

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 35, No. 2, 1965

STUDIES ON THE KINETICS OF THE THERMAL POLYMERIZATION  
OF BUTADIENE UNDER HIGH PRESSURE

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The thermal bulk polymerization of butadiene was investigated at 323 to 368°K under high pressures in the range of 1100 to 5000 kg/cm<sup>2</sup>.

It was observed that the polymerization reaction was not preceded by an induction period, and the polymer yields increased linearly with the reaction time throughout the comparatively long run.

The rate of polymerization was accelerated by increasing the pressure and temperature.

From the apparent initial rate, the activation energies, activation volumes and activation entropies were calculated and the following values were obtained;  $E = 15.1 \sim 19.2$  kcal/mole,  $\Delta V^\ddagger = -8.8 \sim -17.2$  cm<sup>3</sup>/mole and  $\Delta S^\ddagger = -38.0 \sim -24.3$  e. u.

The polymer obtained was insoluble in the ordinary solvents of rubbers, and it was concluded that the polymer is a crosslinked elastic polymer.

## Introduction

Organic reactions under high pressures have been studied by many investigators, and the experiment under high pressures is a useful method for the investigation of the kinetics and mechanism.

Since J. B. Conant<sup>1-3)</sup> reported, it has been well known for a long time that pressure has an accelerating influence on polymerizations, but its quantitative kinetic studies are comparatively small in number. Therefore we have studied the thermal polymerization of butadiene under high pressure from the kinetic view point.

## Experiments

## Materials

Butadiene gas of 99.5% in purity was dried by passing through NaOH and CaSO<sub>4</sub>, and distilled by the trap-to-trap vacuum distillation method using dryice-methanol (195°K) and liquid nitrogen (77°K).

## Apparatus

As the butadiene monomer is gas at room temperature, we used a special capsule to make it react in liquid phase. Fig. 1 shows the reaction vessel. The reaction vessel itself is a usual glass hypodermic

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(Received March 20, 1966)

- 1) J. B. Conant and P. W. Bridgman, *Proc. Nat. Acad. Sci.*, **15**, 680 (1929)
- 2) J. B. Conant and C. O. Tonberg, *J. Am. Chem. Soc.*, **52**, 1659 (1930)
- 3) J. B. Conant and W. R. Peterson, *ibid.*, **54**, 628 (1932)

syringe, and the monomer in the cylinder A is maintained in liquid state at room temperature by supporting the piston B and cap C in the brass-made capsule D.

The pressure transmitting medium is introduced through the hole E into the capsule.

Using this method, it is not necessary to cool the pressure transmitting medium and the piston-cylinder-type high pressure vessel (Fig. 2), before putting the capsule into the vessel. Hence, we can easily heat the reaction system.

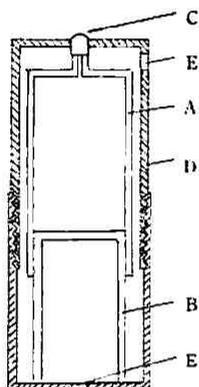


Fig. 1 Reaction vessel  
A: cylinder of glass syringe  
B: piston of glass syringe  
C: cap  
D: brass-made capsule  
E: hole

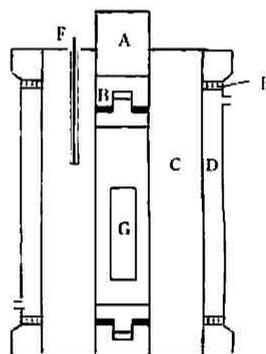


Fig. 2 Piston-cylinder type high pressure vessel  
A: piston  
B: piston-head  
(unsupported area method)  
C: cylinder  
D: jacket  
E: O-ring  
F: thermocouple  
G: reaction vessel

The pressure was generated with the hydraulic press which was the same with those in the experiments of crystallization of polyethylene<sup>4)</sup>.

#### Procedures

The glass syringe which contained 2.1g monomers (3 ml at 195°K) was maintained in the capsule. The pressure transmitting medium used was ethyl alcohol.

The reaction temperature was kept constant within  $\pm 1^\circ\text{C}$  by circulating hot oil into the jacket of the pressure vessel, and measured by an iron-constantan thermocouple inserted in the pressure vessel.

After an appropriate reaction time, the reaction system was cooled by circulating water into the jacket, the pressure was withdrawn and the reaction vessel was removed.

Reaction solutions were poured into a large amount of cold methyl alcohol. The precipitated polymers were dried at 323°K in vacuum until they attained to the constant weight.

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

## Results

The experimental time-yield curves at various pressures and temperatures are illustrated in Figs. 3, 4 and 5.

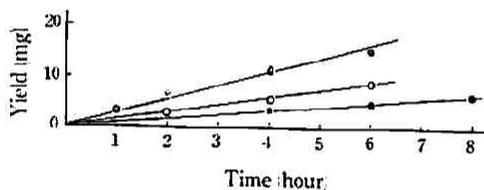


Fig. 3 Time-yield curves at 323°K  
 ●: 1100 kg/cm<sup>2</sup> ○: 3300 kg/cm<sup>2</sup>  
 ◐: 5000 kg/cm<sup>2</sup>

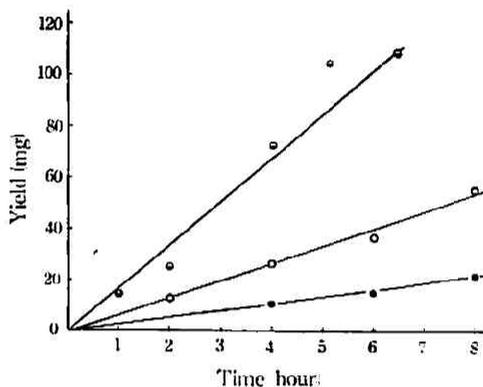


Fig. 4 Time-yield curves at 343°K  
 ●: 1100 kg/cm<sup>2</sup> ○: 3300 kg/cm<sup>2</sup>  
 ◐: 5000 kg/cm<sup>2</sup>

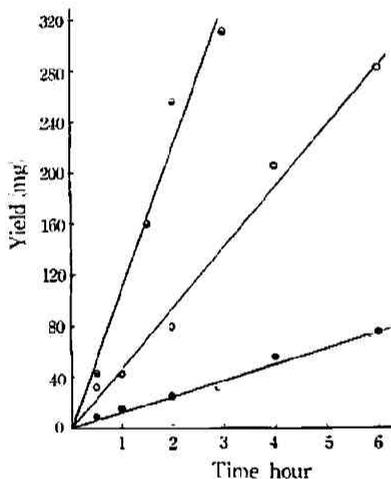


Fig. 5 Time-yield curves at 368°K  
 ●: 1100 kg/cm<sup>2</sup> ○: 3300 kg/cm<sup>2</sup>  
 ◐: 5000 kg/cm<sup>2</sup>

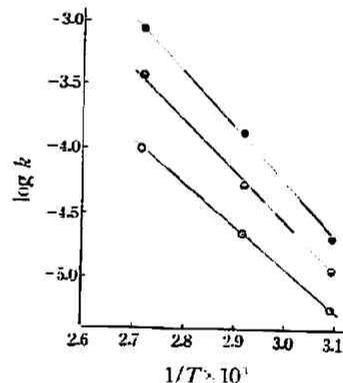


Fig. 6 Arrhenius plots of  $\log k$  vs  $1/T$  at various pressure  
 ○: 1100 kg/cm<sup>2</sup> ◐: 3300 kg/cm<sup>2</sup>  
 ●: 5000 kg/cm<sup>2</sup>

From these results it was observed that the rate of polymerization is increased by increasing the temperature and pressure, and that the polymerization reaction is not preceded by an induction period and the polymer yields increase linearly with the reaction time even in the comparatively long run.

Therefore it is concluded that the apparent initial polymerization rate is zero-order with respect to the monomer concentration as a first approximation.

The initial rate constants ( $k$ ) are obtained from the slopes of the straight lines of Figs. 3, 4 and

5. These values are given in Table 1.

Fig. 6 shows the Arrhenius plots of  $\log k$  against  $1/T$ . They show good straight lines and the activation energies ( $E$ ) calculated from their slopes are given in Table 2.

Table 1 Effect of pressure on the initial rate constant at various temperature

Pressure ( $P$ , kg/cm <sup>2</sup> )	Temperature ( $T$ , °K)	Initial rate constant ( $k \times 10^6$ , min. <sup>-1</sup> )
1100	323	5.95
	343	22.2
	368	99.0
3300	323	11.8
	343	53.8
	368	375
5000	323	20.8
	343	134
	368	871

Table 2 Effect of pressure on the activation energy

Pressure ( $P$ , kg/cm <sup>2</sup> )	Activation energy ( $E$ , kcal/mole)
1100	15.1
3300	17.9
5000	19.2

From the transition state theory, the activation volume ( $\Delta V^\ddagger$ ) and the activation entropy ( $\Delta S^\ddagger$ ) can be calculated by the following formulae;

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

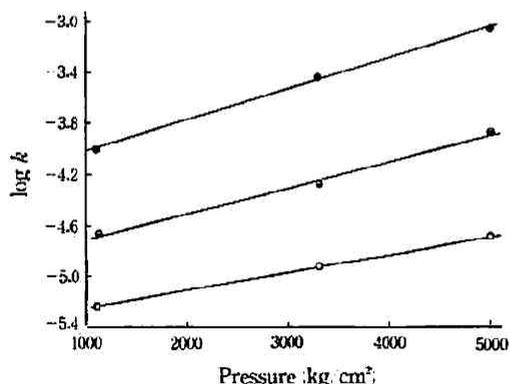


Fig. 7 Plots of  $\log k$  vs pressure at various temperatures

○: 323°K    ◐: 343°K    ●: 368°K

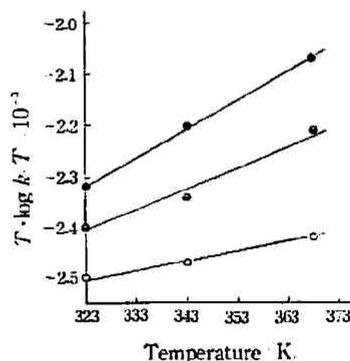


Fig. 8 Plots of  $T \log k/T$  vs temperature at various pressure

○: 1100 kg/cm<sup>2</sup>    ◐: 3300 kg/cm<sup>2</sup>  
●: 5000 kg/cm<sup>2</sup>

$$\left\{ \frac{\partial T \ln(k/T)}{\partial T} \right\}_P = \frac{\Delta S^\ddagger}{R} + \ln \frac{k}{h} \quad (2)$$

where  $k$  is Boltzmann's constant,  $h$  Planck's constant,  $T$  absolute temperature,  $P$  pressure and  $R$  gas constant.

Fig. 7 shows the relationship between  $\log k$  and  $P$ , and the curves come to straight lines which give  $\Delta V^\ddagger$  by eq. (1). The values thus obtained are given in Table 3.

By the similar procedure, we can calculate  $\Delta S^\ddagger$ . Fig. 8 shows the plots of  $T \cdot \log(k/T)$  against  $T$ . In Table 4, we show  $\Delta S^\ddagger$  thus obtained.

Table 3 Effect of temperature on the activation volume

Temperature ( $T$ , °K)	Activation volume ( $\Delta V^\ddagger$ , cm <sup>3</sup> /mole)
323	-8.8
343	-13.3
368	-17.2

Table 4 Effect of pressure on the activation entropy

Pressure ( $P$ , kg/cm <sup>2</sup> )	Activation entropy ( $\Delta S^\ddagger$ , e. u.)
1100	-38.0
3300	-28.8
5000	-24.3

### Considerations

#### Activation volume

Generally,  $\Delta V^\ddagger$  is affected by pressure, and consequently the graph of the plot of  $\log k$  against  $P$  does not come to the straight line, but is quite remarkably curved<sup>5)</sup>. 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. 7 might show the curved lines, but in the case of styrene<sup>6)</sup> and cyclopentadiene<sup>7)</sup> their plots of  $\log k$  against  $P$  were straight lines, and therefore we used the straight line approximation.

From Table 3, it is obvious that  $\Delta V^\ddagger$  is reduced by increasing temperature, and we can obtain the following value as the mean temperature differential;

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

#### Activation entropy

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.

Conant's hypothesis was that the pressure helps the reaction because it aligns the monomer molecules in a way which favours the chain propagation step, in the case of non-ionic solutions. 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 become built into growing polymer chains. The activation

5) E. Whalley, "Advances in Physical Organic Chemistry", Vol. 2, p. 99, Academic Press (London), (1964)

6) F. M. Merret and R. G. W. Norrish, *Proc. Roy. Soc.*, A206, 309 (1951)

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

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  $P > P'$ .

The results shown in Table 4 is consistent with this conclusion, and from this fact Conant's hypothesis is very reasonable.

In connection with this, the thermal polymerization of propylene under high pressure is very interesting<sup>8)</sup>. By a radical catalyst, propylene monomers do not polymerize stereospecifically, but give atactic polymers with low molecular weight. Under high pressure, on the contrary, thermally polymerized polypropylenes have stereospecific structures and high molecular weight.

This fact shows that the stereospecific polypropylene with high molecular weight, which under the ordinary pressure we can produce by the Ziegler-Natta catalyst only, can be obtained by high pressure, in other words, it shows that pressure plays an important role for the monomer orientation.

From the relationship between  $\Delta S^*$  and  $P$ , which gives the nearly straight line, we can obtain the following mean pressure differential of the activation entropy;

$$\left\langle \frac{\Delta \Delta S^*}{\Delta P} \right\rangle = 0.17 \text{ cm}^3/\text{mole-deg.} \quad (4)$$

Compared with eq. (3):

$$\left\langle \frac{\Delta \Delta S^*}{\Delta P} \right\rangle = - \left\langle \frac{\Delta \Delta V^*}{\Delta T} \right\rangle. \quad (5)$$

This relation shows that the following thermodynamic equation is satisfied;

$$\left( \frac{\partial \Delta S^*}{\partial P} \right)_T = - \left( \frac{\partial \Delta V^*}{\partial T} \right)_P. \quad (6)$$

#### Activation energy

As shown in Table 2,  $E$  is slightly increased by increasing pressure.

This rise in the activation energy represents the energy loss of the initial molecules; hence the reaction should be retarded. But in this experiment, therefore, the fact that pressure accelerates polymerization reactions implies that the acceleration is due entirely to the increase in the activation entropy which overcomes the activation energy rise.

#### Polymers

The polymers obtained were insoluble in the ordinary solvents, such as, benzene, toluene, chloroform, carbon tetrachloride and carbon disulfide.

It was concluded that this polymer is a comparatively highly crosslinked elastic polymer.

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