

# Kinetic Studies on the Radical Polymerization of Isopropyl *tert*-Butyl Fumarate Initiated with 2,2'-Azobis(isobutyronitrile) and Dimethyl 2,2'-Azobis(isobutyrate): Rates of Addition and Termination of the Primary Radicals

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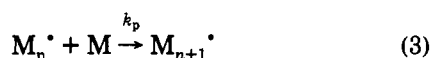
**ABSTRACT:** Kinetic studies were carried out for radical polymerization of isopropyl *tert*-butyl fumarate (iPtBF) initiated with 2,2'-azobis(isobutyronitrile) (AIBN) and dimethyl 2,2'-azobis(isobutyrate) (MAIB) in benzene at 60 °C. The dependence of iPtBF and the initiator concentration on the rate of polymerization ( $R_p$ ) was revealed to change drastically according to the kind of initiators, indicating that the reactivities of the primary radical were important in the polymerization of iPtBF. The concentration of the propagating radical ( $[M^*]$ ) for polymerization of iPtBF was determined from direct observation by ESR spectroscopy. The propagation rate constant was determined at 60 °C to be 0.35 and 0.39 L/mol·s for polymerization with AIBN and MAIB, respectively, from the  $[M^*]$  and  $R_p$ . In order to elucidate the bimolecular termination rate constant ( $k_t$ ), the rate constant for the primary radical formation ( $k_{df}$ ) was determined for both initiators. The  $k_t$  obtained for polymerization with MAIB was 17.5 L/mol·s. In polymerization with AIBN, participation of the primary radical to initiation and termination was examined by the use of  $[M^*]$ ,  $k_t$ , and  $k_{df}$ .

## Introduction

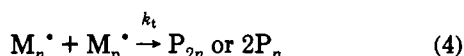
Elementary reactions for radical polymerization are expressed as in eqs 1-5 when chain-transfer reactions are initiation



propagation



termination

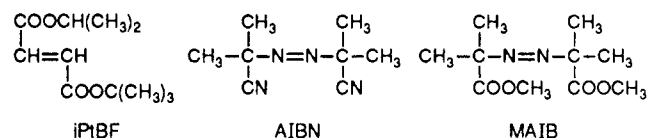


negligible, where I,  $R^*$ , M,  $M^*$ , and P are an initiator, a primary radical, a monomer, a propagating radical, and a resulting polymer, respectively, and  $k_d$ ,  $k_{add}$ ,  $k_p$ ,  $k_t$ , and  $k_{prt}$  represent the rate constants for decomposition of the initiator, addition of the primary radical to the monomer, propagation, bimolecular termination (disproportionation and combination), and primary radical termination, respectively. In ordinary radical polymerizations under appropriate conditions, since reaction of eq 2 is so fast that the rate of initiation is determined with the rate of eq 1 and the bimolecular termination (eq 4) predominantly occurs in the termination step, the reactions in which the primary radical participates; i.e., eqs 2 and 5 can be neglected among these elementary reactions.

We have reported that dialkyl fumarates (DRF) homopolymerize in the presence of radical initiators and their polymerization reactivities increase markedly with an

increase in the bulkiness of the ester substituents.<sup>1-4</sup> It was also confirmed that the rigidity and the stereoregularity of poly(DRF) are varied with the structure of the ester substituents.<sup>3-6</sup> The  $k_p$  and  $k_t$  values for polymerization of diethyl fumarate (DEF) were determined to be  $1.5 \times 10^{-2}$  and 164 L/mol·s, respectively, by means of the rotating-sector method.<sup>7</sup> These values are much lower than those for polymerization of ordinary vinyl monomers. Furthermore, the existence of a high concentration ( $10^{-4}$ - $10^{-6}$  mol/L) of the propagating radical in DRF polymerization systems enables direct observation of it by ESR,<sup>4</sup> leading to a new method for determination of the absolute rate constants.<sup>8-12</sup>

Furthermore, we found recently that the polymerization reactivities of DRFs were drastically changed with the kind of initiators.<sup>13</sup> These phenomena may arise from the low reactivity of DRFs as 1,2-disubstituted ethylene, suggesting that the elementary reactions of eqs 2 and 5 have an important affect on the mechanism of radical polymerization of DRF. Therefore, to examine the influence of the primary radicals on the polymerization of DRFs, the radical polymerization of isopropyl *tert*-butyl fumarate (iPtBF) was carried out with 2,2'-azobis(isobutyronitrile) (AIBN) and dimethyl 2,2'-azobis(isobutyrate) (MAIB), and the kinetics on radical polymerization of iPtBF are discussed in this paper.



## Experimental Section

**Materials.** iPtBF was supplied from Nippon Oil and Fats Co., Ltd., and purified by distillation under a reduced pressure; bp 74 °C (0.5 mmHg);  $d_{25}^{25}$  0.9804. Other DRFs were prepared according to the methods previously reported.<sup>1-4</sup> The purity of all DRFs was checked by <sup>1</sup>H NMR. Commercial AIBN and MAIB were used after recrystallization from ethanol. 1,3,5-Triphenylverdazyl (Verdazyl) was synthesized and purified as described in the literature.<sup>14</sup>

**Table I**  
Radical Polymerization of iPtBF with AIBN and MAIB in Benzene at 60 °C<sup>a</sup>

[iPtBF], mol/L	$R_p \times 10^5$ , L/mol·s		$R_p(\text{MAIB})/R_p(\text{AIBN})$
	AIBN	MAIB	
4.58 <sup>b</sup>	9.79	15.8	1.61
3.66	7.32	14.1	1.93
2.75	3.81	13.0	3.41
1.83	1.43	8.12	5.68
1.37	0.801	5.77	7.20
0.92	0.297	3.41	11.5
0.46	0.0690	1.66	24.1

<sup>a</sup> [initiator] = 0.02 mol/L. <sup>b</sup> In bulk.

**Polymerization Procedures.** Polymerization was carried out in a sealed glass tube. After polymerization for a given time, the content of the tube was poured into a large amount of the precipitant to isolate the polymer. The resulting polymer was dried under vacuum, and the conversion was determined gravimetrically.

**Measurements.** The number- and weight-average molecular weight ( $\bar{M}_n$  and  $\bar{M}_w$ ) and polydispersity ( $\bar{M}_w/\bar{M}_n$ ) were determined by gel permeation chromatography (GPC) at 38 °C in tetrahydrofuran as eluent and calibrated with standard polystyrenes. GPC was performed with Tosoh 8000 series GPC systems.

The measurement of ESR spectra was carried out by the use of a Bruker ESP 300 spectrometer with a variable-temperature control. The typical operation conditions of ESR spectra were as follows: microwave frequency, 9.49 GHz; modulation frequency, 100 kHz; modulation amplitude, 0.1 G; time constant, 655.36 ms. Determination of the absolute radical concentration was performed by using ESR spectra obtained from measurement with a 10-G modulation amplitude to obtain a good signal to noise ratio. No accumulation was carried out for ESR measurement in this study. Radical concentrations were calibrated by using Verdazyl dissolved in iPtBF and benzene in the ESR tube.

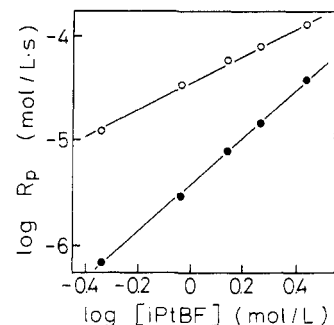
The UV-vis spectra were recorded on a Shimadzu UV-160 spectrophotometer.

## Results and Discussion

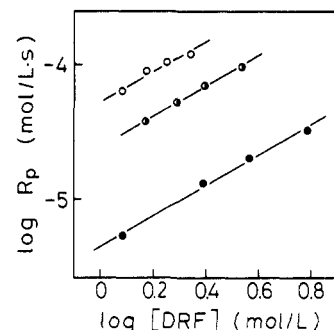
**Polymerization of iPtBF with AIBN and MAIB.** The radical polymerization of iPtBF in bulk or benzene was carried out with two initiators, i.e., AIBN and MAIB, at 60 °C. The polymerization of iPtBF in bulk or at high iPtBF concentration (>3.5 mol/L) proceeded heterogeneously. All polymers obtained in this experiment had polydispersities of 2 or above. Table I shows the rate of polymerization ( $R_p$ ) for polymerization under various iPtBF concentrations and the ratio of  $R_p$  initiated with AIBN and MAIB. As seen in Table I, the  $R_p$  for polymerization of iPtBF with MAIB was much higher than that with AIBN, especially at lower iPtBF concentration, although these initiators have almost the same decomposition rate constants at 60 °C, as follows:  $9.8 \times 10^{-6}$  and  $8.4 \times 10^{-6}$  s<sup>-1</sup> for AIBN<sup>15</sup> and MAIB,<sup>16</sup> respectively.

On the other hand, the molecular weights of the resulting polymers were not appreciably changed with the initiator as compared with  $R_p$ ; e.g.,  $\bar{M}_n(\text{AIBN}) = 5.0 \times 10^4$ ,  $\bar{M}_w/\bar{M}_n(\text{AIBN}) = 2.1$ , and  $\bar{M}_n(\text{MAIB}) = 6.3 \times 10^4$ ,  $\bar{M}_w/\bar{M}_n(\text{MAIB}) = 2.2$  at [iPtBF] = 1.83 mol/L;  $\bar{M}_n(\text{AIBN}) = 0.9 \times 10^4$ ,  $\bar{M}_w/\bar{M}_n(\text{AIBN}) = 2.0$ , and  $\bar{M}_n(\text{MAIB}) = 1.2 \times 10^4$ ,  $\bar{M}_w/\bar{M}_n(\text{MAIB}) = 2.4$  at [iPtBF] = 0.46 mol/L. These results suggested that an actual fraction of primary radicals which participate in initiation in polymerization of iPtBF with AIBN is lower than that of MAIB; i.e., the primary radicals of AIBN are inactivated outside the cage.

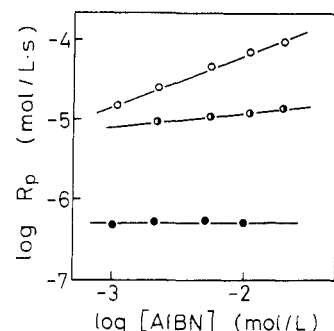
From the relationship between  $R_p$  and the iPtBF concentration (Figure 1), the dependences of iPtBF concentration on  $R_p$  ( $m$  values in eq 6) were determined



**Figure 1.** Dependence of iPtBF concentration on  $R_p$  for polymerization of iPtBF with AIBN (●) and MAIB (○) in benzene at 60 °C; [initiator] = 0.02 mol/L.



**Figure 2.** Dependence of DtBF (○), DiPF (●), and DEF (●) concentration on  $R_p$  for polymerization of DRF with MAIB in benzene at 60 °C; [MAIB] = 0.02 mol/L.



**Figure 3.** Dependence of AIBN concentration on  $R_p$  for polymerization of iPtBF at 60 °C; [iPtBF] = 4.58 mol/L (○) in bulk, 1.83 mol/L (○), and 0.46 mol/L (●) in benzene.

to be 2.2 and 1.2 for polymerization with AIBN and MAIB, respectively.

$$R_p \propto [\text{iPtBF}]^m [\text{initiator}]^n \quad (6)$$

Similar  $m$  values close to unity were observed for polymerization of other DRFs, e.g., di-*tert*-butyl fumarate (DtBF), diisopropyl fumarate (DiPF), and DEF (Figure 2). That is, although the  $m$  values for DtBF, DiPF, and DEF were 2.5, 2.4, and 1.6, respectively, for polymerization with AIBN,<sup>4</sup> the polymerization of these DRFs with MAIB provided 1.1 for the  $m$  value.

Subsequently, the kinetic orders of the initiators,  $n$  value in eq 6, were determined. In polymerization with AIBN, the  $n$  value decreased with a decrease of the iPtBF concentration (Figure 3). Moreover, it was observed that  $R_p$  was independent of the AIBN concentration at 0.46 mol/L of iPtBF; i.e.,  $n \approx 0$ . These results indicate that the termination reaction mechanism depends on the concentration ratio of iPtBF to AIBN; namely, the contribution of the primary radical to termination becomes more important at a low iPtBF concentration. On the other

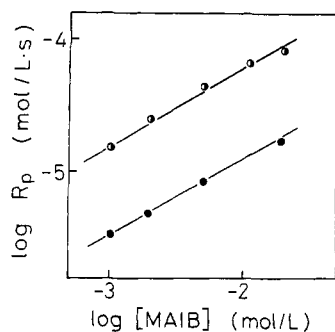


Figure 4. Dependence of MAIB concentration on  $R_p$  for polymerization of iPtBF at 60 °C; [iPtBF] = 1.83 mol/L (●) and 0.46 mol/L (○) in benzene.

Table II  
Dependence of the Concentration of iPtBF ( $m$ ) and Initiator ( $n$ ) on  $R_p$  for Polymerization of iPtBF in Benzene at 60 °C

initiator	$m^a$	$n$ ([DRF], mol/L)
AIBN	2.2	0.65 (4.58 <sup>b</sup> ) 0.19 (1.83) ~0 (0.46)
MAIB	1.2	0.57 (1.83) 0.53 (0.46)

<sup>a</sup> [initiator] = 0.02 mol/L. <sup>b</sup> In bulk.

Table III  
Kinetic Parameters for Polymerization of iPtBF with AIBN and MAIB in Benzene at 60 °C<sup>a</sup>

initiator	$R_p \times 10^5$ , mol/L·s	$[M^*] \times 10^5$ , mol/L	$k_p$ , <sup>b</sup> L/mol·s	$k_d f \times 10^6$ , s <sup>-1</sup>	$k_t$ , <sup>c</sup> L/mol·s
AIBN	0.0690	0.434	0.35	3.53	7500 <sup>d</sup>
MAIB	1.66	9.37	0.39	3.85	17.5

<sup>a</sup> [iPtBF] = 0.46 mol/L, [initiator] = 0.02 mol/L. <sup>b</sup> Calculated from  $k_p = R_p/[M^*][iPtBF]$ . <sup>c</sup> Calculated from  $k_t = 2k_d f/[I]/[M^*]^2$ . <sup>d</sup> This value is invalid for  $k_t$ , because the  $2k_d f/[I]$  value can not be regarded as the initiation rate for polymerization with AIBN (see the text).

hand, the  $n$  values for MAIB were considerably insensitive to the iPtBF concentration (Figure 4), contrary to the drastic change in the  $n$  value observed for polymerization with AIBN.

The  $m$  and  $n$  values in polymerization of iPtBF with AIBN and MAIB are summarized in Table II. From the changes in the  $n$  values with iPtBF concentration and the relationships between  $R_p$  and  $\bar{M}_n$ , the higher  $m$  value in polymerization with AIBN may arise from the consequence of a participation of primary radicals to initiation, namely, a true initiator efficiency, lowered along with the decrease in iPtBF concentration, leading to the predominant primary radical termination in a low iPtBF concentration region. This means that the reactions of eqs 2 and 5 are important in the elementary reactions in polymerization with AIBN. On the other hand, polymerization with MAIB proceeds by a mechanism close to an ordinary radical polymerization, i.e., fast addition of the primary radical to iPtBF and bimolecular termination.

**Determination of  $k_p$  and  $k_t$  Values.** To investigate further the difference in these polymerization kinetics with AIBN and MAIB, the propagating radicals of each polymerization system were examined directly by ESR spectroscopy. The shapes of the ESR spectra obtained for polymerization of iPtBF with AIBN and MAIB were almost the same, but the intensities of these spectra were quite different (Figure 5).

The radical concentrations determined from the ESR spectra are shown in Table III. In the determination of a radical concentration, because the monomer concen-

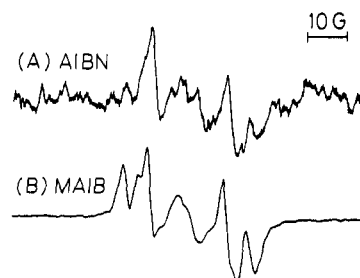


Figure 5. ESR spectra observed during polymerization of iPtBF with AIBN (A) and MAIB (B) in benzene at 60 °C; [iPtBF] = 0.46 mol/L, [initiator] = 0.02 mol/L.

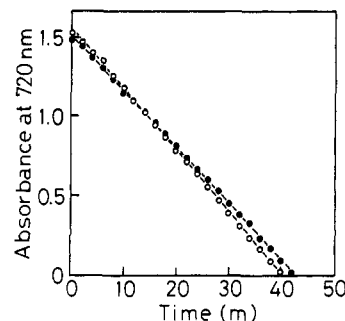


Figure 6. Change of the absorbance at 720 nm with time for polymerization of iPtBF with AIBN (●) and MAIB (○) in benzene in the presence of Verdazyl at 60 °C; [iPtBF] = 0.46 mol/L, [initiator] = 0.02 mol/L.

tration was very low ([iPtBF] = 0.46 mol/L) and ESR measurements were carried out at a low monomer conversion (<2%), the changes in the sensitivity of the ESR spectrometer during the polymerization due to the change in the dielectric constant of the polymerization systems, which was reported to be observed in ESR measurement of the bulk polymerization of methyl methacrylate up to high conversion,<sup>17</sup> were neglected.

The difference in  $R_p$  for polymerizations initiated with MAIB and AIBN is considered to be induced by the difference in the concentration of the propagating radical ( $[M^*]$ ); i.e.,  $[M^*]$  for polymerization with MAIB was about 20 times higher than that with AIBN. In both polymerizations, the propagation rate constants ( $k_p$ ) calculated from the  $R_p$  and  $[M^*]$  values according to eq 7 agreed well with each other as shown in Table III, proving that the  $k_p$  is independent of the initiators.

$$R_p = k_p[M^*][M] \quad (7)$$

In order to elucidate the  $k_t$  value for these polymerizations, a steady-state treatment (eq 8) was adopted.

$$2k_d f[I] = k_t[M^*]^2 \quad (8)$$

The product of  $k_d$  and initiator efficiency ( $f$ ), i.e., the rate constant of primary radical formation, was determined for both initiators by means of radical trapping with Verdazyl.<sup>18</sup> Figure 6 shows the decay of the absorbance of the Verdazyl at 720 nm in the polymerization systems initiated with AIBN and MAIB. The  $k_d f$  values were calculated from the slope of the straight lines and are listed in Table III.

In general, a  $2k_d f/[I]$  value means an initiation rate for ordinary radical polymerization. From studies on iPtBF polymerization with AIBN and MAIB, this assumption is considered to be valid for polymerization with MAIB, whereas the  $2k_d f/[I]$  value may be larger than the initiation rate for polymerization with AIBN because the primary

radicals are found to participate in termination and inactivate outside the cage. Thus, the apparent  $k_t$  value, which was calculated by substitution of the experimental values in eq 8, for polymerization with AIBN was much higher than that with MAIB (Table III) although  $k_t$  for bimolecular termination should be irrespective of the kind of initiators.

Because eq 8 is set up for iPtBF polymerization with MAIB, the  $k_t$  value for bimolecular termination in polymerization of iPtBF was concluded to be 17.5 L/mol·s. However, the  $k_t$  value for polymerization of iPtBF was larger than that of DiPF reported previously.<sup>19</sup> Because the latter value was determined from the decay of the propagating radicals, it represents the true rate constant for bimolecular termination. Accordingly, the former  $k_t$  value may not rule out completely the participation of primary radical termination.

The  $k_p$  and  $k_t$  values obtained with respect to polymerization of iPtBF were extremely small compared to that of vinyl monomers, e.g., styrene<sup>20</sup> and ethyl acrylate<sup>21</sup> ( $k_p$  = 106 and 1300, and  $k_t$  =  $1.08 \times 10^8$  and  $2.7 \times 10^7$  L/mol·s, respectively). Such a tendency was observed for the absolute rate constants for polymerization of DEF and DiPF determined by other methods.<sup>7,19</sup>

**Estimation of the Rate of the Primary Radical Addition and Termination.** In radical polymerization of iPtBF with AIBN, the steady state of the propagating radical should be expressed as in eq 9, which includes the rate of the addition of the primary radical to a monomer (eq 2) and primary radical termination (eq 5).

$$k_{\text{add}}[R^*][M] = k_t[M^*]^2 + k_{\text{prt}}[M^*][R^*] \quad (9)$$

When both the rate of formation and disappearance of the primary radical may be equal, eq 10 is derived, where  $k_{\text{inact}}[R^*]^2$  is the rate of inactivation of the primary radical outside the cage.

$$2k_d[I] = k_{\text{add}}[R^*][M] + k_{\text{prt}}[M^*][R^*] + k_{\text{inact}}[R^*]^2 \quad (10)$$

If the term of inactivation of the primary radical in eq 10 is negligible because of the low concentration of the primary radical, combination of eqs 9 and 10 yields the relationship between  $k_{\text{add}}$  and  $k_{\text{prt}}$  and leads to eq 11 by the use of experimental values for  $[I]$ ,  $[M]$ ,  $[M^*]$ ,  $k_d$ , and  $k_t$ .

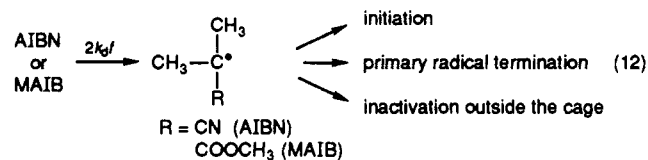
$$k_{\text{prt}}/k_{\text{add}} = 1.06 \times 10^5 \quad (11)$$

Equation 11 indicates that  $k_{\text{prt}}$  is about  $10^5$  times higher than  $k_{\text{add}}$ . Because the monomer concentration was about  $10^5$  times higher than the concentration of the propagating radical, the rate of eq 2 is comparable to that of eq 5, indicating that polymerization is terminated by the primary radicals exclusively in this polymerization condition ( $[i\text{PtBF}] = 0.46$  mol/L and  $[AIBN] = 0.02$  mol/L). This conclusion agrees with the results in Figure 3 and Table II; i.e., the  $n$  value was zero in this condition.

However, in this polymerization, because the inactivation of the primary radicals outside the cage is considered to occur as described in the preceding section, the term of  $k_{\text{inact}}[R^*]^2$  may not be ruled out. The discussion considering the contribution of inactivation outside the cage to the polymerization is required for clarification of the whole kinetics for polymerization of iPtBF with AIBN. But it cannot be achieved at the present time for the difficulty of quantitative estimation of the inactivation outside the cage.

## Conclusion

It is concluded that the primary radical generated from AIBN had a lower initiation reactivity than that from MAIB and acted also as a terminator and inactivated outside the cage in radical polymerization of iPtBF in benzene at 60 °C (eq 12).



Because the true initiator efficiency decreased and the contribution of the primary radical termination gradually increased along with decreasing in iPtBF concentration, the decrease in the polymerization rate is enhanced at a lower iPtBF concentration, resulting in the high  $m$  value for polymerization with AIBN. In the case of MAIB, the initiation is adequately fast so that primary radical termination is almost negligible. Both primary radicals from AIBN and MAIB are tertiary carbon radicals with similar structure, i.e., 2-cyano- and 2-(methoxycarbonyl)-2-propyl radicals, respectively, but quite different kinetics were observed in polymerizations of iPtBF initiated with both initiators. Because such a polymerization behavior depending on the kind of initiators is not observed in ordinary polymerizations of high reactive common vinyl monomers,<sup>13</sup> it may be ascribed to the low reactivity, i.e., extremely low  $k_p$  and  $k_t$  values, of iPtBF as a 1,2-disubstituted ethylene.

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**Registry No.** iPtBF, 105659-63-0; AIBN, 78-67-1; MAIB, 2589-57-3.