From the Department of Organic Synthesis, Faculty of Engineering, Kyushu University,
Fukuoka, Japan

Studies on the Polymerization of Bifunctional Monomers
III. Radical Polymerization of *o*-Divinylbenzene*[,1)]

By CHUJI ASO, TAKANARI NAWATA, and HISASHI KAMAO

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SUMMARY:

In the radical polymerization of *o*-divinylbenzene, soluble polymers were obtained. The content of pendant double bond in the polymer was found to be lower than one for one monomer unit. It was concluded that the intramolecular cyclization reaction occurred during the polymerization. The effects of polymerization temperature and monomer concentration on the cyclization reaction were investigated with the aid of an equation derived kinetically.

ZUSAMMENFASSUNG:

Bei der radikalischen Polymerisation von *o*-Divinylbenzol wurden lösliche Polymere erhalten. Es wurde gefunden, daß der Gehalt an freien Doppelbindungen im Polymeren niedriger war als 1 Doppelbindung pro Grundbaustein. Es wird daraus der Schluß gezogen, daß die intramolekulare Cyklisierungsreaktion während der Polymerisation eintrat. Die Einflüsse der Polymerisationstemperatur und der Monomerkonzentration auf die Cyclisierungsreaktion wurden nach einer kinetisch abgeleiteten Gleichung untersucht.

Introduction

In recent years, a number of papers on cyclopolymerization of 1,6-dien-type compounds have been published²⁾. However, it seems that there have been few studies³⁾ on radical cyclopolymerization of 1,5-dien-type compounds. *o*-Divinylbenzene (*o*-DVB) was employed in this study as one of 1,5-diens, and its polymerization was investigated.

The commercial divinylbenzene (DVB) composed principally of the mixture of *p*-, *m*-DVB and ethylstyrene has been known as a useful crosslinker. HAWARD and SIMPSON reported that some intramolecular reaction occurred during the polymerization of styrene in the presence of commercial DVB⁴⁾. D'ALELIO *et al.* obtained a soluble copolymer of DVB and

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ethylstyrene in the polymerization of commercial DVB with a ZIEGLER-type catalyst, where it was shown that each DVB unit in the copolymer had an unreacted vinyl group[5]. However, any report on the polymerization of pure *o*-DVB has not yet been published.

In this paper, it was concluded that in solution polymerization of *o*-DVB an intramolecular cyclization occurred. Moreover, a composition equation for polymers obtained by a cyclopolymerization mechanism was proposed and dependences of the degree of cyclization reaction on dilution with solvent in polymerization system and on polymerization temperature for the polymerization of *o*-DVB were investigated by the use of this equation.

Experimental

1. *Monomer*

o-DVB was prepared from *o*-xylene (Eastman Kodak's Reagent Grade) according to the procedure reported by HALFORD *et al.*[6]. The IR-spectrum of *o*-DVB thus prepared did not indicate the presence of its isomers, and its gas-chromatogram showed only one peak, the retention time of which is certainly different from those of peaks for commercial DVB (55% content of p-, m-DVB). These facts indicate that the monomer obtained is free from any isomers and impurities. BP.$_{15}$ 78 °C., n_D^{24} 1.5759, d_4^{30} 0.9275.

$C_{10}H_{10}$ (130.19) Calcd. C 92.26 H 7.74
Found C 92.30 H 7.73

2. *Polymerization Procedure*

Polymerization of *o*-DVB was carried out at various temperatures in the presence of α,α'-azobisisobutyronitrile (AIBN) as initiator and of benzene as solvent. A glass tube containing *o*-DVB, AIBN and benzene was sealed under reduced pressure after evacuation of atmosphere and the following replacement with dry nitrogen were repeated several times while this tube was kept in a dry ice-methanol mixture. This tube was then maintained at the polymerization temperature. After the lapse of a given period of time, the content of the tube was poured into enough methanol containing a trace of phenyl-β-naphthylamine as an inhibitor against oxidation or further polymerization. The precipitated polymer was washed thoroughly with methanol and purified by reprecipitation from benzene solution with methanol and dried in vacuo. In such a case that a gelation occurred during polymerization, the insoluble gel was separated by centrifugal separation (10,000 r.p.m.). The sample prepared at 20 °C. was irradiated with an ultra-violet lamp in order to get a reasonable rate of initiation.

3. *Determination of Residual Unsaturation*

Residual unsaturation in the soluble polymer was determined by IR-spectrum analysis and bromination in carbon tetrachloride.

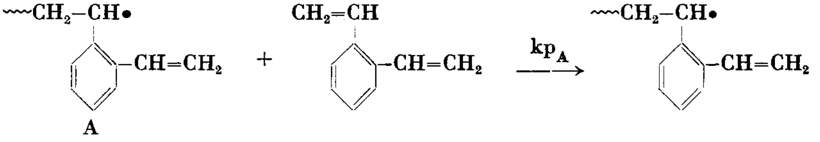
Quantitative infrared analysis was done by comparing absorption intensity of the double bond of polymer with that of *o*-DVB as a standard substance in carbon tetrachloride. In practical, calibration curves were made by plotting the optical densities versus the molarities of styrene and *o*-DVB (monovinyl unit) at 910 cm^{-1} due to C–H deformation vibration of end vinyl group and at 1630 cm^{-1} assigned to C=C stretching vibration respectively. However, while the curves of these two standards at 1630 cm^{-1} were superimposable in good approachment, those at 910 cm^{-1} had slopes (molar extinction coefficients of mono-vinyl unit) considerably different from each other. From this fact, the band at 1630 cm^{-1} was employed for the determination of residual unsaturation in the polymer, and in this work base lines were drawn from the position at 1590 cm^{-1} to that at 1660 cm^{-1} on the spectrum chart*).

Quantitative bromine addition was made as follows. Polymer sample of 50 mg. was dissolved in 10 ml. of carbon tetrachloride in a 100 ml. flask and it was cooled in an ice bath. 20 ml. of 0.1 *N* bromine reagent (carbon tetrachloride solution) pre-cooled was added to the sample solution and the flask was kept at 0 °C. for three hours in the dark. After 15 ml. of 20 % potassium iodide solution was added and the flask was shaken vigorously, the content was completely transfered with 300 ml. of water into a 1 l. flask and was titrated with 0.1 *N* sodium thiosulfate solution while being shaken repeatedly. The presence of a large amount of water was necessary to emulsify the organic layer so that the titration was carried out with ease. The above reaction conditions were chosen based on the experimental results of bromine addition to *o*-DVB monomer, styrene and indene. It was also confirmed that under the above conditions, substitution reaction hardly occurred in the bromination of these monomers.

Kinetics

In a previous study, one of the authors has introduced a composition equation indicating the content of pendant double bond (PDB) in a polymer of divinyl compound, in which the bimolecular chain growth, crosslinking and the unimolecular cyclization were simultaneously considered7). In the present paper, a composition equation is proposed for cyclopolymerization by taking no account of crosslinking reaction.

When *o*-DVB cyclopolymerizes through a head-to-tail addition process, a linear polymer having five-membered rings is to be produced as shown by equation (2). Since the soluble polymer of *o*-DVB has residual unsaturation to some extent, it may be assumed that the following three reactions occur predominantly in the propagation step before a gel point is attained.



(1)

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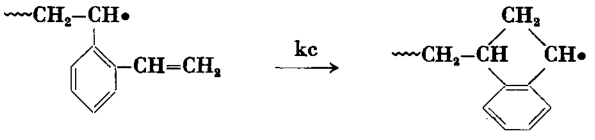
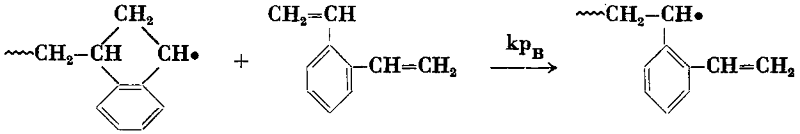
*) The data presented at the symposium of high polymer1) were calculated according to a base line drawn from the position at 1610 cm^{-1} to that at 1660 cm^{-1}. However, since it became clear that this procedure gave lower values than those obtained by bromination method, the data were re-calculated by employing the base line mentioned above.



B

(2)



(3)

If radicals A, B, and a monomer are denoted by $M_A\bullet$, $M_B\bullet$, and M, respectively, and their corresponding concentrations are shown as $(M_A\bullet)$, $(M_B\bullet)$, and (M) in mole/l., the rates of reactions (1), (2), and (3) are written as follows.

$$M_A\bullet + M \longrightarrow M_A\bullet \qquad 2k_{PA}(M_A\bullet)(M) \tag{4}$$

$$M_A\bullet \longrightarrow M_B\bullet \qquad k_c(M_A\bullet) \tag{5}$$

$$M_B\bullet + M \longrightarrow M_A\bullet \qquad 2k_{PB}(M_B\bullet)(M) \tag{6}$$

Equation (4) and (6) give the rate of consumption of *o*-DVB monomer. The factor 2 in those rate expressions is ascribed to the identical reactivities of two unsaturated groups in *o*-DVB. Equation (5) represents the rate of the intramolecular cyclization of radical $M_A\bullet$. This cyclization reaction is believed to be a unimolecular reaction.

If the kinetic chain length is great, it may be assumed that a monomer is consumed only in the propagation reaction so that we have

$$-\frac{d(M)}{dt} = 2k_{PA}(M_A\bullet)(M) + 2k_{PB}(M_B\bullet)(M) \tag{7}$$

PDB is produced by the addition of a monomer to a growing radical and disappears through the cyclization reaction. Therefore, when the concentration of PDB is denoted by (m), the rate of its generation is given by

$$\frac{d(m)}{dt} = 2k_{PA}(M_A\bullet)(M) + 2k_{PB}(M_B\bullet)(M) - k_c(M_A\bullet) \tag{8}$$

Assuming the existence of a steady-state concentration of radical species,

$$k_c(M_A\bullet) = 2k_{PB}(M_B\bullet)(M) \tag{9}$$

Substituting (9) into (7) and (8),

$$-\frac{d(m)}{d(M)} = \frac{2(M)}{2(M) + r_c} \tag{10}$$

where r_c represents the ratio of the rate constants:

$$r_c = k_c/k_{PA}$$

Eq. (10) shows the mole fraction of monomer units having an unreacted vinyl group in total monomer units in the polymer. If the degree of conversion is low, r_c is calculated by eq. (10) with initial monomer concentration (M_0) for (M) and with PDB % found in experimental analysis for $-d(m)/d(M) \times 100$.

At high degree of conversion, the integration of eq. (10) is necessary. Since (m) is zero at an initial stage, eq. (10) may be integrated as follows.

$$(m) = (M_0) - (M) - \frac{r_c}{2} \ln \frac{2(M_0) + r_c}{2(M) + r_c} \tag{11}$$

Providing $(M) = (M_0)(1-x)$,

$$\frac{(m)}{(M_0)x} = 1 - \frac{r_c}{2(M_0)x} \ln \frac{2(M_0) + r_c}{2(M_0)(1-x) + r_c} \tag{12}$$

In eq. (12), the mole fraction of PDB in the polymer is dependent on the degree of conversion x. Eqs. (10) and (12) indicate that the PDB content in the polymer varies as the initial monomer concentration changes if r_c is constant.

Results and Discussion

1. *Characteristics of Polymer*

The results of polymerizations are summarized in Table 1. Soluble polymers were obtained as fine, white powder, and melted at about 400 °C. with decomposition. They are soluble in organic solvents such as aromatic hydrocarbons, chloroform, and carbon tetrachloride. Evaporations of solvent from these solutions left clear and brittle films. In general, the intrinsic viscosity of their benzene solutions was low, while the polymer obtained in bulk polymerization showed considerably high viscosity.

Since the polymerization was stopped before gelation or nearly at gel point in this work, the degree of crosslinking in the insoluble polymer may be low. It seems that the soluble and the insoluble parts in a polymer may have the similar main structure because the IR-spectra of both parts did not show a significant difference.

Table 1. The Results of Polymerization of *o*-DVB in Benzene Solution

Temp. (°C.)	(M_0) [a] (M/l.)	AIBN (mM/l.)	Time (hrs.)	Conversion (%)		Pendant double bond (mole %)		r_c [b] (M/l.)
				Soluble part	Insoluble part	IR-method	Bromine addition	
90	2.67	7	0.5	7.8	12.1	57.2	–	3.60
70	0.58	23	53.8	72.0	0	30.2	–	1.62
70	0.62	27	18.0	60.2	0	28.7	30.1	2.17
70	1.43	44	4.9	10.7	40.7	42.7	–	2.54
70	2.62	10	1.8	5.0	12.1	60.2	–	3.14
70	4.09	7	1.6	3.2	0	71.3	–	3.20
70	6.85[c]	9	1.5	0.9	0	–	–	–
50	1.63	37	6.6	15.0	0	57.5	57.4	2.22
50	2.48	10	11.7	14.1	0	63.5	65.5	2.64
50	4.22	8	1.4	1.1	0	75.0	–	2.81
50	6.99[c]	9	0.8	1.7	0	87.1	–	2.07
30	2.78	24	39.6	3.5	3.9	71.9	–	2.10
30	4.31	8	68.7	0.6	6.5	78.6	–	2.27
20[d]	4.11	36	12.3	6.7	11.8	80.0	–	1.89

[a] Estimated after determining the specific gravity of solution at every temperature.
[b] Estimated by eq. (12) with the use of PDB % found.
[c] Bulk polymerization.
[d] Irradiated with an ultra-violet lamp.

The values of residual unsaturation determined by the two methods bore a reasonable agreement with each other as shown in Table 1. The values from the IR-spectrum analysis were used for the theoretical consideration.

When there existed one unsaturated group per DVB unit in the polymer, the PDB content was evaluated as 100%. However, the observed values of PDB were always lower than 100%, even though those values varied over a wide range from 30 to 90% according to the polymerization conditions as listed in Table 1.

Therefore, it was suggested from solubilities and the low PDB content in polymers that *o*-DVB was converted to a linear polymer having more or less recurring ring units in its main chain formed through a cyclopolymerization mechanism, as shown in eqs. (1), (2), and (3) in the section of kinetics. The ring structure was assumed to be a five-membered ring and further structural studies are under progress in these laboratories.

2. *The Effect of Dilution*

Gelation during polymerization was retarded by dilution of the system, e.g., the degree of conversion reached about 70% without gelation in a solution polymerization with $(M_0) = 0.6$ *M*/l. at 70°C.

It was indicated in Table 1 that the PDB content decreased with decreasing initial monomer concentration at a given polymerization temperature, and therefore the dilution made the cyclization reaction predominant. With selection of appropriate values of r_C several calculated curves of PDB content according to eq. (10) were drawn in Fig. 1, where experimental values at each temperature fell satisfactorily on those corresponding calculated curves except for extremely diluted case.

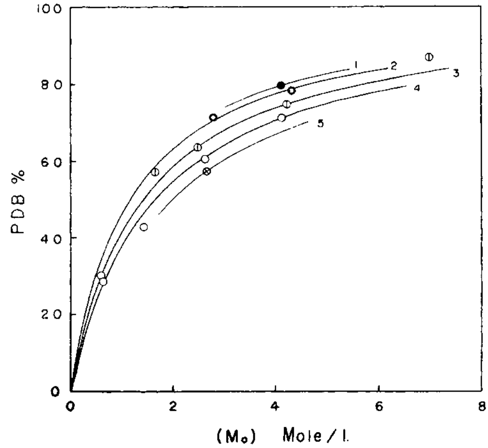


Fig. 1. Pendant double bond mole-% (PDB) *vs.* (M_0): experimental plots and theoretical curses by eq. (10), with the following values of r_C; 2.1, 2.3, 2.8, 3.3, and 4.0 mole/l. for the curves 1, 2, 3, 4, and 5, respectively. ● 20°C.; ◎ 30°C.; ⦶ 50°C.; ○ 70°C.; ⊕ 90°C.

Since the experimental results at the considerably high degree of conversion were involved in this work, r_C values in Table 1 were estimated by eq. (12) under the assumption that both the soluble and the insoluble part in a polymer have the same content of PDB.

Consequently, it may be concluded that r_C is approximately constant at a given reaction temperature in solution polymerization with (M_0) above 2.5 *M*/l., and subsequently the relationship between PDB content in the polymer and monomer concentration is quantitatively represented by eq. (10) or eq. (12).

3. *The Effect of Polymerization Temperature*

It is seen in Fig. 1 that PDB content in the polymer prepared at a given initial monomer concentration decreased with increasing polymerization temperature. The values of log r_c were calculated in accordance with eq. (12) from the experimental results at (M_0) = ca. 2.6 and 4 *M*/l., and plotted against 1/T in Fig. 2. The activation energy for this Arrhenius' plot was estimated to be approximately 1.9 kcal./*M*. This value is the difference of activation energy of the bimolecular propagation reaction, eq. (1), from that of the unimolecular cyclization reaction, eq. (2). It has been known that an activation energy of radical propagation of styrene was about 7.8 kcal./*M*[8]. Therefore, if the addition of *o*-DVB in propagation step (1) is assumed to have a similar nature to that of styrene, the intramolecular cyclization step (2) may have an activation energy of about 10 kcal./*M*.

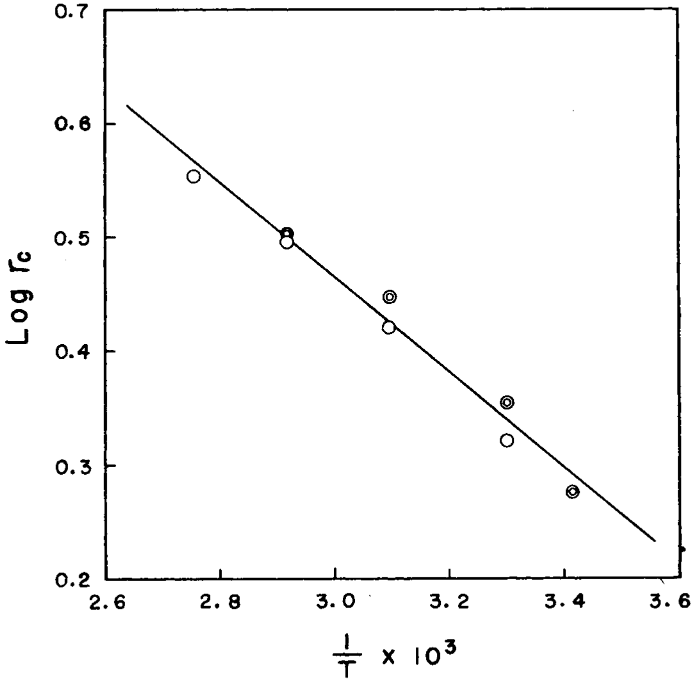
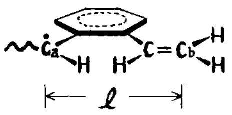
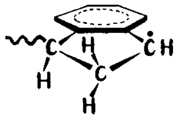


Fig. 2. Log r_c *vs.* 1/T:
(M_0) = ca. 2.6 mole/l. (○); (M_0) = ca. 4.2 mole/l. (◎)

The UV spectrum of *o*-DVB was shown by Fries *et al.*[9], it was also measured in ethyl alcohol in the present work, and there was observed the presence of two broad absorption bands at $\lambda_{max} = 231$ mμ ($\varepsilon_{max} = 2.19 \times 10^4$) and $\lambda_{max} = 257$ mμ ($\varepsilon_{max} = 1.60 \times 10^4$). From this result it may be considered that *o*-DVB has a considerably large resonance energy and its two vinyl groups tend to orient on the same plane with the phenyl group as shown in the following structure C, where two β-carbons of vinyl groups are located mutually at the most separated positions. The propagating radical A is considered to have a similar or somewhat larger



(A)



(B)

(C)

resonance energy in comparison with a styrene radical which has an estimated resonance energy of 20 kcal./*M*[10], while the cyclic radical B may have a smaller energy. It is, therefore, reasonable that the intramolecular cyclization reaction needs a larger activation energy than the addition of monomer.

As for the frequency factor of Arrhenius' plot (Fig. 2), it is impossible to make direct discussion because r_c is the ratio of the rate constants for two reactions having different kinetic orders. To discuss this problem, following treatment was tried assuming a special case.

We first consider a polymerization system under such a special monomer concentration that one double bond of *o*-DVB monomer exists near the carbon C_a of a radical A in the same probability of existence as that of the end PDB of the radical, in other words, a half molecule of *o*-DVB exists in a small space around C_a in which the end PDB can set its location but cannot locate outside.

In first approximation, such a space may be represented by a sphere with the center C_a and the radius l ($l = 4.27$ Å; maximum distance between C_a and C_b). A practical calculation for such a monomer concentration gave a value of 2.6 *M*/l.

We assume now that under such a concentration, both the rates of addition of the PDB and the double bond of *o*-DVB monomer to C_a may be described by eq. (13) as unimolecular reactions, V_c and V_p, respectively.

$$\begin{aligned} V_c &= k_C(M\bullet) \\ V_P &= k'_{PA}(M\bullet) \end{aligned} \tag{13}$$

On the other hand, V_p must be represented also by eq. (14) according to eq. (4) since the monomer concentration in this case is 2.6 *M*/l.

$$V_P = 2k_{PA}(M\bullet) \times 2.6 \tag{14}$$

From eq. (13) and eq. (14),

$$\frac{k_C}{k'_{PA}} = \frac{k_C}{5.2 \times k_{PA}} = \frac{r_C}{5.2} \tag{15}$$

According to eq. (15), consequently, the ratio of the frequency factors corresponding to k_C/k'_{PA}, in which there is no more prevention in comparing, is now made possible to be evaluated by an Arrhenius' plot of r_C. Graphical resolution from Fig. 2 gave 10 as the ratio of these frequency factors. The difference of activation entropies in the two reactions was computed with the aid of the absolute rate equation under an assumption that the transmission coefficient was unity, and found to be about 4.6 e.u.

If the assumptions mentioned above may be permitted, it is infered that, in the polymerization of *o*-DVB, the intramolecular ring closure is more ease than the intermolecular propagation at the point of view of steric factor.

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1) Presented at the Symposium of High Polymer, Osaka, Nov. 14, 1962.

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