^*)/\boldsymbol{R}] \times \exp[-(\Delta \mathrm{H}_{11}{}^* - \Delta H_{12}{}^*)/\boldsymbol{RT}] \qquad (7)$$

Since the activation enthalpies, ΔH^*, are almost invariable with the pressure,[13] the pressure dependence of the reactivity ratios may be attributed to the increment of the relative activation entropies $(\Delta S^*{}_{11}-\Delta S^*{}_{12})$.

Therefore, the relative activation entropies at high pressures, $(\Delta S^*{}_{11}-\Delta S^*{}_{12})_p$, would be equal to that of the atmosphere, $(\Delta S^*{}_{11}-\Delta S^*{}_{12})_1$, in the copolymerization of the nonconjugated monomer and styrene.

Effect of Pressure on the Molecular Weight of the Copolymer. The molecular weights of the copolymer in the St-VC system were not measured directly, but the intrinsic viscosity $[\eta]$ was determined as a approximate indication, whose relation to the copolymer composition is shown in Fig. 6.

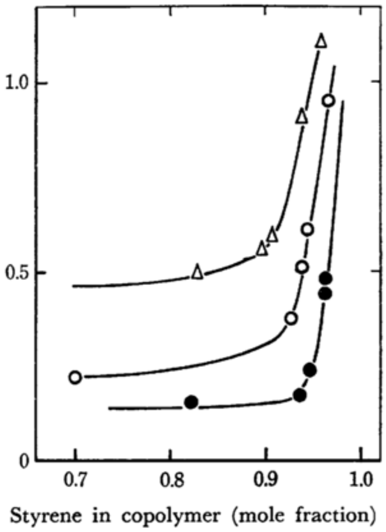

Fig. 6. Effect of pressure on the intrisic viscosity in toluene solution (30°C).
-△-: 3000 kg/cm², -○-: 1000 kg/cm²,
-●-: 1 kg/cm²

Although the reason why these curves rise abruptly at higher styrene contents cannot be explained briefly, the increase in $[\eta]$ with the pressure can be recognized in the figure. This behavior must be due to the acceleration of the chain growth by the pressure.

---

[13] C. Walling and J. Pellon, *J. Am. Chem. Soc.*, **79**, 4782 (1957).