

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 38, NO. 2, 1968

PRESSURE EFFECT ON THE KINETICS OF POLYMERIZATION I

Bulk Polymerization of Vinyl Chloride, Propylene and Butadiene

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The bulk polymerization of vinyl chloride with benzoyl peroxide as the initiator, was carried out at 40° to 70°C under high pressures in the range of 1,170 to 3,900 kg/cm².

These results were considered in comparison with those of radical polymerization of propylene (with benzoyl peroxide as the initiator at 80° to 100°C, 2,800 to 4,000 kg/cm²) and thermal polymerization of butadiene (at 50° to 95°C, 1,100 to 5,000 kg/cm²), from the kinetic viewpoint. In all cases, it was observed that the polymerization reaction was not preceded by any induction periods, and the polymer yields increased linearly with the reaction time throughout the comparatively long runs.

The rate of polymerization was accelerated by increasing pressure and temperature. From the apparent initial rate, the activation energies (E), the activation volumes ($\Delta V^\ddagger$) and the activation entropies ($\Delta S^\ddagger$) were calculated, and the following values were obtained: i) for vinyl chloride, $E=20.6$ to 24.0 kcal/mole, $\Delta V^\ddagger=-4.6$ to -10.4 cm³/mole and $\Delta S^\ddagger=-15.1$ to -2.3 e.u., ii) for propylene, $E=11.9$ to 12.3 kcal/mole, $\Delta V^\ddagger=-9.0$ to -12.7 cm³/mole and $\Delta S^\ddagger=-46.4$ to -42.0 e.u., iii) for butadiene, $E=15.1$ to 19.2 kcal/mole, $\Delta V^\ddagger=-8.8$ to -17.2 cm³/mole and $\Delta S^\ddagger=-38.0$ to -24.3 e.u.

The activation entropies and activation energies were increased by increasing pressure, but the activation volumes showed negative values. Then, the accelerating effect of pressure on the polymerization reaction is entirely ascribed to the increase in the activation entropy which overcomes the rise of activation energy. The latter is considered to retard the rate of the reaction.

From the X-ray diffraction and infrared absorption analyses, following subjects were concluded,

1. The polyvinyl chloride obtained was not different from the ordinary polyvinyl chloride, but the degree of polymerization was increased by increasing pressure, i.e., $\bar{P}=1,470$ to $1,900$ at 50°C.
2. The polypropylene obtained was atactic polypropylene. The degree of polymerization was very low and was unaffected by pressure, i.e., $\bar{P}=14$ to 65 at 80° to 100°C.
3. The polybutadiene obtained was insoluble in the ordinary solvents of rubbers, and was a crosslinked elastic polymer.

Introduction

Organic reactions under high pressures have been studied by many investigators, and the experi-

(Received December 10, 1968)

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ment under high pressure is a useful method for the investigation on the reaction kinetics and mechanism.

After 1929 when Conant reported¹⁾⁻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 kinetic study on the polymerization of the liquefied monomer gases which could be polymerized only under high pressure. From these points of view, we reported previously some results of the investigation on the thermal bulk polymerization of butadiene under high pressure⁴⁾.

The polymerizations of vinyl chloride have been widely studied by many investigators, and now being studied in order to obtain more excellent characteristic polymers. However, the studies on the polymerization under high pressure are scarcely performed, except the report by Imoto *et al.*⁵⁾. They found that vinyl chloride could be thermally polymerized under high pressure, but in our preliminary experiments no polymer could be obtained under such a condition as that of them.

Breitenbach and his collaborator⁶⁾ found that very purely purified vinyl chloride could not polymerize even at 100°C. Consequently, the discrepancy of Imoto's and our results may be attributed to the difference of the purification method of the monomer.

Propylene does not polymerize by a radical process under the low pressure of the order of several tenths of an atmosphere⁷⁾. This fact may be elucidated by the transfer of the kinetic chain to monomer with the formation of inactive allyl radicals. However, it was reported that at high pressure and temperature, *i.e.* at 7,000 atm and 100° or 200°C, propylene was polymerized in the presence of radical initiators, and the resulting polymer had the isotactic configuration⁸⁾.

On the other hand, the radiation-induced polymerization of propylene at high pressure was studied in the pressure range of 5,000 to 16,000 atm at the temperature of 21°, 48° and 83°C, and found that the polymer obtained was an atactic polypropylene⁹⁾.

Zharov *et al.*¹⁰⁾ investigated the solution polymerization of propylene with radical initiators in the pressure range of 3,000 to 8,000 atm. They found that the rate of polymerization was increased with pressure, and the change of the degree of polymerization in the pressure range investigated was negligible. The same results were obtained in our experiments on the bulk polymerization of propylene with benzoyl peroxide as the initiator¹¹⁾.

In the present work, the author will report the results of the kinetic experiment on the bulk

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- 4) J. Osugi, K. Hamanoue and S. Hirayama, *This Journal*, **35**, 103 (1966)
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- 6) J. W. Breitenbach and W. Thury, *Experientia*, **3**, 281 (1947)
- 7) K. E. Weale, *Quart. Rev.*, **16**, 267 (1962)
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- 10) A. A. Zharov, A. L. Berlin and N. S. Enikolopyan, *J. Polymer Sci.*, **C No. 16**, 2313 (1967)
- 11) J. Osugi, K. Hamanoue and T. Tachibana, *This Journal*, **38**, 96 (1968)

polymerization of vinyl chloride with benzoyl peroxide as the initiator and some considerations given to the effect of pressure on the polymerization reactions in comparison with those of radical polymerization of propylene¹¹⁾ and thermal polymerization of butadiene¹²⁾.

Experimentals

Materials

Vinyl chloride monomer was passed through soda lime and calcium chloride in order to eliminate hydrogen chloride and water, and distilled four times by the trap-to-trap vacuum distillation method using dryice-methanol (-78°C) and liquid nitrogen (-190°C) baths.

Extra pure benzoyl peroxide (BPO) used as the initiator was recrystallized with chloroform and methanol and dried in vacuum.

Apparatus

As the vinyl chloride monomer is gas at room temperature, a special capsule was used to make it react in liquid phase. Fig. 1 shows the reaction capsule. It is made of stainless steel, and the

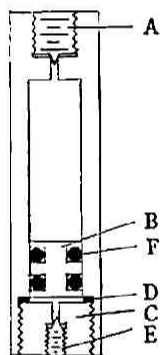


Fig. 1 Reaction capsule

- A: cap
- B: piston
- C: plug
- D: packing
- E: closure screw
- F: O-ring

monomer in the cylinder is maintained in liquid state at room temperature by screwing in the cap (A) and supporting the piston (B) by the plug (C). Before the liquefied monomer gas is charged into the capsule, it is necessary to cool the capsule. In this procedure, the O-ring fixed in the piston (B) shrinks and does not work as a seal, and the monomer leaks out through the interspace between the piston and the cylinder. But this leakage can be prevented with the packing (D) and the closure screw (E).

Procedures

The reaction capsule which contained 3 mg BPO was immersed in the dryice-methanol bath and cooled. Withdrawing the cap (A), the previously cooled monomers (3.5 g vinyl chloride) were charged by the glass hypodermic syringe. As soon as the cap (A) was screwed in, the capsule was immersed in a room temperature methanol bath. Confirming no monomer leakage, the closure screw (E) was withdrawn.

Ethyl alcohol used as the pressure transmitting medium is introduced through the hole of the closure screw (E) into the capsule, and the monomers in the capsule can be compressed by the displacement of the piston (B). Using this method, it is unnecessary to cool the pressure transmitting medium and the high pressure vessel before putting the capsule into the vessel. Hence, it becomes easier to bring the reaction system to the desired temperature. The reaction temperature was kept constant within $\pm 1^\circ\text{C}$ and measured by an iron-constantan thermocouple inserted in the pressure vessel.

The piston-cylinder type high pressure vessel which was described in the previous paper⁴⁾ was used, and the pressure was generated with the hydraulic press which was same as that used in the experiments on crystallization of polyethylene¹²⁾.

After an appropriate reaction time, the reaction system was cooled by circulating cold water into the jacket, the pressure withdrawn and the reaction capsule removed. The reaction capsule was dipped in the dry-ice-methanol bath. Loosening the cap (A), the residual monomers were evaporated by warming slowly the capsule.

The polyvinyl chlorides obtained were dissolved in tetrahydrofuran. These polymers were precipitated with methanol and the solvents were decanted. And the polymers were dried at room temperature in vacuum until they attained to the constant weight.

The relative viscosity of polyvinyl chloride was measured in cyclohexanone at 30°C using an Ubbelohde type viscometer, and from its value the degree of polymerization was calculated using the Arrhenius-Duclaux equation and the Sakurada equation.

Results

The experiments were carried out at various temperature and pressure. The principal experimental results are illustrated in Figs. 2 and 3.

From these results it was observed that the rate of polymerization is increased by increasing temperature and pressure, and that the polymerization reaction is not preceded by any induction period, contrary to the case of the ordinary radical polymerization at atmospheric pressure, where some induction periods are used to be observed.

At constant pressure and temperature, the polymer yields increased linearly to the reaction time even in the comparatively long runs. Consequently it is concluded that the apparent initial polymerization rate is zero-order with respect to the monomer concentration as a first approximation, and the author regards these rates as the apparent initial rate constants in the following discussion.

The apparent initial rates (k_i) are obtained from the slopes of the straight lines of Figs. 2 and 3, etc. These values are given in Table 1. Tables 2 and 3 show our previous results of the radical polymerization of propylene¹¹⁾ and the thermal polymerization of butadiene⁴⁾, respectively.

Fig. 4 shows the Arrhenius plots of $\log k_i$ against $1/T$. They show good straight lines and the activation energies (E) calculated from these slopes are illustrated in Fig. 5, together with the results

12) J. Osugi, K. Hara, N. Hirai and J. Hikasa, *This Journal*, **34**, 59 (1964)

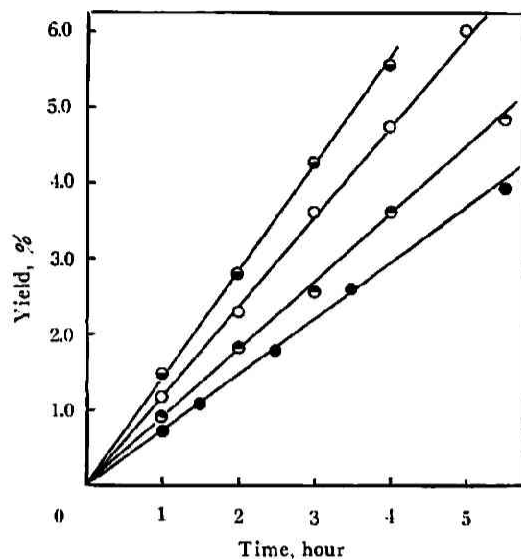


Fig. 2 Polymerization of vinyl chloride at 50°C

● : 3,900 kg/cm² ○ : 3,120 kg/cm²
 ● : 1,950 kg/cm² ● : 1,170 kg/cm²

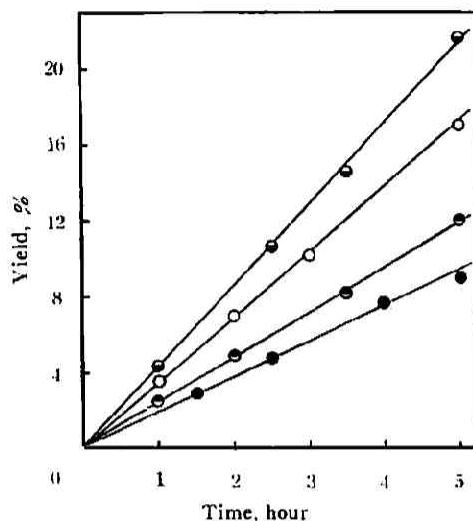
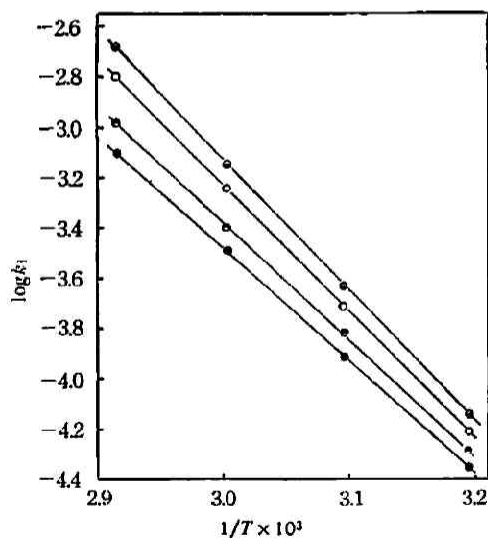


Fig. 3 Polymerization of vinyl chloride at 60°C

● : 3,900 kg/cm² ○ : 3,120 kg/cm²
 ● : 1,950 kg/cm² ● : 1,170 kg/cm²

Fig. 4 Arrhenius plots of $\log k_t$ vs $1/T$ at various pressure

● : 3,900 kg/cm² ○ : 3,120 kg/cm²
 ● : 1,950 kg/cm² ● : 1,170 kg/cm²

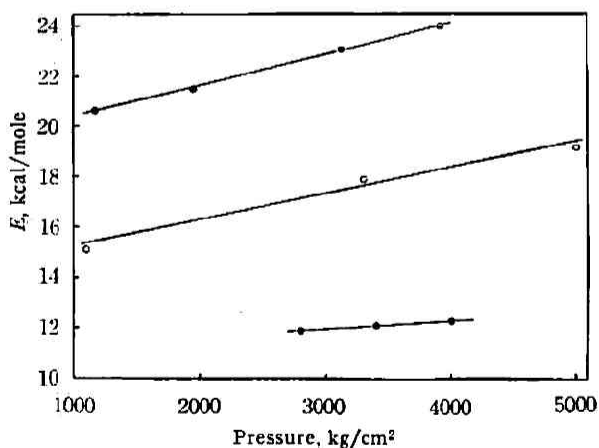


Fig. 5 Effect of pressure on the activation energy

● : vinyl chloride ○ : butadiene
 ● : propylene

Table 1 Effect of pressure on the initial rate at various temperature (Vinyl chloride)

Pressure (P , kg/cm ²)	Temperature (T , °C)	Initial rate ($k_i \times 10^3$, %/min)
1.170	40	4.50
	50	12.3
	60	32.5
	70	79.7
1.950	40	5.17
	50	15.0
	60	40.3
	70	105
3.120	40	6.17
	50	19.7
	60	57.2
	70	158
3.900	40	7.17
	50	23.7
	60	71.8
	70	208

Table 2 Effect of pressure on the initial rate at various temperature (Propylene)

Pressure (P , kg/cm ²)	Temperature (T , °C)	Initial rate ($k_i \times 10^3$, %/min)
2,800	80	8.0
	90	15.5
	100	19.8
3,400	80	10.2
	90	17.1
	100	25.6
4,000	80	12.1
	90	20.6
	100	30.2

Table 3 Effect of pressure on the initial rate at various temperature (Butadiene)

Pressure (P , kg/cm ²)	Temperature (T , °C)	Initial rate ($k_i \times 10^4$, %/min)
1,100	50	5.95
	70	22.2
	95	99.0
3,300	50	11.8
	70	53.8
	95	375
5,000	50	20.8
	70	134
	95	871

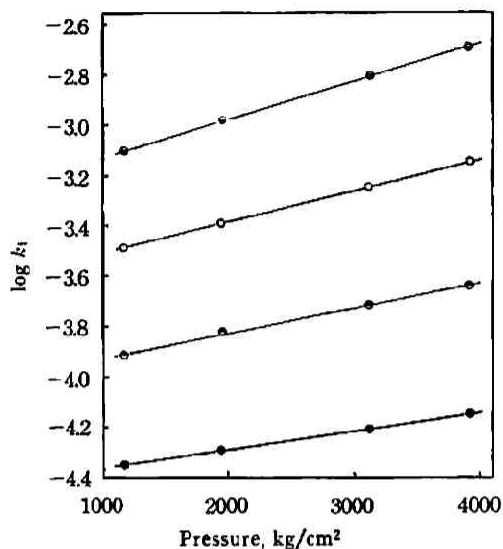


Fig. 6 Plots of $\log k_t$ vs pressure at various temperature

●: 70°C ○: 60°C ▲: 50°C
●: 40°C

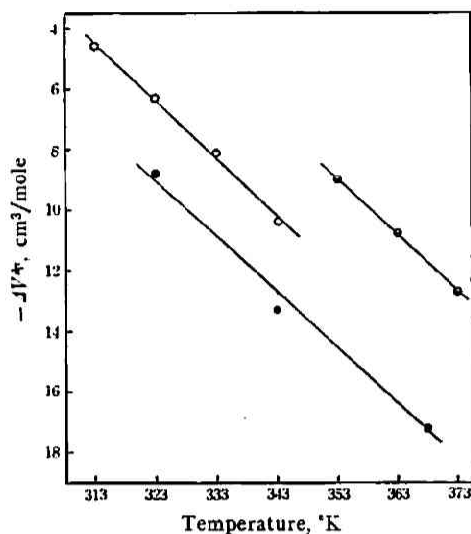


Fig. 7 Effect of temperature on the activation volume

●: propylene ○: vinyl chloride
●: butadiene

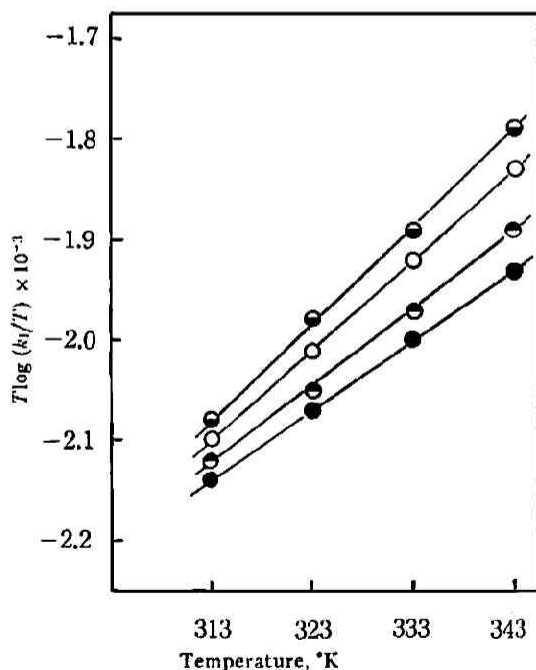


Fig. 8 Plots of $T \log(k_t/T)$ vs temperature at various pressure

●: 3,900 kg/cm² ○: 3,120 kg/cm²
●: 1,950 kg/cm² ●: 1,170 kg/cm²

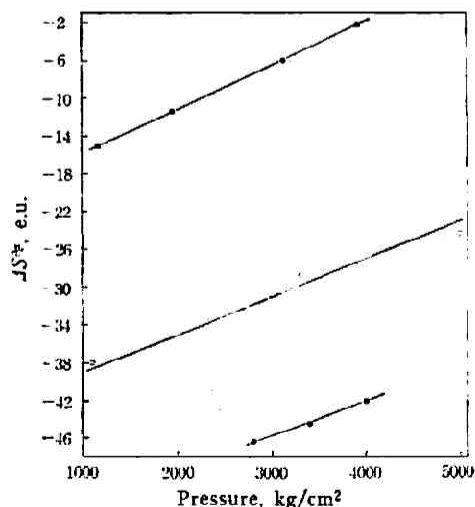


Fig. 9 Effect of pressure on the activation entropy

●: vinyl chloride ○: butadiene
●: propylene

of the previous paper⁴⁾¹¹⁾.

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

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

where

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

is the activation volume of the reaction, i.e., the difference in the volumes of the transition state ($V^\ddagger$) and the initial state (V_{ini}).

Fig. 6 shows the relationship between $\log k_1$ and P , and the curves come to be straight lines which give the apparent activation volumes by equation (1). These values thus obtained are illustrated in Fig. 7, together with the results of the previous paper⁴⁾¹¹⁾.

Similarly the activation entropy can be calculated by the following equation:

$$\left\{\frac{\partial T \ln(k/T)}{\partial T}\right\}_P = \frac{\Delta S^\ddagger}{R} + \ln \frac{k}{h}, \quad (3)$$

where k is Boltzmann's constant, h Planck's constant, T the absolute temperature, P the pressure, R the gas constant and $\Delta S^\ddagger$ the activation entropy of the reaction, i.e., the difference in the entropies of the transition state ($S^\ddagger$) and the initial state (S_{ini}).

Fig. 8 shows the plots of $T \log(k_1/T)$ against T , and the straight line relationships can be obtained. The values of $\Delta S^\ddagger$ obtained from the slopes of the straight lines are illustrated in Fig. 9, together with the results of the previous paper⁴⁾¹¹⁾.

In the polyvinyl chloride solutions, the relationship between the intrinsic viscosity and the relative viscosity can be expressed by the following Arrhenius-Duclaux equation,

$$[\eta] = \frac{1}{C} \ln \eta_{\text{rel}}, \quad (4)$$

where $[\eta]$ is the intrinsic viscosity, η_{rel} the relative viscosity, C the concentration of polyvinyl chloride in gram per liter unit.

The degree of polymerization ($\bar{P}$) can be calculated by the following Sakurada equation.

$$[\eta] = k \log \left(1 + \frac{\bar{P}}{a}\right), \quad (5)$$

where k and a are constants, and Furusawa *et al.*¹⁴⁾ reported that k and a are 0.197 and 500, respectively for polyvinyl chloride in cyclohexanone solution at 30°C.

The author measured the relative viscosity of about 2g/l PVC solutions at 30°C, using cyclohexanone as the solvent. The calculated degrees of polymerization of the polymers which were obtained by the run at 50°C, are given in Table 4. It is obvious from this table that the degrees of polymerization are increased as increasing pressure.

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

14) S. Furusawa and K. Goto, *Kobunshi Kagaku (Chemistry of High polymers)*, **10**, 259 (1953)

Mizushima and his collaborators^{15)~19)} studied extensively the infrared spectra of C-Cl bondings which appear at the region of 550 to 750 cm^{-1} , and found that the wave numbers are varied depending on the molecular structures. They concluded that the suitable infrared absorption bands can be used as the primary measure of the crystallinity in polymers, and in PVC the absorption coefficient ratio of 635 cm^{-1} to 690 cm^{-1} , *i.e.* D_{635}/D_{690} , is the measure of the crystallinity which is due to the syndiotactic structure of the polymer. From infrared absorption spectra, the calculated values of D_{635}/D_{690} are also given in Table 4.

It is clear from the table that no correlations between the pressure and the absorption coefficient ratios can be observed. And also the author can not observe any difference between the polymers obtained and that of commercial PVC concerning to X-ray diffraction spectra. Then, it is concluded that the polymer obtained at high pressure is not different from commercial PVC in the crystallinity and configuration.

In Table 5, the degrees of polymerization of polypropylene are shown¹¹⁾. No effect of pressure on the degree of polymerization is recognized. This polymer is a paste-like material, and easily soluble in benzene and cyclohexane at room temperature. From the infrared spectrum it was found that the polypropylene has the same absorption bands as those of the atactic polypropylene except the band due to the carbonyl group which may be assigned to benzoyloxy group. The appearance of the carbonyl band reflects the very low degree of polymerization.

Table 4 Effect of pressure on the degree of polymerization and the absorption coefficient ratio, (Polyvinyl chloride)

Pressure (P , kg/cm^2)	Degree of polymerization ($\bar{P}$)	D_{635}/D_{690} *
1,950	1,470	1.46
3,120	1,615	1.39
3,900	1,900	1.45

* For commercial PVC, D_{635}/D_{690} is 1.41.

Table 5 Effect of pressure and temperature on the degree of polymerization, (Polypropylene)

Pressure (P , kg/cm^2)	Temperature (T , $^{\circ}\text{C}$)		
	80	90	100
2,800	26	18	24
3,400	65 (76)	22	14
4,000	41	18	17

15) S. Mizushima, T. Shimanouchi, I. Nakagawa and A. Miyake, *J. Chem. Phys.*, **21**, 215 (1953)

16) I. Nakagawa and S. Mizushima, *ibid.*, **21**, 2195 (1953)

17) S. Mizushima and T. Shimanouchi, *ibid.*, **26**, 970 (1957)

18) T. Shimanouchi, S. Tsuchiya and S. Mizushima, *ibid.*, **30**, 1365 (1959)

19) T. Shimanouchi, S. Tsuchiya and S. Mizushima, *Kobunshi (High Polymers, Japan)*, **8**, 202 (1959)

Considerations

Initial polymerization rate

In its most elementary form, a kinetic treatment of the free radical polymerization of a single vinyl monomer has to take into account the rates of four types of component reaction :

A) Rate of production of radicals by initiator decomposition

$$R_d = 2fk_d[C] \quad (6)$$

B) Rate of initiation $R_i = k_i[R\cdot][M]$ (7)

C) Rate of chain growth $R_p = k_p[M][M_n\cdot]$ (8)

D) Rate of termination $R_t = k_t[M_m\cdot]^2$ (9)

Equation (6) refers to the production of two radicals ($R\cdot$) from each molecule of initiator (C) by homolysis, f being the efficiency of the radicals in starting chains. The chain initiation is caused by the addition of $R\cdot$ to the monomer M , and the chain growth proceeds by successive addition of monomer molecules to the chain radicals $M_n\cdot$. The kinetic chains are terminated by the collisions between polymeric radicals which result in disproportionations or combinations.

Assuming that (1) the radical concentrations are in the steady state condition, (2) the rate constant of chain growth is independent of the chain length and (3) the kinetic chain length is very large compared with unity, then we can obtain the following overall rate equation,

$$-\frac{d[M]}{dt} = k_p \left(\frac{k_d f}{k_t} \right)^{\frac{1}{2}} [C]^{\frac{1}{2}} [M] \quad (10)$$

We may assume that equation (6) can be applicable at high pressure and f is nearly equal to one, then,

$$-\frac{d[M]}{dt} = k_p \left(\frac{k_d}{k_t} \right)^{\frac{1}{2}} [C]^{\frac{1}{2}} [M] \quad (11)$$

Equation (11) is well applicable to the process at high pressure²⁰⁾²¹⁾.

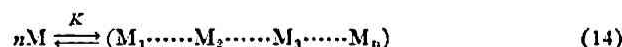
It may be reasonable to assume that in the initial polymerization reaction, the change of the monomer concentration is very small. Then

$$\frac{dX}{dt} = k_p \left(\frac{k_d}{k_t} \right)^{\frac{1}{2}} [C]^{\frac{1}{2}} \quad (12)$$

where X is defined as follows

$$X = \frac{\text{Weights of resultant polymers}}{\text{Weights of initial monomers}} \quad (13)$$

Generally, it is considered that in the polymerization reactions under high pressure, the propagation step is most accelerated by pressure. This means that the pressure somehow aligns the monomer molecules in a manner favorable to polymerization. So, the following equilibrium between the free monomers and the aligned monomer groups may be presumed,

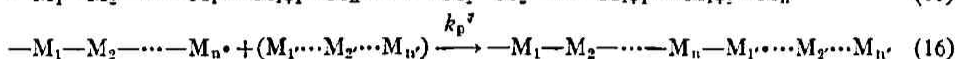
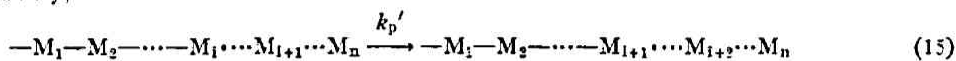


20) T. Imoto, *Kobunshi (High Polymers, Japan)*, 16, 910 (1967)

21) H. Asai and T. Imoto, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, 84, 863 (1963)

In these aligned monomer groups, the propagation reaction may proceed in some fixed direction. And in the propagation step of $-M_1-M_2-M_3-\cdots-M_n\cdot$ to the next aligned monomer group, the addition of the monomer group which has the special orientation to the growing radical may be favorable. Then, in both propagation reactions mentioned above, the reaction is zero-order with respect to monomer concentrations.

Namely,



Assuming the steady state condition, we can obtain the following overall rate equation,

$$-\frac{d[M]}{dt} = (k_p' + k_p'') \left(\frac{k_d}{k_t} \right)^{\frac{1}{2}} [C]^{\frac{1}{2}} = k_p \left(\frac{k_d}{k_t} \right)^{\frac{1}{2}} [C]^{\frac{1}{2}} \quad (17)$$

In the reaction of vinyl chloride polymerization, the reacting system may successively become a heterogeneous system as the reaction proceeds. Then, the mechanisms of the bulk polymerization of vinyl chloride under the pressure of the order of several tenths of an atmosphere are very complicated²²⁾⁻²⁵⁾. Mizutani *et al.*²⁶⁾ reported that the bulk polymerization reaction of vinyl chloride proceeded linearly to the reaction time up to 60% yields, at the several tenths of an atmosphere.

As shown in the previous reports⁴⁾¹¹⁾, the yields of polybutadiene and polypropylene were very small and increased linearly with the reaction time throughout the comparatively long runs. In any cases, it is assumed that these reactions are zero-order with respect to the monomer concentration within the experimental errors.

Activation energy

Putting $k_p(k_d/k_t)^{1/2} = k$, then

$$k_t = k[C]^{1/2}. \quad (18)$$

At the temperatures T_1 and T_2 , the following relation exists.

$$\ln k_{T_1} - \ln k_{T_2} = \ln k_{T_1} - \ln k_{T_2} + \frac{1}{2} \ln \frac{V_{T_2}}{V_{T_1}}, \quad (19)$$

where V is the volume of the system.

The value of the third term at the right-hand side of equation (19) can be estimated from the thermal expansion coefficients of liquids²⁷⁾ and of liquefied propylene⁹⁾ at atmospheric pressure and at high pressure, respectively, and the term can be neglected as a first approximation. Then, the activation energy obtained from k_t nearly corresponds to that of k .

The activation energy thus obtained is made up of three terms,

22) W. I. Bengough and R. G. W. Norrish, *Proc. Roy. Soc.*, **A200**, 301 (1950); **A218**, 149 (1953)

23) M. Magat, *J. Polymer Sci.*, **16**, 491 (1955)

24) E. J. Arlman and W. M. Wagner, *ibid.*, **9**, 581 (1952)

25) W. M. Thomas and M. T. O'shanghnessy, *ibid.*, **11**, 455 (1953)

26) K. Mizutani, T. Morisawa and N. Enari, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **55**, 708 (1952)

27) "American Institute of Physics Handbook", McGraw-Hill, New York (1957)

$$E = \frac{1}{2}E_d + E_p - \frac{1}{2}E_t, \quad (20)$$

where E_d , E_p , and E_t are the activation energies associated with spontaneous decomposition of the initiator, the chain growth and the chain termination respectively.

There are many values concerning those activation energies at atmospheric pressure, for example, E_d is 30 ± 1 kcal/mole for benzoyl peroxide dissociation^{28,29)}, and for styrene^{30,31)} and vinyl acetate^{32,33)} $E_p - \frac{1}{2}E_t$ is 6.5 to 5.5 and 4.7 to 4.4 kcal/mole, respectively. For many other polymerization reactions, these values are nearly the same order. The overall activation energies for radical-initiated polymerizations are, therefore, 21.5 to 19.4 kcal/mole. Thus the values for vinyl chloride, i.e., 20.6~24.0 kcal/mole, may be reasonable.

As shown in Fig. 5, the activation energies of the polymerization of propylene, i.e., 11.9~12.3 kcal/mole, are very small compared with that of the ordinary radical polymerization. From the facts that the overall rate constants are not so much smaller than that of the ordinary radical polymerization, and that the degrees of polymerization are very small, the small activation energy should imply some contribution of the chain transfer step.

The kinetic effects of pressure on the thermal polymerization have not been so extensively studied. But the reaction may follow a different kinetic pattern from that outlined in equations (6) to (9). The exact nature of the chain-initiation process is obscure³⁴⁾, but it probably involves a bimolecular reaction between two molecules of monomer, which may be accelerated with increasing pressure. The rate of thermal initiation is then expressed by an equation of the form,

$$R_{ti} = k_{ti}[M]^2. \quad (21)$$

If equation (6) is replaced by equation (21) in the development of the general kinetic equation, the rate of thermal polymerization reaction is given by

$$-\frac{d[M]}{dt} = k_p \left(\frac{k_{ti}}{k_t} \right)^{\frac{1}{2}} [M]^2. \quad (22)$$

The overall activation energy is again expressible in the form

$$E = \frac{1}{2}E_{ti} + E_p - \frac{1}{2}E_t. \quad (23)$$

In the thermal polymerization of styrene, Bagdasaryan³⁵⁾ obtained E_{ti} to be 23.3 kcal/mole, which is smaller than that of BPO. If we assume $E_p - \frac{1}{2}E_t$ is 4 to 7 kcal/mole, then E would be 15.7 to 18.7 kcal/mole. Goldfinger and Lauterbach³⁶⁾ found E to be 16.0 kcal/mole. Same value is obtained in the thermal polymerization of methyl methacrylate by Walling and Briggs³⁷⁾. Thus the values shown in

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34) C. Walling, "Free Radicals in Solution", John Wiley & Sons, New York (1957)

35) Kh. S. Bagdasaryan, *Uspekhi Khim.*, **17**, 316 (1948)

36) G. Goldfinger and H. Lauterbach, *J. Polymer Sci.*, **3**, 145 (1948)

37) C. Walling and E. R. Briggs, *J. Am. Chem. Soc.*, **68**, 1141 (1946)

Fig. 5, *i.e.*, 15.1~19.2 kcal/mole, may be reasonable.

The overall activation energy of the thermal polymerization is smaller than that of radical polymerization with BPO, which may be due to the smaller value of E_{t1} than E_d .

As shown in Fig. 5, E is slightly increased by increasing pressure. This rise in the activation energy represents the stabilization of the initial molecule caused by its energy loss by pressure, hence the reaction should be retarded. But in these experiments, the polymerization reactions were accelerated by increasing pressure. Then, the accelerating effect is entirely due to the increase in the activation entropy which overcomes the retarding effect due to the rise of the activation energy.

Activation volume

The activation volume is probably easier to understand on an elementary level than other important quantities of activation, *i.e.*, the free energy, enthalpy and entropy. The reason for this is mainly that the atomic position alone tells a good deal about the volume, but the entropy requires knowledge of the vibrations, and the enthalpy and free energy do that of the vibration and the forces. The activation volume should, therefore, be rather useful for the elucidation of the mechanisms of reactions.

From equation (18) one can derive the following equation,

$$\frac{\partial \ln k_1}{\partial P} = \frac{\partial \ln k}{\partial P} - \frac{1}{2} \frac{\partial \ln V}{\partial P}. \quad (24)$$

The second term on the right-hand side is the compressibility term. This term can be estimated from compressibilities of liquefied propylene³⁸⁾ and of many liquids³⁹⁾. As well known, the isothermal compressibilities of a number of liquids are correlated remarkably well by an empirical equation (25) developed by Tait:

$$\frac{V_0 - V_p}{V_0} = C \ln \left(1 + \frac{P}{B} \right). \quad (25)$$

where V_0 and V_p are the volumes of liquid at an atmospheric pressure and at pressure P , respectively, and B and C are positive constants. Using this equation, we can estimate the compressibility of *n*-propyl chloride and *n*-butyl chloride, etc³⁹⁾.

Comparing these estimated values with the left-hand side of equation (24), we can neglect the term which is due to the compressibility, as a first approximation.

Thus, the activation volume obtained from k_1 nearly corresponds to that from k . The activation volumes are in general dependent on the pressure because the initial and transition states usually have different compressibilities, and consequently the graphs, where $\log k$ is plotted against P , are not the straight lines, but are frequently quite remarkably curved⁴⁰⁾. In other words, $\Delta V^\ddagger$ is initially negative and its absolute value is large, but its magnitude falls off as the pressure increases.

Fig. 6 might show the curved lines, but in the cases of styrene⁴¹⁾, cyclopentadiene⁴²⁾ and our

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40) E. Whalley, "Advances in Physical Organic Chemistry Vol. 2", p. 93 Academic Press, (London) (1964)

previously reported butadiene⁴⁰ and propylene⁴¹) their plots of $\log k$ against P were straight lines, and therefore, the author used the straight line approximation.

The activation volume thus obtained is made up of three terms, and from equations (1) and (18) the pressure dependence of k should be given by

$$\frac{RT}{P} \frac{\partial \ln k}{\partial P} = -\Delta V^* = -\frac{1}{2} \Delta V_d^* - \Delta V_p^* + \frac{1}{2} \Delta V_t^*, \quad (26)$$

where ΔV_d^* , ΔV_p^* and ΔV_t^* are the volume changes associated with spontaneous decomposition of the initiator, chain growth and chain termination, respectively.

The decomposition of benzoyl peroxide involves the stretching and breaking of the O-O bond, so that ΔV_d^* is likely to be positive for this reaction, i.e., 4.8 to 9.8 cm³/mole^{42,43}), and k_d will be decreased by pressure. The chain growth is the bimolecular addition process which has the negative value of ΔV_p^* and consequent acceleration by pressure may be expected.

The termination by combination should also have a negative ΔV_t^* , but Merrett and Norrish⁴¹) considered that this reaction between two large radicals is diffusion-controlled and is retarded at high pressure because of the increased viscosity of the medium.

The overall activation volumes obtained are negative and, from the above discussion, ΔV_p^* is the predominantly large negative value which contributes to the sign of ΔV^* . For this reason, according to equation (1) the reaction should be accelerated by pressure.

In the polymerization reaction of propylene, it was concluded that some chain transfer processes should take place. The polymers obtained are not high polymers as shown in Table 5. Therefore, it is quite possible that the bimolecular reaction between two radicals, which terminate the kinetic chains, is not diffusion-controlled. If so, it should be accelerated by pressure and ΔV_t^* may be negative. Then, the value of $|\Delta V^*|$ in equation (26) would be smaller than that of reactions in which the rate of termination is decreased by pressure.

As may be discussed later, ΔV^* decreases linearly with increasing temperature, so one can estimate ΔV^* of vinyl chloride at 80° to 100°C. Comparing these values with that of propylene (cf. Fig. 7), it is found that the activation volume of propylene-polymerization has a smaller negative value than that of vinyl chloride-polymerization.

Brown and Wall investigated the radiation induced polymerization of propylene at 21° to 83°C under high pressure in the range of 5,000 to 16,000 atmospheres⁹). They concluded that the polymerization proceeds by a radical mechanism with a large monomer transfer constant, and ΔV^* is -12.22 cm³/mole at 83°C.

In many γ -irradiation polymerizations, the initiation rates do not depend on pressure, i.e., $\Delta V_{int}^* = 0$. Then, $(\Delta V^*)_{\text{propylene}} = \Delta V_p^* - \frac{1}{2} \Delta V_t^* = -12.22$ cm³/mole, at 83°C.

On the other hand in the present experiment

41) F. M. Merrett and R. G. W. Norrish, *Proc. Roy. Soc. A* **206**, 309 (1951)

42) R. H. Sapiro, B. Raistrick and D. M. Newitt, *J. Chem. Soc.*, **1939** 1761

43) C. Walling and J. Pellon, *J. Am. Chem. Soc.*, **79**, 4786 (1957)

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

$$(\Delta V^\ddagger)_{\text{propylene}} = \frac{1}{2} \Delta V_d^\ddagger + \Delta V_p^\ddagger - \frac{1}{2} \Delta V_t^\ddagger = -9.0 \text{ cm}^3/\text{mole, at } 80^\circ\text{C.}$$

Assuming $\Delta V_d^\ddagger$ of BPO is 4.8 to 9.7 cm³/mole,

$$\Delta V_p^\ddagger - \frac{1}{2} \Delta V_t^\ddagger = -11.4 \sim -13.85 \text{ cm}^3/\text{mole, at } 80^\circ\text{C.}$$

Then, the two values from different initiators agree with each other.

From equation (22) the overall activation volume of the thermal polymerization is again expressible in the form :

$$\Delta V^\ddagger = \frac{1}{2} \Delta V_{ii}^\ddagger + \Delta V_p^\ddagger - \frac{1}{2} \Delta V_t^\ddagger, \quad (27)$$

where $\Delta V_{ii}^\ddagger$ is the volume change associated with bimolecular initiation and should be negative. Since $\Delta V_{ii}^\ddagger$ and $\Delta V_p^\ddagger$ are negative, $-\Delta V^\ddagger$ can be expected to exceed that of polymerization with a radical initiator. Comparing the results in Fig. 7, we can confirm this assumption. The activation volumes are reduced by increasing temperature, and the relationships between $\Delta V^\ddagger$ and T give the nearly straight lines as shown in Fig. 7. From these curves we can obtain the mean temperature differential

Table 6 The mean temperature differential of the activation volume

	Vinyl chloride	Propylene	Butadiene
$\langle \frac{\Delta \Delta V^\ddagger}{\Delta T} \rangle$ (cm ³ /mole-deg.)	-0.19	-0.19	-0.18

of the activation volume as shown in Table 6. From this table it is obvious that these values are nearly constant, and one may obtain the following equation,

$$\langle \frac{\Delta \Delta V^\ddagger}{\Delta T} \rangle = -0.19 \sim -0.18 \text{ cm}^3/\text{mole-deg.} \quad (28)$$

This equation means that the aligned monomer molecules have the larger thermal expansion coefficients than that of activated complexes, and the overall activation volumes have the nearly equal mean temperature differential.

Activation entropy

From equation (18) one can derive the following equation.

$$\frac{\partial T \ln(k_i/T)}{\partial T} = \frac{\partial T \ln(k/T)}{\partial T} + \frac{1}{2} \ln[C] + \frac{1}{2} T \frac{\partial \ln[C]}{\partial T}. \quad (29)$$

In the above equation, $\partial \ln[C]/\partial T$ corresponds to the thermal expansion coefficient. Estimating the orders of the second and third terms at the right-hand side, one can neglect these terms. Consequently, the activation entropy which was obtained from k_i nearly corresponds to that calculated from k .

Polymerization is the reaction in which a number of monomers are combined into one polymer, so that the entropy of the system must be decreased.

Namely, as already mentioned, if we consider the aligned monomer groups, which are generated by pressure, the reaction may be accelerated by increasing pressure. This implies that the compression causes the monomer molecules to lose partly their freedom, with the result that they have less to lose when they come to be built into growing polymer chains. The activation entropy will, therefore, be less negative than that at lower pressure, and the polymerization will be accelerated by a factor of about

$\exp (\Delta S_p^*/R - \Delta S_p'^*/R)$, where $P > P'$. Namely, the main reason for the rate increase is the increase in the value of rate constant of chain propagation. Chain growth is characterized by the negative entropy of activation ΔS^* and the negative values of ΔV^* . The results shown in Fig. 9 are consistent with this conclusion.

In connection with this, the thermal or radical initiated polymerization of propylene under high pressure is very interesting⁸⁾. By a radical catalyst, propylene monomers do not polymerize in the order of several tenths of atmosphere⁷⁾. Under high pressure, on the contrary, thermally or radically polymerized polypropylenes have stereospecific structures and high molecular weight.

This fact shows that the stereospecific polypropylene with high molecular weight can be obtained by high pressure. In other words, it shows that pressure plays an important role for the monomer orientation. Similar results can be found in the polymerization of ethylene⁴⁵⁾ which gives very high density polymers (du-Pont) and that of methyl methacrylate by Walling⁴⁶⁾ or Asai⁴⁷⁾, and that of propylene by Kardos⁴⁸⁾. These facts show that the orientation of monomer caused by high pressure controls the structure of the resulting polymers.

From the relationship between ΔS^* and P , which gives nearly straight lines as shown in Fig. 9, one can obtain the mean pressure differential of the activation entropy as shown in Table 7. From

Table 7 The mean pressure differential of the activation entropy

	Vinyl chloride	Propylene	Butadiene
$\langle \frac{\Delta \Delta S^*}{\Delta P} \rangle$ (cm ³ /mole-deg.)	0.20	0.17	0.17

this table, it is obvious that the value obtained are nearly constant and one can obtain the following equation,

$$\langle \frac{\Delta \Delta S^*}{\Delta P} \rangle = 0.20 \sim 0.17 \text{ cm}^3/\text{mole-deg.} \quad (30)$$

Comparing equation (28) with equation (30),

$$\langle \frac{\Delta \Delta S^*}{\Delta P} \rangle = - \langle \frac{\Delta \Delta V^*}{\Delta T} \rangle. \quad (31)$$

This relation shows that the thermodynamic equation is satisfied.

Degree of polymerization

It may be possible to arrive at some general conclusions concerning the effect of pressure on the radical polymerization⁴³⁾⁴⁴⁾⁴⁹⁾.

1) The radical formation by the unimolecular decomposition of initiators is slightly depressed by pressure, 2) Propagation reactions are strongly accelerated by pressure, 3) Termination reactions are scarcely affected by pressure and may rather be retarded as they become diffusion-controlled.

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49) A. H. Ewald, *Discussions Faraday Soc.*, **22**, 138 (1956)

Then, if there were no other effects, the molecular weight of the polymer would rise. Our results given in Table 4 are consistent with the above conclusions. But in the propylene polymerization, the chain transfer reaction takes place. Approximately, $\bar{P}$ may be equal to the ratio of the propagation rate to the transfer rate. From Table 5 it is obvious that $\bar{P}$ is independent of pressure and has very small values. This means that the transfer reaction with monomers is accelerated nearly as much as the chain propagation by an increase of pressure.

Acknowledgement

The author wishes to express his sincere thanks to Prof. Jiro Osugi for valuable guidance.

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