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PRESSURE EFFECT ON THE KINETICS OF POLYMERIZATION II

Bulk Copolymerization of Vinyl Chloride with Propylene and Isobutylene

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The bulk copolymerizations of vinyl chloride with propylene and isobutylene, using benzoyl peroxide as the initiator, were investigated from the kinetic view point in the temperature range of 50°~70°C and the pressure range 1,950~3,900 kg/cm².

It was observed that the copolymerization reaction at constant monomer composition was not preceded by any induction periods, and the polymer yields increased linearly to the reaction time throughout comparatively long runs. And the reaction was accelerated by increasing pressure and temperature. The rate of copolymerization was decreased by increasing mole fraction of propylene or isobutylene in the monomer mixtures.

The degrees of copolymerization and the melting points of the copolymers were decreased by increasing mole fraction of propylene or isobutylene in the copolymers, but they were increased by increasing pressure.

The monomer reactivity ratios in the copolymerizations of vinyl chloride (M₁) with propylene (M₂) and isobutylene (M₂) at 60°C, were determined as follows; $r_1 = 2.45 \pm 0.12$, $r_2 = 0.09$, $r_1' = 1.54 \pm 0.02$, $r_2' = 0.08$.

From these values, Q - and e -values were calculated as follows; $Q_2 = 0.013$ to 0.015, $e_2 = -1.01$ to -1.05 , $Q_2' = 0.019$ to 0.025, $e_2' = -1.20$ to -1.30 .

Introduction

Since 1929 when Conant reported^{1)~3)}, it has been well known that the pressure has an accelerating influence on polymerizations, but its quantitative kinetic studies are comparatively small in number. Then, we are full of interest in the study on the kinetics of the polymerization of the liquefied monomer gases which could be polymerized only under high pressure. From these points of view, we have already reported the thermal bulk polymerization of butadiene⁴⁾ under high pressure, and the bulk polymerization of propylene⁵⁾ and vinyl chloride⁶⁾ under high pressure using benzoyl

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- 1) J. B. Conant and P. W. Bridgman, *Proc. Nat. Acad. Arts Sci.*, **15**, 680 (1929)
- 2) J. B. Conant and C. O. Tonberg, *J. Am. Chem. Soc.*, **52**, 1659 (1930)
- 3) J. B. Conant and W. R. Peterson, *ibid.*, **54**, 628 (1932)
- 4) J. Osugi, K. Hamanoue and S. Hirayama, *This Journal*, **35**, 103 (1965)
- 5) J. Osugi, K. Hamanoue and T. Tachibana, *ibid.*, **38**, 96 (1968)
- 6) K. Hamanoue, *ibid.*, **38**, 103 (1968)

peroxide as the initiator.

On the other hand, the copolymerization reaction is a process of great theoretical interest and of industrial importance. But only recently have some systematic studies of the effect of pressure on these reactions been reported. In the present work, the author will report the results of the kinetic experiment on the bulk copolymerizations of vinyl chloride with propylene and isobutylene, which are generally difficult to be polymerized with radical initiators, and some considerations given to the effect of pressure on the copolymerization reaction.

The copolymerizations of vinyl chloride (VC) with various monomers have been widely studied by many investigators in order to obtain more excellent characteristic polymers, for example, peroxides-initiated-emulsion copolymerization of VC-isobutylene (IB) by Gleason⁷⁾ and Holdsworth⁸⁾, trialkylboron-initiated copolymerization of VC-ethylene by Zutty⁹⁾, copolymerization of VC-ethylene with Ziegler-type catalyzers by Rust¹⁰⁾. However, the studies, standing on the kinetic viewpoint, are scarcely reported except the reports of Lewis *et al.*¹¹⁾, and Imoto *et al.*¹²⁾. The former studied the bulk copolymerization of VC-IB and determined the monomer reactivity ratios, while the latter the solution copolymerization of VC-propylene (PP) and VC-IB. Moreover, no kinetic study on the copolymerization of VC-PP or VC-IB under high pressure is yet reported.

Experimentals

Materials and Procedures

Monomers and initiator (BPO) were purified by the same method as described in part I⁶⁾.

Monomers being liquefied gases, it is difficult to employ a usual glass hypodermic syringe as the reactor. So, the stainless steel capsule which was the same as described in part I⁶⁾ was used. The reaction capsule, which contained 3 mg BPO, was immersed in the dryice-methanol bath and was cooled.

Previously cooled monomer mixtures (3.5 ml, at -78°C) were charged into the capsule with the glass hypodermic syringe. The reactions were carried out by the same procedure as described in part I.

The copolymers obtained were dissolved in tetrahydrofuran, and precipitated by adding methanol. The precipitated polymers were dried in vacuum at room temperature until they attained to the constant weight.

Intrinsic viscosities $[\eta]$ were determined from the relative viscosities which were measured in cyclohexanone at 30°C using an Ubbelohde type viscometer.

The compositions of copolymers were calculated from chlorine contents which were determined by elementary analysis.

7) A. H. Gleason, U. S. Pat., 2,379,292 (1945)

8) R. S. Holdsworth, W. Mayo *et al.*, U. S. Pat. 3,063,977 (1962)

9) N. L. Zutty, U. S. Pat. 3,051,689 (1962)

10) K. Rust, S. Müllner and M. Gumboldt, U. S. Pat. 3,111,505 (1963)

11) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and W. J. Wenisch, *J. Am. Chem. Soc.*, **70**, 1527 (1948)

12) K. Matsuoka, K. Takemoto and M. Imoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 1941 (1965)

Results and Discussion

The rate of copolymerization

The bulk copolymerization reactions (at 84.8 mole% of VC in monomer mixtures) were carried out at 50° to 70°C under high pressure in the range of 1,950 to 3,900 kg/cm².

The principal experimental results are illustrated in Figs. 1, 2, 3 and 4. From these results it was observed that the rate of copolymerization was increased by increasing pressure and temperature. At constant pressure and temperature, the copolymerization reaction was not preceded by any induction periods, and the polymer yields increased linearly to the reaction time even in the comparatively long runs.

Imoto and his collaborators (*loc. cit.*) measured the rates of the copolymerizations in the systems of vinyl chloride-propylene and vinyl chloride-isobutylene at an atmospheric pressure, using benzene as the solvent and α, α' -azodiisobutyronitrile as the initiator. They found that the yields of these reactions increased linearly to reaction time up to about 20% yields.

The apparent initial rates (k_1) were obtained from the slopes of the straight lines shown in Figs. 1, 2, 3 and 4, etc. These values are given in Tables 1 and 2.

According to the transition state theory¹³⁾, the fundamental equation for the effect of pressure on the rate constant (k) of an elementary reaction is

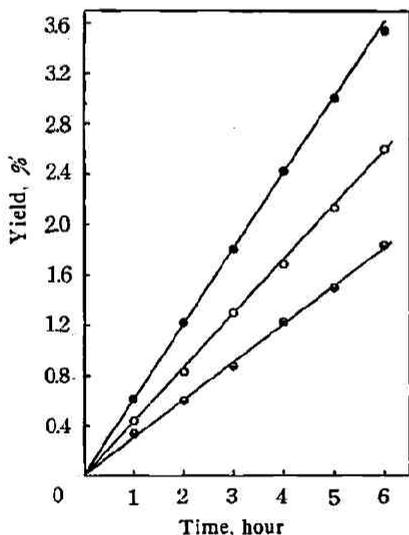


Fig. 1 Copolymerization of vinyl chloride with propylene at 50°C
 ● : 3,900 kg/cm² ○ : 3,120 kg/cm²
 ◐ : 1,950 kg/cm²

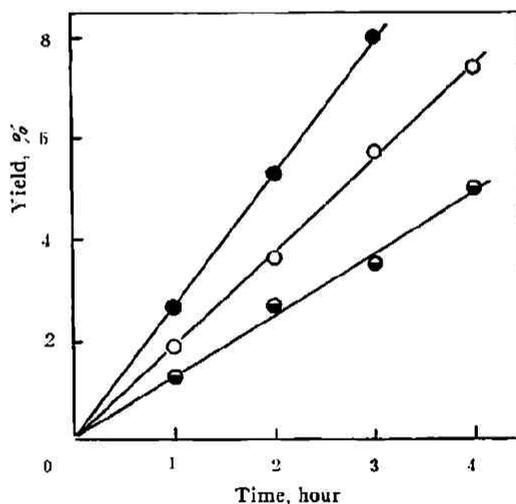


Fig. 2 Copolymerization of vinyl chloride with propylene at 60°C
 ● : 3,900 kg/cm² ○ : 3,120 kg/cm²
 ◐ : 1,950 kg/cm²

13) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935)

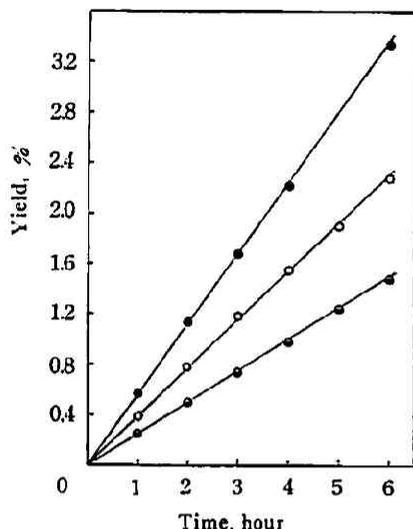


Fig. 3 Copolymerization of vinyl chloride with isobutylene at 50°C

● : 3,900 kg/cm² ○ : 3,120 kg/cm²
◐ : 1,950 kg/cm²

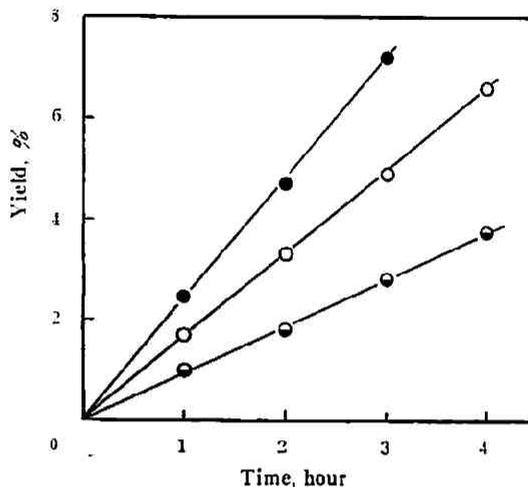


Fig. 4 Copolymerization of vinyl chloride with isobutylene at 60°C

● : 3,900 kg/cm² ○ : 3,120 kg/cm²
◐ : 1,950 kg/cm²

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\ddagger}}{RT}, \quad (1)$$

where

$$\Delta V^{\ddagger} = V^{\ddagger} - V_{\text{Int}}, \quad (2)$$

i.e. ΔV^{\ddagger} , the activation volume of the reaction is the difference between the transition state V^{\ddagger} and the initial state V_{Int} .

If the copolymerization reactions of VC-PP and VC-IB are assumed to proceed through the same reaction mechanism, the ratio of copolymerization rate of one system to that of another might correspond to the ratio of the respective rate constants. Then, considering the results of the previous report⁶⁾, the correlation of $[\Delta V^{\ddagger}]_{\text{VC-PP}}$ to $[\Delta V^{\ddagger}]_{\text{VC-IB}}$ obtained from k_t may correspond to that of

Table 1 Effect of pressure on the initial rate at various temperature (VC-PP)

Pressure (P , kg/cm ²)	Temperature (T , °C)	Initial rate ($k_t \times 10^3$, %/min)
1,950	50	5.0
	60	20.5
	70	76.7
3,120	50	7.17
	60	31.0
	70	130
3,900	50	10.2
	60	43.8
	70	175

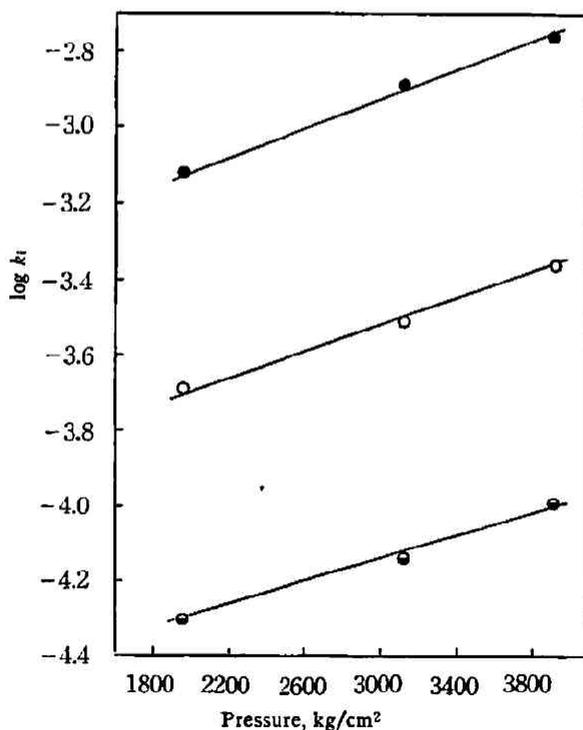
Table 2 Effect of pressure on the initial rate at various temperature (VC-IB)

Pressure (P , kg/cm ²)	Temperature (T , °C)	Initial rate ($k_1 \times 10^3$, %/min)
1,950	50	4.17
	60	16.7
	70	71.7
3,120	50	6.5
	60	28.2
	70	127
3,900	50	9.5
	60	40.5
	70	167

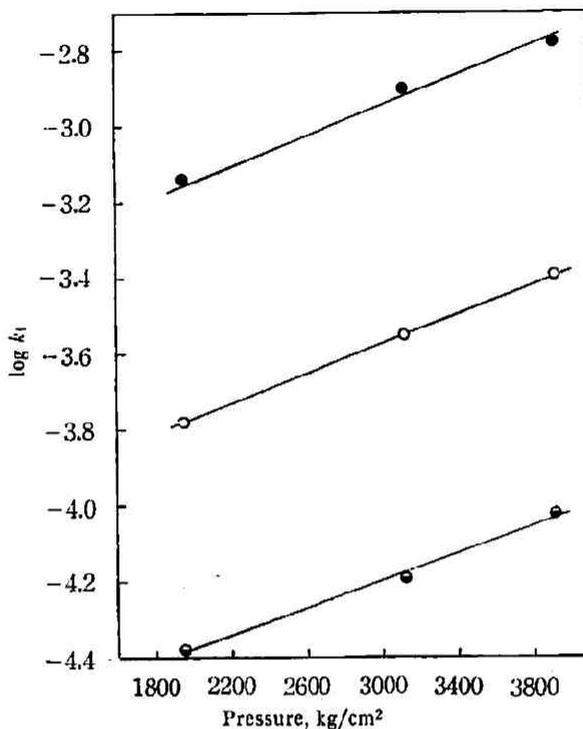
$[\Delta V^*]_{VC-PP}$ to $[\Delta V^*]_{VC-IB}$ which may be obtained from k .

Figs. 5 and 6 show the relationships between $\log k_1$ and P . The plots come to be straight lines, whose slopes give the apparent activation volumes by equation (1). These values thus obtained are given in Table 3.

Figs. 7 and 8 show the Arrhenius plots of $\log k_1$ against $1/T$. They show good straight lines, and activation energies (E) calculated from these slopes are given in Table 4. As shown in Table 3, the

Fig. 5 Plots of $\log k_1$ vs pressure at various temperature (VC-PP)

● : 70°C ○ : 60°C ◐ : 50°C

Fig. 6 Plots of $\log k_1$ vs pressure at various temperature (VC-IB)

●: 70°C ○: 60°C ◐: 50°C

Table 3 Effect of temperature on the activation volume

Temperature (T , °C)	Activation volume (ΔV^\ddagger , cm ³ /mole)	
	VC-PP	VC-IB
50	-10.4	-11.3
60	-11.7	-12.7
70	-13.0	-13.4

Table 4 Effect of pressure on the activation energy

Pressure (P , kg/cm ²)	Activation energy (E , kcal/mole)	
	VC-PP	VC-IB
1,950	29.1	29.5
3,120	30.2	30.7
3,900	31.1	31.6

overall activation volumes are negative, and so, the reaction should be accelerated with increasing pressure by equation (1). The activation volumes are reduced by increasing temperature. These effects of pressure on the rate of copolymerization closely resemble to those observed in most of radical homopolymerizations.

Table 4 shows that activation energies are slightly increased by increasing pressure. This rise in the activation energy may represent the stabilization of the initial molecule owing to its energy loss by pressure, resembling to those observed in most of radical homopolymerizations. The overall activation energies in radical homopolymerizations, such as that of styrene or vinyl acetate, are 21.5~19.4 kcal/mole at an atmospheric pressure. And the author's previous experimental results on vinyl chloride⁶⁾

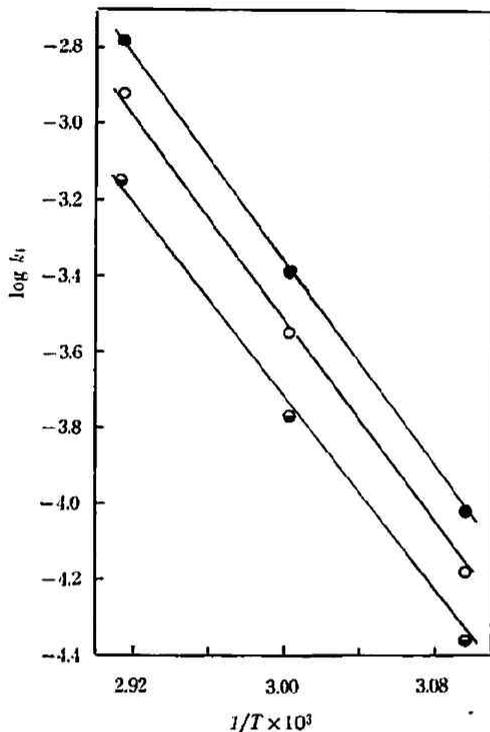


Fig. 7 Arrhenius plots of $\log k_1$ vs $1/T$ at various pressure (VC-PP)

● : 3,900 kg/cm² ○ : 3,120 kg/cm²
 ◐ : 1,950 kg/cm²

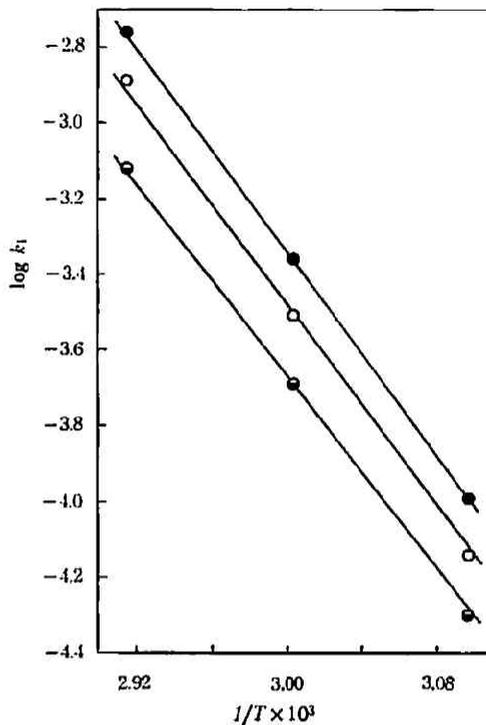


Fig. 8 Arrhenius plots of $\log k_1$ vs $1/T$ at various pressure (VC-IB)

● : 3,900 kg/cm² ○ : 3,120 kg/cm²
 ◐ : 1,950 kg/cm²

are 21.6~24.0 kcal/mole at high pressure. Then, the activation energies of the copolymerizations of vinyl chloride with propylene and isobutylene are comparatively high. This may be due to the fact that propylene and isobutylene are difficult to be homopolymerized in a radical initiating process.

Imoto and his collaborators (*loc. cit.*) obtained the activation energies as $E_{VC-PP}=24.2$ kcal/mole and $E_{VC-IB}=26.5$ kcal/mole in their solution copolymerizations at an atmospheric pressure.

They attributed this difference in activation energies to the steric hindrance of two methyl groups of isobutylene.

A number of examples are known in which 1,2-disubstituted ethylene is very reluctant to copolymerize, whereas the corresponding 1,1'-disubstituted compound reacts easily. This is usually paralleled by the inability of the former material to homopolymerize although the latter will do so; an example is afforded by 1,2-dichloroethylene and vinylidene chloride.

Mark has concluded that the interaction between two substituents of 1,2-disubstituted ethylene is large in its transition state¹⁴⁾, but such steric hindrance does not occur in the case of 1,1'-disubstituted ethylene. Some reactivity ratios show that a reaction occurs more readily with vinylidene chloride than with vinyl chloride.

14) T. Alfrey, Jr, J. J. Bohrer and H. Mark, "Copolymerization", p. 49 Interscience, (1952)

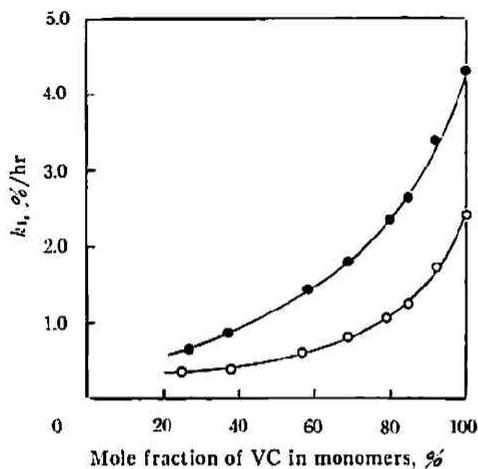


Fig. 9 Copolymerization rate for the system VC-PP at 60°C

● : 3,900 kg/cm² ○ : 1,950 kg/cm²

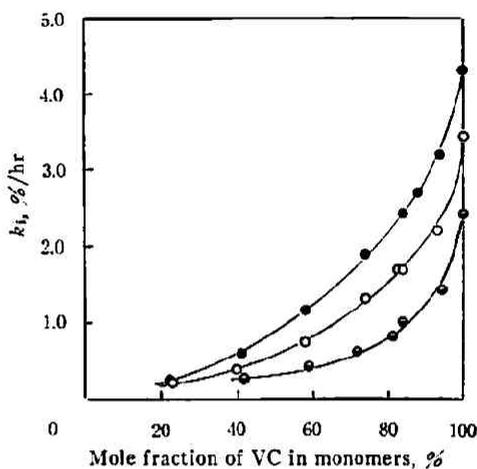


Fig. 10 Copolymerization rate for the system VC-IB at 60°C

● : 3,900 kg/cm² ○ : 3,120 kg/cm²
◐ : 1,950 kg/cm²

In the present experiment under high pressure, the activation energies and the absolute values of activation volumes are higher in the copolymerization of vinyl chloride with isobutylene than those in the copolymerization of vinyl chloride with propylene. But their differences are very small. From the foregoing discussion, therefore, if some steric hindrance, which was considered to be very small, were concerned, its effect may be decreased by pressure.

Figs. 9 and 10 show the relationship between the rate of copolymerization and monomer composition at 60°C.

It is found that the rates of copolymerization are remarkably decreased by increasing mole fraction of propylene or isobutylene in monomer mixtures. As mentioned above, this decrease in the rate of copolymerization may be ascribed to the difficulty of polymerizability of propylene and isobutylene by radical initiators.

Monomer reactivity ratios

The copolymerizations are similar in their general characteristics to the homopolymerization, and display no inherently new features. The main theoretical interest in the copolymerization is the information which they yield on the relative reactivities of different radicals, and consequently on the relation between structure and reactivity.

It is usually assumed that the reactivity of the radical is independent of the chain length, and the reactivity is solely determined by the terminal monomer unit, *i.e.* radicals ending in $-M_1-M_1\cdot$ and $-M_2-M_1\cdot$ are assumed to be equal reactivities towards any given monomer. With two kinds of monomers, M_1 (vinyl chloride) and M_2 (propylene or isobutylene), there are thus only four different propagation reactions as follows:





and



where $M_1 \cdot$ and $M_2 \cdot$ represent the chains ending at M_1 and M_2 monomeric units respectively.

Assuming (1) the radical concentrations are in the steady state condition, *i.e.*, $k_{12}[M_1 \cdot][M_2] = k_{21}[M_2 \cdot][M_1]$ and (2) the kinetic chain length is great, one can obtain the following "copolymer composition equation":

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \quad \left(= \frac{m_1}{m_2} \text{ for low conversion} \right), \tag{7}$$

where $[M_1]$ and $[M_2]$ refer to the monomer composition and m_1 and m_2 to the polymer composition. Two reactivity ratios (r_1 and r_2) of each monomer are defined by the equations,

$$r_1 = \frac{k_{11}}{k_{12}}, \quad r_2 = \frac{k_{22}}{k_{21}}. \tag{8}$$

Let F and f equal to $[M_1]/[M_2]$ and m_1/m_2 respectively, then equation (7) can be rewritten as¹⁵⁾

$$\frac{F}{f} (f - 1) = r_1 \frac{F^2}{f} - r_2. \tag{9}$$

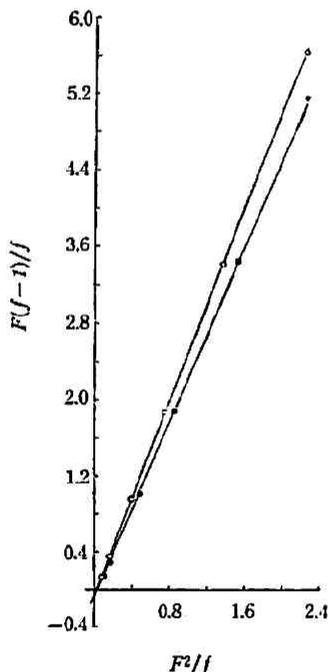


Fig. 11 Fineman-Ross plots for the system VC-PP
● : 3,900 kg/cm² ○ : 1,950 kg/cm²

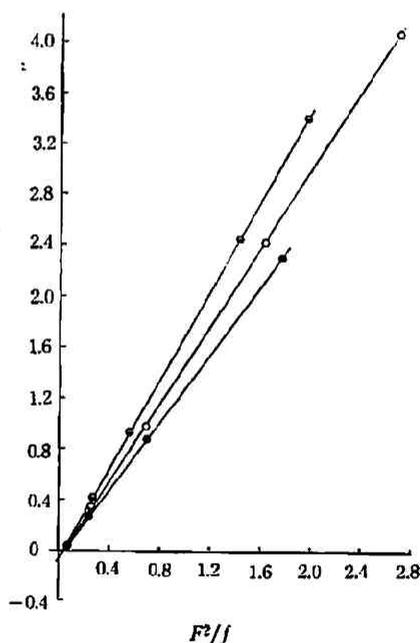


Fig. 12 Fineman-Ross plots for the system VC-IB
● : 3,900 kg/cm² ○ : 3,120 kg/cm²
◐ : 1,950 kg/cm²

15) M. Fineman and S.D. Ross, *J. Polymer Sci.*, 5, 259 (1950)

Pressure Effect on the Kinetics of Polymerization II

129

Table 5 Effect of pressure on the monomer reactivity ratio and Q_2 , e_2 -values

Pressure (P , kg/cm ²)	VC-PP				VC-IB			
	r_1	r_2	Q_2	e_2	r_1	r_2	Q_2	e_2
1,950	2.57	0.09	0.013	-1.01	1.76	0.08	0.019	-1.20
3,120					1.53	0.08	0.022	-1.25
3,900	2.33	0.09	0.015	-1.05	1.33	0.08	0.025	-1.30

Figs. 11 and 12 show the plots of $F(f-1)/f$ against F^2/f . They show good straight lines whose slopes are r_1 and whose intercepts are minus r_2 . The values of r_1 and r_2 thus obtained are given in Table 5. Fig. 13 shows the copolymer composition curves which were calculated from r_1 and r_2 by using equation (7). Excellent agreement was obtained between the experimental values and those obtained from equation (7). It is found that the compositions of vinyl chloride are always higher in the copolymers than in the monomer mixtures. This tendency is more remarkable in the system of vinyl chloride-propylene than in the system of vinyl chloride-isobutylene.

In both the copolymerizations, $r_1 > 1$ and $r_2 \ll 1$. then, from the definition of these ratios (equation 8), the results imply that reactions shown by equations (3) and (5) are more favorable than those of (4) and (6) respectively. This indicates that the active centre of vinyl chloride reacts more readily

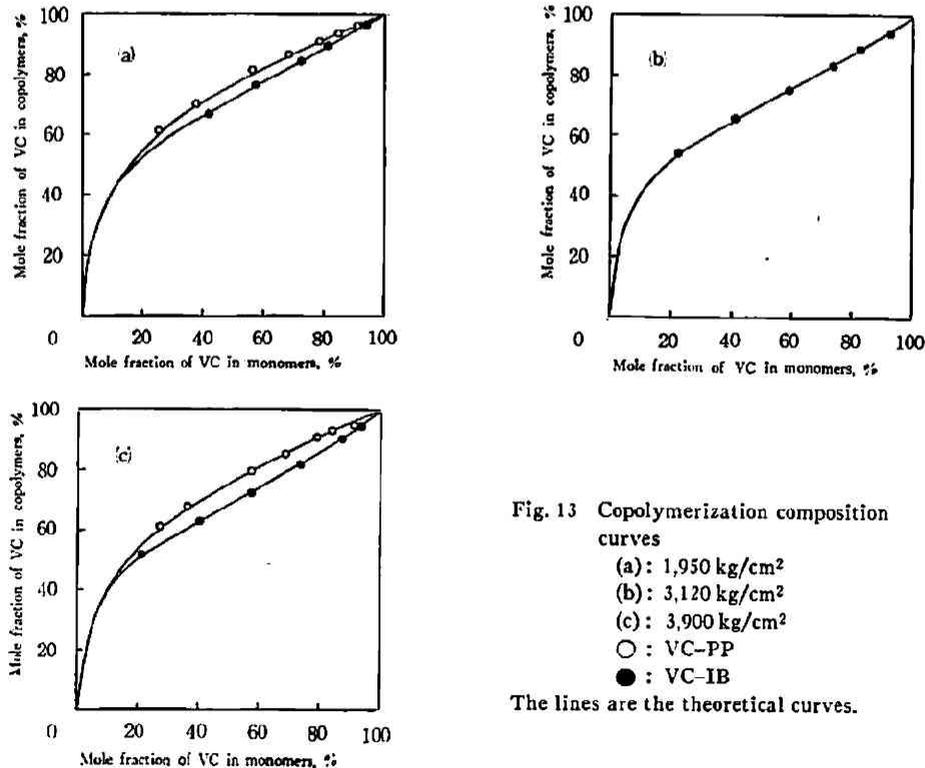


Fig. 13 Copolymerization composition curves

(a): 1,950 kg/cm²
 (b): 3,120 kg/cm²
 (c): 3,900 kg/cm²

○ : VC-PP
 ● : VC-IB

The lines are the theoretical curves.

with its own type of monomer, whereas the active centre of propylene or isobutylene reacts preferentially with vinyl chloride.

The rate constants for various pairs of propagation reactions, e.g. k_{11} , k_{12} , k_{21} and k_{22} may be specifically increased by pressure. But the numerical values of r_1 vary from one to three. If k_{12} is more accelerated than k_{11} , it may be reasonable to consider that r_1 is decreased by pressure. On the other hand, the order of r_2 is very small compared with one, and is independent of pressure. Then, there is no change of r_2 unless k_{22} is more exceedingly changed than k_{21} by pressure. The data on reactivity ratios at an atmospheric pressure have been obtained by Imoto *et al.*, Gleason and Lewis *et al.* as follows:

i) Imoto *et al.*¹²⁾,

$$r_1=2.27, r_2=0.30 \text{ for VC-PP and } r_1=2.11, r_2=0.34 \text{ for VC-IB}$$

ii) Gleason⁷⁾,

$$r_1=4.3, r_2=0 \text{ for VC-IB}$$

iii) Lewis *et al.*¹¹⁾,

$$r_1=2.05 \pm 0.3, r_2=0.08 \pm 0.6 \text{ for VC-IB.}$$

These values are varied according to the experimental conditions. But, for the copolymerization of vinyl chloride with isobutylene, the author's results are substantially near to that of bulk copolymerization by Lewis *et al.*

According to the semi-empirical equation of Alfrey-Price¹⁶⁾¹⁷⁾, the monomer reactivity ratios can be expressed by the following equations,

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2} \exp\{-e_1(e_1 - e_2)\} \quad (10)$$

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1} \exp\{-e_2(e_2 - e_1)\}. \quad (11)$$

Here Q is proportional to the reactivity of the monomer, and e is the quantity describing the charges on monomer structure, the identical charges being assumed for a monomer and for a radical with a terminal unit of the same type.

Evans *et al.*¹⁸⁾¹⁹⁾ have discussed the relation between the resonance stabilization of the radical and the reactivity of monomer, and have suggested that the term Q , defined by Alfrey and Price as a measure of general reactivity, is to be identical with

$$Q = \exp(R_A - R_M) / RT. \quad (12)$$

that is, high reactivity is to be associated with a large gain in resonance in going from the monomer (M) to the corresponding radical (A), i.e., with delocalization energy. If values of $Q_1=0.044$ and $e_1=0.20$ are assigned to vinyl chloride²⁰⁾, we can calculate Q_2 and e_2 from equations (10) and (11). The calculated values are given in Table 5.

16) T. Alfrey, Jr. and C. C. Price, *J. Polymer Sci.*, 2, 101 (1947)

17) C. C. Price, *ibid.*, 1, 83(1946)

18) M. G. Evans, *Discussions Faraday Soc.*, 2, 271 (1947)

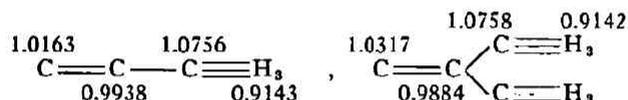
19) M. G. Evans, J. Gergely and E. C. Seaman, *J. Polymer Sci.*, 3, 866 (1948)

20) L. J. Young, *ibid.*, 54, 411 (1961).

Generally Q is larger in conjugated monomers than in nonconjugated monomers. The results of Table 5 are consistent with these conclusions. Namely, the hyperconjugation of propylene which has one methyl group and one double bond is smaller than that of isobutylene which has two methyl groups and one double bond. Then, Q -value of the former must be smaller than that of the latter.

By the use of the simple LCAO molecular orbital method we can calculate π -electron densities of propylene and isobutylene, taking account of the hyperconjugation model and heteroatom model of the methyl group²¹⁾²²⁾. The calculated values are as follows:

i) Hyperconjugation model



ii) Heteroatom model



We may define the charge density of π -electron on the double bond by the following equation,

$$\xi = 2 - q, \quad (13)$$

where q is the sum of the π -electron density on the carbon atoms which participate in the double bonding. Then, $\xi > 0$ and $\xi < 0$ mean the positive and negative characters of the double bond, respectively.

In either case of model (i) or (ii), ξ is negative, and $|\xi_{\text{IB}}|$ is larger than $|\xi_{\text{PF}}|$. Thus, the e -value is proportional to ξ , e.g. vinyl chloride which has an electrophilic substituent has positive ξ , i.e., positive e , and isobutylene or propylene which has an electron-donating substituent has negative ξ , i.e., negative e . In Table 5, values of e_2 are negative and $|e_{\text{IB}}|$ are larger than $|e_{\text{PF}}|$. These results are consistent with the foregoing discussion on ξ .

Young (*loc. cit.*) has collected the monomer reactivity ratios in the copolymerizations of isobutylene with various monomers. From these data he calculated Q_2 and e_2 , and obtained the values of 0.033 and -0.96 respectively. Imoto *et al.* (*loc. cit.*) reported $Q_2=0.02$ and $e_2=-0.4$ for both propylene and isobutylene. These values mentioned above are the data in the experiments under an atmospheric pressure. But the author's data at high pressure are nearly close to that of Young.

From equations (10) and (11) we have

$$r_1 r_2 = \exp\{-(e_1 - e_2)^2\}. \quad (13)$$

As shown in Table 5, r_2 is independent of pressure but r_1 is decreased by increasing pressure, and so $r_1 r_2$ must be decreased by increasing pressure. This means that, in equation (13), $|e_1 - e_2|$ must be increased by increasing pressure.

In the previous paper⁶⁾, the author considered that monomers were aligned by pressure. Then,

21) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", p. 131 John Wiley & Sons, New York, (1961)

22) T. Yonesawa *et al.*, "Ryoshi Kagaku Nyumon (Introduction to the Quantum Chemistry) Vol 1", p. 55, Kagaku-dōjin (1963)

propylene or isobutylene may be affected by the inductive effect which is caused by the alignment of vinyl chloride molecules. So, ξ_2 , *i.e.*, e_2 may be increased to a large negative value. On the contrary, ξ_1 , *i.e.*, e_1 may be increased to a large positive value by the alignment of propylene or isobutylene. Consequently, $|e_1 - e_2|$ is increased by pressure, that is, $r_1 r_2$ must be decreased by increasing pressure.

From equation (1), r_1 and r_2 may be expressible in the form

$$\frac{\partial \ln r_1}{\partial P} = -\frac{\Delta V_{11}^* - \Delta V_{12}^*}{RT} \quad (14)$$

$$\frac{\partial \ln r_2}{\partial P} = -\frac{\Delta V_{22}^* - \Delta V_{21}^*}{RT} \quad (15)$$

where ΔV_{ij}^* is the activation volume of the propagation reaction between radical ($M_i\cdot$) and monomer (M_j). In the copolymerization of vinyl chloride with isobutylene, the relationship between $\log r_1$ and P is illustrated in Fig. 14. Extrapolating to $P=1$, we obtain $\log r_1=0.312$, *i.e.*, $r_1=2.05$, which is equal to the value of Lewis *et al.* ($r_1=2.05\pm 0.3$). Then, from the tangent at $P=1$, we can calculate

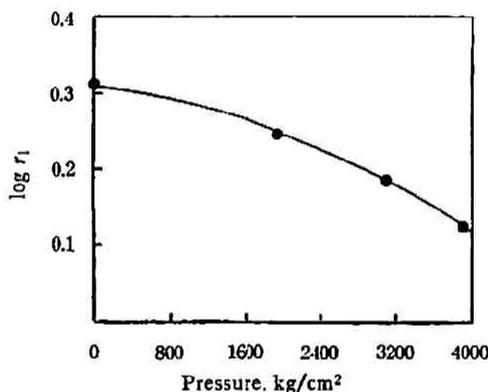


Fig. 14 Plot of $\log r_1$ vs pressure for the system VC-IB

$\Delta V_{11}^* - \Delta V_{12}^*$ (*i.e.*, $1.2 \sim 1.6 \text{ cm}^3/\text{mole}$). Since, r_2 is independent of pressure, ΔV_{22}^* is equal to ΔV_{21}^* .

In the bulk copolymerization of vinyl chloride with propylene, the monomer reactivity ratios have not yet been obtained at an atmospheric pressure, so, the author calculated $\Delta V_{11}^* - \Delta V_{12}^*$ from the present two experimental values of r_1 . The value thus obtained is $1.4 \text{ cm}^3/\text{mole}$, and ΔV_{22}^* is equal to ΔV_{21}^* .

In both the copolymerization reactions, ΔV_{12}^* is slightly smaller than ΔV_{11}^* or may be equal to ΔV_{11}^* and ΔV_{22}^* is equal to ΔV_{21}^* . Generally, ΔV_{11}^* and ΔV_{22}^* may be different from each other because they are the activation volumes of different monomers in the homopolymerization. Consequently, the above conclusion concerning ΔV_{1j}^* implies that the transition state in the propagation step is affected mainly by the terminal structure of the growing radical.

Lamb and Weale²³⁾ investigated the bulk copolymerization of styrene with methyl methacrylate

23) J. A. Lamb and K. E. Weale, *Symp. Phys. and Chem. of High Pressure*, (Soc. Chem. Ind. London), p. 229 (1963)

and diethyl fumarate up to 3,500 atm at 60°C, with benzoyl peroxide as the initiator. In these two systems the reactivity ratios were found to change very little or to decrease slightly with pressure increase. But, for the solution copolymerizations of acrylonitrile with styrene and methyl methacrylate, Burkhart and Zutty²⁴⁾ reported that r_1r_2 increased and tended to approach unity as the pressure increased. A large number of monomer combinations have been examined by Asai *et al.*²⁵⁾²⁶⁾. They concluded that the effect of pressure on the change of r_1r_2 is positive in the copolymerization of a pair of conjugated monomers, but the effect is negative or zero in the copolymerizations of the other pair of monomers. On the other hand, Mitani *et al.*²⁷⁾²⁸⁾ concluded in their copolymerizations of crotonaldehyde with various vinyl monomers that the above mentioned regularity of a pair of conjugated monomer is questionable.

From the foregoing discussion, it may be concluded that the effect of pressure on the monomer reactivity ratio contains many questionable factors at present and, therefore, it is difficult to give any satisfactory explanation to these complicated effects until the structure of the transition state is more precisely known. Consequently we might conclude that the reactivity ratios of the copolymerizations of vinyl chloride with propylene and isobutylene are as follows:

- i) For VC-PP; $r_1=2.45\pm 0.12$, $r_2=0.09$
- ii) For VC-IB; $r_1=1.54\pm 0.22$, $r_2=0.08$

Properties of copolymers

The copolymers of vinyl chloride with propylene are white but they become slightly brown when the mole fraction of propylene in copolymers is over 39%.

The copolymers of vinyl chloride with isobutylene become slightly brown as the mole fraction of isobutylene in copolymers is over 25%, and become glutinous materials with further increase of the mole fraction of isobutylene, and at about 46% isobutylene they become brown cohesive materials.

The infrared absorption spectra of the copolymers are illustrated in Figs. 15 and 16. They show different spectra from that of polyvinyl chloride. Namely, the absorption bands of $\nu_a(\text{CH}_2)$ and $\nu(\text{CH})$, which appear at 2,920 cm^{-1} and 2,967 cm^{-1} respectively in PVC, overlap with that of $\nu_a(\text{CH}_2)$ which appears at 2,960 cm^{-1} in the copolymers. Then the shapes of absorption curves are gradually varied by the change of copolymer compositions.

New bands, which do not appear in PVC, are found at 1,450 cm^{-1} and 1,380 cm^{-1} in the copolymers of vinyl chloride with propylene. The former band may be assigned to $\delta_a(\text{CH}_2)$ and $\delta(\text{CH}_2)$, and the latter to $\delta_s(\text{CH}_3)$ which is due to propylene.

In the copolymers of vinyl chloride with isobutylene, new bands are found at 1,470 cm^{-1} , 1,395 cm^{-1} and 1,370 cm^{-1} . The band at 1,470 cm^{-1} is assigned to $\delta_a(\text{CH}_2)$ and those at 1,395 cm^{-1} and 1,370

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

25) H. Asai and T. Imoto, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)* **84**, 871 (1963); **85**, 152, 155 (1964)

26) H. Asai, *ibid.*, **85**, 247, 252, 312, 347 (1964)

27) T. Imoto, Y. Ogo, S. Goto and T. Mitani, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1371 (1966)

28) T. Mitani, Y. Ogo and T. Imoto, *ibid.*, **70**, 1217 (1967)

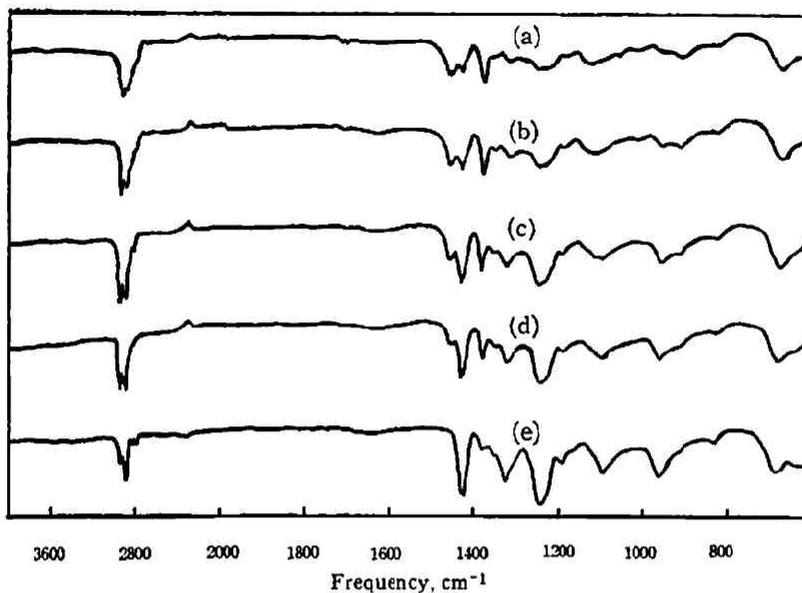


Fig. 15 Infrared absorption spectra of VC-PP copolymers
 (a): 38.5% (b): 29.8% (c): 18.7% (d): 13.2% (e): PVC
 The numbers indicate the mole % of propylene in copolymers.

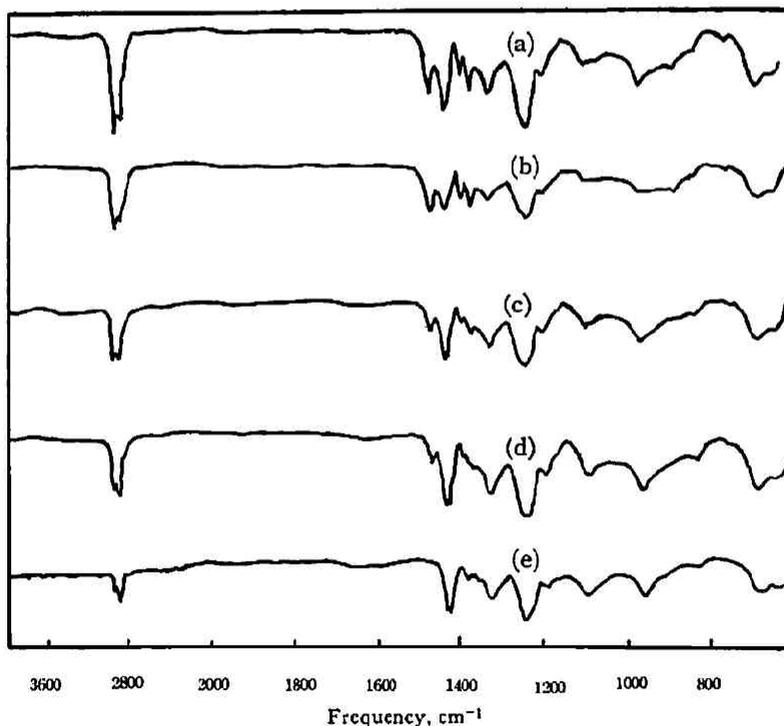


Fig. 16 Infrared absorption spectra of VC-IB copolymers
 (a): 17.2% (b): 23.2% (c): 9.3% (d): 5.6% (e): PVC
 The numbers indicate the mole % of isobutylene in copolymers.

cm^{-1} to $\delta_s(\text{CH}_3)$ which are due to isobutylene. The intensities of these new bands are increased with increasing mole fractions of propylene and isobutylene as shown in Figs. 15 and 16.

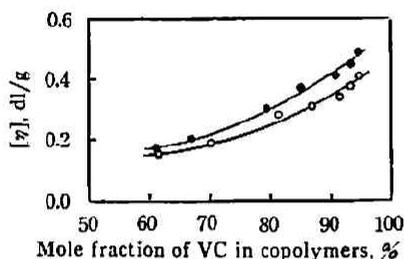


Fig. 17 The relationships between $[\eta]$ and copolymer composition for VC-PP
 ● : 3,900 kg/cm² ○ : 1,950 kg/cm²

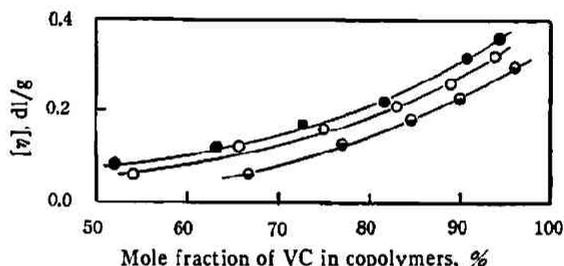


Fig. 18 The relationships between $[\eta]$ and copolymer composition for VC-IB
 ● : 3,900 kg/cm² ○ : 3,120 kg/cm²
 ◐ : 1,950 kg/cm²

The molecular weight of the copolymer was not determined, but the intrinsic viscosity in cyclohexanone was measured, and this gives an approximate indication of the pressure effect on the molecular weight. The relationships between the intrinsic viscosity $[\eta]$ and the compositions of copolymers are shown in Figs. 17 and 18. Obviously, $[\eta]$ is increased by pressure, and at constant pressure, it is

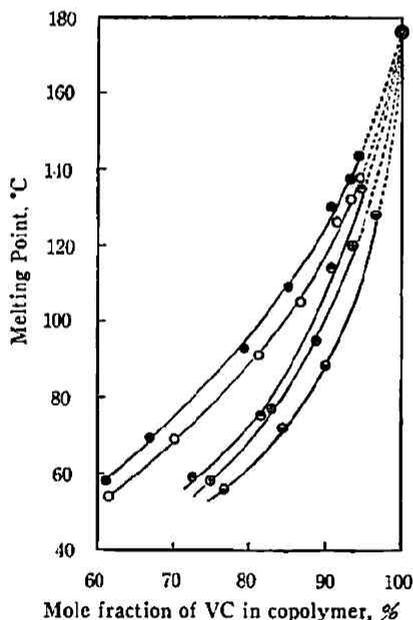


Fig. 19 The relationships between the melting point and copolymer composition
 ● : VC-PP (3,900 kg/cm²)
 ○ : VC-PP (1,950 kg/cm²)
 ▲ : VC-IB (3,900 kg/cm²)
 ⊕ : VC-IB (3,120 kg/cm²)
 ◑ : VC-IB (1,950 kg/cm²)

increased by increasing mole fraction of vinyl chloride in copolymers. And the intrinsic viscosities of vinyl chloride-propylene copolymers are always higher than those of vinyl chloride-isobutylene copolymers. The rise of molecular weight by pressure may be due to the accelerating effect of pressure on the propagation steps, closely resembling to those observed in the homopolymerization.

Fig. 19 shows the relationship between the melting point and the composition of copolymers. It shows the same phenomenon as the intrinsic viscosity, that is, the melting point is increased by pressure, and at constant pressure it is increased by increasing mole fraction of vinyl chloride in copolymers, ultimately approaching to that of polyvinyl chloride. And the melting points of vinyl chloride-propylene copolymers are always higher than those of vinyl chloride-isobutylene copolymers.

The resulting copolymers are soluble in polar solvents such as tetrahydrofuran, dimethyl formamide, cyclohexanone, nitrobenzene and acetone, but are insoluble in methanol, water and ether.

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