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The Copolymerization of Dimethallylidenepentaerythritol and Dicrotylidenepentaerythritol with Maleic Anhydride*[1]

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Dimethallylidenepentaerythritol (DMAPE) and dicrotylidenepentaerythritol (DCPE) have been copolymerized with maleic anhydride (Manh), using benzoyl peroxide as an initiator. From the results of the UV spectrum concerning the rate of copolymerization, it was found that the copolymerization might proceed on the *pseudo*-terpolymerization of the charge transfer complex-allylidene group-Manh. The following functional group reactivity ratios were calculated at 60°C in these systems:

DMAPE(M_1)-Manh(M_2)
$r_{1c}K=0.77$, $r_{2c}K=0.058$
$r_1=0.05$, $r_2=0.025$
DCPE(M_1)-Manh(M_2)
$r_{1c}K=0.89$, $r_{2c}K=0.057$
$r_1=0.02$, $r_2=0.020$

It has already been pointed out that maleic anhydride (Manh) is copolymerized alternately with various vinyl monomers.[1-10]

In a previous experiment paper,[11] the copolymerization of diallylidenepentaerythritol (DAPE) and Manh was carried out as one of a series of studies of the copolymerization of DAPE; then the behavior of the radical copolymerization was investigated by means of kinetic equations derived by assuming a *pseudo*-tersystem.

On the other hand, 2-vinyl-1,3-dioxolane (VDOL) has been further copolymerized with Manh, and the difference in the copolymerizations between mono- and di-allylidene cyclic acetal compounds with Manh has been studied.[12]

In this paper, the copolymerizations of dimethallylidenepentaerythritol (DMAPE) and dicrotylidenepentaerythritol (DCPE), which are α,α'- and β,β'-substitution products of DAPE respectively, with Manh will be reported; the functional reactivity ratios will be estimated, and the in-

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*[1] Studies of Polymerization of Diallylidenepentaerythritol. VIII.

1) T. Alfrey and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).

2) C. C. Price, *ibid.*, **1**, 83 (1946).

3) C. C. Price, *ibid.*, **3**, 772 (1948).

4) C. C. Price, *Discuss. Faraday Soc.*, **2**, 304 (1947).

5) P. D. Bartlett and K. Nozaki, *J. Amer. Chem. Soc.*, **68**, 1495 (1946).

6) C. Walling, E. R. Briggs, K. B. Woltsirn and F. R. Mayo, *ibid.*, **70**, 1537, 1544 (1948).

7) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

8) F. M. Lewis, C. Walling, W. Cumming, E. R. Briggs and E. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1519 (1948).

9) S. Iwatsuki and Y. Yamashita, *Makromol. Chem.*, **89**, 205 (1965); **104**, 263 (1967).

10) S. Iwatsuki and Y. Yamashita, *J. Polym. Sci., Part A-1*, **5**, 1753 (1967).

11) T. Ouchi and M. Oiwa, *Kogyo Kagaku Zasshi*, 1713, **73**, (1970).

12) T. Ouchi and M. Oiwa, *ibid.*, **73**, 1717 (1970).

fluence of substituents on the reactivity of copolymerization will be discussed.

Experimental

Materials. The DMAPE and DCPE were synthesized by a previously-reported method.[13] The Manh was purified by the recrystallization and vacuum distillation of a commercial product.

The benzoyl peroxide (BPO) used as an initiator and the solvents were purified by the conventional method.

Copolymerization Procedure. A glass ampoule was charged with prescribed amounts of each monomer, BPO, and benzene in such a way that the concentration of DMAPE or DCPE was kept constant. The ampoule was then sealed off under a vacuum and set in a thermostated water bath at 60±0.1°C, without stirring, for the time necessary to give less than 10% of conversion. A hydroquinone/benzene solution was added to the reaction solution to inhibit further polymerization, and the polymer was precipitated from an excess of dehydrated ether. The polymer thus obtained was washed repeatedly with ether in the Soxhlet extractor and dried under reduced pressure to a constant weight.

Analysis of the Copolymer. The composition of the resulting copolymer was determined by C and H elementary analysis. The residual unsaturation was calculated by the determination of the bromine value of the resulting copolymer according to a previously-described method.[14]

The UV spectrum was measured by means of an Ito Chodenpa apparatus, Model QU-3, in chloroform with a quartz cell over the range of 352—358 mμ and at room temperature.

Results and Discussion

The Ratio of "Charged" to "Reacted" Vinyl Groups. The copolymerizations were carried out at 60°C under various concentrations and ratios of the functional groups in the monomer feed. The relations among the residual unsaturation and the monomer and copolymer compositions are plotted in Figs. 1 and 2. From Figs. 1 and 2, it can be found that the DMAPE or DCPE mole fraction in copolymer increases with an increase in that in the monomer over the range of 0.3—0.4, and also with an increase in the feed concentration of DMAPE or DCPE. On the other hand, the residual unsaturation of the polymer tends to decrease with a decrease in the DMAPE or DCPE mole fraction and in the concentration in the monomer feed.

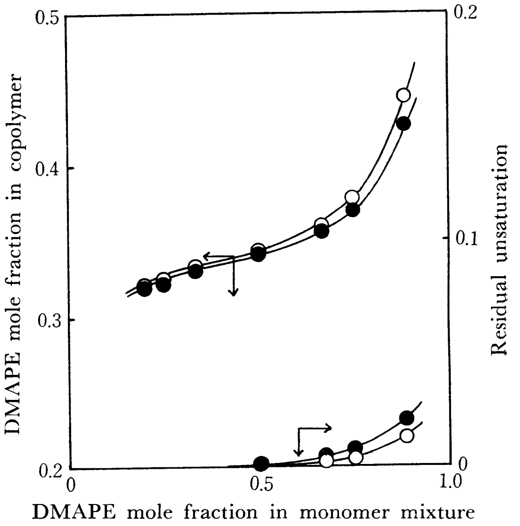

Fig. 1. Relation of the monomer compositions to the copolymer composition and the residual unsaturation.

(DMAPE-Manh)

○: (DMAPE)=0.208 mol/*l*

●: (DMAPE)=0.416 mol/*l*

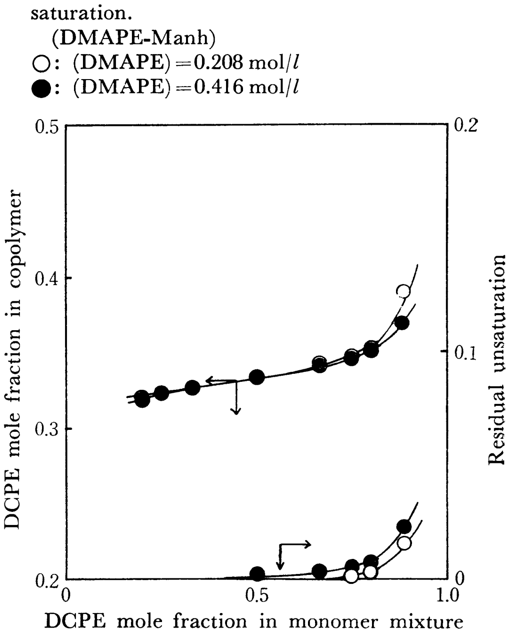

Fig. 2. Relation of the monomer composition to the copolymer composition and the residual unsaturation.

(DCPE-Manh)

○: (DCPE)=0.277 mol/*l*

●: (DCPE)=0.555 mol/*l*

When all the allylidene-compound units in a copolymer have unreacted pendant double bonds without any cyclization or crosslinking, the ideal bromine values of the copolymer are indicated by BV_{id}; the ratio of the experimental bromine value (BV_{ex}) to BV_{id}, that is, BV_{ex}/BV_{id}, indicates the residual unsaturation.

When the concentrations of the allylidene compounds and the Manh in the copolymer are $d(M_1)$ and $d(M_2)$, and when those of the allylidene group and the Manh in it are $d(m_1)$ and $d(m_2)$ respectively, the following relation may be obtained:

$$d(m_1)/d(m_2) = (2-BV_{ex}/BV_{id})d(M_1)/d(M_2)$$

The relations between charged and reacted vinyl

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[13] T. Ouchi, S. Tatsuno, T. Nakayama and M. Oiwa, This Bulletin, **43**, 2241 (1970).

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

groups are plotted in Figs. 3 and 4. The reacted methallylidene- or crotylidene-group fraction tends to increase with an increase in the charged methallylidene- or crotylidene-group fraction, and also with a decrease in its concentration. It may be expected that the formation of the CT complex is related to the propagation reaction.

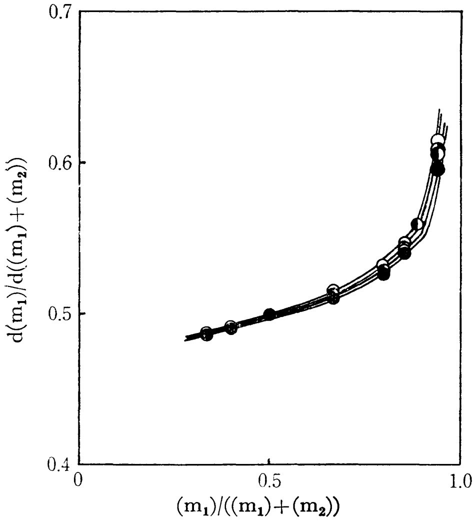


Fig. 3. The relation between charged and reacted vinyl group fraction.
DMAPE(M_1)—Manh(M_2)
○: $(m_1)=0.416$ vinyl group/*l*
◐: $(m_1)=0.554$ vinyl group/*l*
◑: $(m_1)=0.666$ vinyl group/*l*
●: $(m_1)=0.832$ vinyl group/*l*
—: logical curves

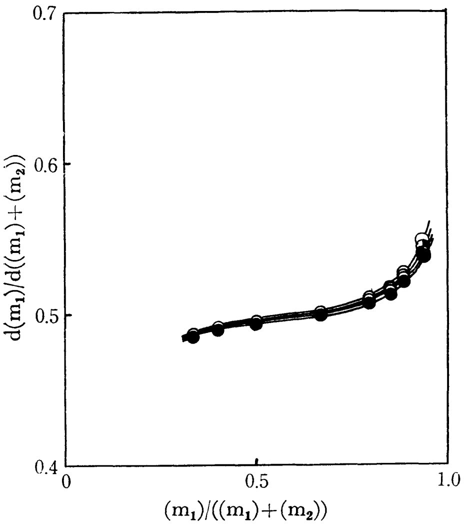


Fig. 4. The relation between charged and reacted vinyl group fraction.
DCPE(M_1)-Manh(M_2)
○: $(m_1)=0.554$ vinyl group/*l*
◐: $(m_1)=0.668$ vinyl group/*l*
◑: $(m_1)=0.832$ vinyl group/*l*
●: $(m_1)=1.110$ vinyl group/*l*
—: logical curves

The Relation between the Charged Composition and the Rate of Copolymerization. The dependence of the monomer composition and concentration upon the rate of copolymerization is shown in Fig. 5. The rate of copolymerization reaches a maximum at the feed ratio of 1 : 2, regardless of the monomer concentration.

A similar tendency was also recognized in the DCPE-Manh system.

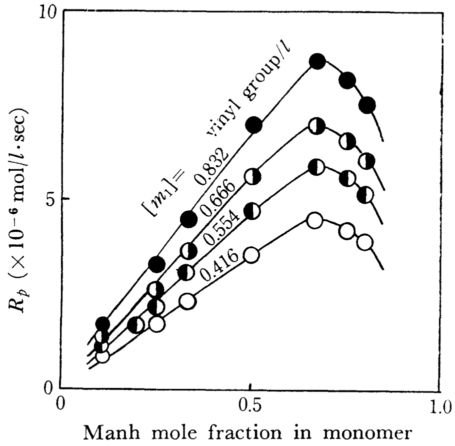


Fig. 5. Plots of the rate of copolymerization against the monomer composition in benzene at 60°C.
DMAPE-Manh

The Continuous-variation Method. The *Q* and *e* values for the functional group of DMAPE have already been calculated as 0.05 and −0.48, while those of DCPE have been obtained as 0.01

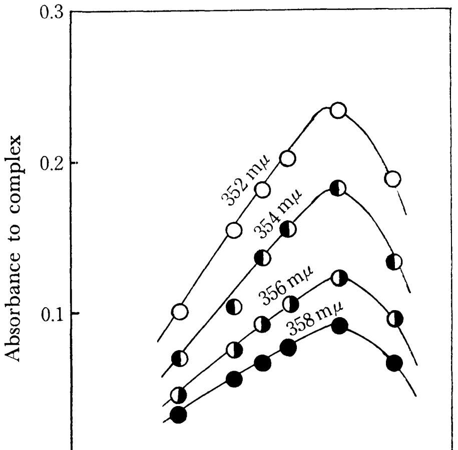
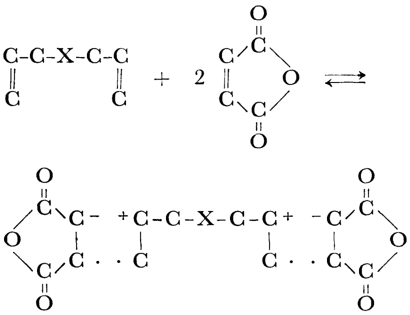


Fig. 6. The continuous variation method.
DMAPE-Manh
Solvent: chloroform, room temp.

and −0.32, respectively.[15] As the Q and e values of Manh are also 0.23 and 2.25,[16] the complex formation between such monomer pairs may be expected. Further, when DMAPE and Manh were mixed, no color appeared, but it was found according to the optical analysis, that is, according to the continuous-variation method, that a 1 : 2 complex formation occurred between the monomer[17] (Fig. 6).

A similar tendency was observed in the DCPE-Manh system.

These molecular complexes are probably CT complexes with the following structure, if we can make an analogy with the results of *p*-dioxen and Manh:[9–10]



CT Complex

The Kinetic Analysis. The copolymerizations of DMAPE and DCPE with Manh were kinetically investigated by a previously-reported method.[1]

The *pseudo*-terpolymerization of the CT complex-allylidene group-Manh is dealt with assuming that the complex is attacked on the side of Manh, assuming that the active growing chain ends become allylidene radicals. Here, m_1 denotes an allylidene group; m_2, Manh; C or m_1m_2, the complex; $m_1\cdot$, an allylidene radical, and $m_2\cdot$, a Manh radical. The following elementary reactions can then be presumed to hold in the copolymerization of these allylidene compounds and Manh:

		Rate Const.
Complex Formation	$m_1 + m_2 \rightleftarrows m_1m_2(C)$	k_1 k_{-1}
Propagation	$m_1\cdot + C \rightarrow m_1\cdot$	k_{1c}
	$m_1\cdot + m_1 \rightarrow m_1\cdot$	k_{11}
	$m_1\cdot + m_2 \rightarrow m_2\cdot$	k_{12}
	$m_2\cdot + C \rightarrow m_1\cdot$	k_{2c}
	$m_2\cdot + m_1 \rightarrow m_1\cdot$	k_{21}
	$m_2\cdot + m_2 \rightarrow m_2\cdot$	k_{22}

If a steady state is assumed for the radicals and the complex, Eq. (1) can be derived:

$$\frac{F}{1-f} = A\left(\frac{1}{B+F}\right)\left(\frac{f}{1-f}\right) - C \qquad (1)$$

where $r_1=k_{11}/k_{12}$, $r_2=k_{22}/k_{21}$, $r_{1c}=k_{1c}/k_{12}$, $r_{2c}=k_{2c}/k_{21}$, $K=k_1/k_{-1}$, $F=(m_1)/(m_2)$, $f=d(m_1)/d(m_2)$, and

$$A = \frac{r_{2c}K(m_1)+r_2}{r_1},\quad B = r_{2c}K(m_1),\quad C = \frac{r_{1c}K(m_1)+1}{r_1} \qquad (2)$$

The values of A, B, and C can be obtained by the trial-and-error method according to Eq. (1). The relation of $F/(1-f)$ *vs.* $f/(1-f)(B+F)$ is plotted in Fig. 7, when (m_1) is the 0.666 vinyl group/l on the DMAPE-Manh system. It is found that a straight line is obtained when B is 0.04. Therefore, A and C are estimated to be 1.30 and 31.3 respectively from this slope and intercept. A similar example of the DCPE-Manh system is shown in Fig. 8.

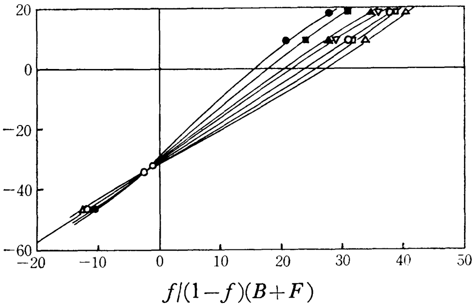


Fig. 7. Plots of $F/(1-f)$ *vs.* $f/(1-f)(B+F)$.
DMAPE-Manh
$[m_1]=0.666$ vinyl group/l
△ $B=0$, □ $B=0.03$, ○ $B=0.04$
▽ $B=0.08$, ▲ $B=0.10$, ■ $B=0.20$
● $B=0.30$

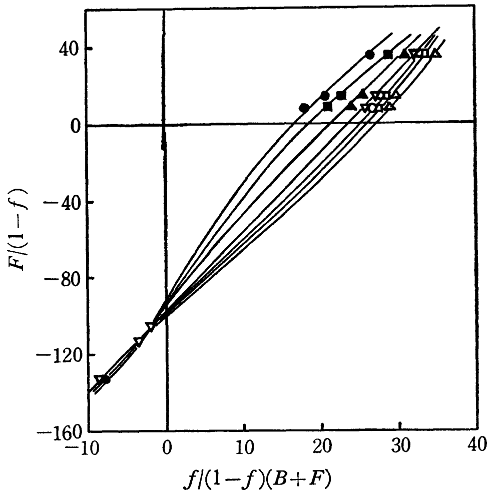


Fig. 8. Plots of $F/(1-f)$ *vs.* $f/(1-f)(B+F)$.
DCPE-Manh
$(m_1)=1.110$ vinyl group/l
△ $B=0$, □ $B=0.03$, ○ $B=0.05$,
▽ $B=0.06$, ▲ $B=0.10$, ■ $B=0.20$,
● $B=0.30$

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[15] T. Ouchi, S. Tatsuno, T. Nakayama and M. Oiwa, *Kogyo Kagaku Zasshi.*, **73**, 607 (1970).

[16] G. E. Ham, "Copolymerization," Interscience Pub., New York (1964), p. 859.

[17] P. Job, *Ann. Chim.*, **9**, 113 (1928).

By varying the m_1 concentration, the A, B, and C values are obtained by the same procedure; the relations among A, B, and C *vs.* (m_1) are plotted in Figs. 9—11. Straight lines are obtained in every case, as was expected on the basis of Eq. (2).

From these slopes and intercepts, the parameters of copolymerization can be estimated to be as in Table 1.

From Table 1, it can be found that $r_{1c}K$ values became DAPE < DMAPE < DCPE, and that r_1 and r_2 values decreased unlike as in the case of $r_{1c}K$ in the order of DCPE < DMAPE < DAPE.

The values of r_{1c}, r_{2c} were much larger than those of r_1 and r_2 in allylidene compounds-Manh systems because the K values were presumed to be very small; therefore, it seemed that the propagation radicals reacted preferentially with the functional groups of the complex rather than with the monomer. If the K values are taken to be equal in these systems, such a tendency was observed in the order of DAPE < DMAPE < DCPE; the influence of an α- or β-methyl group on the reactivity of the functional group was thus recognized. Since the $r_{1c}K$ values were larger than $r_{2c}K$, $K_{1c} > K_{2c}$; this suggests that the addition rate of allylidene radicals to the complex is larger than that of Manh radicals, as had been expected.

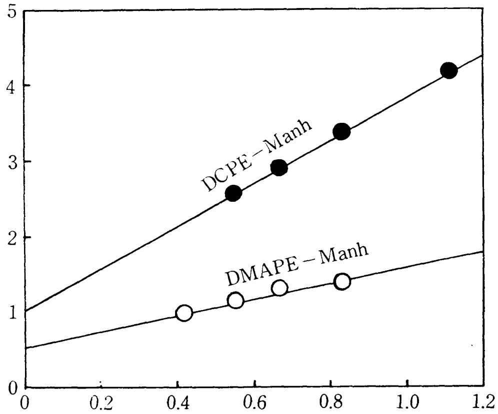

Fig. 9. Plots of A *vs.* (m_1).

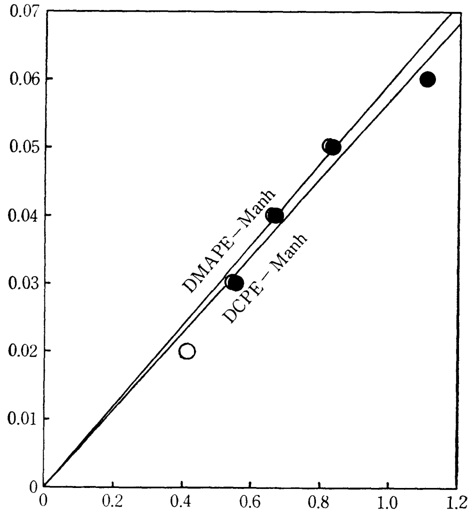

Fig. 10. Plots of B *vs.* (m_1).

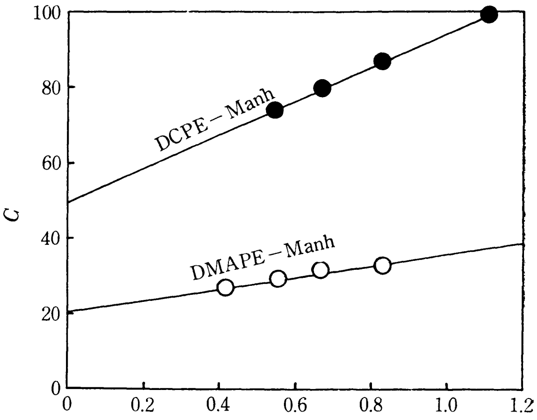

Fig. 11. Plots of C *vs.* (m_1).

TABLE 1. THE PARAMETERS OF COPOLYMERIZATION

M_2	$r_{1c}K$	$r_{2c}K$	r_1	r_2
DMAPE	0.77	0.058	0.05	0.025
DCPE	0.89	0.057	0.02	0.020
DAPE	0.76	0.055	0.08	0.030

The curves of the relation between charged and reacted vinyl group fractions agreed well with the experimental results shown in Figs. 3 and 4.

Summarizing the above results, three significant facts can be pointed out:

1) DMAPE or DCPE and Manh are copolymerized easily with a radical initiator to give the alternating copolymer, whereas neither one can be polymerized with a radical initiator. 2) The rate of copolymerization reaches a maximum at the feed ratio of 1 : 2. 3) The formation of the 1 : 2 CT complex between DMAPE or DCPE and Manh may proceed by way of a *pseudo*-terpolymerization of the allylidene group - Manh - the CT complex.