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Kinetic Study of the Polymerization of Diallyl Carbonate*1

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The polymerization of diallyl carbonate was carried out at 60°C, benzoyl peroxide being used as the initiator; here it has been discussed kinetically from the point of view of cyclopolymerization. The rate of polymerization, R_p, was not proportional to the square root or the first power of the initiator concentration, (I), but $R_p/(I)^{1/2}$ and $(I)^{1/2}$ bore a linear relationship. The rate of polymerization, the residual unsaturation, and the degree of polymerization decreased with a decrease in the monomer concentration. The relation between the rate of polymerization over the degree of polymerization, $R_p/\bar{P}_{n,0}$ and the monomer concentration, (M), was also linear, as in $R_p/(I)^{1/2}$ and $(I)^{1/2}$. The ratio of the rate constant of the unimolecular cyclization reaction to that of the bimolecular propagation reaction of the uncyclized radical, K_c, was estimated to be 4.0 mol/*l* from the dependence of the residual unsaturation on the monomer concentration.

It is well known that diallyl-compounds undergo cyclopolymerization.[1-9] It seems, however, that there have been few detailed studies of kinetic treatment on the basis of cyclopolymerization.

Holt and Simpson[1] have studied, with a number of diallyl esters, the statistical theory of gelation; they have found that the conversion at the gelation point was greater than would be calculated for the formation of networks from tetrafunctional monomers, and that the divergence from theory could be partly explained as resulting from a loss of unsaturation by cyclization. In their report they also proposed a reaction scheme for the polymerization of the diallyl ester; however, the kinetics based on the scheme were not clarified in detail, for their consideration contained the assumption that the reactivities of the uncyclized radical with an adjacent pendant double bond and of the cyclized radical were equivalent.

On the other hand, we have presented in detail the kinetics of the polymerization of diallyl phthalate;[10] in this paper the two radicals mentioned above were individually treated.

In the present experiment, the polymerization of diallyl carbonate was carried out; by employing the kinetic equations derived in a previous paper, we will kinetically discuss our results from the standpoint of cyclopolymerization.

Experimental

Materials. The diallyl carbonate was prepared by the ester exchange reaction of diethyl carbonate with allyl alcohol according to the procedure of Adelson and Dannenberg.[11] A portion of clean sodium (about 4 g) was cut into small pieces and then added to 230 g of absolute allyl alcohol. After all the sodium had been dissolved, 120 g of diethyl carbonate was added; the mixture was refluxed under a Vigreux column, and then ethyl alcohol was taken off overhead. The residue was taken up in 100 m*l* of benzene, and water-washed several times, after which the benzene was distilled off. The residue was distilled under reduced pressure and then redistilled just before use; bp 90—91°C/50 mmHg, d_4^{20} 0.969 (lit,[11] bp 95—97°C/57—61 mmHg). The purity of the diallyl carbonate was confirmed by the complete disappearance of the absorption due to the ethyl group in its NMR spectrum.

The benzoyl peroxide (BPO) was purified by repeated precipitations from a chloroform solution by the addition of methanol.

*1 Studies of the Polymerization of Diallyl-compounds. V.

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The benzene was washed thoroughly with concentrated sulfuric acid and then with distilled water until it became neutral; it was then dried on calcium chloride and distilled over metallic sodium.

Polymerization Procedure. Polymerizations were carried out in glass ampoules (10—50 m*l* capacity), using dry benzene as the solvent and BPO as the initiator. Measured amounts of diallyl carbonate, BPO, and benzene were placed in a glass ampoule, which was then degassed twice in the usual manner and flushed with nitrogen. The ampoule was then sealed under a vacuum and transferred into a thermostat regulated at the desired temperature.

After a definite reaction time, the ampoule was removed from the thermostat and the polymer was separated by pouring the contents into a tenfold volume of methanol containing hydroquinone, and also by centrifuging.

The polymer thus obtained was then washed repeatedly with methanol and dried *in vacuo* until a constant weight was attained. The conversion was calculated on the weight of the dry polymer obtained.

The polymer was then purified by dissolving it in benzene and by subsequent reprecipitation in methanol.

Analyses of the Polymer. The residual unsaturation of the purified polymer was determined by the method of Simpson *et al.*[12]; the polymer was dissolved in benzene, saponified in excess alcoholic potassium hydroxide, and neutralized with hydrochloric acid, and then the free allyl alcohol was determined by the bromide-bromate technique. Tests on pure diallyl esters showed that this could be done within an estimated error of $\pm 1.5\%$. The results were expressed as percentages of pure diallyl carbonate.

The molecular weight of the polymer was measured with a vapor-pressure osmometer, Hewlett Packard 302.

Results and Discussion

Kinetics of the Diallyl Ester. In a previous paper,[10] the kinetics of the polymerization of diallyl phthalate was discussed in detail on the basis of cyclopolymerization; the kinetic equations were derived by assuming steady-state conditions, conditions which were based on the following reaction scheme:

Decomposition: $\mathrm{I} \longrightarrow 2\mathrm{R}\cdot$ $2k_d(\mathrm{I})$

Initiation: $\mathrm{R}\cdot + \mathrm{M} \longrightarrow \mathrm{M}\cdot$ $2k_i(\mathrm{R}\cdot)(\mathrm{M})$

Cyclization: $\mathrm{M}\cdot \longrightarrow \mathrm{M_c}\cdot$ $k_c(\mathrm{M}\cdot)$

Propagation:
$\mathrm{M}\cdot + \mathrm{M} \longrightarrow \mathrm{M}\cdot$ $2k_p(\mathrm{M}\cdot)(\mathrm{M})$
$\mathrm{M_c}\cdot + \mathrm{M} \longrightarrow \mathrm{M}\cdot$ $2k_{cp}(\mathrm{M_c}\cdot)(\mathrm{M})$

Chain transfer:
$\mathrm{M}\cdot + \mathrm{M} \longrightarrow \mathrm{P} + \mathrm{M}\cdot^*$ $2k_{t_1}(\mathrm{M}\cdot)(\mathrm{M})$
$\mathrm{M_c}\cdot + \mathrm{M} \longrightarrow \mathrm{P} + \mathrm{M}\cdot^*$ $2k_{t_2}(\mathrm{M_c}\cdot)(\mathrm{M})$

Re-initiation: $\mathrm{M}\cdot^* + \mathrm{M} \longrightarrow \mathrm{M}\cdot$ $2k_i'(\mathrm{M}\cdot^*)(\mathrm{M})$

Stabilization: $\mathrm{M}\cdot^* + \mathrm{M}\cdot^* \longrightarrow \mathrm{M}^* - \mathrm{M}^*$ $k_{t_3}(\mathrm{M}\cdot^*)^2$

where I denotes an initiator; M, a diallyl ester monomer; P, the polymer; R·, the initiator radical; M·, the uncyclized radical; $\mathrm{M_c}\cdot$, the cyclized radical, and M·*, the degraded radical.

If a steady state is assumed for the different types of radicals, Eqs. (1)—(4) can be obtained:

$$(\mathrm{R}\cdot) = fk_d(\mathrm{I})/k_i(\mathrm{M}) \tag{1}$$

$$(\mathrm{M}\cdot) = \frac{2fk_d(\mathrm{I}) + 2k_i'(2fk_d(\mathrm{I})/k_{t_3})^{1/2}(\mathrm{M})}{2k_{t_1}(\mathrm{M}) + k_ck_{t_2}/(k_{cp} + k_{t_2})} \tag{2}$$

$$(\mathrm{M_c}\cdot) = \frac{\{k_c/2(k_{cp} + k_{t_2})(\mathrm{M})\}\{2fk_d(\mathrm{I}) + 2k_i'(2fk_d(\mathrm{I})/k_{t_3})^{1/2}(\mathrm{M})}{2k_{t_1}(\mathrm{M}) + k_ck_{t_2}/(k_{cp} + k_{t_2})} \tag{3}$$

$$(\mathrm{M}\cdot^*) = (2fk_d(\mathrm{I})/k_{t_3})^{1/2} \tag{4}$$

The rate and the degree of polymerization were then obtained as Eqs. (5) and (6), in which it was assumed that the dimer, M*–M*, produced by stabilization was present in the polymer recovered.

$$\begin{aligned} R_p &= 2k_i(\mathrm{R}\cdot)(\mathrm{M}) + 2(k_p + k_{t_1})(\mathrm{M}\cdot)(\mathrm{M}) \\ &\quad + 2(k_{cp} + k_{t_2})(\mathrm{M_c}\cdot)(\mathrm{M}) + 2k_i'(\mathrm{M}\cdot^*)(\mathrm{M}) \\ &= \{2fk_d(\mathrm{I}) + 2k_i'(2fk_d(\mathrm{I})/k_{t_3})^{1/2}(\mathrm{M})\} \\ &\quad \times \left\{1 + \frac{2(k_p + k_{t_1})(\mathrm{M}) + k_c}{2k_{t_1}(\mathrm{M}) + k_ck_{t_2}/(k_{cp} + k_{t_2})}\right\} \end{aligned} \tag{5}$$

$$\begin{aligned} \bar{P}_{n,o} &= R_p/\{2k_{t_1}(\mathrm{M}\cdot)(\mathrm{M}) + 2k_{t_2}(\mathrm{M_c}\cdot)(\mathrm{M}) + k_{t_3}(\mathrm{M}\cdot^*)^2\} \\ &= \left\{1 + \frac{2(k_p + k_{t_1})(\mathrm{M}) + k_c}{2k_{t_1}(\mathrm{M}) + k_ck_{t_2}/(k_{cp} + k_{t_2})}\right\} \\ &\quad \times \left\{\frac{fk_d(\mathrm{I}) + k_i'(2fk_d(\mathrm{I})/k_{t_3})^{1/2}(\mathrm{M})}{2fk_d(\mathrm{I}) + k_i'(2fk_d(\mathrm{I})/k_{t_3})^{1/2}(\mathrm{M})}\right\} \end{aligned} \tag{6}$$

Here f denotes the efficiency of the initiation of the chain radicals by R·.

On the other hand, the rate of the formation of the pendant double bonds in the polymer is given by:

$$\begin{aligned} \mathrm{d}m/\mathrm{d}t &= 2k_i(\mathrm{R}\cdot)(\mathrm{M}) + 2k_p(\mathrm{M}\cdot)(\mathrm{M}) - k_c(\mathrm{M}\cdot) \\ &\quad + 2k_{cp}(\mathrm{M_c}\cdot)(\mathrm{M}) + 4k_{t_1}(\mathrm{M}\cdot)(\mathrm{M}) \\ &\quad + 4k_{t_2}(\mathrm{M_c}\cdot)(\mathrm{M}) + 2k_i'(\mathrm{M}\cdot^*)(\mathrm{M}) \\ &= \{2fk_d(\mathrm{I}) + 2k_i'(2fk_d(\mathrm{I})/k_{t_3})^{1/2}(\mathrm{M})\} \\ &\quad \times \left\{2 + \frac{2(k_p + k_{t_1})(\mathrm{M})}{2k_{t_1}(\mathrm{M}) + k_ck_{t_2}/(k_{cp} + k_{t_2})}\right\} \end{aligned} \tag{7}$$

By combining Eqs. (5) and (7), the following equation was obtained for evaluating K_c, the probability of cyclization which is characteristic of each monomer.

$$\left(F - \frac{2\beta}{1 + 2\beta}\right)^{-1} = \frac{(1 + 2\alpha)(1 + 2\beta)}{1 + 3\alpha + 2\alpha\beta} + \frac{(1 + 2\beta)^2}{2(1 + 3\alpha + 2\alpha\beta)(1 + \beta)} \cdot K_c \cdot \frac{1}{(\mathrm{M})} \tag{8}$$

12) W. Simpson, T. Holt and R. J. Zetie, *J. Polymer Sci.*, **10**, 489 (1953).

where F is the ratio of the amount of the residual pendant double bonds in the polymer to that of the polymerized diallyl ester monomer, $dm/d(M)$, while α, β, and K_c are k_{t1}/k_p, k_{t2}/k_{cp}, and k_c/k_p respectively.

If the kinetic chain length is sufficiently large and if the dimer, M*–M*, produced by stabilization is not present in the polymer recovered, the loss of the monomer by the initiation, chain transfer, and re-initiation reactions is negligible compared with that by the propagation reaction. The above equations may, therefore, be simplified as follows:

$$R_p = 2k_p(M\cdot)(M) + 2k_{cp}(M_c\cdot)(M)$$
$$= \{2fk_d(I) + 2k_i'(2fk_d(I)/k_{t3})^{1/2}(M)\} \times \left\{\frac{2k_p(M) + k_ck_{cp}/(k_{cp} + k_{t2})}{2k_{t1}(M) + k_ck_{t2}/(k_{cp} + k_{t2})}\right\} \quad (9)$$

$$\bar{P}_{n,o} = R_p/\{2k_{t1}(M\cdot)(M) + 2k_{t2}(M_c\cdot)(M)\}$$
$$= \frac{2k_p(M) + k_ck_{cp}/(k_{cp} + k_{t2})}{2k_{t1}(M) + k_ck_{t2}/(k_{cp} + k_{t2})} \quad (10)$$

$$dm/dt = 2k_p(M\cdot)(M) - k_c(M\cdot) + 2k_{cp}(M_c\cdot)(M)$$
$$= \{2fk_d(I) + 2k_i'(2fk_d(I)/k_{t3})^{1/2}(M)\} \times \left\{\frac{2k_p(M) - k_ck_{t2}/(k_{cp} + k_{t2})}{2k_{t1}(M) + k_ck_{t2}/(k_{cp} + k_{t2})}\right\} \quad (11)$$

From Eqs. (9) and (11) we obtain:

$$(1 - F)^{-1} = \frac{1}{1 + \beta} + \frac{2}{K_c}\cdot(M) \quad (12)$$

The combination of Eqs. (9) and (10) gives:

$$R_p/\bar{P}_{n,o} = 2fk_d(I) + 2k_i'(2fk_d(I)/k_{t3})^{1/2}(M) \quad (13)$$

Polymerization Results. The bulk polymerization of diallyl carbonate was investigated under different initiator concentrations at 60°C; the time-conversion curves are shown in Fig. 1. The initial rates of polymerization as calculated from the slope of the straight lines shown in Fig. 1 are summarized in Table 1; they are not proportional to the square root or to the first power of the initiator concentration, as had been expected from Eq. (9).

Table 1. Influence of the initiator on the rate of polymerization of diallyl carbonate (in bulk, at 60°C)

(I) mol/l	$R_p\times10^5$ mol/l·sec	$(R_p/(I)^{1/2})\times10^5$ (mol/l)$^{1/2}$·sec^{-1}	$(R_p/(I))\times10^5$ sec^{-1}
0.4	6.84	10.24	16.2
0.2	3.64	8.13	18.2
0.1	2.05	6.47	20.5
0.06	1.44	5.91	24.1

The influence of the monomer concentration was studied by measuring the rate of polymerization, the residual unsaturation, and the degree of poly-

Table 2. Results of polymerization of diallyl carbonate at 60°C ((BPO)=0.2 mol/l, in benzene)

(M) mol/l	$R_p\times10^5$ mol/l·sec	R_{us}[a]	$\bar{P}_{n,o}$[b]	$(R_p/\bar{P}_{n,o})\times10^7$ mol/l·sec
6.82	3.64	0.379	77	4.72
4.54	3.12	0.341	75	4.16
3.41	2.47	0.306	67	3.69
2.27	2.05	0.253	63	3.25
1.70	1.82	0.237	56	3.25
1.14	—	0.224	51	—

a) The residual unsaturation is the degree of unsaturation of the molecule expressed as a percentage of pure diallyl carbonate and was obtained by the analysis of the polymer less than 10% conversion.

b) The initial degree of polymerization was obtained by the extrapolation from the experimental results shown in Fig. 2.

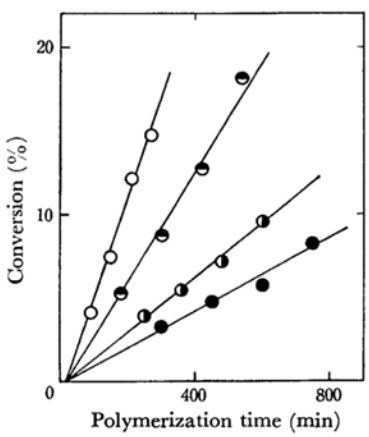

Fig. 1. Time-conversion curves in the bulk polymerization of diallyl carbonate at 60°C.
(I)=0.4(○), 0.2(◓), 0.1(◑), 0.06(●) mol/l

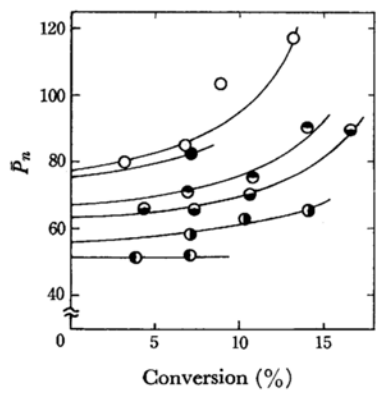

Fig. 2. Dependence of the degree of polymerization on conversion.
Polymerization temperature, 60°C
(I)=0.2 mol/l; (M)=6.82(○), 4.54(●), 3.41(◓), 2.27(◒), 1.70(◑), 1.14(◐) mol/l

merization at a constant initiator concentration ((I)=0.2 mol/l) at 60°C. The results obtained are given in Table 2.

The conversion dependence of the degree of polymerization is shown in Fig. 2. It had a tendency to increase with an increase in the conversion, and to become smaller with a decrease in the monomer concentration. Similar tendencies were observed in the previous work[10] for the polymerization of diallyl phthalate. These results may be attributed to an increase in the probability of the crosslinking reaction as the polymerization proceeds.

The values of the initial degree of polymerization, $\bar{P}_{n,o}$, as extrapolated from the experimental results shown in Fig. 2, are plotted against the monomer concentration in Fig. 3.

In Fig. 4, the relation between the residual unsaturation of the polymer, R_{us}, and the monomer concentration is plotted. Both $\bar{P}_{n,o}$ and R_{us} tend to decrease with a decrease in the monomer concentration.

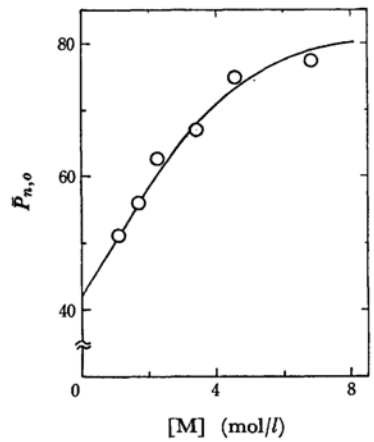

Fig. 3. Dependence of the initial degree of polymerization on monomer concentration.
Polymerization temperature, 60°C, (I)=0.2 mol/l

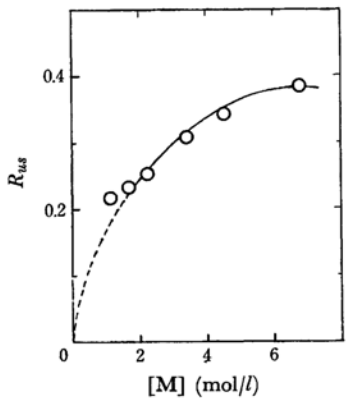

Fig. 4. Relation between the residual unsaturation and the monomer concentration.
Polymerization temperature, 60°C, (I)=0.2 mol/l

Also, as is shown in Figs. 2 and 3 and in Table 2, the initial degree of polymerization was sufficiently large; therefore, as has been mentioned above, the simplified kinetic equations, *e. g.*, Eqs. (9)—(12), can be used instead of the more elaborate ones, *e. g.*, Eqs. (5), (6) and (8), for the polymerization of diallyl carbonate.

Dependence of the Degree of Polymerization on the Initiator and Monomer Concentrations. From Eq. (10) it may be kinetically expected that the degree of polymerization will be independent of the initiator concentration. The degree of polymerization of the polymers obtained under different initiator concentrations, *e. g.*, (I)=0.4, 0.2, 0.1, and 0.06 mol/l, were determined to be 86, 82, 86, and 83 respectively; they were nearly identical, regardless of the initiator concentration. The polymers analyzed were all of about 5% conversion. This agreement between the kinetics and the experimental results may support the idea that the use of the simplified kinetic equations is justifiable.

On the other hand, the dependence of the initial degree of polymerization on the monomer concentration is shown in Fig. 3. By comparing the results with Eq. (10), we obtained the following results : $(\bar{P}_{n,o})_{M\to 0}=k_{cp}/k_{t2}\simeq 42$, $(\bar{P}_{n,o})_{M\to\infty}=k_p/k_{t1}\simeq 80$. These results suggest that the reactivities of the uncyclized radical and the cyclized radical are not equivalent. If the reactivities of the two radicals are equivalent, as has been shown by Holt and Simpson,[1] the degree of polymerization should be independent of the monomer concentration.

Influence of the Initiator and Monomer Concentrations on the Rate of Polymerization. When the monomer concentration is kept constant and the initiator concentration is varied, it may be kinetically expected from Eq. (9) that $R_p/(\mathrm{I})^{1/2}$ *vs.*

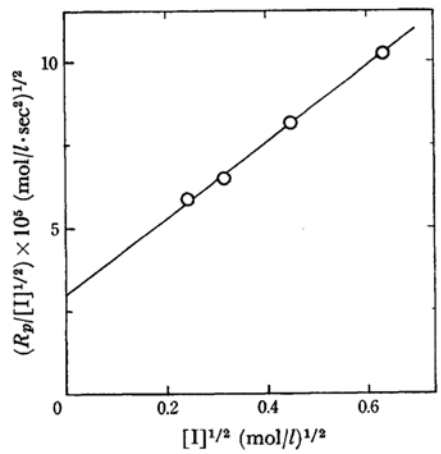

Fig. 5. Plot of $R_p/(\mathrm{I})^{1/2}$ *vs.* $(\mathrm{I})^{1/2}$.
Polymerization temperature, 60°C
(M)=6.82 mol/l

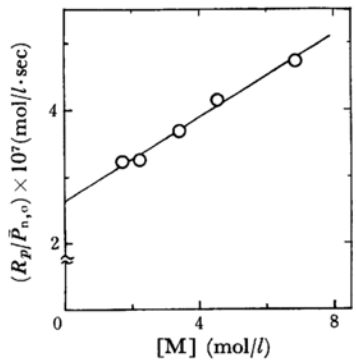

Fig. 6. Plot of $R_p/\bar{P}_{n,o}$ *vs.* (M).
Polymerization temperature, 60°C
(I)=0.2 mol/*l*

$(I)^{1/2}$ will be a straight line.*2

Similarly, if the initiator concentration is kept constant and the monomer concentration is varied, a linear relationship between $R_p/\bar{P}_{n,o}$ and (M) may be expected from Eq. (13).

These results are plotted in Figs. 5 and 6, in which the fit of the experimental data to the linear relationship is fairly good. From the slope and the intercept of the straight line shown in Fig. 5, fk_d and $k_t'/k_{t3}^{1/2}$ were estimated to be 0.74×10^{-6} sec^{-1} and 0.23×10^{-4} $(l/mol\cdot sec)^{1/2}$ respectively, while in Fig. 6, fk_d and $k_t'/k_{t3}^{1/2}$ were 0.67×10^{-6} sec^{-1} and 0.30×10^{-4} $(l/mol\cdot sec)^{1/2}$, values in good agreement with the values in Fig. 5.

Estimation of K_c. The ratio of the rate constant of the unimolecular cyclization reaction to that of the bimolecular propagation of the uncyclized radical, K_c, was evaluated by applying Eq. (12) to the experimental measurements of the dependence of the residual unsaturation on the monomer concentration.

*2 Eq. (9) can be written as follows:

$$\frac{R_p}{(I)^{1/2}} = \{2fk_d(I)^{1/2} + 2k_i'(2fk_d/k_{t3})^{1/2}(M)\} \times \left\{\frac{2k_p(M) + k_ck_{cp}/(k_{cp}+k_{t2})}{2k_{t1}(M) + k_ck_{t2}/(k_{cp}+k_{t2})}\right\}$$

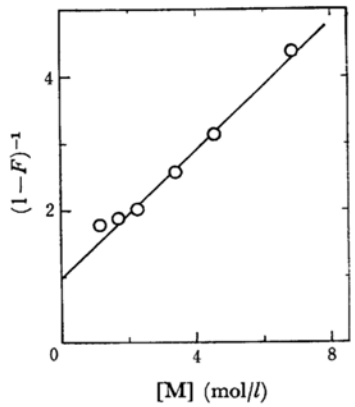

Fig. 7. Plot of $(1-F)^{-1}$ *vs.* (M).
Polymerization temperature, 60°C
(I)=0.2 mol/*l*

The plot $(1-F)^{-1}$ *vs.* (M) is shown in Fig. 7; it has a good linear relationship, as was predicted by Eq. (12). K_c was estimated to be 4.0 mol/*l* from the slope of the straight line.

On the other hand, if the uncyclized and cyclized radicals were not individually treated as by Holt and Simpson,[1] the following equation would be obtained:

$$(1-F)^{-1} = (2k_p/k_c)(M)$$

It is obvious, however, that this equation is not sufficient to account for the experimental data shown in Fig. 7.

In cyclopolymerization, K_c is the critical factor determining the microstructure of the polymer; it may be interpreted as twice the monomer concentration necessary for the rate of the bimolecular propagation reaction to equal that of the unimolecular cyclization.[13] Thus, the monomer concentration of diallyl carbonate required for the two processes to proceed at an equal rate is 2.0 mol/*l*, which corresponds to about a 70% dilution of the pure monomer.

13) W. E. Gibbs, *J. Polymer Sci.*, **A2**, 4815 (1964).