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THE POLYMERIZATION OF PROPYLENE UNDER HIGH PRESSURE

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The bulk polymerization of propylene, with benzoyl peroxide as the initiator, was studied at the pressures of 2,800, 3,400 and 4,000 kg/cm², and at the temperatures of 80, 90 and 100°C, respectively. It was found that the rate of polymerization was always accelerated by increasing pressure and temperature. From the initial rates, the activation volumes, the activation energies and the activation entropies were calculated and the following values were obtained: $\Delta V^{\ddagger}=-9.0\sim-12.7\mathrm{cm^3/mole}$, $E=11.9\sim12.3\mathrm{kcal/mole}$ and $\Delta S^{\ddagger}=-46.4\sim-42.0$ e. u. The polymer obtained was a paste-like material, being easily soluble in benzene and cyclohexane at room temperature. It was concluded from the infrared spectrum that the polymer was the atactic polypropylene with low degree of polymerization.

Introduction

The investigations of many types of reactions at high pressures have provided the fundamental informations on the mechanism of reaction, especially, on the structure of activated complex. The first general studies of polymerization at high pressures were made about forty years ago¹⁾²⁾. The accelerating effect of pressure on the free radical polymerization of olefines has been subsequently proved to be a rather general phenomenon³⁾⁴⁾.

At low pressures the radical induced polymerization of propylene does not take place³⁾. It was found that at high pressure and temperature, *i. e.* at 7,000 atm and 100 and 200°C, propylene was polymerized in the presence of radical initiators to yield polypropylene and it was partially in the isotactic configuration⁵⁾.

On the other hand, the radiation induced polymerization of propylene at high pressures was studied in the pressure range of 5,000~16,000 atm and at the temperatures of 21, 40 and 83°C⁶⁾. It was found that the polymer obtained was the atactic polypropylene and the rate of polymerization was increased with pressure. Recently, the radical induced polymerization of propylene in benzene solution was investigated in the pressure range of 5,000~8,000 atm and at the temperatures of 80 and 100°C⁷⁾. It was found that the rate of polymerization was accelerated by pressure.

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1) P. W. Bridgman and J.B. Conant, *Proc. Nat. Acad. Arts Sci.*, 15, 680 (1929)

2) J. B. Conant and C. O. Tongberg, *J. Am. Chem. Soc.*, 52, 1659 (1930)

3) K. E. Weale, *Quart Rev.*, 16, 267 (1962)

4) K. Kinkel, *Ber. Bunsenges. Physik. Chem.*, 70, 1030 (1966)

5) A. A. Zharov, U. V. Kissin, O. N. Pirrov and N. S. Enikolopyan, *Vysokomol. Soed.*, 6, 962 (1964)

6) D. W. Brown and L. A. Wall, *J. Phys. Chem.*, 67, 1016 (1963); *J. Polymer Sci.*, C No. 4, 1151 (1963)

7) A. A. Zharov, Al. Al. Berlin and N. S. Enikolopyan, *J. Polymer Sci.*, C No. 16, 2313 (1967)

In this work. the kinetic investigation of bulk polymerization of propylene with benzoyl peroxide as the initiator was performed at the pressures of 2,800, 3,400 and 4,000 kg/cm^2 and at the temperatures of 80, 90 and 100°C, respectively.

Experimentals

Materials

Propylene monomer of 99% or more in purity, was purified by the trap to trap vacuum distillation method using dry ice-methanol (−77°C) and liquid nitrogen (−196°C).

Benzoyl peroxide (BPO) was recrystallized with chloroform and methanol, and dried in vacuum.

The guranteed benzene and cyclohexane treated with the ordinary purification method were used as the solvents.

Apparatus

The high pressure apparatus used consists of three separate parts. namely, manual pump, intensifier and high pressure vessel. The detail of these apparatus were already reported[8][9]. Bourdon gauge used was of the ordinary type and corrected by means of a free piston gauge. The stainless steel capsule was used, which may be described in the following paper[10].

Procedures

For polymerization experiments at high pressures, the monomer liquid was introduced into the capsule, which contained 5 mg BPO, by means of the glass syringe. The reaction mixture in the capsule was compressed by introducing the pressure transmitting medium (ethanol) from the pressure intensifier into the high pressure vessel. Then, the high pressure vessel in the thermostat was heated to a definite temperature by the electrical heater. After an appropriate reaction time the monomer was removed and the residual polymer was dried overnight in vacuum to obtain a constant weight. The polymer obtained was dissolved in benzene, precipitated with methanol and then the solvents were decanted. The polymer was dried overnight in vacuum in order to measure the infrared spectra and the molecular weights.

The infrared spectra of polymers were obtained by using the Model Hitachi E. P. I.-S 2 Infrared spectrometer.

The molecular weight of polymer was measured by the cryoscopic method with cyclohexane as the solvent, and the viscosity in benzene was measured at 25°C.

Results and discussion

The experimental results at various pressures and temperatures are shown in Fig. 1.

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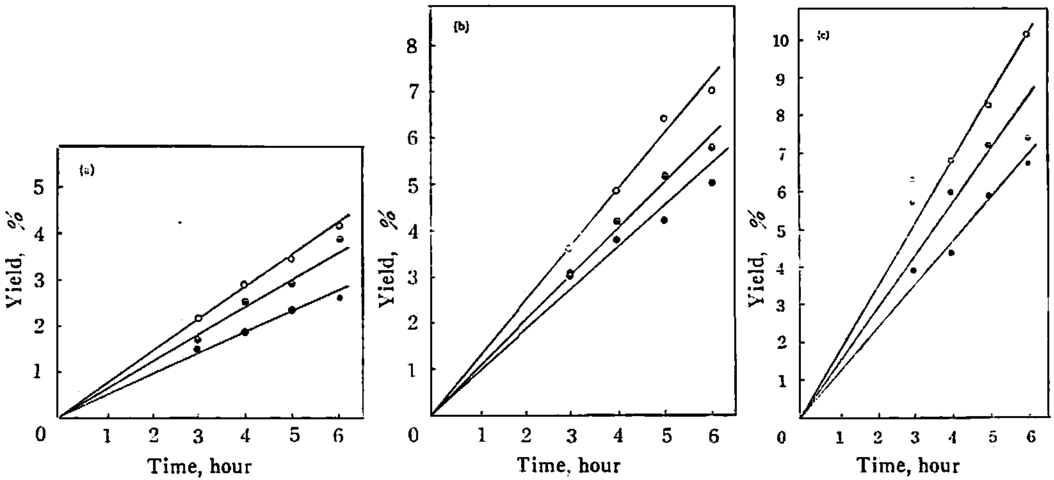
[8] R. Kiyama, *This Journal*, **19**, 1 (1945)

[9] T. Mizukami, *ibid.*, **35**, 51 (1965)

[10] K. Hamanoue, *ibid.*, **38**, 103 (1968)



(a): 80°C ○: 4,000 kg/cm²
(b): 90°C ◒: 3,400 kg/cm²
(c): 100°C ●: 2,800 kg/cm²

Fig. 1 Polymerizations of propylene

From these results it is clear that the rate of polymerization is accelerated by increasing pressure and temperature, and the yields of the polymer increase linearly with the reaction time. In addition, the induction period is not found. Therefore, it is assumed that the overall rate of polymerization is zero-order with respect to the monomer concentration. The initial rates of polymerization were calculated from the slopes of the straight lines of Fig. 1. The results are given in Table 1.

Considering the results of the discussion on the rate constant, which may be described in the following paper[10), we may regard these rates as the apparent initial rate constants in the following discussion.

Table 1 The initial rate ($k\times 10^3$, %min^{-1})

Pressure (kg/cm²)	Temperature (°C)		
	80	90	100
2,800	8.0	15.5	19.8
3,400	10.2	17.1	25.6
4,000	12.1	20.6	30.2

The transition state theory developed by Eyring *et al.*[11) shows that the rate constant, k, of reaction depends on the free energy of activation ($\Delta G^{\ne}$) as expressed by the following equation,

$$k=\kappa\frac{kT}{h}\exp\left(-\frac{\Delta G^{\ne}}{RT}\right), \qquad (1)$$

where κ is the transmission coefficient, generally assumed to be unity, k Boltzmann's constant, h Planck's constant, R the gas constant and T the absolute temperature. The fundamental equation for the effect of pressure on the reaction rate, on the basis of the transition state theory is deduced.

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11) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Book Company, Inc., New York and London (1941)

$$\left(\frac{\partial \ln k}{\partial P}\right)_T=-\frac{\Delta V^{\neq}}{RT}, \qquad (2)$$

where P is pressure and $\Delta V^{\neq}$ is the activation volume. Generally, the activation volume is affected by pressure[12], but it may be assumed that the activation volume is not affected by pressure in the small range of pressure.

Fig. 2 shows the plots of $\ln k$ against P. From their slopes, the activation volumes are calculated and given in Table 2, which shows the activation volumes decrease with increasing temperature.

Table 2 Effect of temperature on the activation volume

Temperature (T, °C)	Activation volume ($\Delta V^{\neq}$, cm^3/mole)
80	−9.0
90	−10.8
100	−12.7

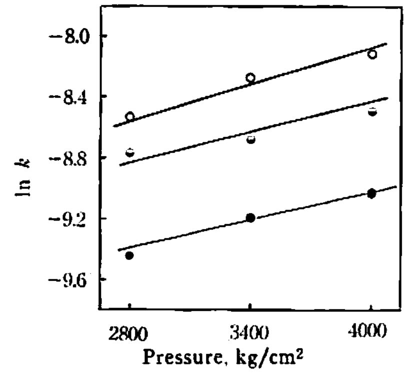

Fig. 2 Effect of presure on the rate of reaction at various temperatures
○: 100°C ◒: 90°C ●: 80°C

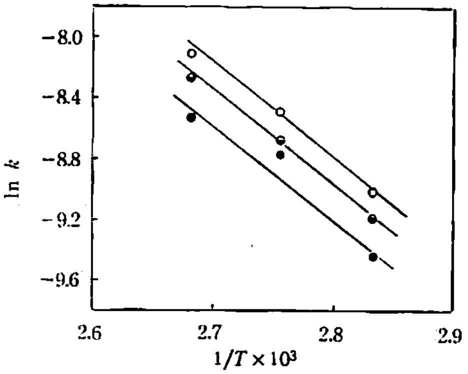

Fig. 3 Effect of temperature on the rate of reaction at various pressures
○: 4,000 kg/cm² ◒: 3,400 kg/cm²
●: 2,800 kg/cm²

The activation energy (E) is defined by the following equation, namely, the Arrhenius equation,

$$\ln k=\ln A-\frac{E_a}{RT}, \qquad (3)$$

where A is the frequency factor.

Fig. 3 shows the plots of $\ln k$ against $1/T$. From their slopes the activation energies are calculated and shown in Table 3. The activation energies increase with pressure.

Table 3 Effect of pressure on the activation energy

Pressure (P, kg/cm^2)	Activation energy (E, kcal/mole)
2,800	11.9
3,400	12.1
4,000	12.3

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[12] H. S. Golinkin, W. G. Laidlaw and J. B. Hyne, *Can. J. Chem.*, **44**, 2193 (1966)

Similarly the activation entropy ($\Delta S^{\neq}$) can be calculated by the following equation ;

$$\left\{\frac{\partial T\ln(k/T)}{\partial T}\right\}_P=\frac{\Delta S^{\neq}}{R}+\ln\frac{k}{h} \tag{4}$$

Fig. 4 shows the plot of $T\ln(k/T)$ against T.

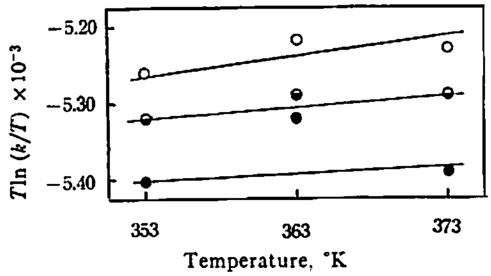

Fig. 4 Plots of $T\ln(k/T)$ vs temperature at various pressures
○ : 4,000 kg/cm² ◒ : 3,400 kg/cm²
● : 2,800 kg/cm²

From their slopes, the activation entropies are calculated and shown in Table 4.

Table 4 Effect of pressure on the activation entropy

Pressure (P, kg/cm²)	Activation entropy ($\Delta S^{\neq}$, e. u.)
2,800	−46.4
3,400	−44.4
4,000	−42.0

As shown in Table 4, the activation entropies are negative and their absolute values decrease with increasing pressure. According to Conant's hypothesis, the monomer molecules are aligned by pressure. This means that the freedoms of the monomer molecules are decreased by pressure. The decrease of the freedom has the correlation with the variation of entropy. On the other hand, polymerization is the process of negative entropy, because a number of monomers are combined into one polymer. Therefore, the activation entropy of polymerization at high pressure should be less negative than that at low pressure. In other words, it seems that the monomer molecules are put in order by pressure before forming the transition state. Thus, the accelerating effect of pressure on polymerization is entirely ascribed to the increase of the activation entropy with pressure, which overcomes the opposite contribution of the activation energy to the polymerization rate.

The activation volume calculated from the overall rates of polymerization is a composite function,

$$\Delta V^{\neq}=\Delta V_p^{\neq}+\frac{1}{2}\Delta V_d^{\neq}-\frac{1}{2}\Delta V_t^{\neq}, \tag{5}$$

if the following equation is valid:

$$R=k_p\left(\frac{k_d f}{k_t}\right)^{1/2}[\mathrm{M}][\mathrm{I}]^{1/2}. \tag{6}$$

Equation (6) is the overall rate of radical induced polymerization[13]. In equation (5), the suffixes p, d

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[13] P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press (1953)

and t represent the propagation step, the decomposition step and the termination step, respectively.

For the decomposition of BPO $\Delta V_d^{\neq}$ is positive14), but $\Delta V^{\neq}$ is yet negative as shown in Table 2. This implies that $\Delta V_p^{\neq}$ is negative and the predominant term in equation (5). The propagation step is the process of forming a large number of new bonds. Thus, $\Delta V_p^{\neq}$ should be negative.

The activation energy is small compared with that of the ordinary free radical polymerization. From the facts that the overall rate constant agrees with that of the ordinary free radical polymerization and the degree of polymerization is low, the small activation energy should imply some contribution of the chain transfer step.

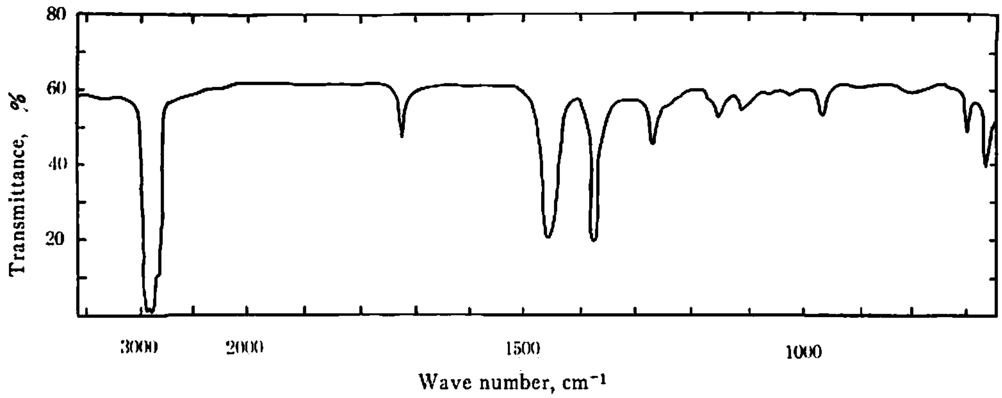

Fig. 5 Infrared spectrum of polymer

The infrared spectrum of the polymer obtained is shown in Fig. 5, which has the same absorption bands as those of the atactic polypropylene15)–17), except the band due to the carbonyl group at 1725 cm^{-1}.

The appearance of the carbonyl band reflects the relatively low molecular weight of the polymer. The decomposition of BPO can be formulated as shown in equation (7).

Table 5 The degree of polymerization

Pressure (kg/cm^2)	Tempreature (°C)		
	80	90	100
2,800	26	18	24
3,400	65(76*)	22	14
4,000	41	18	17

*: obtained from viscosity18)

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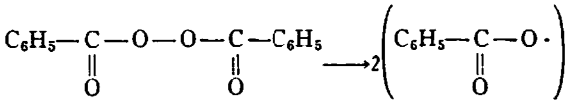
14) C. Walling and J. Pellon, *J. Am. Chem. Soc.*, 79, 4786 (1957)

15) J. P. Loungo, *J. Appl. Polymer Sci.*, 3, 302 (1960)

16) M. C. Tobin, *J. Phys. Chem.*, 64, 216 (1960)

17) T. Miyazawa, *J. Chem. Phys.*, 43, 4034 (1965)

18) J. B. Kinsinger and R.E. Hughes, *J. Phys. Chem.*, 63, 2002 (1959)



$$C_6H_5-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-C_6H_5 \longrightarrow 2\left(C_6H_5-\underset{\underset{O}{\|}}{C}-O\cdot\right) \qquad (7)$$

Then it is expected that the polymer obtained contains benzoyloxy radical (C_6H_5-COO·) as an end group.

In Table 5 the degrees of polymerization of the polymer are shown. The effect of pressure on the degree of polymerization may be small. The polymer obtained is a paste-like material and easily soluble in benzene and cyclohexane at room temperature.

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