BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2863—2870 (1970)

The Polymerization of Di-(β-methacrylyloxypropionaldehyde)-pentaerythritolacetal[*1]

Tatsuro OUCHI, Yorihiro IMASE and Masayoshi OIWA*

* *Department of Applied Chemistry, Faculty of Engineering, Kansai University, Senriyama, Suita-shi, Osaka*

(Received October 18, 1969)

The polymerization of di-(β-methacrylyloxypropionaldehyde)-pentaerythritolacetal (DβMPP) and the copolymerizations of DβMPP with styrene (St) and acrylonitrile (AN) have been carried out at 60°C, using benzoyl peroxide as an initiator. They have then been discussed kinetically from the point of view of cyclopolymerization. The results can be summarized as follows:

1) The relation among the rate of polymerization, R_p, the initiator concentration, (I), and the monomer concentration, (M), can be expressed by the following equations;

$$R_p/(\mathrm{I})^{1/2} = A(\mathrm{I})^{1/2} + B$$
$$R_p/(\mathrm{M}) = C(\mathrm{M}) + D$$

where A, B, C, and D are constant.

2) The ratio of the rate constant of the unimolecular cyclization reaction to that of the bimolecular propagation reaction of the uncyclized radical, k_c/k_p, was 22.0 mol/*l*.

3) The copolymerization of DβMPP proceeded primarily by means of cyclocopolymerization, and the ratio of the cyclization rate to the vinyl propagation also decreased with an increase in the comonomer fraction in the copolymer.

4) The following reactivity ratios were estimated on the basis of the Smets-Roovers equation:

System	$K_c = k_c/k_{11}$	$K_c' = k_c/k_{12}$	$r_1 = k_{11}/k_{12}$	$r_2 = k_{22}/k_{21}$	$r_c = k_{c1}/k_{c2}$
DβMPP(M_1)-St(M_2)	12.7	2.54	0.20	0.35	0.32
DβMPP(M_1)-AN(M_2)	12.7	5.08	0.40	0.35	0.61

As one of a series of studies of the polymerization of diallylidenepentaerythritol (DAPE), di-(β-methacrylyloxypropionaldehyde) - pentaerythritol (DβMPP) was prepared from DAPE and methacrylic acid; it was then confirmed to be a pure product. Although a patent has been previously published regarding the synthesis of DβMPP, its method is still far from clear.[1] On the present paper, it is well known that divinyl-compounds undergo cyclopolymerization.[2-4]

In the present paper, the polymerization of DβMPP will be discussed kinetically from the point of view of cyclopolymerization by modifying the Minoura and Mitoh method,[3] and the correlation with the rate constants will be investigated.

The copolymerizations of DβMPP with styrene (St) and acrylonitrile (AN) will also be carried out, and then the reactivity ratios will be estimated according to the Roovers and Smets procedure.[5]

Experimental

Materials. DβMPP was prepared as follows. A mixture of 310 g (1.46 mol) of DAPE, 372 m*l* (4.38 mol) of methacrylic acid, and 0.3 g of *p*-toluenesulfonic acid as an initiator was heated in a flask fitted with a reflux condenser at 55—60°C for 8—10 hr, the mixture was then washed with water to remove any unreacted methacrylic acid. Benzene was added, whereupon two layers formed; the product remaining in the benzene layer was separated and treated with sodium hydrosulfite to remove the dark color. After the benzene had been distilled under reduced pressure, the residual solution was filtered through an activated silica-charcoal layer to remove any haziness and foreign particles. The final product gave 90% of a light brown liquid and was confirmed to be DβMPP by the determination of the infrared spectrum, the molecular weight (MW), the saponification value (SV), and the bromine value (BV). $d_D^{20} = 1.1353$, $n_D^{20} = 1.4735$.

Found: C, 59.29; H, 7.41%; MW, 382.3; BV, 84.99; SV, 289.9. Calcd for $C_{19}H_{28}O_8$: C, 59.36; H, 7.34%; MW, 384.4; BV, 83.14; SV, 291.9.

St and AN, used as the comonomers, benzoyl per-

[*1] Studies of the Polymerization of Diallylidenepentaerythritol. IX.

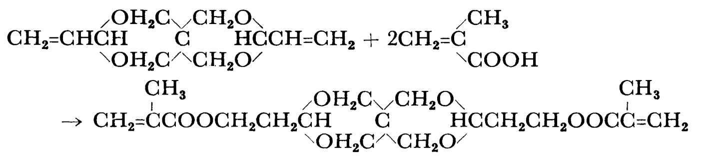
1) F. Fekete, U. S. 2975156 (1961).

2) C. Aso, T. Nawata and H. Kamao, *Makromol. Chem.*, **68**, 1 (1963).

3) Y. Minoura and M. Mitoh, *J. Polym. Sci., Part-A*, **3**, 2149 (1965).

4) S. G. Matsoyan, *ibid.*, **52**, 189 (1961).

5) J. Roovers and G. Smets, *Makromol. Chem.*, **60**, 89 (1963).



$$CH_2{=}CHCH{<}\begin{matrix}OH_2C\\OH_2C\end{matrix}{>}C{<}\begin{matrix}CH_2O\\CH_2O\end{matrix}{>}HCCH{=}CH_2 + 2CH_2{=}C{<}\begin{matrix}CH_3\\COOH\end{matrix}$$

$$\rightarrow CH_2{=}\overset{CH_3}{\overset{|}{C}}COOCH_2CH_2CH{<}\begin{matrix}OH_2C\\OH_2C\end{matrix}{>}C{<}\begin{matrix}CH_2O\\CH_2O\end{matrix}{>}HCCH_2CH_2OOC\overset{CH_3}{\overset{|}{C}}{=}CH_2$$

DβMPP

oxide (BPO), and the solvents were purified by the conventional method.

Polymerization Procedure. A glass ampoule was charged with the prescribed amount of each monomer, a solvent, and BPO; it was then degassed, sealed off under a vacuum, and set, without stirring, in a thermostated water bath at 60±0.1°C. The reaction solution was poured into a large amount of petroleum ether, and the polymer which was thus precipitated was centrifuged, filtered, and then dried *in vacuo* until a constant weight was attained. The conversion was less than 10%. The homopolymer was then purified from benzene-petroleum ether. The copolymers obtained on DβMPP-St and DβMPP-AN systems were also reprecipitated from benzene-petroleum ether and acetone-petroleum ether respectively.

Analyses of the Polymer and Copolymer. The polymer was dissolved in benzene, saponified in excess alcoholic potassium hydroxide, and neutralized with hydrochloric acid; then the residual unsaturation of the polymer was determined by the method of Siggia.[6] The molecular weight of the polymer was determined by means of a vapor-pressure osmometer (Hewlett Packard Model-302) at 37°C, using benzene as the solvent.

The composition of the resulting copolymer was determined by C, H, and N elementary analysis. The residual unsaturation of the copolymer was also calculated according to the Siggia method.[6]

The infrared spectra were measured by applying the potassium bromide-pellet technique to the polymer and the salt-plate method to the monomer on a Shimadzu infared spectrophotometer, Model IR-27.

The Kinetics of Polymerization

The preliminary experiment showed that the rate of the cyclization reaction was larger than that of the propagation reaction of the uncyclized radical on the polymerization of DβMPP. Therefore, the kinetics of the polymerization of DβMPP was discussed according to a modification of the Minoura *et al.* procedure.

The kinetic equations on the following reaction scheme were derived by assuming a steady-state condition:

		Rate const.
Decomposition of initiator	$I \rightarrow 2R\cdot$	k_d
Initiation	$R\cdot + M \rightarrow M\cdot$	k_i
Cyclization	$M\cdot \rightarrow M_c\cdot$	k_c
Propagation	$M\cdot + M \rightarrow M\cdot$	k_p
	$M_c\cdot + M \rightarrow M\cdot$	k_{cp}
Termination	$M_c\cdot + M_c\cdot \rightarrow P_c$	$\alpha^2 k_t$
	$M_c\cdot + M\cdot \rightarrow P_c'$	$\alpha\beta k_t$
	$M\cdot + M\cdot \rightarrow P$	$\beta^2 k_t$

(1)

where I denotes an initiator; M, a monomer; P_c, P_c', and P, the polymers; R·, the initiator radical; M·, the uncyclized radical, and M_c·, the cyclized radical. α and β are certain constants introduced to simplify the following algebraic treatment; the rate constants of the three termination reactions are, of course, determined by the values of α and β.

Here the crosslinking may be neglected as having been treated with the initial state.

If a steady state is assumed for the different types of radicals, Eqs. (2)—(4) can be obtained:

$$(R\cdot) = fk_d(I)/k_i(M) \tag{2}$$

$$(M\cdot) = \frac{(2/\alpha)(2fk_d/k_t)^{1/2}(I)^{1/2}\{k_{cp}(M)+(\alpha/2)(2fk_dk_t)^{1/2}(I)^{1/2}\}}{k_c+(2\beta/\alpha)\{k_{cp}(M)+(\alpha/2)(2fk_dk_t)^{1/2}(I)^{1/2}\}} \tag{3}$$

$$(M_c\cdot) = \frac{(k_c/\alpha)(2fk_d/k_t)^{1/2}(I)^{1/2}}{k_c+(2\beta/\alpha)\{k_{cp}(M)+(\alpha/2)(2fk_dk_t)^{1/2}(I)^{1/2}\}} \tag{4}$$

$$\text{or}\quad \alpha(M_c\cdot) + \beta(M\cdot) = (2fk_d/k_t)^{1/2}(I)^{1/2} \tag{5}$$

Here, f denotes the efficiency of the initiator.

The Rate Polymerization. Consequently, the rate of polymerization is given in Eq. (6);

$$\begin{aligned} R_p &= -d(M)/dt \\ &= 2k_p(M\cdot)(M) + 2k_{cp}(M_c\cdot)(M) \qquad (6) \\ &= (2k_{cp}/\alpha)(2fk_d/k_t)^{1/2}(I)^{1/2}(M) \\ &\times\frac{1+(2k_p/k_{cp})\{(k_{cp}/k_c)(M)+(\alpha/2k_c)(2fk_dk_t)^{1/2}(I)^{1/2}\}}{1+(2\beta/\alpha)\{(k_{cp}/k_c)(M)+(\alpha/2k_c)(2fk_dk_t)^{1/2}(I)^{1/2}\}} \qquad (7) \end{aligned}$$

Eqaution (7) can be developed as:

$$R_p = R_o\{1+(a-b)x-b(a-b)x^2+\cdots\cdots\} \tag{8}$$

where:

$$R_o = (2k_{cp}/\alpha)(2fk_d/k_t)^{1/2}(I)^{1/2}(M)$$

$$a = 2k_p/k_{cp},\quad b=2\beta/\alpha$$

and:

$$x = (k_{cp}/k_c)(M) + (\alpha/2k_c)(2fk_dk_t)^{1/2}(I)^{1/2} \tag{9}$$

From the results of the investigation of residual unsaturation, it was found that the rate of cyclization was far faster than that of propagation, namely,

$$k_c(M\cdot) \gg k_p(M\cdot)(M) \tag{10}$$

Therefore,

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[6] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 3rd ed., J. Wiley & Sons, New York and London (1963), p. 301.

$$k_c \gg k_p(\mathrm{M}) \tag{11}$$

Both k_p and k_{cp} may be assumed to be almost of the same order. Equation (11) is, then given by:

$$k_c \gg k_{cp}(\mathrm{M}) \tag{12}$$

The second term of x in Eq. (9) is rewritten as:

$$(\alpha/2k_c)(2fk_dk_t)^{1/2}(\mathrm{I})^{1/2} = (\alpha/2k_c)k_t^{1/2}R_i^{1/2} \tag{13}$$

where R_i is the rate of initiation.

Generally, R_i is of an order of about 10^{-8}, and k_t is about 10^8—10^6; then, $\alpha \leq 1$ in the case of a radical polymerization such as is described in this experiment. Therefore, the second term of x in Eq. (9) is influenced only by $1/k_c$.

As will be described later, the value of k_p/k_c is 0.046 l/mol. The rate constant of the propagation reaction in radical polymerization is in the range of 10—10^3; therefore, the value of $1/k_c$ is very small.

In view of these considerations, x is very small, and x^2, x^3 and other higher terms in Eq. (8) may be neglected.

Considering this approximation, R_p may be indicated as in the following equation:

$$\begin{aligned}R_p &= R_0\{1+(a-b)x\}\\ &= (2k_{cp}/\alpha)(2fk_d/k_t)^{1/2}(\mathrm{M})\\ &\quad\times [1+\{2k_p/k_{cp}-(2\beta/\alpha)\}\{(k_{cp}/k_c)(\mathrm{M})\\ &\qquad + (\alpha/2k_c)(2fk_dk_t)^{1/2}(\mathrm{I})^{1/2}\}]\end{aligned} \tag{14}$$

Accordingly, if the monomer concentration is kept constant and the initiator concentration is varied, Eq. (14) can be written as follows:

$$R_p/(\mathrm{I})^{1/2} = A(\mathrm{I})^{1/2} + B \tag{15}$$

where:

$$\begin{aligned}A &= (k_{cp}/k_c)(2fk_d)(2k_p/k_{cp}-2\beta/\alpha)(\mathrm{M}) = \text{const.}\\ B &= (2k_{cp}/\alpha)(2fk_d/k_t)^{1/2}(\mathrm{M})\\ &\quad\times \{(2k_p/k_{cp}-2\beta/\alpha)(k_{cp}/k_c)(\mathrm{M})+1\} = \text{const.}\end{aligned} \tag{16}$$

Similarly, when the initiator concentration is kept constant and the monomer concentration is varied, Eq. (14) can be written as follows:

$$R_p/(\mathrm{M}) = C(\mathrm{M}) + D \tag{17}$$

where:

$$\left.\begin{aligned}C &= (2k_{cp}/\alpha)(2fk_d/k_t)^{1/2}(2k_p/k_{cp}-2\beta/\alpha)(k_{cp}/k_c)(\mathrm{I})^{1/2}\\ &= \text{const.}\\ D &= (k_{cp}/k_c)(2fk_d)(2k_p/k_{cp}-2\beta/\alpha)(\mathrm{I})\\ &\quad + (2k_{cp}/\alpha)(2fk_d/k_t)^{1/2}(\mathrm{I})^{1/2} = \text{const.}\end{aligned}\right\} \tag{18}$$

The Residual Unsaturation of the Polymer. On the other hand, the rate of the formation of the pendant double bonds in the polymer is given by:

$$\mathrm{d(m)}/\mathrm{d}t = 2k_p(\mathrm{M}\cdot)(\mathrm{M})+2k_{cp}(\mathrm{M}_c\cdot)(\mathrm{M})-k_c(\mathrm{M}\cdot) \tag{19}$$

From Eqs. (6) and (19), we obtain:

$$\mathrm{d(m)}/\mathrm{d(M)} = 1-\frac{k_c(\mathrm{M}\cdot)}{2(\mathrm{M})(k_p(\mathrm{M}\cdot)+k_{cp}(\mathrm{M}_c\cdot))} \tag{20}$$

The combination of Eqs. (3), (4), and (20) gives:

$$\frac{1}{(\mathrm{M})(1-\mathrm{d(m)}/\mathrm{d(M)})}-\frac{k_p}{k_c} = \frac{k_{cp}}{2k_{cp}(\mathrm{M})+\alpha(2fk_dk_t)^{1/2}(\mathrm{I})^{1/2}}$$

which, on rearrangement, gives:

$$\frac{1}{1-2R_{us}}-\frac{1}{1+E(\mathrm{I})^{1/2}/2(\mathrm{M})} = (2k_p/k_c)(\mathrm{M}) \tag{21}$$

where:

$$2R_{us} = \mathrm{d(m)}/\mathrm{d(M)},\ E = \alpha(2fk_dk_t)^{1/2}k_{cp}$$

Results and Discussion

Polymerization of DβMPP. The conditions and the results of polymerization are summarized in Tables 1 and 2. From these tables, it is obvious that the rate of polymerization is not proportional to the square root nor to the first power of the initiator concentration, nor is it proportional to either the first or the second power of the monomer concentration, as was to be expected from Eqs. (15) and (17).

TABLE 1. RESULTS OF POLYMERIZATION OF DβMPP IN BENZENE AT 60°C, (M)=1.48 mol/l

(I) ($\times 10^{-3}$ mol/l)	R_p ($\times 10^{-6}$ mol/$l\cdot$sec)	BV*	$2R_{us}$*	$\bar{P}_n$*
10.0	12.8	4.24	0.102	107
7.50	11.0	4.28	0.103	124
5.00	9.05	4.32	0.104	155
2.50	6.36	4.45	0.107	223
1.20	4.40	4.53	0.109	310

* The values were obtained by extrapolating to zero for the conversion.

TABLE 2. RESULTS OF POLYMERIZATION OF DβMPP IN BENZENE AT 60°C, (I)=5.00×10^{-3}mol/l

(M) (mol/l)	R_p ($\times 10^{-6}$ mol/$l\cdot$sec)	BV*	$2R_{us}$*	$\bar{P}_n$*
2.95	19.1	7.98	0.192	342
2.22	14.0	6.82	0.164	243
1.48	9.05	4.32	0.104	155
1.03	6.18	2.62	0.063	105
0.738	4.31	2.04	0.049	71

* The value were obtained by extrapolating to zero for the conversion.

Since the value of residual unsaturation, $2R_{us}$, was very small, the rate of the cyclization reaction might be far faster than that of the propagation reaction. That is, the residual unsaturation decreased with a decrease in the monomer concentration.

Influence of the Initiator and Monomer Concentrations on the Rate of Polymerization. When the monomer concentration is varied, it may be kinetically expected from Eq. (15) that the plots of $R_p/(I)^{1/2}$ *vs.* (I) will be a straight line.

Similarly, if the initiator concentration is kept constant and the monomer concentration is varied, a linear relationship between $R_p/(M)$ and (M) may be expected on the basis of Eq. (17).

The results are plotted in Fig. 1, in which the fit of the experimental data to the linear relationship is fairly good. From the slopes and intercepts of the straight line shown in Fig. 1, *A*, *B*, *C*, and *D* were estimated to be 7.00×10^{-6}, 1.27×10^{-4}, 2.65×10^{-7}, and 5.68×10^{-6} respectively. Thus, the following ratios of the rate constant were calculated from the above values:

$$2fk_d = 6.95\times10^{-5}\,\mathrm{sec}^{-1}$$

$$2k_{cp}/\alpha\sqrt{k_t} = 1.14\times10^{-2}\,l^{1/2}/\mathrm{mol}^{1/2}\cdot\mathrm{sec}^{1/2}$$

$$(2k_p/k_{cp}-2\beta/\alpha)(k_{cp}/k_c) = 4.52\times10^{-2}\,l/\mathrm{mol}$$

Here, $2fk_d$ of the order of 10^{-5} seems to be pertinent when BPO is used as an initiator.

On the other hand, $2k_{cp}/\alpha\sqrt{k_t}$ of the order of 10^{-2} suggests that the termination between two $M_c\cdot$ may be very fast. Therefore, $(2k_p/k_{cp}-2\beta/\alpha)(k_{cp}/k_c)$ of the order of 10^{-2} may be presumed to be much cyclized by this polymerization.

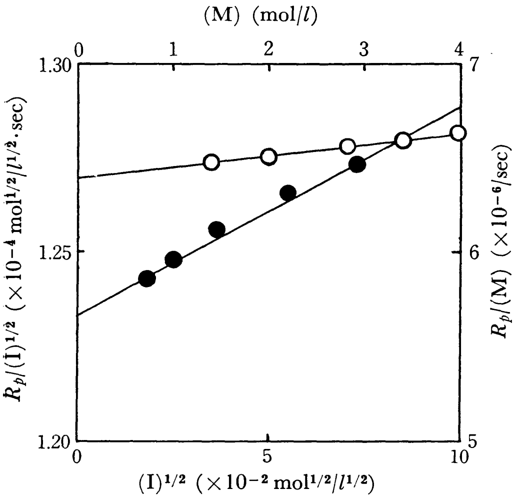

Fig. 1. Plots of $R_p/(I)^{1/2}$ *vs.* $(I)^{1/2}$ and $R_p/(M)$ *vs.* (M).

The Residual Unsaturation. If the monomer concentration is kept constant, the residual unsaturation is almost independent of the initiator concentration; the ratio of cyclization is almost never related to the initiator concentration, as is shown in Table 1. The ratio of the rate constant of the unimolecular cyclization reaction to that of the bimolecular propagation of the uncyclized radical, k_c/k_p, was evaluated by means of Eq. (21). *E* was then calculated to be 1.46 mol$^{1/2}$/$l^{1/2}$ on the basis of the previous rate constants. Accordingly, the plots of $\{1/(1-2R_{us})-(1+E(I)^{1/2}/2(M))\}$ *vs.* (M) are shown in Fig. 2; there is a good linear relationship, as was predicted by Eq. (21). The k_c/k_p value was estimated to be 22.0 mol/*l* from the slope of the straight line.

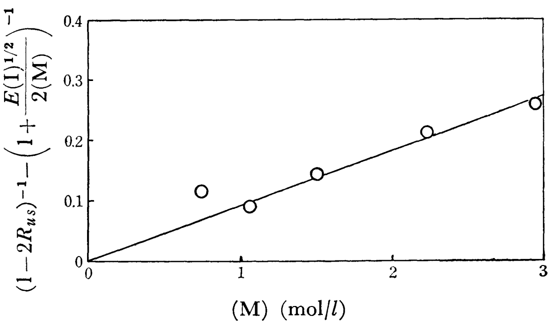

Fig. 2. Plots of $\left\{(1-2R_{us})^{-1}-\left(1+\frac{E(I)^{1/2}}{2(M)}\right)^{-1}\right\}$ *vs.* (M).

As the rate of cyclization was larger than the propagation of uncyclized radicals, the previous kinetic equations may be suitable for the polymerization of DβMPP. By combining k_c/k_p and $(2k_p/k_{cp}-2\beta/\alpha)(k_{cp}/k_c)$, the following rate constant could be obtained;

$$(k_{cp}/k_c)(2\beta/\alpha) = 4.58\times10^{-2}\,l/\mathrm{mol}$$

Accordingly, it was presumed that the propagation of the cyclized radical was almost equal to that of uncyclized radicals.

The degree of polymerization, $\overline{P}_n$, is small, and it then decreases with a decrease in the monomer concentration and with an increase in the initiator concentration, as is shown in Tables 1 and 2.

Copolymerization Results. The curves of the monomer and copolymer compositions are shown in Fig. 3. It was found that the azeotropic copolymers were prepared in both systems; DβMPP was copolymerized with St and AN. On the other hand, it might be seen that the rate of copolymerization had a minimum, but was almost

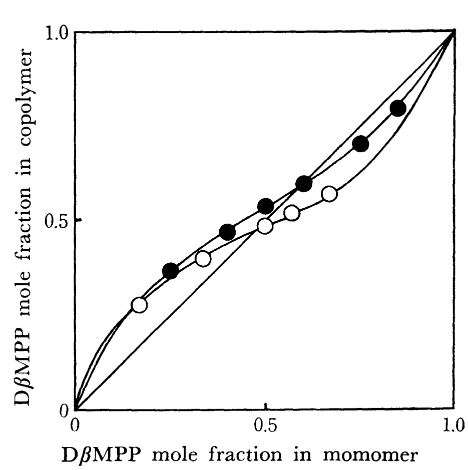

Fig. 3. Monomer - copolymer composition curves.
○: DβMPP-St, ●: DβMPP-AN,
—: calculated curve

independent of the monomer composition.

The Residual Unsaturation of the Copolymer. The ideal bromine value of the copolymer denotes BV_{id} when all the DβMPP units in polymer have pendant double bonds without any cyclization or crosslinking reaction, and the ratio of the experimental bromine value (BV_{ex}) to BV_{id} defines the residual unsaturation. Accordingly, the value of BV_{ex}/BV_{id} becomes 1.0 without any cyclization or crosslinking reaction, and it then decreases with an increase in those reactions.

The relation between the copolymer composition and the residual unsaturation is shown in Fig. 4. It was found that the residual unsaturation decreased with an increase in the DβMPP mole fraction in the copolymer, while the degree of cyclization increased. Such a tendency was more obvious in DβMPP-AN than in DβMPP-St because St was polymerized more easily than AN.

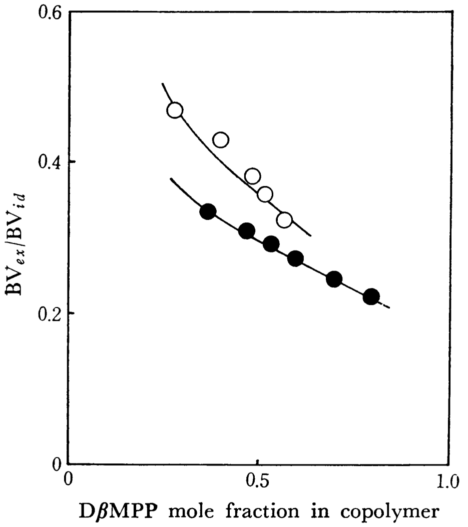

Fig. 4. Correlation of the copolymer composition to the residual unsaturation.

○: DβMPP-St, ●: DβMPP-AN,
—: calculated curve

The Determination of the Reactivity Ratio. The degree of cyclization to propagation was very large in those copolymerizations, as has been described previously.

Although the apparent monomer reactivity ratios could be calculated by the well-known Fineman-Ross method, the true monomer reactivity ratios could not be obtained.

In this experiment, the Smets-Roovers equation was applied to these copolymerizations, and then the reactivity ratios were calculated.

That is, the following reaction scheme was based on these copolymerizations:

$$M_1\cdot + M_1 \rightarrow M_1\cdot \qquad k_{11}(M_1\cdot)(M_1)$$

$$M_1\cdot + M_2 \rightarrow M_2\cdot \qquad k_{12}(M_1\cdot)(M_2)$$

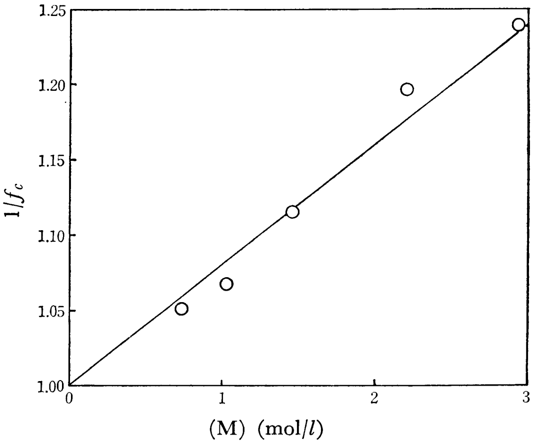

Fig. 5. Plots of $1/f_c$ vs. (M) on polymerization of DβMPP at 60°C; [BPO]$=5.00\times10^{-3}$ mol/l.

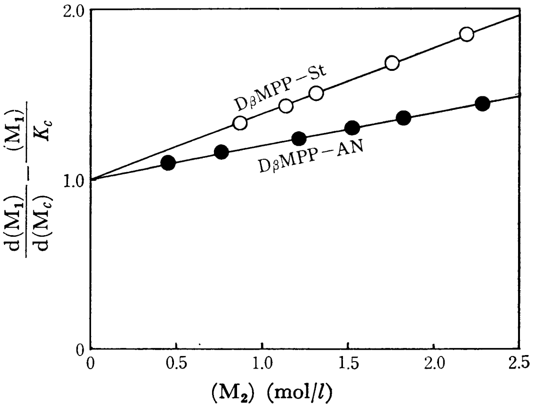

Fig. 6. Plots of $\left(\frac{d(M_1)}{d(M_c)}-\frac{(M_1)}{K_c}\right)$ vs. (M_2).

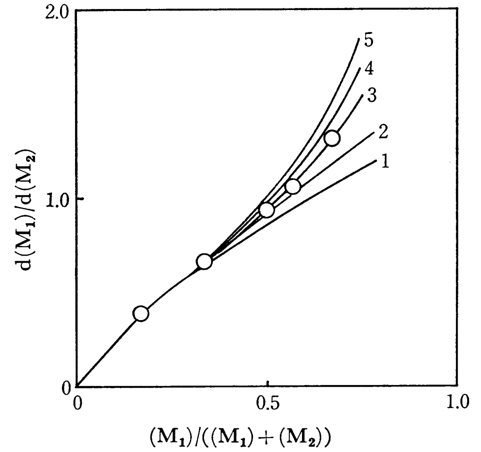

Fig. 7. Plots of $(M_1)/((M_1)+(M_2))$ vs. $d(M_1)/d(M_2)$.

DβMPP(M_1)-St(M_2)

$r_2=0.35$ 1: $r_c=0.10$, 2: $r_c=0.20$, 3: $r_c=0.30$
4: $r_c=0.40$, 5: $r_c=0.50$,
○: experimental value

$$\begin{array}{ll}
\mathrm{M_1}\cdot \rightarrow \mathrm{M}_c\cdot & k_c(\mathrm{M_1}\cdot) \\
\mathrm{M}_c\cdot + \mathrm{M_1} \rightarrow \mathrm{M_1}\cdot & k_{c1}(\mathrm{M_c}\cdot)(\mathrm{M_1}) \\
\mathrm{M}_c\cdot + \mathrm{M_2} \rightarrow \mathrm{M_2}\cdot & k_{c2}(\mathrm{M_c}\cdot)(\mathrm{M_2}) \\
\mathrm{M_2}\cdot + \mathrm{M_1} \rightarrow \mathrm{M_1}\cdot & k_{21}(\mathrm{M_2}\cdot)(\mathrm{M_1}) \\
\mathrm{M_2}\cdot + \mathrm{M_2} \rightarrow \mathrm{M_2}\cdot & k_{22}(\mathrm{M_2}\cdot)(\mathrm{M_2})
\end{array}$$

Here M_1 denotes a divinyl monomer; M_2, a comonomer; $M_1\cdot$ and $M_2\cdot$, the uncyclized radical, and $M_c\cdot$, the cyclized radical.

If a stationary state is assumed for the different types of radicals, Eqs. (22)—(24) can be derived:

$$\frac{\mathrm{d(M_1)}}{\mathrm{d(M_2)}} = \frac{\mathrm{(M_1)}}{\mathrm{(M_2)}} \times \frac{r_1\mathrm{(M_1)}+\mathrm{(M_2)}+K_c'}{\left\{r_2\mathrm{(M_2)}+\mathrm{(M_1)}+K_c'\left[\dfrac{r_2\mathrm{(M_2)}+\mathrm{(M_1)}}{r_c\mathrm{(M_1)}+\mathrm{(M_2)}}\right]\right\}} \tag{22}$$

$$\frac{\mathrm{d(M_1)}}{\mathrm{d(M}_c)} = 1 + \frac{\mathrm{(M_1)}}{K_c} + \frac{\mathrm{(M_2)}}{K_c'} \tag{23}$$

$$\frac{\mathrm{d(M_2)}}{\mathrm{d(M}_c)} = \mathrm{(M_2)}\left\{1+r_2\frac{\mathrm{(M_2)}}{\mathrm{(M_1)}}\right\}\left\{\frac{1}{K_c'}+\frac{1}{r_c\mathrm{(M_1)}+\mathrm{(M_2)}}\right\} \tag{24}$$

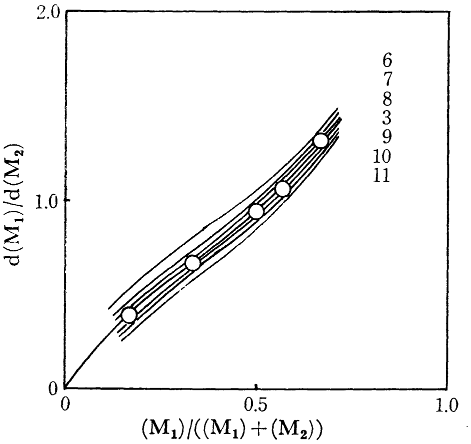

Fig. 8. Plots of $(M_1)/((M_1)+(M_2))$ *vs.* $d(M_1)/d(M_2)$.

DβMPP(M_1)-St(M_2)

$r_c=0.30$ 6: $r_2=0.20$, 7: $r_2=0.25$, 8: $r_2=0.30$
3: $r_2=0.35$, 9: $r_2=0.40$, 10: $r_2=0.45$
11: $r_2=0.50$, ○: experimental value

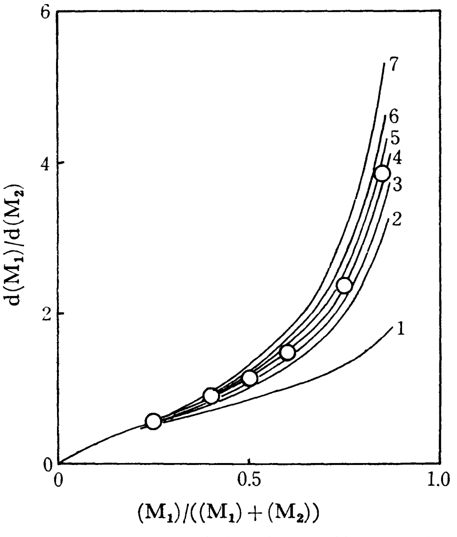

Fig. 9. Plots of $(M_1)/((M_1)+(M_2))$ *vs.* $d(M_1)/d(M_2)$.

DβMPP(M_1)-AN(M_2)

$r_2=0.35$ 1: $r_c=0.10$, 2: $r_c=0.40$, 3: $r_c=0.50$,
4: $r_c=0.60$ 5: $r_c=0.70$, 6: $r_c=0.80$,
7: $r_c=1.00$, ○: experimental value

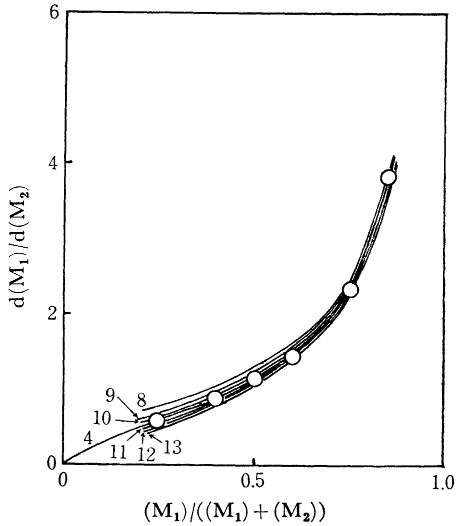

Fig. 10. Plots of $(M_1)/((M_1)+(M_2))$ *vs.* $d(M_1)/d(M_2)$.

$r_c=0.60$ 8: $r_2=0.20$, 9: $r_2=0.25$, 10: $r_2=0.30$,
4: $r_2=0.35$, 11: $r_2=0.40$, 12: $r_2=0.45$,
13: $r_2=0.50$, ○: experimental value

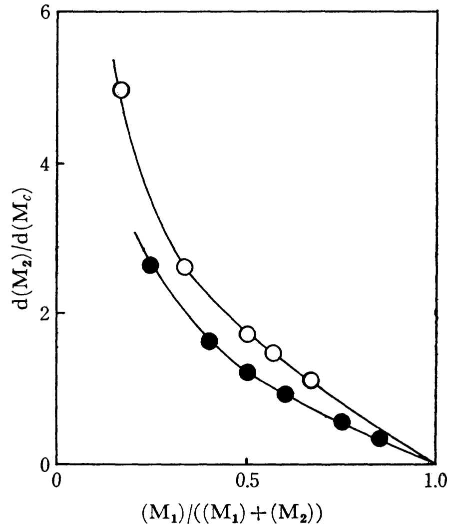

Fig. 11. Plots of $(M_1)/((M_1)+(M_2))$ *vs.* $d(M_2)/d(M_c)$.

○: DβMPP(M_1)-St(M_2)
●: DβMPP(M_1)-AN(M_2)
—: calculated curve

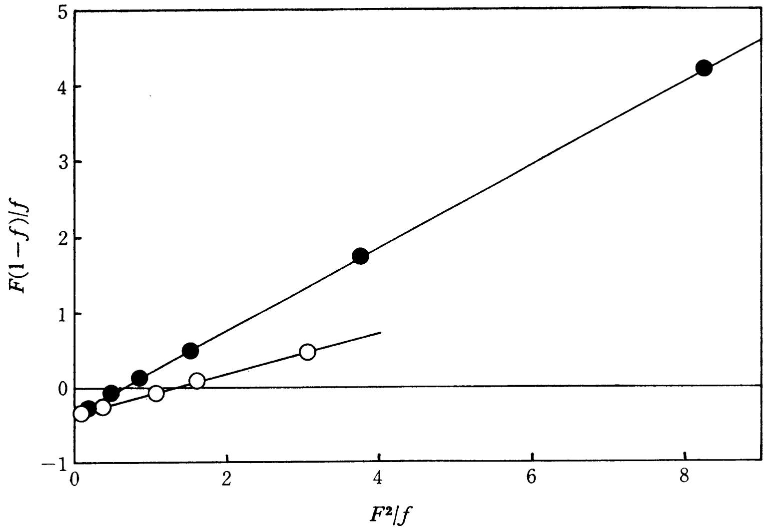

Fig. 12. Fineman-Ross plots.
○: DβMPP(M_1)-St(M_2), ●: DβMPP(M_1)-AN(M_2)

where $r_1=k_{11}/k_{12}$, $r_2=k_{22}/k_{21}$, $r_c=k_{c1}/k_{c2}$, $K_c=k_c/k_{11}$, and $K_c'=k_c/k_{12}$; d(M_1), d(M_2), and d(M_c) then denote M_1, M_2, and M_c respectively in the copolymer.

On the other hand, the relation between the fraction of cyclized units, f_c, and the monomer concentration is given in Eq. (25):

$$1/f_c = 1 + (\mathrm{M})/K_c \qquad (25)$$

The plots of $1/f_c$ *vs.* (M) are shown in Fig. 5 by using the data of the previously-reported homopolymerization of DβMPP; they have a good linear relationship, as was predicted from Eq. (25). K_c was estimated to be 12.7 mol/*l* from the slope of the straight line.

The correlations of $\{d(M_1)/d(M_c)-(M_1)/K_c\}$ to (M_2) are plotted in Fig. 6; they have a good linear relationship, and the K_c' values were calculated to be 2.54 on DβMPP-St and 5.08 on DβMPP-AN from these slopes.

From the values of K_c and K_c', the r_1 values were estimated to be 0.20 on DβMPP(M_1)-St(M_2) and 0.40 on DβMPP(M_1)-AN(M_2).

Then r_2 and r_c were determined from Eqs. (22) and (24) according to the trial-and-error method. The theoretical curves are compared with the experimental results in Figs. 7 and 8 (DβMPP-St) and Figs. 9 and 10 (DβMPP-AN). A good agreement between them is seen at $r_2=0.35$ and $r_c=0.30$ on DβMPP-St and $r_2=0.35$ and $r_c=0.60$ on DβMPP-AN.

By using these values, the relations between $(M_1)/((M_1)+(M_2))$ and $d(M_2)/d(M_c)$ are plotted in Fig. 11. The values calculated from Eq. (24) agreed very closely with the experimental values. Accordingly, the monomer reactivity ratios obtained might be proper for the copolymerizations.

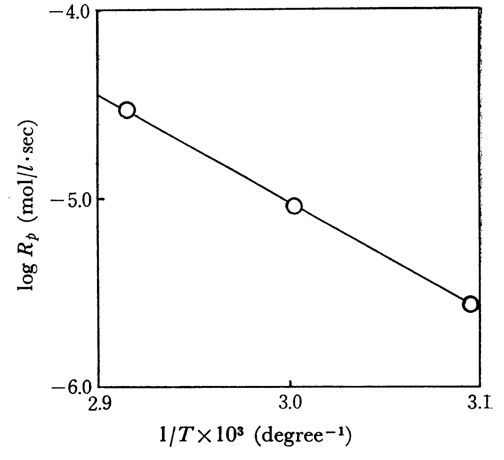

Fig. 13. Arrhenius plots.
(M) = 1.48 mol/*l*, (I) = 5.00×10^{-3} mol/*l*

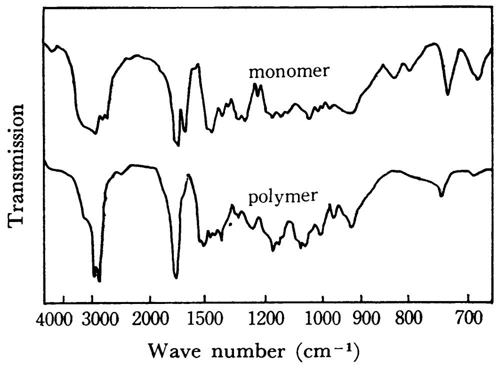

Fig. 14. Infrared spectra of DβMPP monomer and polymer.

If the cyclization and crosslinking reaction are neglected, the apparent monomer reactivity ratios can be obtained by the well-known Fineman-Ross method. The following results were estimated from the slopes and the intercepts of the straight line shown in Fig. 12:

DβMPP(M_1)-St(M_2)	$r_1'=0.27$,	$r_2'=0.35$
DβMPP(M_1)-AN(M_2)	$r_1'=0.55$,	$r_2'=0.35$

Activation Energy. To determine the overall activation energy, the polymerization of DβMPP was carried out at 50, 60, and 70°C. The plots of the logarithm of R_p *vs.* $1/T$ are shown in Fig. 13. The apparent activation energy was calculated to 26.5 kcal/mol from the slope of the obtained straight line. The value was almost equal to those of the normal vinyl polymerizations.

IR Spectrum. The infrared spectra of the resulting monomer and polymer are shown in Fig. 14. The absorption peaks at 1625, 1740, and 2930 cm^{-1} are assigned to C=C, $\rangle$C=O, and CH_3 respectively. The absorptions of the cyclic acetal compound are also presented in the range of 1200—1040 cm^{-1}. In spite of the initial state, the C=C band at 1625 cm^{-1} on the polymer almost disappears; therefore, it was found that the cyclization reaction was preferential upon the polymerization of DβMPP.

On the other hand, DβMPP was gelated with a high conversion; we will later report on such crosslinking.