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The Cyclopolymerization of Triallyl Citrate

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The radical polymerization of triallyl citrate was carried out at 60 °C, benzoyl peroxide being used as the initiator and benzene as the solvent; here it has been considered kinetically in terms of cyclopolymerization. Thus, the kinetic equations for the polymerization of the triallyl ester were first derived by an extension of the kinetic treatment for the cyclopolymerization of the diallyl ester. Next, they were applied to the polymerization of triallyl citrate. In consequence, the following results were obtained: (i) the rate of polymerization, R_p, was not proportional to either the square root or first power of the initiator concentration, [I]; rather, $R_p/[I]^{1/2}$ and $[I]^{1/2}$ had a linear relationship, (ii) the relation between the rate of polymerization over the degree of polymerization, $R_p/\bar{P}_{n,o}$, and the monomer concentration, [M], was also linear, and (iii) the ratio of the unimolecular cyclization reaction to the bimolecular propagation reaction of the uncyclized radical, K_c, was estimated to be 4.5 mol/l from the dependence of the residual unsaturation on the monomer concentration.

In our previous papers,[1-4] the polymerizations of various diallyl esters of dicarboxylic acids have been kinetically discussed in detail in terms of cyclopolymerization and allyl polymerization, including the degradative chain transfer[5] characteristic of allyl compounds.

The present paper will be concerned with the polymerization kinetics of triallyl citrate; the kinetic treatment for the polymerization of the diallyl ester involving the intramolecular cyclization reaction is developed for application and the radical polymerization results are discussed in detail.

Experimental

Materials. The triallyl citrate was prepared by the esterification of citric acid with allyl alcohol according to the literature[6]; bp 130 °C/0.005 mmHg, d_4^{20} 1.135 (lit. bp 207—208 °C/12 mmHg, d_4^{17} 1.1358). The purity of triallyl citrate was confirmed further by spectral and chemical analyses.

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

The benzene was distilled over metallic sodium after purification by the usual method.

Polymerization Procedure. Measured amounts of triallyl citrate, BPO, and benzene were placed in a glass ampoule (10—50 ml capacity), which was then evacuated under reduced pressure and flushed with nitrogen. The ampoule was then sealed under a vacuum and put into a thermostat regulated at 60±0.1 °C.

After a definite reaction time, the polymer thus produced was precipitated by pouring the reaction mixture into more than a tenfold volume of cooled petroleum ether. The polymer thus obtained was then washed repeatedly with petroleum ether and dried *in vacuo* until a constant weight was obtained. The percentage conversion was calculated from the weight of the polymer isolated. The polymer was then purified by dissolving it in acetone and by subsequent reprecipiation with petroleum ether.

Analyses of the Polymer. The unreacted pendant allyl groups of the purified polymer were determined by the method of Simpson *et al.*[7] The polymer was dissolved in methanol and saponified in excess potassium hydroxide, and then the free allyl alcohol was determined by the bromide–bromate technique. The residual unsaturation of the polymer was then expressed as percentages of the corresponding pure triallyl citrate.

The number-average molecular weight of the polymer was measured with a Hewlett-Packard 302 vapor pressure osmometer in acetone at 37 °C.

Results and Discussion

Kinetics. The polymerization mechanism of triallyl citrate must be virtually equivalent to that of the diallyl ester.[1] Thus, the following reaction scheme can be presented for the polymerization of triallyl citrate; in the scheme it is assumed that the three allyl groups of triallyl citrate behave equivalently and that the possibility of a bicyclo-intramolecular propagation[8] accompanying the formation of a bicyclic ring is negligible, as will be discussed later.

Decomposition:	$I \longrightarrow 2R\cdot$	$2k_d[I]$
Initiation:	$R\cdot + M \longrightarrow M\cdot$	$3k_i[R\cdot][M]$
Cyclization:	$M\cdot \longrightarrow M_c\cdot$	$2k_c[M\cdot]$
Propagation:	$M\cdot + M \longrightarrow M\cdot$	$3k_p[M\cdot][M]$
	$M_c\cdot + M \longrightarrow M\cdot$	$3k_{cp}[M_c\cdot][M]$
Chain transfer:	$M\cdot + M \longrightarrow P + M\cdot*$	$3k_{t1}[M\cdot][M]$
	$M_c\cdot + M \longrightarrow P + M\cdot*$	$3k_{t2}[M_c\cdot][M]$
Re-initiation:	$M\cdot* + M \longrightarrow M\cdot$	$3k_i'[M\cdot*][M]$
Stabilization:	$M\cdot* + M\cdot* \longrightarrow M*\text{–}M*$	$k_{t3}[M\cdot*]^2$

where I denotes an initiator; M, a triallyl citrate monomer; P, the polymer; R·, the initiator radical; M·, the initial radical derived from the attack of a radical on M (the uncyclized radical); $M_c\cdot$, the radical formed by the intramolecular cyclization of M· (the cyclized radical), and M·*, the radical derived from the abstraction of an allylic hydrogen of M by the growing polymer chain (the degraded radical).

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

$$[R\cdot] = 2fk_d[I]/3k_i[M] \tag{1}$$

$$[M\cdot] = \frac{2fk_d[I]+3k_i'(2fk_d[I]/k_{t3})^{1/2}[M]}{3k_{t1}[M]+2k_ck_{t2}/(k_{cp}+k_{t2})} \tag{2}$$

$$[M_c\cdot] = \frac{\{2k_c/3(k_{cp}+k_{t2})[M]\}\{2fk_d[I]+3k_i'(2fk_d[I]/k_{t3})^{1/2}(M)\}}{3k_{t1}[M]+2k_ck_{t2}/(k_{cp}+k_{t2})} \tag{3}$$

$$[M\cdot*] = (2fk_d[I]/k_{t3})^{1/2} \tag{4}$$

where f denotes the efficiency of the initiation of chain radicals by R•.

In previous papers on the polymerization of diallyl esters,[1-3] the kinetic equations were derived for two cases. In one case, where the loss of a monomer by initiation, chain termination, and re-initiation reaction is not negligible compared with that by the propagation, the kinetic chain length is small. In the other case, where the propagation reaction is predominant, the kinetic chain length is quite large and the simplified kinetic equations can, therefore, be used instead of the elaborate ones. In the polymerization of triallyl citrate investigated in this paper, the degree of polymerization was quite large, as can be seen in Table 2: therefore, the polymerization of triallyl citrate is of the latter type, as for the diallyl esters of aliphatic dicarboxylic acids.[2,3]

Thus, the rate of polymerization is given by:

$$\begin{aligned} R_p &= 3k_p[\mathrm{M}\cdot][\mathrm{M}] + 3k_{cp}[\mathrm{M_c}\cdot][\mathrm{M}] \\ &= \{2fk_d[\mathrm{I}]+3k_i'(2fk_d[\mathrm{I}]/k_{t3})^{1/2}[\mathrm{M}]\} \\ &\quad\times\left\{\frac{3k_p[\mathrm{M}]+2k_ck_{cp}/(k_{cp}+k_{t2})}{3k_{t1}[\mathrm{M}]+2k_ck_{t2}/(k_{cp}+k_{t2})}\right\} \end{aligned} \tag{5}$$

The initial degree of polymerization is also given by:

$$\begin{aligned} \bar{P}_{n,o} &= R_p/(3k_{t1}[\mathrm{M}\cdot][\mathrm{M}]+3k_{t2}[\mathrm{M_c}\cdot][\mathrm{M}]) \\ &= \frac{3k_p[\mathrm{M}]+2k_ck_{cp}/(k_{cp}+k_{t2})}{3k_{t1}[\mathrm{M}]+2k_ck_{t2}/(k_{cp}+k_{t2})} \end{aligned} \tag{6}$$

The combination of Eqs. (5) and (6) gives:

$$R_p/\bar{P}_{n,o} = 2fk_d[\mathrm{I}]+3k_i'(2fk_d[\mathrm{I}]/k_{t3})^{1/2}[\mathrm{M}] \tag{7}$$

On the other hand, the rate of the formation of the pendant unreacted allyl groups in the polymer is given by:

$$\mathrm{d[allyl]}/\mathrm{d}t = 6k_p[\mathrm{M}\cdot][\mathrm{M}] + 3(1-\alpha)k_{cp}[\mathrm{M_c}\cdot][\mathrm{M}] \tag{8}$$

where α denotes the ratio of the non-consecutive cyclization as seen in the polymerization of diallyl terephthalate[4] to the consecutive intramolecular cyclization in the same monomer unit.

Equation (8) is true in the absence of crosslinking reactions, since these reactions will consume the pendant unreacted allyl groups in the polymer. However, in the early stage of polymerization, the loss of allyl groups by the crosslinking reaction should be small compared with that during propagation.

By using Eqs. (2) and (3), we obtain:

$$\begin{aligned} \mathrm{d(allyl)}/\mathrm{d}t &= \{2fk_d[\mathrm{I}]+3k_i'(2fk_d[\mathrm{I}]/k_{t3})^{1/2}[\mathrm{M}]\} \\ &\quad\times\left\{\frac{6k_p[\mathrm{M}]+2(1-\alpha)k_ck_{cp}/(k_{cp}+k_{t2})}{3k_{t1}[\mathrm{M}]+2k_ck_{t2}/(k_{cp}+k_{t2})}\right\} \end{aligned} \tag{9}$$

Equatins (5) and (9) give:

$$\begin{aligned} -\frac{\mathrm{d[allyl]}}{\mathrm{d[M]}} &= 3R_{us} \\ &= \frac{6k_p[\mathrm{M}]+2(1-\alpha)k_ck_{cp}/(k_{cp}+k_{t2})}{3k_p[\mathrm{M}]+2k_ck_{cp}/(k_{cp}+k_{t2})} \end{aligned} \tag{10}$$

where R_{us} denotes the degree of unsaturation of the polymer.

From Eq. (10) we obtain:

$$(3R_{us})_{\mathrm{M}\to 0} = 1 - \alpha \tag{11}$$

On the other hand, the rearrangement of Eq. (10) gives:

$$(2-3R_{us})^{-1} = \frac{1}{1+\alpha} + \frac{3(1+x)}{2(1+\alpha)}\cdot\frac{1}{K_c}[\mathrm{M}] \tag{12}$$

where $x=k_{t2}/k_{cp}=(\bar{P}_{n,o})^{-1}_{\mathrm{M}\to 0}$, $K_c=k_c/k_p$.

Polymerization Results. The bulk polymerization of triallyl citrate was investigated under different initiator concentrations at 60 °C; the initial rates of polymerization as calculated from the slope of the straight lines of the time-conversion curves, are summarized in Table 1; they are proportional neither to the square root nor to the first power of the initiator concentration, as was observed in the polymerization of diallyl esters.[1-4]

TABLE 1. RELATION BETWEEN THE RATE OF POLYMERIZATION AND INITIATOR CONCENTRATION IN THE BULK POLYMERIZATION OF TRIALLYL CITRATE AT 60 °C

[I] (mol/l)	$R_p\times 10^5$ (mol/l·s^{-1})	$(R_p/[\mathrm{I}]^{1/2})\times 10^4$ (mol/l·s^{-2})$^{1/2}$	$(R_p/[\mathrm{I}])\times 10^3$ (s^{-1})
0.01	1.39	1.39	1.39
0.02	2.31	1.63	1.16
0.04	3.42	1.71	0.86
0.10	8.24	2.61	0.82

TABLE 2. POLYMERIZATION OF TRIALLYL CITRATE (60 °C, [BPO]=0.02 mol/l, Solvent; benzene)

[M] (mol/l)	$R_p\times 10^5$ (mol/l·s^{-1})	$\bar{P}_{n,o}$	R_{us}
3.63	2.33	—	0.500
2.42	1.20	58.9	0.465
1.82	0.74	52.3	0.435
1.21	0.45	44.2	0.405
0.73	0.25	36.5	0.362
0.40	0.13	29.5	0.327

On the other hand, the influence of the monomer concentration on the rate of polymerization, the residual unsaturation, and the degree of polymerization was also examined at a constant initiator concentration at 60 °C. The results obtained are given in Table 2.

Figure 1 shows the relation between the residual unsaturation, R_{us}, and the monomer concentration; R_{us} tends to decrease with a decrease in the monomer con-

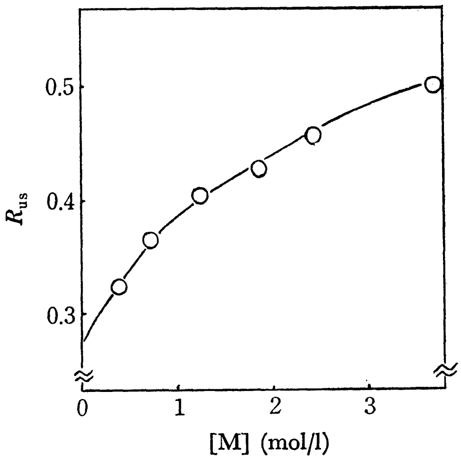

Fig. 1. Dependence of R_{us} on monomer concentration.

centration, and it reaches 0.284 by the extrapolation of the monomer concentration to zero. Thus, α is estimated from Eq. (11) to be 0.148.

Now, it should be noted that R_{us} must be 0.667 if neither cyclization nor crosslinking reaction occurs; conversely, it reaches zero in an infinitely diluted solution if the bicyclo-intramolecular cyclization reaction occurs completely. On the other hand, in the absence of the bicyclo-intramolecular cyclization, R_{us} approaches 0.333, assuming that the intramolecular cyclization reaction occurs only in the same monomer unit. Consequently, the result obtained above, *i.e.*, $(R_{us})_{M\to 0}=0.284$, may be understood by considering the absence of the bicyclo-intramolecular cyclization and the occurrence of the non-consecutive intramolecular addition reaction, as was observed in the polymerization of diallyl terephthalate.[4,9,10]

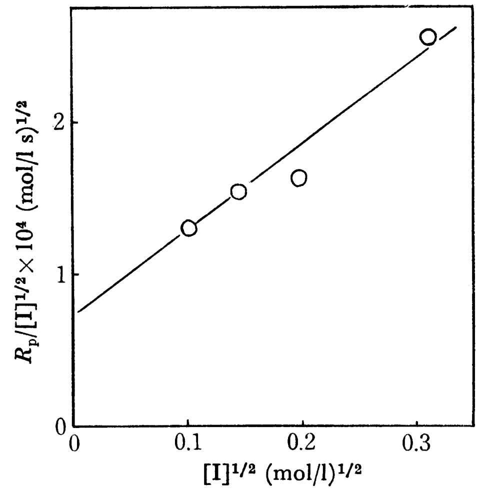

Fig. 2. Relationship between $R_p/[I]^{1/2}$ and $[I]^{1/2}$ based on Eq. (6).

Kinetic Evaluation. Figure 2 shows the relation between $R_p/[I]^{1/2}$ and $[I]^{1/2}$ based on the data of Table 1; there is a fairly good linear relationship, as can be expected from Eq. (5). 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] can be expected from Eq. (7) (See Fig. 3). These results seem to demonstrate the validity of the kinetics discussed in the previous section.

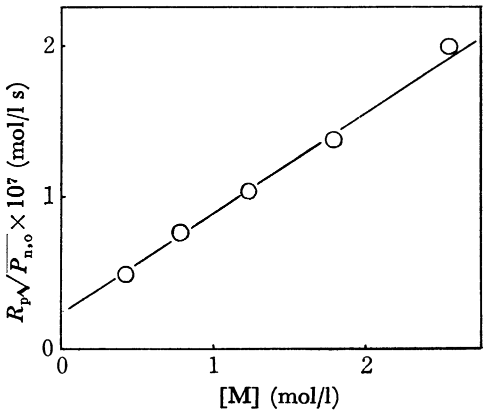

Fig. 3. Relationship between $R_p\sqrt{\bar{P}_{n,o}}$ and [M] based on Eq. (9).

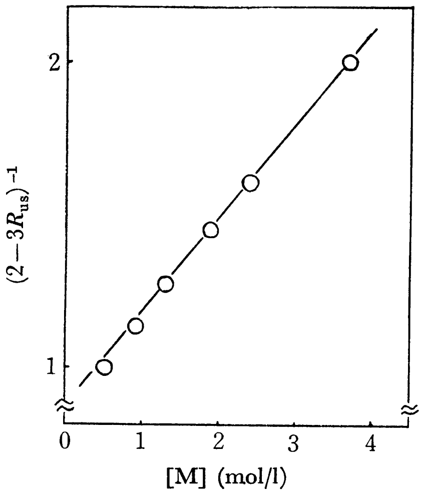

Fig. 4. Evaluation of K_c based on Eq. (14).

On the other hand, the ratio of the unimolecular cyclization reaction to that of the bimolecular propagation reaction of the uncyclized radical, K_c, can be obtained from the dependence of the residual unsaturation on the monomer concentration by employing Eq. (12), since, in the early stage of polymerization, the crosslinking reaction is negligible and the deviation of R_{us} from 0.667 can predominantly be attributed to the intramolecular cyclization reaction. Figure 4 shows the plot of $(2-3R_{us})^{-1}$ *vs.* [M]; there is a good linear relationship, and K_c was estimated to be 4.5 mol/l from the slope of the straight line. K_c is a critical factor determining the microstructure of the polymer; the monomer concentration required for obtaining the polymer carrying 50% of the cyclic recurring unit is 3.0 mol/l, which corresponds to around a 82.5% dilution of the pure monomer.

Now, it should be noted that the values of K_c for diallyl phthalate and diallyl succinate, which are considered to be diallyl esters structurally corresponding to triallyl citrate, are 7.5 mol/l[1] and 2.8 mol/l[3] respectively, in which the free rotation between the two ester groups is possible in diallyl succinate, whereas in diallyl phthalate it is impossible. Thus, the fact that the value of the K_c of triallyl citrate is intermediary between those of diallyl phthalate and diallyl succinate suggests a limited rotation among the three ester groups; we may imagine the structural feature of triallyl citrate to be that the three allyl groups are symmetrical about the hydroxide group. From such a standpoint, the equivalency of the three allyl groups of triallyl citrate mentioned above can also be understood.

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