NOTES

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The Polymerization of Dimethallylidenepentaerythritol and Dicrotylidenepentaerythritol[*1]

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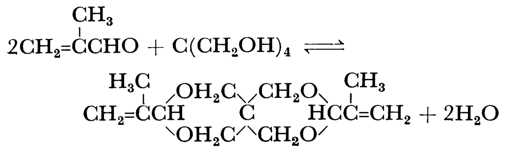
In a previous paper, the polymerization of diallylidenepentaerythritol (DAPE) has been kinetically investigated by means of degradative, effective chain transfers by the allylidene groups, and by means of cyclization by the two double bonds.[1]

This paper will deal with the polymerization of dimethallylidenepentaerythritol (DMAPE) and dicrotylidenepentaerythritol (DCPE), and with the influence of α,α'- or β,β'-methyl groups on the chain transfer and the cyclization.

Experimental

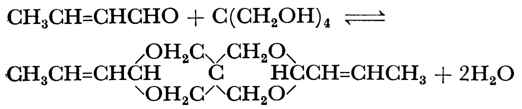
Materials. DMAPE was prepared from methacrolein and pentaerythritol by the procedure of Komori and his co-workers,[2] using phosphoric acid - phosphorus pentoxide as the catalyst; mp 115—116°C (lit,[2] 115—116°C).



$$2CH_2{=}\overset{CH_3}{\overset{|}{C}}CHO + C(CH_2OH)_4 \rightleftharpoons CH_2{=}\overset{H_3C}{\overset{|}{C}}CH\begin{matrix}\diagup OH_2C\diagdown\diagup CH_2O\diagdown\\ C\\ \diagdown OH_2C\diagup\diagdown CH_2O\diagup\end{matrix}H\overset{CH_3}{\overset{|}{C}}C{=}CH_2 + 2H_2O$$

DMAPE

DCPE was prepared from crotonaldehyde and pentaerythritol by the method of Weihe and Schweitzer[3] and was purified by recrystallization from methanol-water; mp 57.5—58.0°C (lit,[3] 58°C).



$$CH_3CH{=}CHCHO + C(CH_2OH)_4 \rightleftharpoons CH_3CH{=}CHCH\begin{matrix}\diagup OH_2C\diagdown\diagup CH_2O\diagdown\\ C\\ \diagdown OH_2C\diagup\diagdown CH_2O\diagup\end{matrix}HCCH{=}CHCH_3 + 2H_2O$$

DCPE

Polymerization Procedure. DMAPE and DCPE were polymerized in benzene at 80°C with benzoyl peroxide as a radical initiator. The monomer, solvent, and initiator were charged in an ampoule; after having been degassed by the freeze-thaw method, the ampoule was sealed under a vacuum. The sealed tubes were then set in a thermostated water bath; later they were taken out into a large amount of petroleum ether and the polymers were separated by using the centrifuged, after which they were dried *in vacuo*. The conversion of the polymer was less than 10%.

Measurements of the Residual Unsaturation and the Degree of Polymerization. The residual unsaturation was calculated from the bromine value (BV) according to the usual bromite-bromate method.[4]

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.

Results and Discussion

The conditions and the results of polymerization are summarized in Tables 1 and 2. The values of residual unsaturation and degree of polymerization shown in Tables 1 and 2 are estimated by extrapolating to zero for conversion.

If the monomer concentration is kept constant, the plots of the rate of polymerization against the initiator concentration are found to be as shown in Fig. 1 by using the values listed in Tables 1 and 2. It is found that the rate of polymerization is proportional to the first power of the initiator concentration. If the relation of $([\mathrm{I}]/R_p-a)^{-1}$ *vs.* [M] is plotted by means of the trial-and-error method, the straight-line relationship is obtained when the values are 3.0×10^3 sec (DMAPE) and 2.0×10^4 sec (DCPE) respectively (Figs. 2 and 3). Therefore, b and c values are calculated from those slopes and intercepts as follows:

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

[1] T. Ouchi and M. Oiwa, *Kogyo Kagaku Zasshi*, **72**, 746 (1969).

[2] T. Agawa, T. Ishikawa, N. Tamiya and S. Komori, *Shikizai*, **37**, 338 (1964).

[3] A. Weihe and O. Schweitzer (to Deutsche Gold und Silber Scheideanstalt); U. S. 2739121 (1956).

[4] I.P. Losev and O.Y. Fedotoba, "Praktikum po Khimii Vysokopolimernykh Soedinenii," Gosudarstvennoe Nauchno-Tekhnicheskoe Izdatelstvo Khimicheskoi Literatury, Moskova.

DMAPE $b = 2.53 \times 10^5$ sec, $c = 0.243$ mol/l
DCPE $b = 2.00 \times 10^7$ sec, $c = 0.044$ mol/l

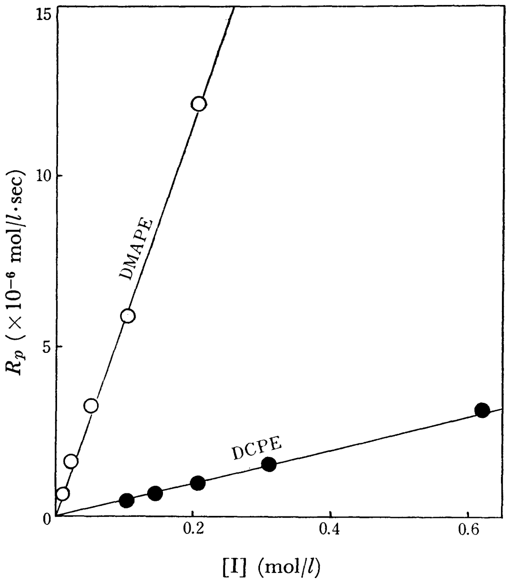


Fig. 1. Plots of rate of polymerization against the initiator concentration.

The degradative chain transfer occurred more readily on DCPE than on DMAPE. The low rate of polymerization on DCPE is due to the steric hindrance of β,β'-methyl groups.

If the monomer concentration is kept constant, the residual unsaturation does not depend on the initiator concentration. If the initiator concentration is kept constant, the residual unsaturation de-

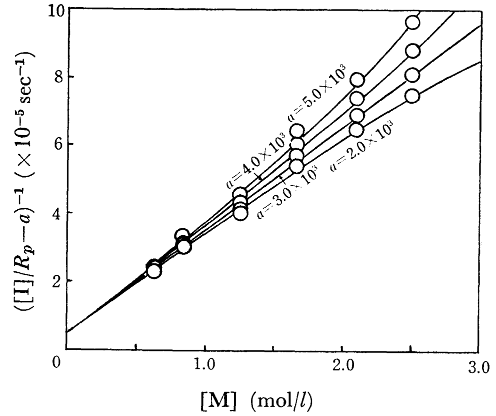


Fig. 2. Plots of ([I]/R_p−a)$^{-1}$ *vs.* [M] obtained on the polymerization of DMAPE.

Table 1. The polymerization of DMAPE (80°C)

[BPO] ($\times 10^{-1}$ mol/l)	[DMAPE] (mol/l)	R_p ($\times 10^{-6}$ mol/l·sec)	BV	$2R_{us}$	Molecular weight $\bar{M}_n$	Degree of polymerization $\bar{P}_n$
2.064	2.081	12.15	62.71	0.943	1807	7.52
1.032	2.081	5.89	62.80	0.944	1812	7.54
0.516	2.081	3.23	62.83	0.945	1822	7.58
0.206	2.081	1.62	62.77	0.944	1817	7.56
0.103	2.081	0.64	62.91	0.946	1806	7.52
1.032	2.497	6.71	63.05	0.948	1896	7.89
1.032	1.664	5.02	62.19	0.935	1805	7.51
1.032	1.248	3.81	60.85	0.915	1694	7.05
1.032	0.832	2.92	58.66	0.882	1629	6.78
1.032	0.624	2.22	56.23	0.845	1416	5.89

Table 2. The polymerization of DCPE (80°C)

[BPO] ($\times 10^{-1}$ mol/l)	[DCPE] (mol/l)	R_p ($\times 10^{-6}$ mol/l·sec)	BV	$2R_{us}$	Molecular weight $\bar{M}_n$	Degree of polymerization $\bar{P}_n$
6.193	2.081	3.120	65.73	0.988	840	3.50
3.096	2.081	1.584	65.67	0.987	839	3.49
2.064	2.081	0.971	65.71	0.988	845	3.52
1.445	2.081	0.680	65.65	0.987	853	3.55
1.032	2.081	0.491	65.75	0.989	841	3.50
2.064	4.162	1.696	66.24	0.996	973	4.05
2.064	3.121	1.301	65.98	0.992	901	3.75
2.064	1.561	0.693	65.51	0.985	819	3.41
2.064	1.040	0.507	65.25	0.981	805	3.35

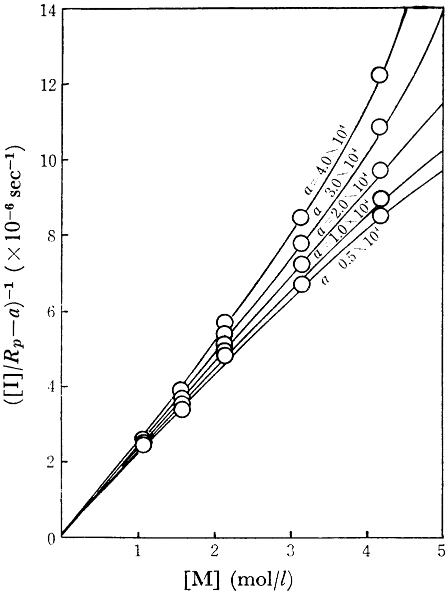


Fig. 3. Plots of $([I]/R_p-a)^{-1}$ *vs.* [M] obtained on the polymerization of DCPE.

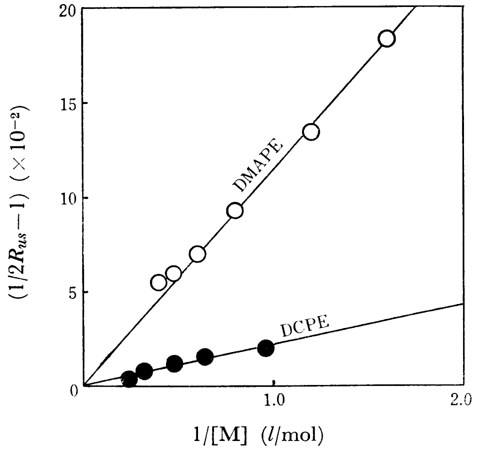


Fig. 4. Plots of $(1/2R_{us}-1)$ *vs.* 1/[M].

creases with the decrease in the monomer concentration; accordingly, there is a tendency to cyclize easily. The plots of $(1/2R_{us}-1)$ against 1/[M] are, then, shown in Fig. 4. Straight lines through the point of origin are obtained. Using their slopes, the c values of DMAPE and DCPE are computed as 0.226 mol/l and 0.044 mol/l respectively. These values agree very closely with those obtained from the trial-and-error method. Here the c value of DCPE is very small because the cyclization was sterically hindered by β,β'-methyl groups.

The degree of polymerization does not depend on the initiator concentration, but increases with the increase in the monomer concentration. It is natural that the degree of polymerization of DCPE is small, because β,β'-methyl groups influence the propagation and termination. The plots of $R_p/\bar{P}_n$ against [I] and of $(2a[M]+bc)R_p/\bar{P}_n[I]$ against [M] are shown in Fig. 5. Straight lines are obtained; therefore, this experimental fact seems to agree with the previous equation.[1]

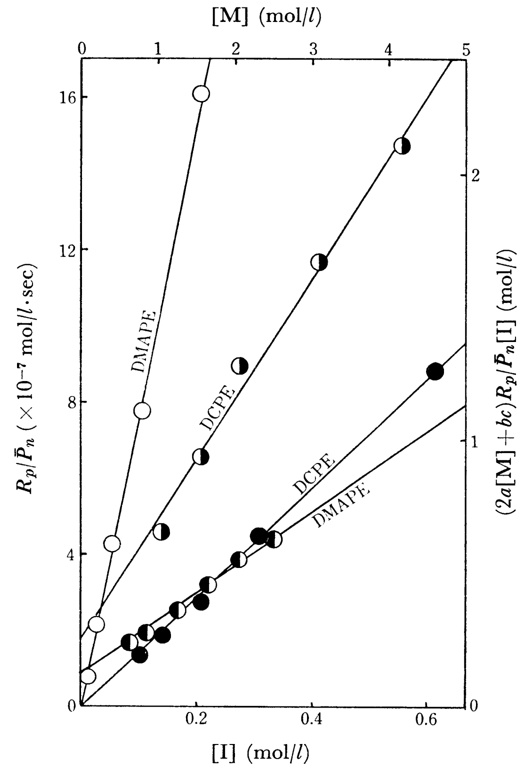


Fig. 5. Plots of $R_p/\bar{P}_n$ *vs.* [I] and $(2a[M]+bc)R_p/\bar{P}_n[I]$ *vs.* [M].

Conclusion

The polymerization of DMAPE and DCPE, which are α,α'- and β,β'-substituted derivatives of DAPE, in the initial stage were explained kinetically according to the equations suggested in a previous paper.[1] The parameters of copolymerization for three monomers are summarized in Table 3.

TABLE 3. THE PARAMETERS OF COPOLYMERIZATION

Monomer	a ($\times 10^3$ sec)	b ($\times 10^4$ sec)	$\frac{k_c}{2(k_p+k_{tr}+k_{tr}^*)[M]}$
DMAPE	3.0	2.53×10	0.118
DCPE	20.0	2.00×10^3	0.022
DAPE	2.0	5.66	0.276

From the above results, it was found that $k_c/2(k_p+k_{tr}+k_{tr}^*)[M]$ were in the order of DAPE$>$DMAPE$>$DCPE, and that the cyclization was sterically hindered by methyl groups.

The *a* and *b* values varied in the following sequence:

DAPE < DMAPE < DCPE

It seemed that the degradative chain transfer occurred more readily on the methallylidene and crotylidene groups that on the allylidene group. It may be considered that allylidene groups can be resonanced easily to stabilize with methyl groups, and to hypercojugate.