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THE PENULTIMATE EFFECT ON COPOLYMERIZATION UNDER HIGH PRESSURE

BY YOSHIAKI OGO AND TATSUYA IMOTO

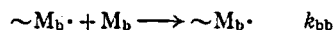
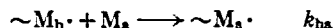
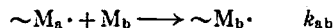
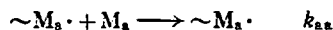
As one of investigations about the effects of pressure on chemical reactions, several copolymerizations, such as styrene-maleic anhydride, styrene-fumaronitrile, fumaronitrile-1,1-diphenylethylene, fumaronitrile-methylmethacrylate, fumaronitrile-vinylphenylether, fumaronitrile- α -methylstyrene, fumaronitrile-methylacrylate, fumaronitrile-*trans*-stilbene and maleic anhydride-cyclopentene, were studied under the pressure up to 7,000 kg/cm².

The copolymer compositions were affected by pressure with a few exceptions. The effect of pressure on these copolymerization reactions can be explained in terms of the penultimate effect, which has been proposed by Merz *et al.* to account for the influence of remote monomer unit on copolymerization. High pressure is generally presumed to be effective for the eliminating of the penultimate effect on copolymerization.

Introduction

The radical copolymerization under high pressures has been studied by several groups of workers in recent years and 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. The quantitative treatments of radical copolymerization have generally assumed that the reactivity of a growing free radical is determined solely by its terminal monomer unit.

In the ordinary copolymerization process, there are four possible ways in which a monomer can add.



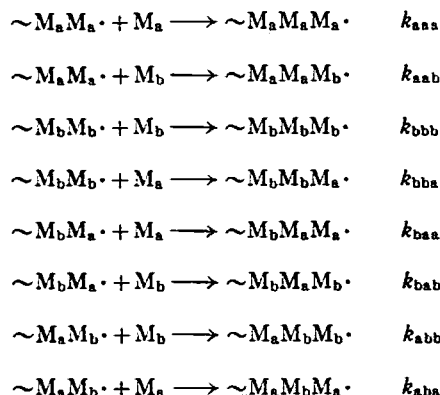
where $\sim M_a \cdot$ and $\sim M_b \cdot$ represent the chains ending in the M_a and M_b monomer unit, respectively, and the parameter, $r_1 = k_{aa}/k_{ab}$ and $r_2 = k_{bb}/k_{ba}$ are defined as monomer reactivity ratios.

A copolymer composition equation, which is derived from the foregoing four propagating steps in copolymerization, cannot satisfactorily represent the experimental results in some cases. In 1948 Merz *et al.*¹⁾ proposed that there are instances where the penultimate unit might influence the addition of

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1) E. Mertz, T. Alfrey and G. Goldfinger, *J. Polymer Sci.*, 1, 75 (1947)

monomers to the growing free radical. On these systems eight propagating steps were envisioned considering that the reactivity of a growing chain in copolymerization might be influenced by the nature of the penultimate unit.



An equation was derived, but no experimental demonstrations were given by the authors. It was further suggested that confirmation would be difficult to obtain. The equation unfortunately contained an error in published form. It is probable that this fact accounted for the lack of broad application initially.

Employing the nomenclature generally used, the corrected equation is

$$n = \frac{1 + \frac{r_1' x(r_1 x + 1)}{r_1' x + 1}}{1 + \frac{r_2' \frac{r_2 + x}{x}}{r_2' + x}} = \frac{d(M_a)}{d(M_b)} \quad (1)$$

$$r_1 = \frac{k_{aaa}}{k_{aab}}, \quad r_1' = \frac{k_{aaa}}{k_{bab}}$$

$$r_2 = \frac{k_{bbb}}{k_{bba}}, \quad r_2' = \frac{k_{abb}}{k_{aba}}$$

In 1951 Ham and Fordyce²⁾ reported that the chain rich in fumaronitrile (styrene as comonomer) and containing styrene as the last added unit exhibited a greatly decreased reactivity with fumaronitrile monomer. For this copolymerization the conventional copolymerization equation cannot be applied.

If $r_2 = r_2' = r_2''$ in equation (1), then

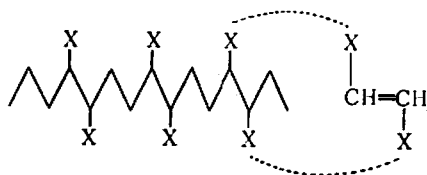
$$n - 1 = \frac{r_1' x(r_1 x + 1)}{r_1' x + 1}, \quad (2)$$

Barb³⁾ utilized this equation in interpreting the data of Ham and Fordyce with moderate agreement.

2) G. E. Ham and R. G. Fordyce, *J. Am. Chem. Soc.*, **73**, 1187 (1951)

3) W. G. Barb, *J. Polymer Sci.*, **11**, 117 (1953)

The clear implication was that the effects of repulsion could be partially treated in terms of the influence of a penultimate comonomer unit as follows.



Accordingly, an unusual pressure effect has been expected on these copolymerization systems because the volume of transition state would be abnormally large in order to interact between the adding monomer and the remote unit of polymer radical.

In an effort to quantitatively determine the penultimate effect, we have investigated some copolymerization under high pressure.

In the following section, some results obtained on copolymerization having the penultimate effect will be reported. However, it may be noticed that for simplicity's sake only the results and discussion without experimentals will be described in this paper.

Styrene-maleic anhydride system ⁴⁾

Fig. 1 shows the copolymer composition calculated from equation (2) at various pressures. The solid curves based on the r_1 , r_2 values listed in the Table 1 were the best fit for the experimental data. The ratio r_1'/r_1 which means the degree of the penultimate effect decreased from 2.8 to 1.7 with increasing pressure from 1 to 4,000 kg/cm².

The effect of pressure on the rate of chemical reactions can be related to the volume change from the initial state to the transition state with van't Hoff's equation,

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^\ddagger}{RT}, \quad (3)$$

where ΔV^\ddagger is an activation volume. Assuming that ΔV^\ddagger does not vary with pressure, equation (3) leads to

$$\ln \frac{(k)_P}{(k)_1} = -\frac{\Delta V^\ddagger}{RT}(P-1) \approx -\frac{\Delta V^\ddagger}{RT}P, \quad (4)$$

where $(k)_P$ and $(k)_1$ are the rate constants at P kg/cm² and the atmosphere, respectively.

By substituting $r_1 = k_{\text{StStSt}}/k_{\text{StStMA}}$ and $r_1' = k_{\text{MAStSt}}/k_{\text{MAStMA}}$ into equation (4), the following equations are obtained. In this case, subscript St and MA used instead of a and b represent styrene and maleic anhydride.

$$\left(\frac{\partial \ln r_1}{\partial P}\right)_T = \left[\frac{\partial \ln (k_{\text{StStSt}}/k_{\text{StStMA}})}{\partial P}\right]_T = -\frac{(\Delta V^\ddagger_{\text{StStSt}} - \Delta V^\ddagger_{\text{StStMA}})}{RT} \quad (5)$$

4) G. Enomoto, Y. Ogo and T. Imoto, *Makromol. Chem.*, **138**, 19 (1970)

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$$\left(\frac{\partial \ln r_1'}{\partial P}\right)_T = \left[\frac{\partial \ln(k_{MAStSt}/k_{MAStMA})}{\partial P}\right]_T = -\frac{(\Delta V^\ddagger_{MAStSt} - \Delta V^\ddagger_{MAStMA})}{RT} \quad (6)$$

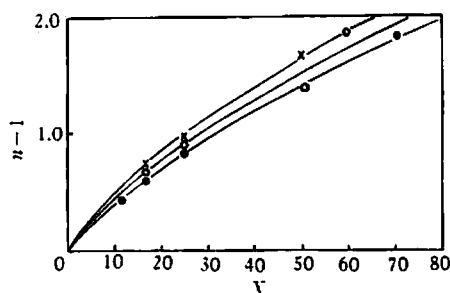


Fig. 1 Copolymer composition curves calculated from penultimate model

—x— 1 kg/cm², —○— 2000 kg/cm²
—●— 4000 kg/cm²

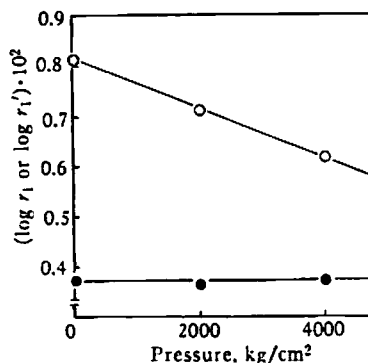


Fig. 2 Effect of pressure on the monomer reactivity ratios

—●— r_1
—○— r_2

Table 1 The monomer reactivity ratios calculated from penultimate model

Pressure (kg/cm ²)	r_1	r_1'	r_1'/r_1
1	0.023	0.065	2.8
2,000	0.022	0.055	2.5
4,000	0.023	0.042	1.7

According to equations (5) and (6), we can expect a difference of the activation volume on the copolymerization reactions. As shown in Fig. 2, a plot of $\log r_1$ or r_1' against pressure was linear. $\Delta V^\ddagger_{MAStSt} - \Delta V^\ddagger_{MAStMA}$ was calculated 2.6 cm³/mole. The constancy of the reactivity ratios with pressure lead to $\Delta V^\ddagger_{StStSt} = \Delta V^\ddagger_{StStMA}$.

Since the activation volume of the propagation reactions of styrene ΔV^\ddagger_{StSt} has been known to be -11.5 cm³/mole from the data of Nicholson and Norrish⁵⁾.

$$\Delta V^\ddagger_{StStSt} = \Delta V^\ddagger_{MAStSt} = -11.5 \text{ cm}^3/\text{mole}$$

$$\Delta V^\ddagger_{MAStMA} = \Delta V^\ddagger_{MAStSt} - 2.6 = -14.1 \text{ cm}^3/\text{mole}$$

These facts indicate that the copolymerization reaction with maleic anhydride and polymer chain which possess the maleic anhydride unit preceding the active styrene chain end especially increase with pressure, $\Delta V^\ddagger = -14.1 \text{ cm}^3/\text{mole}$.

On the other, the following equations were derived from the preceding penultimate model equation by Miller and Nielsen⁶⁾.

$$P_{StStSt} = r_1 x (r_1 x + 1), \quad P_{StStMA} = 1 / (r_1 x + 1)$$

$$P_{MAStSt} = r_1' x / (1 + r_1' x), \quad P_{MAStMA} = 1 / (1 + r_1' x)$$

$$P_{MAStMA} = r_2 x / (x + r_2), \quad P_{MAStMA} = x / (x + r_2)$$

5) A. E. Nicholson and R. G. W. Norrish, *Discuss. Faraday Soc.*, **22**, 97, 104 (1956)6) R. L. Miller and L. E. Nielsen, *J. Polymer Sci.*, **46**, 303 (1960)

$$P_{\text{SiMAMA}} = r_2' / (x + r_2'), \quad P_{\text{SiMARI}} = x / (x + r_2')$$

where P_{MASiMA} is the instantaneous probability of the adding monomer of type MA to a growing chain ending in MA-St.

The probability of occurrence among all the sequences of type MA of a sequence exactly m units long is $W_n(m)$

$$W_n(m) = P_{\text{MASiSt}} P_{\text{SiSiMA}} P_{\text{SiSiSt}}^{m-2} \quad m \geq 2 \quad (7)$$

$$W_n(m) = P_{\text{MASiMA}} \quad m = 1 \quad (8)$$

At the molar ratio (maleic anhydride/styrene), $x=150$, pressure 1 and 4,000 kg/cm², the sequence distribution of copolymer was calculated from equations (7) and (8), as shown in Fig. 3. When the effect of unit other than terminal on the reactivity of a growing chain with adding monomer is considered ($m=1$), the sequence distribution of copolymer obtained under 4,000 kg/cm² increased as compared with the sequence distribution of copolymer obtained under atmosphere.

Ang and Harwood⁷⁾ investigated the infrared spectra of styrene-maleic anhydride copolymer. On the basis of these data obtained, the authors mentioned that the phenyl absorption at 700 cm⁻¹ was found to be independent of sequential environment and this absorption proved useful in determining the copolymer compositions. In contrast, the phenyl absorption at 759 cm⁻¹ proved to be sensitive to the sequential environment and use was made of this feature to measure sequence distribution in the copolymer.

The ratio (A_{759}/A_{700}) of the absorbance at 759 cm⁻¹ to that at 700 cm⁻¹ for a given copolymer was used to calculate the fraction (f_{MASiMA}) of the styrene unit centered in MA-St-MA triads in copolymers.

$$f_{\text{MASiMA}} = \frac{a - A_{759}/A_{700}}{a - c} \quad (9)$$

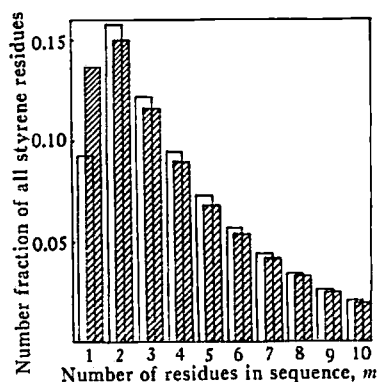


Fig. 3 Number distribution of styrene residues calculated from penultimate model, $x=150$
 □: 1 kg/cm², ■: 4,000 kg/cm²

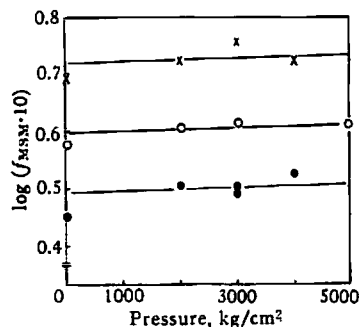


Fig. 4 Effect of pressure on f_{MSM}
 ● $x=43.1$
 ○ $x=25.3$
 × $x=12.6$

7) T. L. Ang and H. J. Harwood, *Am. Chem. Soc., Polymer Preprints*, **5**, No. 1, 306 (1964)

Equation (9) can be written by the following equation (10), where $a=0.725$, the A_{753}/A_{700} value observed for polystyrene and where $c=0.110$, the A_{753}/A_{700} value observed for alternating copolymers.

$$f_{\text{MAStMA}} = [0.725 - (A_{753}/A_{700})]/0.615 \quad (10)$$

Fig. 4 shows the dependence of $\log f_{\text{MAStMA}}$ on the reaction pressure. Evidently, the value of f_{MAStMA} increased with pressure. These facts suggest that a high pressure favored the formation of MA-St-MA type copolymer.

It may be concluded from the results of these investigations that the copolymerization reaction with maleic anhydride and the polymer chain which possess the maleic anhydride unit preceding the active styrene chain end especially increase with pressure.

Styrene-fumaronitrile system⁸⁾

The penultimate effect would be due to the steric or polar strain between substituents of polymer radical and monomer. If the major factor on the penultimate effect is the polar strain between them, the force on this strain should obey Coulomb's equation:

$$F = \left(\frac{1}{4\pi\epsilon} \right) \left(\frac{q_1 q_2}{r^2} \right) \quad (11)$$

where ϵ is the dielectric constant of the solvent, r the distance between substituents and q_1, q_2 the electric charge. On the styrene-fumaronitrile copolymerization system, the value of F is relatively small in pure acetone as the solvent. The reason is that the cyano groups are so dispersed that the mean value of r is large since the copolymers are easily soluble in this solvent and ϵ is also large (20.7, 25°C). On the other hand, the value of F in poor solvent (acetone-benzene mixture) is relatively large compared with in acetone since the average distance between both cyano groups and the dielectric constant are small. From these considerations, it seemed reasonable to assume that the copolymer compositions in such two kinds of the solvents are not consistent with each other, the penultimate effects are shown markedly in acetone-benzene mixture compared with in pure acetone. The results of experiments are shown in Fig. 5. It has been found from Fig. 5 that the copolymer composition did not depend on the kind of the solvent and the major factor of the penultimate effect are due to the steric hindrance between the monomer and the cyano group presented near the end of polymer radical.

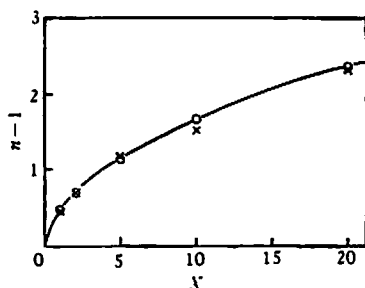


Fig. 5 Styrene-fumaronitrile copolymer composition curve (atmospheric pressure)

The mole ratio of monomer to solvent is 1/12

○: in acetone,

×: in acetone-benzene equimolar mixture

8) G. Enomoto, Y. Ogo and T. Imoto, *Nippon Kagaku Zasshi*, (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **91**, 804 (1960)

In the copolymerization of styrene and fumaronitrile, the fumaronitrile content of copolymer cannot be increased beyond 40 mole % regardless to the concentration of fumaronitrile in the monomer. In this behavior, fumaronitrile differs from most monomers incapable of adding to themselves, such as maleic and citraconic anhydride. In copolymerization with most monomers these latter rapidly approach the level of 50 mole % content in the copolymer. If there is no effect due to the preceding unit (behind the penultimate unit) any significant value of k_{FNStFN} should lead to the alternating copolymer FN-St-FN-St-FN-St-FN. It follows that k_{FNStFN} so defined is of limited importance in styrene-fumaronitrile copolymerization. Subscript FN represents fumaronitrile.

Molecular models of styrene-fumaronitrile copolymers shows that a 1-1 copolymer would impose improbable requirements of steric and polar strain. However, the structure



where FN-St-St units alternate with FN-St units, allows resonable conformation of substituents to impose minimum strain and dipole interaction consistent with copolymer existence. This structure contains precisely 40% fumaronitrile corresponding closely to the limiting experimental value.

It follows that there is a substantial influence in the copolymerization of monomers where polar and steric restrictions exist due to the units beyond the penultimate. Thus, if

$$\frac{k_{\text{StStFNStSt}}}{k_{\text{StStFNStFN}}} = \frac{k_{\text{FNStFNStSt}}}{k_{\text{FNStFNStFN}}}$$

it is possible to account for the observed results in styrene-fumaronitrile copolymerization.

From the above considerations, the following pen-penultimate equation (12) which best demonstrates the observed results with styrene-fumaronitrile copolymerization was derived by Ham *et al.*⁹⁾. The essence of the progression is that r' and r_2' in penultimate equation are replaced by $r_1''(r_1'x+1)/(r_1''x+1)$ and $r_2''(r_2'x+1)/(r_2''x+1)$, respectively. Of course, if r_2 , r_2' and r_2'' may be equated to zero, further simplification are possible.

$$n-1 = \left[\frac{r''x(r'x+1)}{r''x+1} \right] (rx+1) / \left[\frac{r''x(r'x+1)}{r''x+1} \right] + 1 \quad (12)$$

In this case r ($k_{\text{StStSt}}/k_{\text{StStFN}}$) is for additions to the growing radical —St-St·, there is no influence exerted by units more remote. However, r' ($k_{\text{FNStStFNStSt}}/k_{\text{FNStStFNStFN}}$ or more precisely $k_{\text{StStFNStSt}}/k_{\text{StStFNStFN}}$) and r'' ($k_{\text{FNStFNStSt}}/k_{\text{FNStFNStFN}}$) is for additions to units ending in —FN-St·, there is sub-

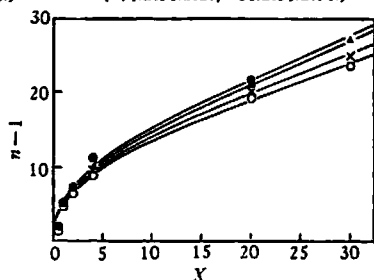


Fig. 6 Styrene-fumaronitrile copolymer composition curves calculated from pen-penultimate model (monomer: 50.00, azobisisobutironitrile: 0.03, acetone: 49.97 wt %)
 ●: 1kg/cm² ▲: 2,000kg/cm²
 ×: 3,000kg/cm² ○: 4,000kg/cm²

9) G. E. Ham, *J. Polymer Sci.*, **45**, 169 (1960)

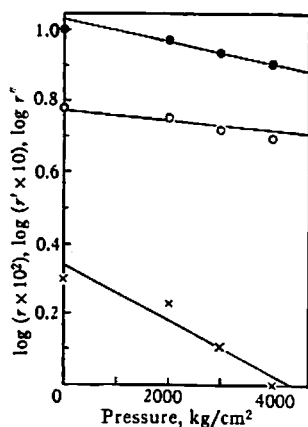
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Table 2 Effect of pressure on r , r' and r''

Pressure (kg/cm ²)	r	r'	r''
1	0.060	1.00	2.0
2,000	0.057	0.94	1.7
3,000	0.053	0.87	1.3
4,000	0.050	0.80	1.0

monomer: 50.00wt%, azobisisobutyronitrile: 0.03wt%, acetone: 99.97 wt %, at 60°C

Fig. 7 Effect of pressure on r , r' and r'' ○: $r = k_{\text{StStSt}}/k_{\text{StStStFN}}$ ●: $r' = k_{\text{FNStStFNStSt}}/k_{\text{FNStStFNStFN}}$ ×: $r'' = k_{\text{FNStStFNStSt}}/k_{\text{FNStStFNStFN}}$

stantial influence by more distant units.

The copolymer composition curves calculated from equation (12) are shown in Fig. 6. Evidently it depends on pressure. The pressure dependency of r , r' and r'' calculated by the least square mean method (Table 2) were shown Fig. 7 as the van't Hoff plot. The differences of the activation volume on the copolymerization reactions were calculated from Fig. 7 as follows,

$$\Delta V^*_{\text{StStSt}} - \Delta V^*_{\text{StStFN}} = 1 \text{ cm}^3/\text{mole}$$

$$\Delta V^*_{\text{FNStStFNStSt}} - \Delta V^*_{\text{FNStStFNStFN}} = 2 \text{ cm}^3/\text{mole}$$

$$\Delta V^*_{\text{FNStFNStSt}} - \Delta V^*_{\text{FNStFNStFN}} = 5 \text{ cm}^3/\text{mole}$$

Since the activation volume of the propagation reactions of styrene has been known to be $-11.5 \text{ cm}^3/\text{mole}$ ⁵⁾ as described in preceding section, the activation volumes of the copolymerization reaction were obtained.

$$\Delta V^*_{\text{p}} = \Delta V^*_{\text{StStSt}} = -11.5 \text{ cm}^3/\text{mole}$$

$$\Delta V^*_{\text{StStFN}} = -12.5 \text{ cm}^3/\text{mole}$$

$$\Delta V^*_{\text{FNStStFNStSt}} = \Delta V^*_{\text{FNStFNStSt}} = \Delta V^*_{\text{StStSt}}$$

$$\Delta V^*_{\text{FNStStFNStFN}} = -13.5 \text{ cm}^3/\text{mole}$$

$$\Delta V^*_{\text{FNStFNStFN}} = -16.5 \text{ cm}^3/\text{mole}$$

It may be concluded from the results of this experiment that the copolymerization reaction between the polymeric radical possessing fumaronitrile as penultimate unit and the fumaronitrile increases with pressure, especially the influence of pressure on the addition of the FN-St-FN-St chain end to FN is the largest, considering from the magnitude of the value of activation volume as $|ΔV^*_{\text{FNSiFNSiFN}}| > |ΔV^*_{\text{FNSiSiFNSiFN}}| > |ΔV^*_{\text{FNSiFNSiSi}}|$.

Fumaronitrile-1,1-diphenylethylene system⁸⁾

A number of 1,2-disubstituted ethylene do not polymerize readily, if at all, at the ordinary pressure in the presence of radical-producing initiators. From the consideration of the interference of fumaronitrile monomer on copolymerization as the penultimate effect, it seems most reasonable to conclude that fumaronitrile does not homopolymerize.

A similar result was obtained by Newitt and his colleagues¹⁰⁾ with 1,1-diphenylethylene. After the reaction at 5,000 kg/cm² for prolonged periods at 120°C, a solid product was isolated and identified as a dimer, and 1,1-diphenylethylene would not also homopolymerize.

However, fumaronitrile and 1,1-diphenylethylene gave only a low yield of copolymer and the conversion increased with pressure in our experimental conditions. The copolymer was obtained yield of 0.4% at 90°C under 100 kg/cm² for 67 hours. On the other hand, the copolymer was obtained readily under 3,000~5,000 kg/cm².

The IR spectra of the copolymer obtained are shown in Fig. 8. Strong absorption bands of 2,240 cm⁻¹ due to cyano group, 1,700 cm⁻¹ due to carbonyl group and 1,603, 759 and 700 cm⁻¹ due to phenyl group were observed. Since the absorption bands of 2,240 cm⁻¹ was essentially weak even if fumaronitrile was present in excess, fumaronitrile would polymerize as the shape of >C=C<. The strong peak of the spectra at 1,700 cm⁻¹ is carbonyl band from benzoylperoxide. The molecular weight of copolymer would be fairly small from the fact that this absorption is very sharp even when the concentration of the copolymer are relatively low. The peaks at 1,603, 759 and 700 cm⁻¹ are due to the phenyl group of 1,1-diphenylethylene and benzoylperoxide.

Fig. 9 shows the molecular weight plotted against nitrogen content of copolymer. This copolymerization is so complicated that its copolymerization mechanism cannot be imagined. However,

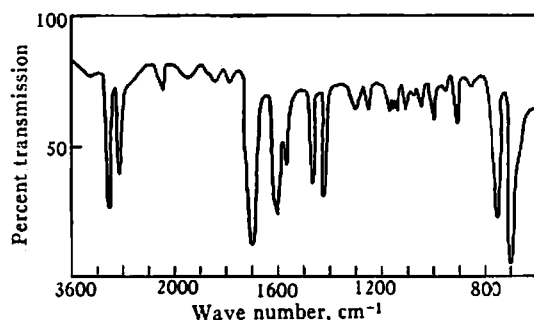


Fig. 8 IR spectra of fumaronitrile-1,1-diphenylethylene copolymer (fumaronitrile: 0.0568, 1,1-diphenylethylene: 0.0568, tetrahydrofuran: 0.0123, benzoylperoxide: 0.021 mole, 90°C, 3,000 kg/cm²)

10) R. H. Sapiro, R. P. Linstead and D. M. Newitt, *J. Chem. Soc.*, 1937, 1784

considering the facts that the dissociation of benzoylperoxide decreases with pressure and that tetrahydrofuran as solvent is the typical chain transfer agent, the value of nitrogen contents was plotted against the molecular weight of copolymer as shown in solid line in Fig. 9. These relations were calculated from the following molecular formula.

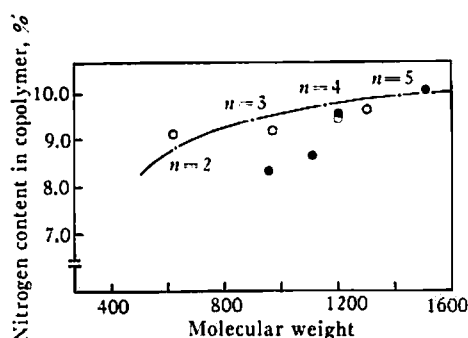
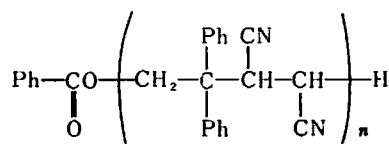


Fig. 9 The relation between nitrogen content and molecular weight in fumaronitrile-1,1-diphenylethylene copolymer at 90°C

○: Monomer concentration is constant (mole ratio of fumaronitrile to 1,1-diphenylethylene is 1 : 1) and pressure is 3,000, 3,500 and 5,000 kg/cm² from left to right, respectively.

●: Pressure is constant (5,000 kg/cm²) and monomer concentration is 0.27, 0.36, 0.58 and 0.73 fumaronitrile fraction from left to right, respectively.

It was found from Fig. 9 that the molecular weight of copolymer varied from 600 to 1,300 with increase of pressure from 3,000 up to 5,000 kg/cm².

The propagation reaction on this copolymerization system would depend on the reaction between 1,1-diphenylethylene radical end and fumaronitrile monomer in consideration of radical stability. Accordingly, the penultimate effect occurs on this system. As is well known, when a number of compounds are allowed to polymerize readily under high pressure, the molecular weight increases. This copolymerization system, especially is affected by pressure as shown in Fig. 9 with regard to pressure dependency on nitrogen content. The penultimate effect of fumaronitrile monomer is presumed to disappear readily under high pressure.

The conversion of fumaronitrile monomer shown in Fig. 10 was calculated from the yield and elementary analysis on the nitrogen content of the copolymer in a 1 : 1 molar ratio of monomer and various copolymerization time. The apparent overall rate constants at each pressure were evaluated from the slope of conversion-time curves. These rate constants were plotted according to van't Hoff's equation (4) in Fig. 11. The overall activation volumes on this copolymerization system were determined from the slope of this line in Fig. 11 as -25 cm³/mole. Strict comparison is not feasible on this value of activation volume, because the copolymer did not give sufficient yield below 3,000 kg/cm², and the activation volume under atmosphere could not be calculated exactly. However, the value of activation volume under atmospheric pressure on this copolymerization system would be considerably

larger than the values expected for customary copolymerization reaction that is recognized in the range from -10 to $-20\text{ cm}^3/\text{mole}$. This discrepancy may be responsible for the penultimate effect.

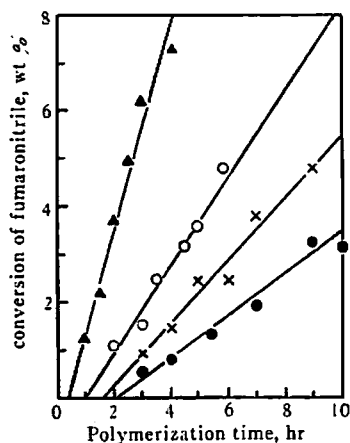


Fig. 10 The overall copolymerization rates for fumaronitrile-1,1-diphenylethylene system (monomer: 5.56, tetrahydrofuran: 1.23, benzoylperoxide: 0.002 mole, 90°C)
 Δ : 5,000 kg/cm², \circ : 4,000 kg/cm²
 \times : 3,500 kg/cm², \bullet : 3,000 kg/cm²

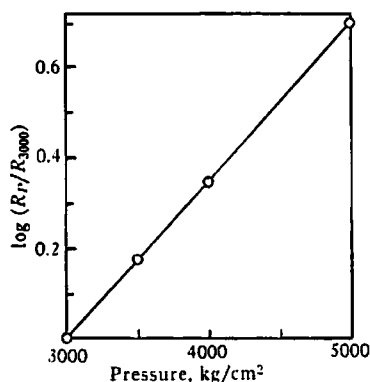


Fig. 11 van't Hoff plots for fumaronitrile-1,1-diphenylethylene system

The product having 2 or 3 monomeric units would be present in the copolymer mixture because of their low molecular weight. In this case, the penultimate effect between polymer radical and initiator fragment should be taken into account. There is no definite experimental evidence that the penultimate effect on the initiator fragment reported for the ethylene-carbon tetrachloride telomerization system¹¹⁾ are negligible in this case. However, the pressure dependency on the molecular weight is fairly large compared with the value in the literature. For example, the molecular weights of trichloroethylene-vinylacetate copolymer are 1,550~1,630 at atmosphere and 2,150~2,410 at 4,000 kg/cm²¹²⁾, and it has been generally assumed on high pressure polymerization that the reason for the molecular weight increase with pressure is that the polymerization rates are probably diffusion-controlled and the rate of termination will decrease as the pressure is raised. In this experiment, the effect of pressure on the molecular weight is not so marked as for the usual copolymerization because of the low molecular weight. Therefore, as in the case of fumaronitrile-1,1-diphenylethylene copolymerization, the penultimate effect of fumaronitrile is presumed to readily disappear under high pressure.

Fumaronitrile-methylacrylate, -vinylphenylether, - α -methylstyrene and -methylmethacrylate system⁸⁾

11) C. Walling, "Free Radical in Solution", p. 257, John Wiley and Sons (1957)

12) M. G. Gonikberg, R. I. Baikova and V. M. Zhulin, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 1164 (1962)

The Penultimate Effect on Copolymerization under High Pressure

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Fumaronitrile copolymerized with methylacrylate and vinylphenylether as vinyl type comonomer and α -methylstyrene and methylmethacrylate as vinylidene type comonomer. The experimental conditions and results, together with those of other comonomers such as styrene and 1,1-diphenylethylene, are given in Tables 3 and 4. All copolymerization reactions were done the same conditions.

Fumaronitrile content in the copolymer with styrene increased with pressure. In the case of copolymerization with methylacrylate, the copolymer composition was not affected by pressure. The

Table 3 Copolymerization of fumaronitrile with vinyl type comonomer,
molar ratio of comonomer 1 : 1

Comonomer	Total comonomer (wt%)	Azobisisobutyronitrile (wt%)	Acetone (wt%)	Pressure (kg/cm ²)	Temperature (°C)	Nitrogen in copolymer (wt%)	Fumaronitrile in copolymer (mole %)
Styrene	50.1	0	49.9	1	60	11.74	39.86
	50.1	0	49.9	2,000	60	12.57	41.80
	50.1	0	49.9	7,000	60	12.68	42.14
Methylacrylate	43.3	0.21	56.3	1	54	3.58	10.88
	43.3	0.21	56.5	2,000	54	3.40	10.33
	43.3	0.21	56.5	3,000	54	3.47	10.54
	43.3	0.21	56.5	4,000	54	3.87	11.76
Vinylphenylether	40.5	0.19	59.3	1	54	13.65	48.6
	40.5	0.19	59.3	4,000	54	13.88	49.4
	40.5	0.19	59.3	5,000	54	—	—

Table 4 Copolymerization of fumaronitrile with vinylidene type comonomer,
molar ratio of comonomer 1 : 1

Comonomer	Total comonomer (wt%)	Initiator (wt%)	Solvent (wt%)	Pressure (kg/cm ²)	Temperature (°C)	Nitrogen in copolymer (wt%)	Fumaronitrile in copolymer (mole %)
Methylmethacrylate	51.3	azobisisobutyronitrile	acetone				
	51.3	0.003	48.7	1	60	2.75	9.61
	51.3	0.003	48.7	2,750	60	2.54	8.89
α -Methylstyrene	51.3	0.003	48.7	4,650	60	1.98	6.96
		azobisisobutyronitrile	acetone				
	48.7	0.12	51.2	1	50	12.89	45.87
	48.7	0.12	51.2	2,000	50	12.71	45.33
	48.7	0.12	51.2	2,450	50	12.80	45.60
	48.7	0.12	51.2	4,100	50	12.91	45.93
Diphenylethylene		benzoylperoxide	tetrahydrofuran				
	43.4	3.0	53.6	3,000	90	9.10	50
	43.4	3.0	53.6	3,500	90	9.20	50
	43.4	3.0	53.6	4,000	90	9.36	50
	43.4	3.0	53.6	5,000	90	9.65	50

reason for this result is that the penultimate effect is negligible since the fumaronitrile content in this copolymer is only 10%. The fumaronitrile content of copolymer was 48~50% when the copolymerization with vinylphenylether was carried out. Alternating copolymer is presumed to be readily formed under these conditions since both comonomers scarcely homopolymerize. These facts suggest that the penultimate effect is present in this system. It was found, as might have been expected, that the fumaronitrile content of the copolymer increased with pressure.

However, the pressure effect of the copolymerization with vinylidene type comonomer was somewhat different from those with vinyl type comonomer, as shown in Table 4. The penultimate effect was expected since the composition of the copolymer with α -methylstyrene are very similar to alternating copolymer compared with those of copolymer with styrene. However, fumaronitrile content of copolymer was not affected by pressure. The fumaronitrile content of under 10% in the copolymer with methylmethacrylate is lower than this of copolymer with methylacrylate and the fumaronitrile content of this copolymer decreased with pressure. The reason for this unfavorable result is probably as follows. α -Methylstyrene depolymerizes readily because of their low ceiling temperature. In such a monomer, depolymerization is suppressed and chain propagation reaction accelerated by pressure. Accordingly, it seems most reasonable to conclude that the elimination of the penultimate effect by pressure was balanced with the acceleration of the propagation by pressure.

The penultimate effect is negligible in the case of copolymerization with methylmethacrylate because of low fumaronitrile content. However, from the consideration of reverse tendency about fumaronitrile content with pressure, it has been suggested that the effect of pressure on the propagation reaction of methylmethacrylate is fairly larger than those of other vinyl monomers. Some attempts have been made to estimate the pressure dependency on the propagation reaction from those on the chain transfer reaction¹³⁾, no direct measurement on the pressure dependency of the propagation reaction about methylmethacrylate has ever been reported in the literature. A more detailed study about the elementary reaction on polymerization under high pressure may offer a valuable information on the penultimate effect on copolymerization.

The penultimate effect on the copolymerization with 1,1-diphenylethylene would appear, since both comonomers, as well as vinylphenylether, did not homopolymerize and form alternating copolymer. In Table 4, fumaronitrile content of the copolymer is not affected by pressure. The value in this table, however, shows the estimation calculated from the molecular weight without initiator chain end. Considering the fact discussed in the preceding section that the molecular weight increases with pressure and the overall activation volume is fairly large on this copolymerization system, the copolymer having a large amount of fumaronitrile based on molecular weight including the initiator chain end is presumed to be readily formed under high pressure.

The above mentioned results were listed in Table 5. The copolymerization of fumaronitrile with styrene, 1,1-diphenylethylene and vinylphenylether having small e -value proceeded at sufficient rate under high pressure and the composition of the copolymers were very similar to the composition of alternating copolymer. The penultimate effect on the copolymerization systems with fumaronitrile

13) V. M. Zhulin, M. G. Gonikberg, A. L. Goff and V. N. Zagorbinina, *Vysokomol. Soed.*, A11, 777 (1969)

showed a tendency to decrease with increasing pressure. High pressure is presumed to be effective for eliminating the penultimate effect on the copolymerization.

Table 5 Effect of pressure on the fumaronitrile content in copolymer

Comonomer	Fumaronitrile content
Styrene	increase
Vinylphenylether	increase
Methylacrylate	none
α -Methylstyrene	none
1,1-Diphenylethylene	increase
Methylmethacrylate	decrease

Fumaronitrile—*trans*-stilbene system¹⁴⁾

The copolymer obtained was a yellowish substance and the IR spectra of the copolymer are shown in Fig. 12. On the basis of these spectra, it seemed reasonable to assume that fumaronitrile copolymerizes as the shape of $\begin{array}{c} \text{CN} \\ | \\ -\text{C}-\text{C}- \\ | \\ \text{CN} \end{array}$ and does not copolymerize by cyano bond since cyano group absorption is strongly recognized at $2,240\text{cm}^{-1}$. The peak of the spectra at $1,700\text{cm}^{-1}$ is the carbonyl band from benzoylperoxide and the absorptions at $1,603$, 759 and 700cm^{-1} show the phenyl group from the *trans*-stilbene.

The variations of copolymer yield with polymerization time at 90°C are shown in Fig. 13. The rate of copolymerization was accelerated by pressure. However, the yields were considerably small

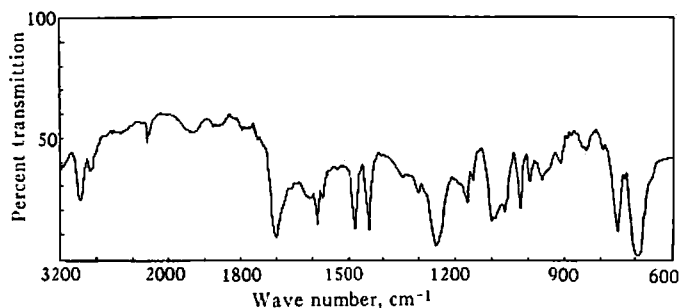
Fig. 12 IR spectra of fumaronitrile—*trans*-stilbene copolymer

Table 6 Elementary analysis and molecular weight of copolymer

Pressure (kg/cm ²)	Elementary analysis (%)				Molecular weight
	C	H	O	N	
100	81.97	5.47	4.35	8.21	2,000
2,000	81.99	5.44	3.99	8.53	2,500
3,000	81.57	5.47	4.24	8.72	1,600
4,000	81.28	4.47	4.52	8.73	2,000

14) G. Enomoto, Y. Ogo and T. Imoto, *Memoirs of the Faculty of Eng. Osaka City Univ.*, **11**, 61 (1970)

and the effect of polymerization time was not so marked as for the effect of pressure.

The result of elementary analysis and molecular weight of copolymer is shown in Table 6. The copolymers are all of very low molecular weight and the molecular weight are not affected by pressure. These facts suggest that this copolymerization system is different from the customary copolymerization using radical initiator. However, there is no definite evidence that this is due to the different copolymerization mechanism.

As shown in Table 6, the content of nitrogen in the copolymer increased with pressure. These facts indicate that the fumaronitrile rich copolymer is easy to be formed under high pressure because its penultimate effect tends to disappear with pressure and is in agreement with our previous conclusion.

Maleic anhydride-cyclopentene system¹⁵⁾

The copolymer composition curves on this system are shown in Fig. 14. The penultimate effect is also expected on this system. Detailed studies are in progress.

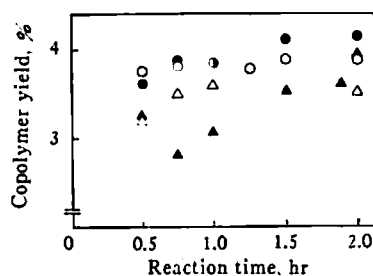


Fig. 13 Effect of pressure on copolymerization yield

▲: 100kg/cm² △: 2,000kg/cm²
●: 3,000kg/cm² ○: 4,000kg/cm²

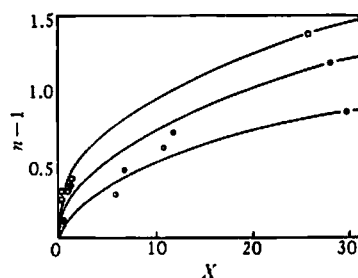


Fig. 14 Copolymer composition curves for maleic anhydride-cyclopentene system at 60°C, in benzene solution, azobisisobutyronitrile as initiator

○: 1kg/cm² ●: 2,000kg/cm²
■: 4,000kg/cm²

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*Faculty of Engineering
Osaka City University
Sugimotocho, Sumiyoshi
Osaka, Japan*

15) M. Yokawa, Y. Ogo and T. Imoto, "Oral Presentation at 13th High Pressure Conference", Tokyo (1971); *Makromol. Chem.*, in press