Communications to the Editor

"Fast" Radical Polymerization of Sterically Hindered Dialkyl Fumarates as 1,2-Disubstituted Ethylenes

Takayuki Otsu* and Masahiro Yoshioka

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

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Radical polymerization of monosubstituted as well as 1,1-disubstituted ethylenes has widely been studied as they polymerize readily with several initiating species. The polymerization reactivity of such monomers on the basis of their polarity, resonance, and steric factors of the substituents has also been reported in the literature. On the other hand, 1,2-disubstituted ethylenes showed reluctance to undergo radical homopolymerization due to the steric hindrance of the substituents.[1] However, we reported[2] in 1981 that dialkyl fumarates (DRF), even with bulky alkyl ester groups such as isopropyl and *tert*-butyl groups, could be polymerized with a radical initiator to get a polymer having a substituted polymethylene structure and a high molecular weight. Such substituted polymethylenes are expected to show new properties due to their rigid structure, different from ordinary vinyl polymers produced from monosubstituted and 1,1-disubstituted ethylenes.[2d]

The salient features of radical polymerization of DRF monomers are as follows: (i) polymerization reactivities deduced from the rate of polymerization (R_p) and the molecular weight of the resulting polymers increase with the increase in the bulkiness of the ester substituents,[2] (ii) the flexibility (rigidity) and the stereoregularity of the resulting polymers depend sensitively upon the structure of the substituents,[3] and (iii) both the absolute rate constants for propagation and termination (k_p and k_t) are extremely low as compared with those of ordinary vinyl monomers.[4] These characteristics are closely related to one another, and they arise essentially from the less reactivity of sterically hindered DRF monomers and of propagating poly(DRF) radicals consisting of a substituted polymethylene structure.

In our previous studies[2] on the radical polymerization of 1,2-disubstituted DRF monomers in bulk, wherein 2,2′-azobis(isobutyronitrile) (AIBN) was mainly used as the initiator, we pointed out that high polymerization reactivity could be accomplished with a relatively high concentration of initiator (~10^{-2} mol/L) due to their less reactivity. Also the observed R_p was lower in every case when compared with the value for monosubstituted or 1,1-disubstituted vinyl monomers.

Recently, in the radical polymerization of DRF monomers with a different initiator, i.e., dimethyl 2,2′-azobis(isobutyrate) (MAIB), an alternating azo compound (Scheme I), a much higher value of R_p was found apart from the difference in the rates of the primary radical formation.[5] Surprisingly, this value was even higher than those observed with conventional vinyl monomers under identical conditions. Therefore, we have taken up a systematic study on the radical polymerization of DRF monomers and other vinyl monomers with AIBN and MAIB, and the results are being reported herein.

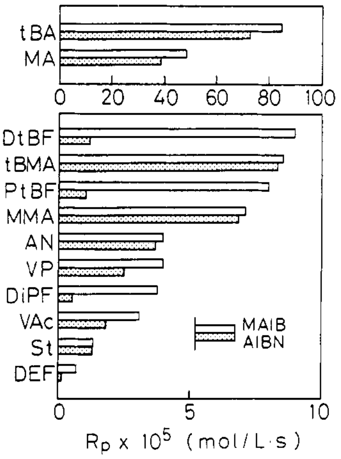


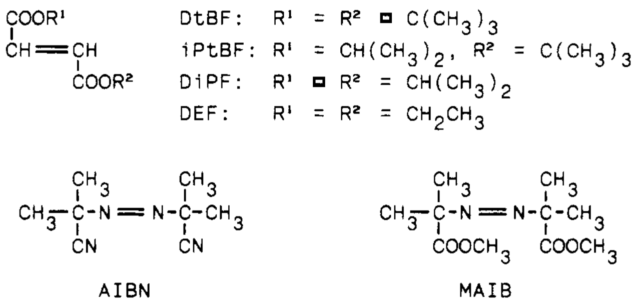
Figure 1. Comparison of R_p for the radical polymerization of DRF and various vinyl monomers initiated with MAIB and AIBN. Polymerization conditions: [Monomer] = 1.5 mol/L, [Initiator] = 0.02 mol/L, in benzene at 60 °C.

Table I
R_p, k_p, k_t, and $k_p/k_t^{0.5}$ Values for the Radical Polymerization of Various Monomers at 60 °C

monomer	R_p[a] × 10^5, mol/L·s	k_p,[b] L/mol·s	k_t,[b] L/mol·s	$k_p/k_t^{0.5}$, (L/mol·s)$^{0.5}$
DtBF	9.00	0.46	11.2	0.14
iPtBF	8.01	0.39	17.5	0.093
MMA	7.09	367	18.7 × 10^6	0.085
St	1.32	176	7.2 × 10^7	0.021

[a] [Monomer] = 1.5 mol/L, [MAIB] = 0.02 mol/L, in benzene. [b] k_p and k_t for DRF were determined by the ESR method.[4c,4d] The values for MMA and St are in the literature (refs 8 and 9, respectively).

Scheme I



$(CH_3)_2C(CN)-N{=}N-C(CN)(CH_3)_2$

$(CH_3)_2C(COOCH_3)-N{=}N-C(COOCH_3)(CH_3)_2$

Figure 1 indicates the value of R_p obtained in the radical polymerization of di-*tert*-butyl fumarate (DtBF), isopropyl *tert*-butyl fumarate (iPtBF), diisopropyl fumarate (DiPF), and diethyl fumarate (DEF) and other vinyl monomers with AIBN and MAIB in benzene at 60 °C. Although similar tertiary carbon-centered radicals are generated from both AIBN and MAIB in almost the same rates,[6] DtBF, iPtBF, DiPF, and DEF showed quite different values of R_p with these two initiators. The ratios R_p(MAIB)/R_p(AIBN) were determined to be 7.83, 7.49, 7.13, and 4.53 for DtBF, iPtBF, DiPF, and DEF, respectively, in accordance with the steric hindrance of the ester

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substituents. These differences in R_p may be due to the fact that the primary radical generated from AIBN which has a low initiation reactivity may participate in primary radical termination and hence inactivates outside the cage.[4d] The reason for the difference in behaviors of the primary radicals of AIBN and MAIB is not clear at the present stage, but the formation of a ketene imine radical[7] from AIBN might be one of the reasons for the low initiation reactivity of AIBN.

The R_p in the polymerization of methyl methacrylate (MMA) and styrene (St) is independent of the initiator; i.e., R_p(MAIB)/R_p(AIBN) is 1.04 for both monomers. Acrylonitrile (AN) and methyl acrylate (MA) show small differences in R_p (R_p(MAIB)/R_p(AIBN) = 1.08 and 1.25 for AN and MA, respectively), and a nonconjugative monomer such as vinyl acetate (VAc) has a large R_p(MAIB)/R_p(AIBN) value (1.71). The ratios for *tert*-butyl methacrylate (tBMA), *tert*-butyl acrylate (tBA), and vinyl pivalate (VP) are 1.03, 1.17, and 1.60, which are almost the same as those for MMA, MA, and VAc, respectively, indicating that the steric factors play no significant role in the polymerization of monosubstituted and 1,1-disubstituted ethylenes. From these results, we may infer that the differences in R_p using two different initiators, which may widely be related to the monomer reactivity, are not only true in polymerization of DRF monomers but also for ordinary vinyl monomers.

When the absolute R_p of DRF monomers is compared with those of the vinyl monomers, it is observed that R_p(AIBN) for DRF monomers is smaller than those for any other monomer used in the present work. However, it has been marvelously revealed that R_p for DRF monomers initiated with MAIB is comparable or more than R_p of the other vinyl monomers. Figure 1 indicates that R_p of DtBF with MAIB is the largest among the polymerization of many kinds of vinyl monomers except for acrylates. In addition, the molecular weights of the resulting polymers showed a tendency similar to that of R_p.

From these results, we conclude that R_p is dominated by the ratio of k_p to $k_t^{0.5}$ regardless of the absolute values of the rate constants[5] (Table I); i.e., both R_p and $k_p/k_t^{0.5}$ are in the following order: DtBF > iPtBF > MMA > St. In other words, even if the monomers have tremendously low k_p values (in fact, k_p values for DRF monomers are about 10^3 times smaller than those for MMA and St) due to the steric hindrance, they can produce a polymer with an adequate speed because the k_t values are smaller enough to compensate for the k_p.

References and Notes

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(5) Generally, R_p for ordinary radical polymerization with bimolecular termination is represented by the following equation; $R_p = (2k_df/k_t)^{0.5}k_p[\text{Monomer}][\text{Initiator}]^{0.5}$ (Odian, G. *Principles of Polymerization*, 2nd ed.; Wiley: New York, 1981; p 186), where k_d and f are the decomposition rate constant and the efficiency of the initiator, respectively.

(6) The rates of primary radical formation ($2k_df$[Initiator]) for both initiators in the polymerization of iPtBF at 60 °C were confirmed to be almost identical by means of the 1,3,5-triphenylverdazyl trapping method;[4d] $2k_df$[Initiator] are 1.41×10^{-7} and 1.54×10^{-7} mol/L·s for AIBN and MAIB, respectively, where [iPtBF] and [Initiator] are 0.46 and 0.02 mol/L, respectively.

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Registry No. DtBF, 7633-38-7; iPtBF, 105659-63-6; MAIB, 2589-57-3; AIBN, 78-67-1; DiPF, 7283-70-7; DEF, 623-91-6.