Studies of the Polymerization of Diallyl Compounds. XXXVII. Copolymerizations of Diallyl Phthalate with Dialkyl Fumarates

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Synopsis

Diallyl phthalate (DAP) was copolymerized with dialkyl fumarates, including diethyl fumarate (DEF), di-*n*-butyl fumarate (DBF), and di-*n*-octyl fumarate (DOF) by using 2,2′-azobisisobutyronitrile as an initiator at 60°C. Both rate and degree of copolymerization were quite enhanced compared with the homopolymerization of DAP and the maximum rate was found at the molar ratio of 1:1 in the monomer feed. The cyclization of DAP was almost exclusively suppressed in the copolymerization. Gelation was promoted from 25% of the gel-point conversion for the DAP homopolymerization to 9% of the minimum one observed. Copolymerizability of DAP (M_1) with dialkyl fumarates (M_2) was quite high, with the following monomer reactivity ratios M_2, r_1, r_2: DEF, 0.01, 1.25; DBF, 0.02, 1.01; DOF, 0.02, 0.96. These results are discussed in mechanistic detail.

INTRODUCTION

In our previous articles[1-4] we have compared in detail the polymerization behavior of methyl allyl and diallyl esters of maleic and fumaric acids as a part of a study program concerned with the radical polymerization of allyl esters of unsaturated acids. Thus it was found that in the polymerization of fumarates the rate and degree of polymerization are quite high compared with maleates and gelation occurs at low conversion; these were attributed to the high reactivity of the fumaric double bond for polymerization and, moreover, the reduction of a degradative chain transfer reaction which is characteristic of allyl polymerization compared with normal vinyl polymerization, implying the change from allyl polymerization to a vinyl-type polymerization.

This interesting polymerization behavior of allyl fumarates prompted us to explore the copolymerization of diallyl dicarboxylates with dialkyl fumarates since we have investigated in detail the polymerization of diallyl dicarboxylates in terms of cyclopolymerization, cyclocopolymerization, and gelation.[5] In this article diallyl phthalate (DAP) as a typical, commercially important diallyl dicarboxylate is chosen for the copolymerization with diethyl fumarate (DEF), di-*n*-butyl fumarate (DBF), and di-*n*-octyl fumarate (DOF); the effects of dialkyl fumarates on the copolymerization, cyclization, and gelation behavior of DAP were examined in detail.

EXPERIMENTAL

Materials

All monomers, commercially available reagents, were distilled *in vacuo* under nitrogen before use.   2,2'-Azobisisobutyronitrile (AIBN) as an initiator was purified by a conventional method.

Copolymerization Procedure

Copolymerization was carried out as described in a previous article.[6]

After a definite reaction, the copolymer produced was precipitated by pouring the reaction mixture into a large amount of precipitant: petroleum ether–*n*-hexane mixture was used for DAP–DEF copolymerization, the petroleum ether volume fraction of which was high in the copolymerization system with the large molar fraction of DAP in the monomer feed, while chilled methanol (−78°C) was used for DAP–DBF and DAP–DOF copolymerizations.   The isolation of copolymer from the reaction mixture was also checked by gel permeation chromatography (GPC) as described previously.[7]

The copolymer thus obtained was then washed repeatedly with precipitant and dried *in vacuo* until a constant weight was obtained.   The percentage conversion was calculated from the weight of the isolated copolymer.   The copolymer was then purified by dissolving it in benzene and subsequently reprecipitating carefully with precipitant to remove exclusively the low-molecular-weight copolymer since in the low-molecular-weight copolymer the analytical results including the copolymer composition and the unreacted double bonds may be influenced by elementary reactions other than propagation reactions and, thus, complicate the interpretation of the analytical results obtained.

Analyses of Copolymers

The purified copolymers obtained at less than 10% conversion were analyzed as follows: First, the composition of the DAP–DEF copolymers was calculated from the carbon content determined by elementary analysis and checked also from their UV spectra in dioxane solutions using the absorption band at 275.5 nm.   For DAP–DBF and DAP–DOF copolymers only the UV spectra were used for composition determination.   Second, the unreacted pendant double bonds of the DAP units incorporated into the copolymer were calculated from the iodine value determined by the Wijs method.

The molecular weight and the polydispersity coefficient $\overline{M}_w/\overline{M}_n$ of the nonfractionated copolymers obtained before reprecipitation were determined by GPC.   Measurements were carried out with a Waters Associates model ALC/GPC 501 apparatus at room temperature under the following conditions: solvent, tetrahydrofuran; polystyrene gel column combination, 10^3, 10^4, and 10^5 Å (Waters designation); polymer concentration, 0.5% (w/v); and flow rate, 1 mL/min.

The gel fraction of the copolymer samples obtained at conversion beyond the gel point was separated by extracting the sol fraction with benzene as the extracting reagent.

RESULTS AND DISCUSSION

Dependence of Copolymerization Rate on Monomer Composition

DAP has been copolymerized with several vinyl monomers, including styrene,[8] methyl methacrylate,[9] acrylonitrile,[9] methyl acrylate,[10] vinyl chloride,[11] vinyl acetate,[10] ethylene,[12] and a series of α-olefins.[13] Figure 1 shows relationships between the relative rate of copolymerization, which is expressed as the ratio of the rate of copolymerization to that of homopolymerization under the same conditions, and the feed monomer composition. The relative rate tended to decrease, on the whole, with an increase in the mole fraction of DAP in feed; this may be ascribable to degradative chain transfer of the growing chain radicals to DAP. Also, the pattern of change was different according to the kind of co-monomer, varying from a linear drop in the case of a conjugated monomer such as styrene to a sharply angled curve at low feed mole fraction of DAP in the case of an unconjugated monomer such as ethylene. This situation may be interpreted on the basis of the facts that the ability of growing radicals to abstract the allylic hydrogen of DAP decreases with an increase in the conjugation of comonomer and, in addition, the possibility of the allyl radical to reinitiate the comonomer has a reverse dependence. Here it should be noted that all vinyl monomers of interest have completely high polymerizability compared with DAP.

However, dialkyl fumarates as internal olefins have only comparable polymerizability to DAP although it was thought that dialkyl fumarates show no homopolymerizability before Bengough's investigation.[14] Thus we can expect
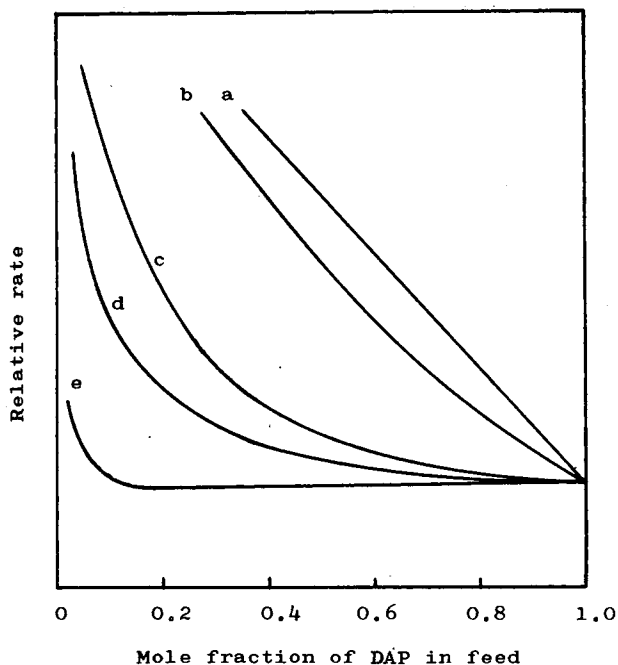

Fig. 1. Relationship between relative rate and monomer composition in the copolymerization of DAP with vinyl monomers: (a) styrene or methyl methacrylate, (b) methyl acrylate or acrylonitrile, (c) vinyl chloride, (d) vinyl acetate, and (e) ethylene.

quite a different relationship between the rate of copolymerization and the feed monomer composition as is evident from the high rate of polymerization of methyl allyl fumarate[4] and diallyl fumarate[3] compared with diallyl dicarboxylates; Figure 2 shows the results of the bulk copolymerization of DAP with DEF, DBF, and DOF using 0.1 mol/L of AIBN at 60°C. In all copolymerizations remarkable rate enhancement was observed. This kind of rate feature is quite usual for copolymerization between monomer combinations accompanied by the formation of the charge transfer complex. In this connection, the formation of the charge transfer complex between the monomer pairs was examined UV spectroscopically; however, no red shift of the absorption spectra was observed. It is also noteworthy that the maximum rate was found at the molar ratio of 1:1 in the monomer feed although DAP has two double bonds. This rather peculiar rate dependence on monomer composition is discussed below in detail.

Copolymerizability and Cyclization

Figure 3 shows the copolymer composition curves for the bulk copolymerization of DAP with DEF, DBF, and DOF; the copolymerizability of DAP with dialkyl fumarates was quite high independent of the alkyl substituent of fumarates.

In our previous articles[10,15] it was suggested that the copolymerization of DAP with various monovinyl monomers obeys the cyclocopolymerization mechanism proposed by Roovers and Smets.[16] Thus the effect of dialkyl fumarates on the cyclopolymerization of DAP was examined by measuring the unreacted pendant double bonds of the DAP units incorporated into the copolymer. Figure 4 shows the dependence of the residual unsaturation R_{us}, on the feed monomer composition in the bulk copolymerization of DAP with DEF, where R_{us} is expressed
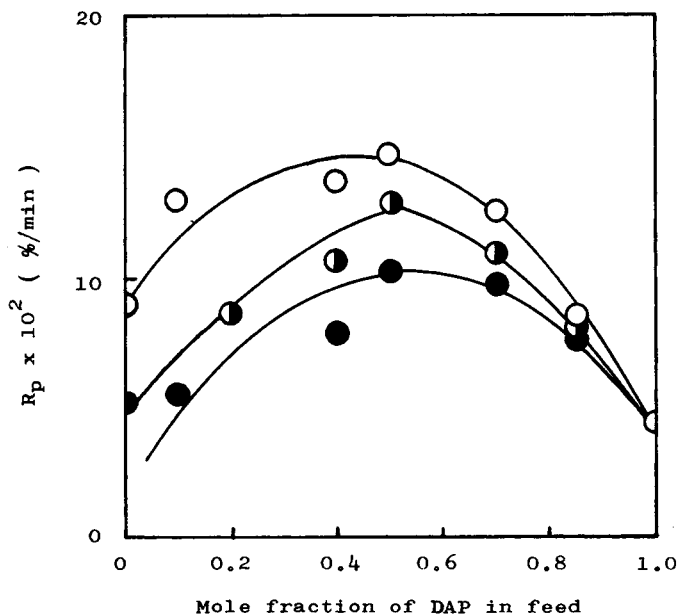

Fig. 2. Dependence of R_p on monomer composition in the bulk copolymerization of DAP with (O) DEF, (◑) DBF, and (●) DOF using 0.1 mol/L of AIBN at 60°C.
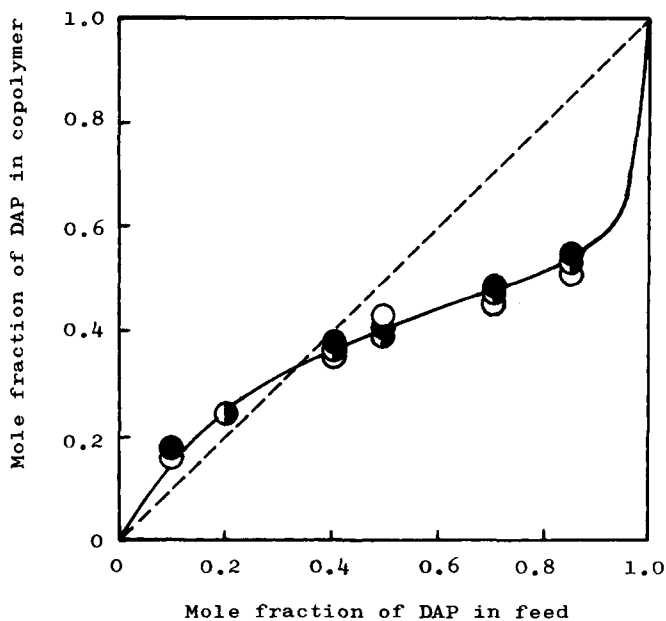
Fig. 3. Copolymer composition curves for the bulk copolymerization of DAP with (O) DEF, (◖) DBF, and (●) DOF at 60°C.

as the molar ratio of the unreacted pendant allyl groups to the total allyl groups of the DAP units incorporated into the copolymer.   The values of R_{us} were always above 0.45 independent of monomer composition, as opposed to the value of 0.28 of the DAP homopolymer obtained under the same polymerization conditions. Now it should be noted that the residual unsaturation is related to the intramolecular cyclization or the crosslinking reaction of DAP accompanying the loss of the two double bonds; R_{us} must be 0.5 if no cyclization or crosslinking reactions occur.   Thus the results shown in Figure 4 suggest that the cyclization of DAP is almost prohibited by the action of DEF, although in this work the crosslinking
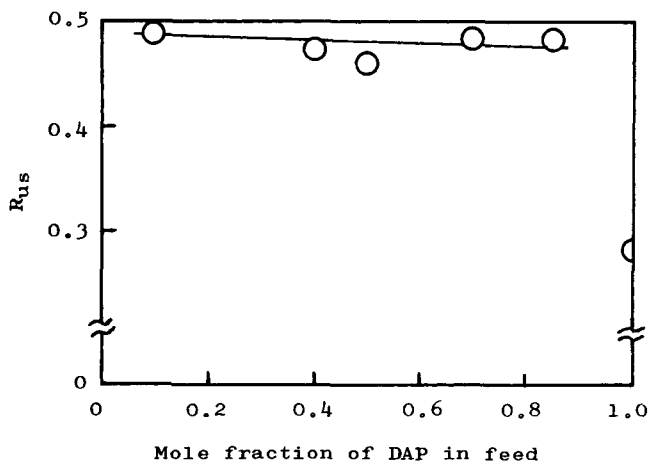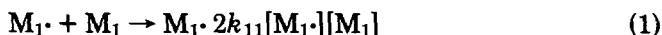

Fig. 4. Dependence of R_{us} on monomer composition in the bulk copolymerization of DAP with DEF at 60°C.

reaction is negligible because the copolymers were obtained at low conversion and soluble in such solvents as acetone and benzene.

In the copolymerization of divinyl monomer (M_1) bearing two equivalent double bonds with monovinyl monomer (M_2), if the intramolecular cyclization of M_1 is not considered, as is the case in this work, reactions (1)–(4) can be given as the propagation reactions for copolymerization:

$$M_1\cdot + M_1 \rightarrow M_1\cdot \ 2k_{11}[M_1\cdot][M_1] \tag{1}$$

$$M_1\cdot + M_2 \rightarrow M_2\cdot \ k_{12}[M_1\cdot][M_2] \tag{2}$$

$$M_2\cdot + M_1 \rightarrow M_1\cdot \ 2k_{21}[M_2\cdot][M_1] \tag{3}$$

$$M_2\cdot + M_2 \rightarrow M_2\cdot \ k_{22}[M_2\cdot][M_2] \tag{4}$$

On the basis of this reaction scheme the copolymer composition eq. (5) is derived[17–19]:

$$\frac{d[M_1]}{d[M_2]} = \frac{2[M_1]}{[M_2]} \cdot \frac{2r_1[M_1] + [M_2]}{2[M_1] + r_2[M_2]} \tag{5}$$

where $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$. Here it should be noted that the monomer reactivity ratios r_1 and r_2 determined by using eq. (5) correspond to those for one double bond of DAP.

The monomer reactivity ratios for the copolymerization of DAP (M_1) with dialkyl fumarates (M_2) were estimated from Fineman–Ross plots[20] according to eq. (5) as follows; M_2, r_1, r_2; DEF, 0.01, 1.25; DBF, 0.02, 1.01; DOF, 0.02, 0.96. Note that the M_1 radical reacts almost exclusively with an M_2 monomer, in reasonable conformity with the suppression of cyclization of DAP by the action of dialkyl fumarates.

Gelation

In our previous article[4] it was found that gelation occurs at 6% in the bulk polymerization of methyl allyl fumarate although for the bulk polymerization of DAP the gel conversion is 25%. In this connection, it is expected that the gelation of DAP should be promoted by the copolymerization with dialkyl fumarates. Thus we examined in detail the gelation in the bulk copolymerization of DAP with DEF; in Figure 5 is shown the relationship between the gel-point conversion and the feed monomer composition, along with the results of the bulk copolymerizations of DAP with DBF and DOF at the molar ratio of 1:1 in the monomer feed. Gelation was quite promoted with an increase in the mole fraction of DEF although the minimum gel point was observed at about 10 mol % of DAP in the monomer feed. Also, the promotion of gelation was depressed with increased bulkiness of the alkyl substituents of fumarates in the order DEF, DBF, and DOF.

As reasons for this type of enhanced gelation of DAP, we can consider the following points: (1) the primary chain length is increased, (2) the unreacted pendant double bonds responsible for the crosslinking reaction are easier to leave on the primary chain, and (3) the crosslinking reaction of the unreacted pendant double bonds of the prepolymer with the growing chain radicals is enhanced by the copolymerization with dialkyl fumarates. The latter two factors are easily understood in terms of the suppression of cyclization and the high copolymerizability mentioned above.
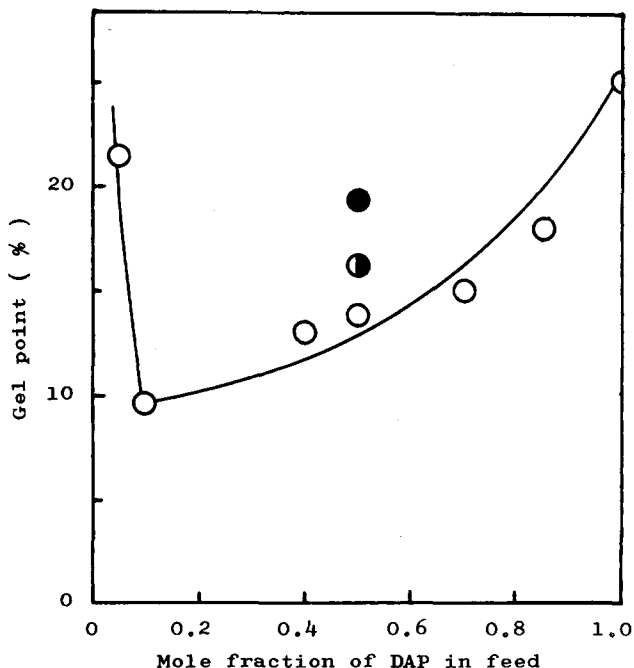
Fig. 5. Dependence of gel point on monomer composition in the bulk copolymerization of DAP with (O) DEF, (◑) DBF, and (●) DOF at 60°C.

The enlargement of polymer chain length was then examined in detail by GPC; Figure 6 shows the GPC curves of the DAP–DEF copolymers obtained at 4.1–5.7% conversion under different monomer compositions in feed. Evidently, the primary chain length and the occurrence of crosslinking reaction were enhanced with an increase in the mole fraction of DEF in the monomer feed. These were further confirmed as follows: GPC curves were analyzed by using the calibration curve obtained with standard samples of monodisperse polystyrene to estimate
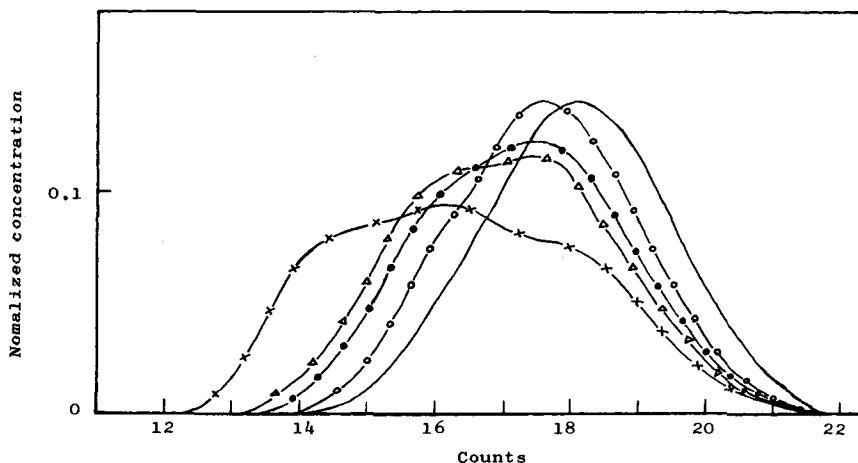

Fig. 6. GPC curves of the copolymers obtained under different feed monomer composition in the bulk copolymerization of DAP with DEF at 60°C; DAP mole fraction, conversion (%); (—) 0.85, 4.8; (—O—) 0.70, 4.1; (—●—) 0.50, 4.6; (—△—) 0.40, 5.7; (—×—) 0.10, 5.3.
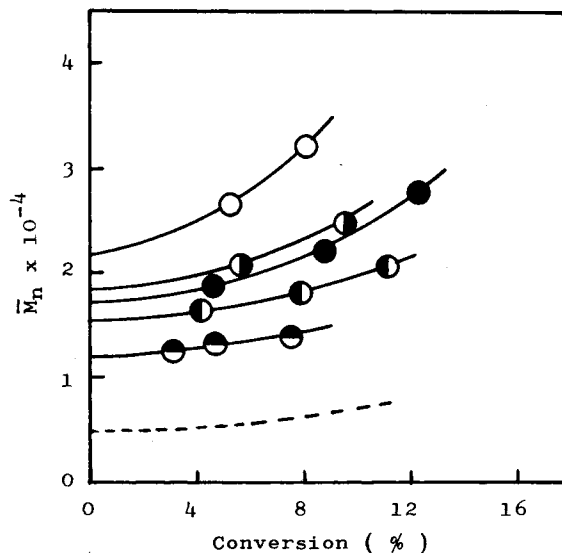
Fig. 7. Dependence of $\overline{M}_n$ on conversion for the DAP–DEF copolymers obtained in bulk at 60°C under different monomer compositions; DAP mole fraction: (◒) 0.85, (◓) 0.70, (●) 0.50, (◐) 0.40, and (○) 0.10. The dotted line is referred to the homopolymerization of DAP for comparison.

the number-average and weight-average molecular weights $\overline{M}_n$ and $\overline{M}_w$; Figures 7 and 8 show the dependences of $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ on conversion in the bulk co-polymerization of DAP with DEF. The molecular weight $\overline{M}_{n,0}$ of the initial polymer is then obtained by extrapolating the $\overline{M}_n$-conversion relationship of Figure 7 to zero conversion. Thus the primary chain length $m + n$ can be cal-culated from the data of the copolymer composition and $\overline{M}_{n,0}$, in which the structure of noncrosslinked copolymer is assumed as $\{DAP\}_m\{DEF\}_n$; evi-dently, the primary chain length was enlarged in a reasonable coincidence with enhanced gelation.

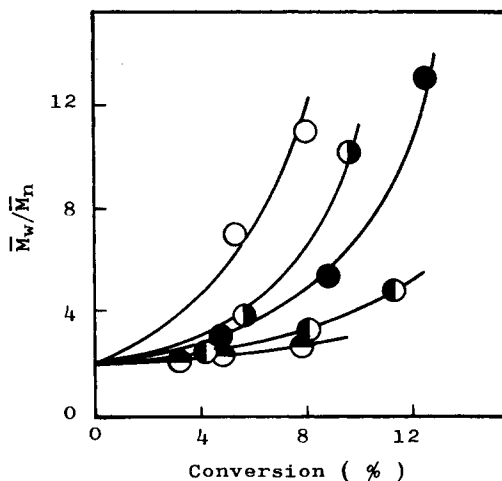Fig. 8. Dependence of $\overline{M}_w/\overline{M}_n$ on conversion for the DAP–DEF copolymers obtained in bulk at 60°C under different monomer compositions; DAP mole fraction: (◒) 0.85, (◓) 0.70, (●) 0.50, (◐) 0.40, and (○) 0.10.

Mechanistic Discussion

The following reaction scheme can be presented for the copolymerization of diallyl dicarboxylate (M_1) with dialkyl fumarate (M_2), in light of the polymerization mechanism of diallyl dicarboxylates[21,22] and the propagation reactions for the cyclocopolymerization of divinyl monomer with monovinyl monomer[16]:
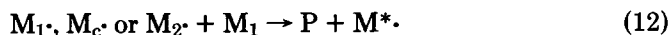
Decomposition:

$$I \rightarrow 2R\cdot \qquad (6)$$

Initiation:

$$R\cdot + M_1 \rightarrow M_1\cdot \qquad (7)$$

$$R\cdot + M_2 \rightarrow M_2\cdot \qquad (8)$$

Cyclization:

$$M_1\cdot \rightarrow M_c\cdot \qquad (9)$$

Propagation:

$$M_1\cdot, M_c\cdot \text{ or } M_2\cdot + M_1 \rightarrow M_1\cdot \qquad (10)$$

$$M_1\cdot, M_c\cdot \text{ or } M_2\cdot + M_2 \rightarrow M_2\cdot \qquad (11)$$

Chain transfer:

$$M_1\cdot, M_c\cdot \text{ or } M_2\cdot + M_1 \rightarrow P + M^*\cdot \qquad (12)$$

Reinitiation:

$$M^*\cdot + M_1 \rightarrow M_1\cdot \qquad (13)$$

$$M^*\cdot + M_2 \rightarrow M_2\cdot \qquad (14)$$

Stabilization:

$$M^*\cdot + M^*\cdot \rightarrow M^* - M^* \qquad (15)$$

I denotes an initiator; P, the polymer; $R\cdot$, the initiator radical; $M_c\cdot$, the cyclized radical formed by the intramolecular cyclization of $M_1\cdot$; and $M^*\cdot$, the allyl radical derived from the abstraction of an allylic hydrogen of M_1 by the growing polymer chain.

For the full understanding of the copolymerization results mentioned above we can first point out the reduction of the chain transfer reaction [eq. (12)] and the fast $M_1\cdot + M_2$ reaction compared with the homopolymerization of DAP: The ability of $M_2\cdot$ of a conjugated radical to abstract an allylic hydrogen of DAP is quite small compared with that of $M_1\cdot$ of an unconjugated radical, and the relative concentration of $M_2\cdot$ to $M_1\cdot$ becomes large in the copolymerization because of the high reactivity of M_2 monomer with the M_1 growing radical. Thus the chain transfer reaction which is characteristic of allyl polymerization and is essentially a termination reaction for a dead polymer chain would be increasingly reduced with.an increase in the mole fraction of dialkyl fumarate in the monomer feed. In addition, the $M^*\cdot + M_2$ reinitiation reaction should be favored compared with the $M^*\cdot + M_1$ reaction. These result in the increase of both rate and degree of polymerization although the charge transfer complex between the two monomers

could not be detected.   It should also be noted that the fast $M_1 \cdot + M_2$ reaction competes with the cyclization [eq. (9)] for the propagation of M_1 growing radical, thus leading to the suppression of cyclization; this is also a reason for our finding of the maximum rate at the molar ratio of 1:1 in the monomer feed, although it should be, at the same time, recalled that the homopolymerizability of dialkyl fumarates is very low compared with normal vinyl monomer and only comparable to that of diallyl dicarboxylates.   In connection with the latter fact, the steric factor resulting in the low homopolymerizability of dialkyl fumarates may be reduced by the copolymerization with DAP, leading to the enhanced copolymerizability.

Finally, the increased degree of polymerization, the suppression of cyclization, and the high copolymerizability should cause the enhanced gelation in the copolymerization of diallyl dicarboxylates with dialkyl fumarates.

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