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Reactivity of Primary Radicals in the Radical Polymerization of Dialkyl Fumarates Initiated with Dimethyl 2,2′-Azobis(isobutyrate) and 2,2′-Azobis(isobutyronitrile)

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ABSTRACT: Radical polymerizations of some dialkyl fumarates (DRFs) and ordinary vinyl monomers (monosubstituted and 1,1-disubstituted ethylenes) were carried out with dimethyl 2,2′-azobis(isobutyrate) (MAIB) and 2,2′-azobis(isobutyronitrile) (AIBN) as initiators. The overall polymerization reactivities of the DRFs have been found to dramatically change depending on the structure of the primary radicals used, while polymerization of the vinyl monomers was not appreciably influenced by the initiators. To investigate the difference in the reactivities of the primary radicals (i.e., 2-(methoxycarbonyl)-2-propyl and 2-cyano-2-propyl) in polymerizations of DRFs initiated with MAIB and AIBN, radical copolymerizations of DRFs with methyl methacrylate (MMA) and methacrylonitrile (MAN) were examined. Furthermore, polymerizations of DRFs with MAIB and AIBN were carried out in the presence of trace amounts of MMA and MAN, and the polymerization behaviors were compared with those for the polymerizations in the absence of MMA and MAN.

Introduction

Contrary to ordinary vinyl monomers (monosubstituted and 1,1-disubstituted ethylenes), 1,2-disubstituted ethylenes show particular characteristics in radical polymerization.[1] We have studied the radical polymerization of dialkyl fumarates (DRFs) as sterically hindered 1,2-disubstituted ethylenes and have found the following features for DRF polymerization.[1-9] The polymers produced from DRFs consist of a less-flexible substituted polymethylene structure.[1,2] The structure of the ester substituents seriously influences the polymerization reactivities and the stereoregularity of the resulting polymers.[3-5] The effects of the ester substituents on the polymerization behaviors may arise from the exceptionally small propagation and termination rate constants due to the low reactivities of the sterically hindered DRFs and of the propagating poly(DRF) radicals as substituted polymethylene.[1,6-9]

Recently, we have also found that the polymerization reactivities of DRFs, which were deduced from the yields and the molecular weights of the resulting polymers, increase when dimethyl 2,2′-azobis(isobutyrate) (MAIB) is used as initiator instead of 2,2′-azobis(isobutyronitrile) (AIBN).[9-11] Several reports have been published with respect to the different behaviors of the primary radicals from MAIB and AIBN, i.e., 2-(methoxycarbonyl)-2-propyl and 2-cyano-2-propyl.[12-16] For example, the self-reactions of both primary radicals were studied to estimate the ratio of combination to disproportionation in termination for the radical polymerization of methyl methacrylate (MMA) and methacrylonitrile (MAN).[12,13] ESR studies of the decomposition of MAIB revealed the formation of a persistent radical during the decomposition.[14,15] In the polymerization of di-*n*-butyl itaconate, it was reported that different ESR spectra were obtained depending on whether MAIB or AIBN was used as initiator.[16]

In this study, the radical polymerizations of several DRFs and ordinary vinyl monomers were carried out with MAIB and AIBN, and the polymerization reactivities were investigated. Moreover, the reactivities of the primary radicals from MAIB and AIBN toward DRFs were examined from the radical copolymerizations of DRFs with MMA and MAN.

Experimental Procedures

Materials. Isopropyl *tert*-butyl fumarate (iPtBF) was supplied by Nippon Oil and Fats Co., Ltd., and distilled under a reduced pressure before use. Di-*tert*-butyl fumarate (DtBF), diisopropyl fumarate (DiPF), and diethyl fumarate (DEF) were prepared according to the methods previously reported.[1] Commercially available MMA and MAN were purified by distillation under a reduced pressure. Other monomers were purified by conventional methods. Commercial MAIB and AIBN were used after recrystallization from ethanol.

Polymerization Procedures. Polymerization and copolymerization were carried out in a degassed glass tube at 60 °C. After polymerization for a given time, the contents of the tube were poured into a large amount of precipitant to isolate the polymer. The resulting polymer was dried under vacuum, and the conversion was determined gravimetrically. The composition of the iPtBF–MMA copolymer was determined from the peak intensities of the ^{1}H NMR spectra of the copolymers (3.3–3.9 ppm for OCH_3 of the MMA unit and 4.6–5.3 ppm for OCH of the iPtBF unit), and the composition of the iPtBF–MAN copolymer was determined by elemental analysis (nitrogen content). The monomer reactivity ratios (r_1 and r_2) were determined by a nonlinear least-squares method.[17]

Measurements. The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were determined by gel permeation chromatography (GPC) at 38 °C with tetrahydrofuran as eluent. Standard polystyrenes were used for calibration. GPC was carried out with a TOSOH 8000 series GPC system.

^{1}H NMR spectra were recorded on a JEOL GX-400 spectrometer with deuteriochloroform and tetramethylsilane as solvent and internal standard, respectively.

ESR measurements were carried out at 60 °C in a degassed ESR tube by means of a Bruker ESP-300 spectrometer. Typical operation conditions were as follows: microwave frequency, 9.5 GHz; modulation frequency, 100 kHz; modulation amplitude, 1 G; time constant, 655.36 ms. The intensity of the ESR spectra was determined from a double integration of the spectra.

Results and Discussion

Radical Polymerization of DRFs and Ordinary Vinyl Monomers with MAIB and AIBN. Table I shows the results of the radical polymerization of various monomers with MAIB and AIBN in benzene at 60 °C, where these initiators have almost the same decomposition

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Table I
Radical Polymerization of DRFs and Ordinary Vinyl Monomers with MAIB and AIBN in Benzene at 60 °C[a]

	MAIB			AIBN			
monomer	$R_p \times 10^5$, mol/L·s	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$R_p \times 10^5$, mol/L·s	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	R_p(MAIB)/R_p(AIBN)
DtBF	9.00	5.2	2.5	1.15	2.1	2.9	7.83
iPtBF	8.01	4.7	2.2	1.07	3.9	2.0	7.49
DiPF	3.78	2.0	2.6	0.53	1.3	2.5	7.13
DEF	0.68			0.15			4.53
St	1.32	0.7	2.0	1.27	0.8	1.8	1.04
MMA	7.09	2.3	2.3	6.82	2.3	2.3	1.04
tBMA	8.54	4.9	2.3	8.32	4.8	2.2	1.03
MA	48.1	16.0	1.7	38.5	15.3	1.9	1.25
tBA	84.7	31.6	1.7	72.3	29.9	1.9	1.17
AN	3.98			3.67			1.08
VAc	3.06	1.5	2.0	1.79	1.2	2.2	1.71
VP	3.94	2.9	1.9	2.47	2.4	2.0	1.60

[a] [Monomer] = 1.5 mol/L, [initiator] = 0.02 mol/L.

rate constants.[9] The ratios of the polymerization rates (R_p) for the initiators, i.e., R_p(MAIB)/R_p(AIBN), in the polymerization of ordinary monosubstituted and 1,1-disubstituted ethylene monomers were found to range from 1.0 to 1.7. In the polymerization of conjugative monomers such as styrene (St) and MMA, the polymerization reactivity was independent of the type of initiator. Acrylonitrile (AN) and methyl acrylate (MA) showed slight differences in R_p and $\bar{M}_n$, and a nonconjugative monomer, vinyl acetate (VAc), showed a relatively large R_p(MAIB)/R_p(AIBN). In the polymerization of these ordinary vinyl monomers, it was confirmed that a steric effect of the substituent did not seriously contribute to the difference in the polymerization reactivities with both initiators, because the changes in R_p and $\bar{M}_n$ in the polymerizations of *tert*-butyl methacrylate (tBMA), *tert*-butyl acrylate (tBA), and vinyl pivalate (VP) were found to be almost same as those of MMA, MA, and VAc, respectively.

On the other hand, in the case of DRFs, the polymerization reactivities in the polymerization with MAIB were much higher than those with AIBN. R_p(MAIB)/R_p(AIBN) values were found to be 4.5–7.8 for DRFs, and these values increase with increasing bulkiness of the ester substituents of the DRFs. Accordingly, it was concluded that the reactivity of the primary radicals toward the monomers greatly affects the overall polymerization reactivity in the polymerization of DRFs.

The $\bar{M}_n$ values for poly(DRF)s with MAIB and AIBN were also found to be different, but the differences in $\bar{M}_n$ were smaller than those in R_p. The number of polymer chains produced, which was estimated from R_p and $\bar{M}_n$ in Table I, is reduced in the polymerization of DRFs with AIBN rather than that with MAIB. This may suggest that the fraction of incorporation of the primary radical of AIBN into polymer formation decreases and the primary radical of AIBN partly inactivates outside the cage; i.e., the real initiator efficiency of AIBN is lower than that of MAIB. This consideration is supported by the detailed kinetic studies for the polymerization of iPtBF with AIBN and MAIB reported in the previous paper.[9] We pointed out that a part of the primary radicals of AIBN participated in termination and inactivated outside the cage for polymerization of iPtBF and that the primary radicals of MAIB exclusively entered in initiation. These different behaviors of the primary radicals lead to the large values of R_p(MAIB)/R_p(AIBN) in the polymerization of DRFs.

Table II
Results of Radical Copolymerization of iPtBF (M_1) with MMA and MAN (M_2) in Bulk at 60 °C

[M_1], mol % in feed	time, h	convn, %	R_{cop}, %/h	[M_1], mol % in copolymer
		M_2 = MMA[a]		
0	0.25	4.27	17.1	0
21.9	0.5	5.78	11.6	~0
41.1	0.6	4.95	8.25	2.56
59.7	0.75	4.29	5.72	5.83
80.7	1	2.27	2.27	15.3
90.9	4.5	5.91	1.31	50.3
100	1	7.81	7.81	100
		M_2 = MAN[b]		
0	3	2.16	0.72	0
20.2	1	0.67	0.67	1.25
46.6	1	0.63	0.63	0.93
60.3	5.2	2.13	0.41	1.69
68.9	9.25	2.04	0.22	3.07
79.5	11	1.01	0.09	4.32
92.0	100	trace		
100	1	9.45	9.45	100

[a] [AIBN] = 0.02 mol/L. [b] [MAIB] = 0.02 mol/L.

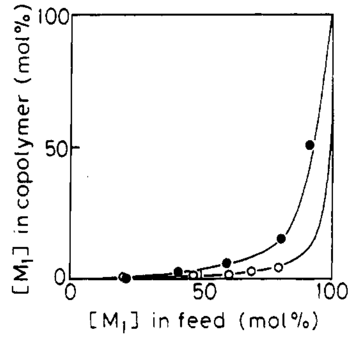
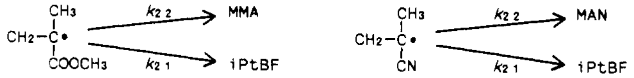


Figure 1. Comonomer–copolymer composition curves for bulk copolymerization of iPtBF (M_1) with MMA (●) and MAN (○) (M_2) at 60 °C.

Scheme I



Copolymerization of DRFs with MMA and MAN. To evaluate the reactivity of the primary radicals derived from MAIB and AIBN toward DRFs, we carried out the copolymerization of iPtBF (M_1) with MMA and MAN (M_2) at 60 °C. Copolymerizations were initiated with an appropriate initiator which does not prevent an accurate determination of copolymer compositions by ^{1}H NMR spectroscopy and elemental analysis; i.e., AIBN and MAIB were used for the iPtBF–MMA and iPtBF–MAN copolymerizations, respectively. Table II and Figure 1 show the results of the copolymerization and comonomer–copolymer composition curves, respectively.

When MAN was used as M_2, the apparent rate of copolymerization (R_{cop}) was lower over the whole range of comonomer compositions than the homopolymerization rates of both comonomers, and it decreased remarkably with increasing concentration of iPtBF in the feed. No copolymer could be isolated for the copolymerization at a comonomer composition >90 mol % of iPtBF.

The r_1 and r_2 determined for each copolymerization system are shown in Table III, indicating that the reactivities of iPtBF are much lower than those of M_2. To estimate quantitatively the reactivity of poly(MMA) and poly(MAN) radicals toward iPtBF, the cross-propagation rate constant (k_{21}) was calculated from eq 1 by using r_1 and k_{22} (Scheme I), where k_{22} is a propagation rate constant

Table III
Copolymerization Parameters in Copolymerization of DRF (M_1) with MMA and MAN (M_2) at 60 °C

M_2	r_1	r_2	k_{22}, L/mol·s	k_{21},[a] L/mol·s	ref
			M_1 = iPtBF		
MMA	0.32	42	315[b]	7.5	this work
MAN	~0	78	26[c]	0.33	this work
			M_1 = DiPF		
MMA	0.17	23	315[b]	14	20
MAN	~0	85	26[c]	0.31	20

[a] Calculated from the following equation: $k_{21} = k_{22}/r_2$. [b] Reference 18; at 25 °C. [c] Reference 19; at 25 °C.

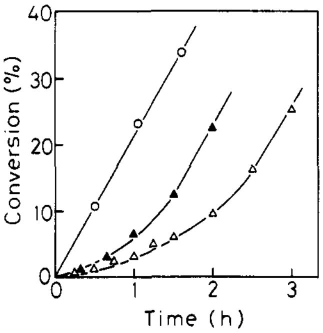


Figure 2. Time–conversion curves for polymerization of DtBF with MAIB in the presence and absence of MAN in benzene at 60 °C; [DtBF] = 1.5 mol/L, [MAIB] = 0.02 mol/L, [MAN] = 0 (○), 5.0 × 10^{-4} (▲), and 1.0 × 10^{-3} (△) mol/L.

for the homopolymerization of MMA and MAN.

$$k_{21} = k_{22}/r_2 \qquad (1)$$

Table III shows the k_{21} values obtained for each copolymerization system, indicating that a poly(MMA) radical had 23 times higher reactivity toward iPtBF than a poly(MAN) radical. The observed difference in reactivity for the polymer radicals may be emphasized by the lower reactivity of the tertiary carbon centered polymer radicals toward sterically hindered iPtBF.

This conclusion is also supported by the results of the copolymerization of DiPF (M_1) with MMA and MAN (M_2).[20] The monomer reactivity ratios in these copolymerizations are listed in Table III, leading to the same conclusion as described above.

Radical Polymerization of DRFs in the Presence of a Trace Amount of MAN. In the copolymerization of DRF with MAN, R_{cop} was very low at the low MAN concentration in the feed. Therefore, the polymerization of DRF initiated with MAIB and AIBN was carried out in the presence of a trace amount of MAN ([MAN] = 10^{-3}–10^{-4} mol/L).

Figure 2 shows the time–conversion curves for the polymerization of DtBF with MAIB in the presence and absence of MAN. The initial polymerization rate decreased upon addition of MAN and then gradually increased to a rate identical to that observed for the polymerization in the absence of MAN. When the MAN concentration was doubled, the acceleration of the polymerization rate was retarded. In the polymerization initiated with AIBN, a similar effect was observed (Figure 3); i.e., the presence of a trace amount of MAN decreased the polymerization rate. On the other hand, when MMA was present in the polymerization system of DtBF, no change in polymerization rate was observed (Figure 3). These results indicate that an existence of MAN retards the DtBF polymerization and the polymerization rate increases with consumption of MAN. Similar retardation by MAN was also observed for the polymerization of DiPF and DEF. The molecular weight and polydispersity of the polymers obtained from the polymerization in the presence of MAN increased with polymerization time (Table IV), indicating that higher molecular weight polymers were produced along with the polymerization.

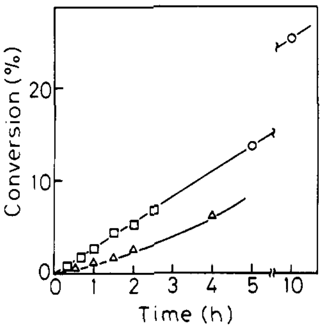


Figure 3. Time–conversion curves for polymerization of DtBF with AIBN in the presence and absence of MAN and MMA in benzene at 60 °C; [DtBF] = 1.5 mol/L, [AIBN] = 0.02 mol/L, [MAN] = [MMA] = 0 (○) mol/L, [MAN] = 1.0 × 10^{-3} (△) mol/L, [MMA] = 1.0 × 10^{-3} (□) mol/L.

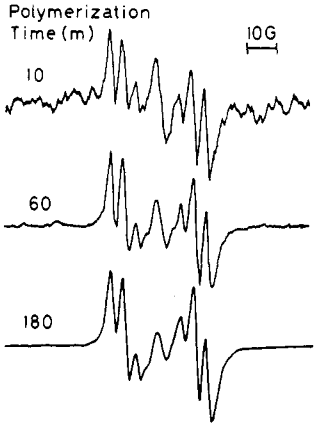


Figure 4. ESR spectra observed during polymerization of DtBF with MAIB in the presence of MAN in benzene at 60 °C; [DtBF] = 1.5 mol/L, [MAIB] = 0.02 mol/L, [MAN] = 1.0 × 10^{-3} mol/L.

Table IV
Results of Polymerization of DtBF with MAIB and AIBN in the Presence of MAN in Benzene at 60 °C[a]

initiator	time, h	convn, %	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
MAIB	0.25	0.81	0.7	2.3
	0.75	2.60	0.8	2.5
	1.25	5.06	0.9	2.9
	2	9.65	1.2	3.4
	3	25.3	1.7	4.0
AIBN	0.5	0.58	0.6	2.1
	1.5	1.79	0.6	2.3
	4	6.25	0.8	2.8

[a] [DtBF] = 1.5 mol/L, [initiator] = 0.02 mol/L, [MAN] = 1.0 × 10^{-3} mol/L.

When AIBN is used as initiator, it should be noted that not only MAN added to the polymerization systems but also MAN produced in situ from the disproportionation of the primary radicals affect the polymerization reactivity. However, because the disproportionation of the primary radical of AIBN was reported[14,15] to occur less frequently, the effect was considered to be low.

Since propagating poly(DRF) radicals are easily detectable by ESR spectroscopy,[1,6–9] ESR measurements of the propagating radical for the polymerization of DtBF with MAIB in the presence of MAN at 60 °C were carried out. The ESR spectra obtained at different polymerization times (Figure 4) were basically the same, but the relative intensity of the central signal was lowered with

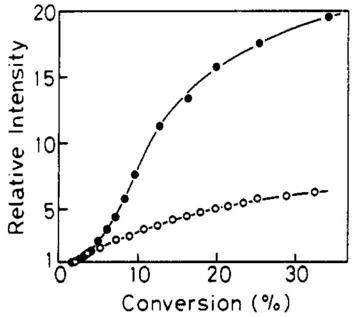
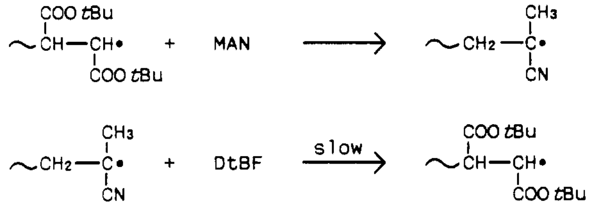


Figure 5. Changes in intensity of the ESR spectra observed during polymerization of DtBF with MAIB in the presence and absence of MAN in benzene at 60 °C; [DtBF] = 1.5 mol/L, [MAIB] = 0.02 mol/L, [MAN] = 0 (○) and 1.0×10^{-3} (●) mol/L.

Scheme II



polymerization time. On the other hand, the whole intensity of the spectra changed remarkably as the polymerization proceeded (Figure 5), where the changes in the intensity do not represent accurately the changes in the propagating radical concentration, because the sensitivity of the ESR spectrometer should be corrected by the change in dielectric constant of the polymerization system.[21] In fact, the intensity of the ESR spectra increased even in the absence of MAN at 60 °C (Figure 5), although it is supposed from a linear relationship up to 30% conversion in Figure 2 that the propagating radical concentration is constant.

The changes in the intensity of the ESR spectra for DtBF polymerization in both the presence and the absence of MAN were quite different, indicating that in the presence of MAN the propagating radical concentration increases along with the polymerization.

From these results, it was concluded that the polymerization rate, the molecular weight of the resulting polymer, and the propagating radical concentration were lowered when the polymerization of DtBF was carried out in the presence of a trace amount of MAN. The decrease in the polymerization reactivity may be caused by the formation of the analogue of the 2-cyano-2-propyl radical from the addition of the propagating radical to MAN (Scheme II). That is, the propagating radical having MAN as a terminal unit has a low reactivity to DtBF, leading to a decrease in the polymerization reactivity.

Conclusion

In the polymerization of DRFs, the polymerization reactivity dramatically decreased when AIBN was used as initiator instead of MAIB, suggesting that a reactivity of primary radicals from the initiators seriously contributes to the polymerization reactivity in the polymerization of DRFs. From the results for the copolymerization of DRFs with MMA and MAN and for the polymerization of DRFs in the presence of a trace amount of MAN, a poly(MAN) radical was found to have a much lower reactivity toward DRFs than a poly(MMA) radical. Since these polymer radicals can be regarded as a model for the primary radical of AIBN and MAIB, it was concluded that the quite different polymerization reactivities for the polymerization of DRFs with MAIB and AIBN resulted from the difference in the reactivities of the primary radicals. From the fact that the polymerization rates were scarcely affected by the kind of initiator in the polymerization of ordinary vinyl monomers, we suppose that the difference in reactivity of the radicals is due to the low reactivity of the sterically hindered DRFs. It is interesting that this difference in reactivity of the radicals toward DRFs was observed despite similar polar and resonance effects of the substituents of the radicals.

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