***meso* and *racemo* Additions in Propagation for Radical Polymerization of Dialkyl Fumarates II. Determination of the Absolute Rate Constants**

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(Received March 14, 1991)

ABSTRACT: The propagation process in radical polymerization of dialkyl fumarates (DRF) was investigated. The propagation rate constants (k_p) for some DRFs were determined by ESR spectroscopy. It was revealed that k_p increased with the introduction of a bulky *tert*-butyl ester group in the following order: di-*tert*-butyl fumarate > methyl *tert*-butyl fumarate > dimethyl fumarate. The absolute rate constants for *meso* and *racemo* additions were elucidated by the combination of the k_p and the probability of *meso* addition, which was determined by ^{13}C NMR spectroscopy.

KEY WORDS Dialkyl Fumarate / Radical Polymerization
/ Electron Spin Resonance / Propagation Rate Constant
/ *meso* Addition / *racemo* Addition /

Dialkyl fumarates (DRF) with bulky ester alkyl groups homopolymerize readily to give high molecular weight poly(substituted methylene)s (Scheme 1).^{1–5} We have revealed that the polymerization reactivity of DRF increases in the following order: di-*tert*-butyl fumarate (DtBF) > diisopropyl fumarate (DiPF) $\approx$ methyl *tert*-butyl fumarate (MtBF) > dimethyl fumarate (DMF). This order is consistent with the increase in the bulkiness of the ester alkyl groups, and has been interpreted as consequence of the decrease in a rate of bimolecular termination between less-flexible poly-(DRF) radicals, relative to a rate of propagation.^{4,5}

Rate constants for propagation (k_p) and termination (k_t) are popularly determined by the analysis of non-steady state by means of a rotating sector.⁶ Recently, however, it has been

demonstrated that ESR spectroscopy is also an another powerful tool for elucidation of the rate constants at non-steady and steady states.^{7–12} In polymerization of DRF, the propagating poly(DRF) radicals are detectable easily under usual polymerization conditions by ESR without any special technique and apparatus,^{4,13–15} leading to the facile determination of the rate constants. For example, we have already determined the k_p and k_t for polymerizations of isopropyl *tert*-butyl fumarate initiated with dimethyl 2,2'-azobisisobutyrate (MAIB) or 2,2'-azobisisobutyronitrile by use of the ESR method.¹² Furthermore, recent results indicate that k_p of DiPF is considerably larger than that of diethyl fumarate (DEF),^{13–15} suggesting that an increase in the propagation rate contributes to overall polymerization reactivity as well as retardation of termination by the introduction of bulky substituents.

In the preceding paper,¹⁶ we have determined the probabilities of *meso* and *racemo* additions, P_m and P_r , respectively, in propagation

Scheme 1

of DRF by means of restricted *trans* mode opening of the double bond, and revealed the dependence of the P_m on polymerization temperature by using ^{13}C NMR spectroscopy.

In this study, to obtain the information of propagation mechanisms for polymerization of DRFs, the k_p values for polymerization of DMF, MtBF and DtBF are determined by the ESR method, and the absolute values of k_m and k_r are evaluated from the combination of the k_p and P_m .

EXPERIMENTAL

DRFs were prepared and purified according to the methods previously reported.¹⁻⁴ Commercial MAIB as a radical initiator was used after recrystallization from ethanol. 1,3,5-Triphenylverdazyl was synthesized and purified as described in the literature.¹⁷

Polymerization was carried out in a sealed glass tube, similarly to the method described in the preceding paper.¹⁶

The measurement of ESR spectra was carried out by the use of a Bruker ESP-300 spectrometer with a variable temperature control. The operating conditions of ESR spectra were as follows; microwave frequency, 9.49 GHz; modulation frequency, 100kHz; modulation amplitude, 0.1 G; time constant, 655.36 ms.

RESULTS AND DISCUSSION

Figure 1 shows the time-conversion relationships for radical polymerization of DMF, MtBF and DtBF in benzene with MAIB at 60°C. The rates of polymerization (R_p) calculated from the slopes of the curves are listed in Table I, indicating that R_p increases in a following order; DtBF > MtBF > DMF, agreeing with the previous reports.⁴

The propagating radical of each polymerization system was observed directly by ESR spectroscopy. The shapes of the ESR spectra obtained for the polymerization of

DMF, MtBF and DtBF (Figure 2) are consistent with that of other DRFs reported previously,^{4,13-15} indicating that the ESR

Figure 1. Time-conversion relationships for radical polymerization of DMF (○), MtBF (◐), and DtBF (●) in benzene with MAIB at 60°C: [DRF] = 1.0 mol l⁻¹; [MAIB] = 0.02 mol l⁻¹.

Table I. Determination of propagation rate constant (k_p) for radical polymerization of DRF at 60°C^a

DRF	$R_p \times 10^5$	$[\text{M}^\cdot] \times 10^4$	k_p
	mol l ⁻¹ s ⁻¹	mol l ⁻¹	l mol ⁻¹ s ⁻¹
DtBF	5.14	1.11	0.46
MtBF	0.95	0.41	0.23
DMF	0.14	0.24	0.058

^a [DRF] = 1.0 mol l⁻¹; [MAIB] = 0.02 mol l⁻¹ in benzene.

Figure 2. ESR spectra observed during radical polymerization of (A) DMF, (B) MtBF, and (C) DtBF in benzene with MAIB at 60°C: [DRF] = 1.0 mol l⁻¹; [MAIB] = 0.02 mol l⁻¹.

spectra arise from the propagating radicals. The absolute propagating radical concentration ($[M\cdot]$) was measured from the intensity of these spectra in a steady state by the use of the verdazyl as a standard,¹² as shown in Table I. Table I also includes the k_p values for these DRFs, which were calculated from the R_p and $[M\cdot]$ according to eq 1.

$$k_p = R_p / [M\cdot][DRF] \quad (1)$$

The obtained k_p values are much smaller than those for polymerization of ordinary vinyl monomers, and are in agreement with the k_p for other DRFs ($k_p(30^\circ\text{C}) = 0.015$ and $0.31 \text{ l mol}^{-1} \text{ s}^{-1}$ for DEF¹⁴ and DiPF,¹⁵ respectively). Moreover, it is clear that the k_p obtained increases with the increase of R_p , i.e., both the k_p and R_p increase in the order of DtBF > MtBF > DMF. However, the R_p for DtBF was 36.7 times larger than that for DMF, while the k_p for DtBF was only 7.7 times larger, indicating that not only the increase in the k_p but also the decrease in k_t contribute to the higher polymerization reactivities of DRF bearing a bulky *tert*-butyl group.

The increase in k_p by introduction of the bulky ester groups is likely to contradict the steric hindrance in propagation. It was considered that a propagating manner of these DRFs should be clarified and discussed in order to interpret the increase of k_p .

In the preceding paper,¹⁶ the differences in free energies of activation for *meso* and *racemo* additions ($\Delta G_m^\ddagger - \Delta G_r^\ddagger$) at 60°C were determined, from which P_m values at 60°C were calculated to be 0.73, 0.57 and 0.47 for DtBF, MtBF and DMF, respectively (Table II).

The P_m obtained can be correlated to the rate constants for *meso* and *racemo* additions (k_m and k_r , respectively) in propagation (eq 2).¹⁸

$$P_m / P_r = k_m / k_r \quad (2)$$

Because the k_p may be expressed as eq 3, the absolute k_m and k_r values can be obtained by

Table II. Probability of *meso* addition and absolute rate constants for *meso* and *racemo* additions in radical polymerization of DRF at 60°C

DRF	P_m^a	k_m^b	k_r^b
		$\text{l mol}^{-1} \text{ s}^{-1}$	$\text{l mol}^{-1} \text{ s}^{-1}$
DtBF	0.73	0.55	0.21
MtBF	0.57	0.26	0.19
DMF	0.47	0.054	0.061

^a Calculated from $\Delta G_m^\ddagger - \Delta G_r^\ddagger$ at 60°C (see ref 16).

^b Calculated from eq 2 and 3 using k_p and P_m (see the text).

the combination of the P_m and k_p values.

$$k_p = P_m k_m + P_r k_r \quad (3)$$

The k_m and k_r obtained for polymerization of DMF, MtBF and DtBF at 60°C are listed in Table II. The both k_m and k_r increased with the introduction of *tert*-butyl group as substituent, but the magnitude of increase in k_m (from 0.054 for DMF to 0.55 for DtBF) was larger than that in k_r (from 0.061 for DMF to 0.21 for DtBF). Therefore, it is concluded that the larger k_p for DtBF originates mainly from the increase in the value of k_m .

In the radical polymerization of ordinary vinyl monomers, since the stereochemical structure of the penultimate unit is determined by the addition of the attacking monomer to the propagating radical, the direction of addition and the opening mode of carbon-to-carbon double bond cannot be distinguished each other. On the other hand, in the case of polymerization of DRF, the direction of addition dominates the configuration of the bond which is newly formed by the addition, i.e., P_m . The k_m and k_r values determined in this work mean the preference of *meso* and *racemo* additions, respectively.

In conclusion, the k_p for polymerization of DtBF, MtBF and DMF at 60°C was determined from the concentration of the propagating radical by the ESR method, indicating that the high polymerization reactivity of

DRF having a *tert*-butyl group was induced from both the increase in k_p and the decrease in k_t . Moreover, the absolute rate constants for *meso* and *racemo* additions, k_m and k_r , which are obtained from the combination of k_p and P_m , increase (especially in the case of k_m) by the introduction of a *tert*-butyl group into ester substituents, leading to the highest k_p and P_m values of DtBF.

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18. Since there are possibilities of head-to-head or tail-to-tail propagation as well as head-to-tail in the case of MtBF, P_m , k_p and k_m determined in the present and preceding papers mean apparent values.