Macromolecules **1992,** *25,* 2713–2716

Determination of Absolute Rate Constants for Radical Polymerization of Dialkyl Itaconates with Various Ester Groups by Electron Spin Resonance Spectroscopy

Takayuki Otsu,* Kenichi Yamagishi, and Masahiro Yoshioka

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

Received October 15, 1991; Revised Manuscript Received January 27, 1992

ABSTRACT: Electron spin resonance spectroscopy was used to determine the absolute rate constants for the radical polymerization of eight kinds of dialkyl itaconates (DRI) with various ester groups with dimethyl 2,2′-azobis(isobutyrate) (MAIB) in benzene at 60 °C. It was found that the polymerization rate (R_p) depended mainly on the structure of the ester substituents. Propagation rate constants (k_p) for all DRIs were determined to be much smaller (0.2–3.9 M^{-1} s^{-1}) than those for ordinary vinyl monomers and were found to decrease as the ester substituents of the DRIs became bulkier. Termination rate constants (k_t) for all DRIs were also determined to be smaller ((1.4–64.1) × 10^3 M^{-1} s^{-1}) than those for ordinary vinyl monomers and were revealed to be lowered with increasing bulkiness of their ester substituents. From these results, the relationships between the rate constants and R_p were discussed.

Introduction

We have studied the radical polymerizations of some 1,2-disubstituted ethylenes, e.g., fumaric and maleic acid derivatives, in order to synthesize rigid vinyl polymers.[1,2] A polymer produced from 1,2-disubstituted ethylenes consists of a substituted polymethylene structure and shows new properties different from those of ordinary vinyl polymers with a flexible chain structure.[1d] We have also investigated the radical polymerization of 1,1-disubstituted ethylenes having bulky substituents.[3]

Among 1,1-disubstituted ethylenes, dialkyl itaconates (DRI) are well-known to show a high polymerization reactivity.[4,5] In the polymerization of DRI, the relationship between the structure of the ester substituents and the polymerization reactivity has been studied in detail.[3b] It was established that the introduction of ester alkyl groups such as isopropyl and *tert*-butyl decreased the polymerization reactivity of DRI. This is in contrast to the fact that in the polymerization of dialkyl fumarates (DRF) the bulkiness serves to enhance the overall polymerization reactivity.[1]

Generally, rate constants for propagation (k_p) and termination (k_t) are determined by analysis of a non-steady state by the use of a rotating sector method.[6] Recently, however, it has been demonstrated successfully that electron spin resonance (ESR) spectroscopy can also be used as another tool for the elucidation of the rate constants at a non-steady state as well as a steady state in the case when the concentration of propagating radicals is high enough to be detected by ESR spectroscopy.[7–12] In the radical polymerization of DRF, the propagating radicals are easily detectable under the usual polymerization conditions by ESR spectroscopy without any special technique and apparatus, because of a slow rate of bimolecular termination between less flexible polymer radicals.[1] We have already determined the rate constants for the radical polymerization of DRF and discussed them in relation to the structure of the ester groups.[13]

Sato and co-workers[9] have reported the determination of k_p and k_t for the polymerization of di-*n*-butyl itaconate (DnBI) and methyl phenethyl itaconate (MPI) by ESR spectroscopy, but the effect of the structure of the alkyl esters as substituents of DRIs on the rate constants has rarely been studied.

The present study deals with the determination of k_p and k_t in the polymerization of various DRIs (shown in Chart I) with the help of ESR spectroscopy. A correlation between the structure of the substituents and the rate constants has also been established.

Experimental Section

Materials. Commercial diethyl (DEI), di-*n*-butyl (DnBI), diisobutyl (DiBI), and di-*sec*-butyl (DsBI) itaconates were used after distillation under reduced pressure; bp 81 °C/2 mmHg for DEI, 145 °C/10 mmHg for DnBI, 98 °C/3 mmHg for DiBI, and 84 °C/1 mmHg for DsBI.

Bis(cyclohexylmethyl) (DCHMI), diisopropyl (DiPI), and dicyclohexyl (DCHI) itaconates were prepared by the esterification of the itaconic anhydride with the corresponding alcohol in the presence of *p*-toluenesulfonic acid as a catalyst, followed by distillation under reduced pressure; bp 156 °C/0.5 mmHg for DCHMI, 72 °C/1 mmHg for DiPI, and 148 °C/0.5 mmHg for DCHI.

Di-*tert*-butyl itaconate (DtBI) was synthesized from itaconic acid with isobutene in dioxane in the presence of a nonaqueous ion-exchange resin (Amberlyst 15) and purified by distillation under reduced pressure; bp 82 °C/1 mmHg.

Dimethyl 2,2′-azobis(isobutyrate) (MAIB) and 2,2′-azobis(2,4,4-trimethylpentane) (ATMP) used as initiators were recrystallized from ethanol. 1,3,5-Triphenylverdazyl (Verdazyl) was synthesized and purified as described in the literature;[14] λ_{max} = 720 nm and $\epsilon_{max} = 4.37 \times 10^3$. The other reagents were used after routine purifications.

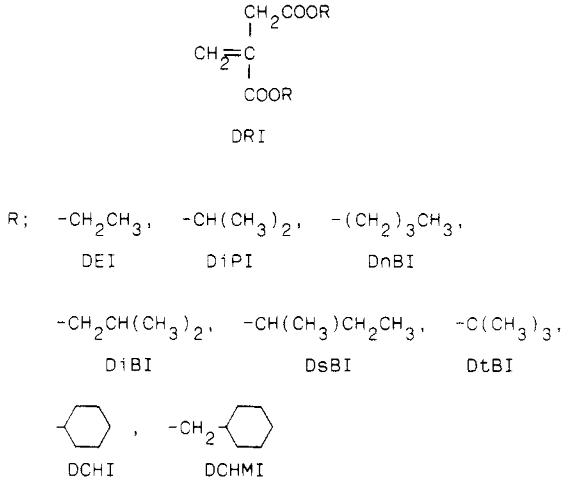
Polymerization Procedures. Radical polymerization of DRI was carried out in a degassed glass tube with MAIB in benzene at 60 °C. After polymerization for a given time, the contents of the tube were poured into a large amount of aqueous methanol to isolate the polymer. The conversion was calculated from the weight of the polymer dried under vacuum.

Measurements. ESR measurements were carried out at 60 °C in a degassed sealed ESR tube by using a Bruker ESP-300 spectrometer with a TE mode cavity. The typical operation conditions of the ESR measurements were as follows: modulation frequency, 100 kHz; modulation amplitude, 0.5 G; time constant, 655.36 ms. Determination of the propagating radical concentration was performed by using ESR spectra obtained from the accumulation of two scans with 10-G modulation amplitude, wherein the change in the sensitivity of the ESR spectrometer was neglected because the ESR mesurements were carried out at very low conversion (<2%).

UV–vis spectra were recorded on a Shimadzu UV-160 spectrophotometer at 60 °C.

0024-9297/92/2225-2713$03.00/0

Chart I



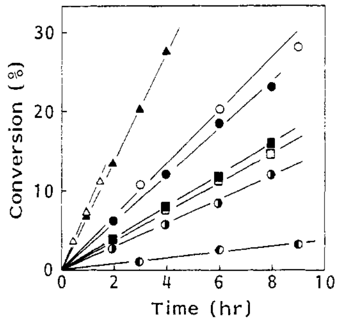


Figure 1. Time–conversion relationships for radical polymerizations of DRIs with MAIB in benzene at 60 °C ([DRI] = 1.5 M, [MAIB] = 0.02 M); (○) DnBI; (●) DiBI; (◑) DsBI; (◐) DtBI; (△) DCHMI; (▲) DCHI; (□) DEI; (■) DiPI.

Table I
Determination of Absolute Rate Constants for Radical Polymerization of DRI with MAIB in Benzene at 60 °C[a]

DRI	$R_p \times 10^5$, M s^{-1}	[P•] × 10^6, M	k_p,[b] M^{-1} s^{-1}	$k_d f \times 10^6$, s^{-1}	f[c]	k_t[d] × 10^{-3}, M^{-1} s^{-1}
DEI	0.76	1.3	3.7	3.0	0.36	64.1
DiPI	0.82	5.2	1.1	3.3	0.40	5.0
DnBI	1.40	2.7	3.5	3.1	0.36	16.9
DiBI	1.27	3.1	2.7	3.8	0.45	15.6
DsBI	0.60	6.2	0.6	3.8	0.46	4.0
DtBI	0.13	4.4	0.2	2.7	0.33	5.6
DCHI	2.82	8.2	2.3	2.4	0.28	1.4
DCHMI	3.16	5.3	3.9	2.4	0.29	3.4

[a] [DRI] = 1.5 M, [MAIB] = 0.02 M. [b] Calculated from $k_p = R_p/[\mathrm{DRI}][\mathrm{P}^\bullet]$. [c] $k_d = 8.4 \times 10^{-6}$ s^{-1}.[17] [d] Calculated from $k_t = 2k_d f\,[\mathrm{I}]/[\mathrm{P}^\bullet]^2$.

Results and Discussion

Radical Polymerization. The radical polymerizations of the various DRIs were carried out with MAIB in benzene at 60 °C. Figure 1 shows time–conversion relationships for these polymerizations. The polymerization rate (R_p) was determined from the initial slopes (less than ca. 10%) of the curves in the figure, and the values are given in Table I. The R_p has been found to depend mainly on the structure of the ester substituents. For example, in the polymerizations of the four DRIs having butyl groups, when the bulkiness of the ester substituents increased from primary to tertiary, R_p decreased in the following order: DnBI ≃ DiBI > DsBI > DtBI. It has been pointed out earlier that R_p increases with increasing bulkiness of the ester substituents in DRF polymerization, i.e., *tert*-butyl > *sec*-butyl > isobutyl ≃ *n*-butyl esters, which is mainly interpreted by the retardation of bimolecular termination due to the rigidity of the polymer chain.[1] However, in DRI polymerization, the structure of the ester substituents does not influence the termination rate much, because poly(DRI)s are members of the poly(1,1-disubstituted ethylene)s, which are less flexible than the poly(monosubstituted ethylene)s but more flexible than substituted polymethylenes such as poly(DRF). Moreover, it should be noted that DCHMI and DCHI bearing cyclohexyl groups show a higher polymerization reactivity than other DRIs. Such behavior may be interpreted on account of the bulky substituents on these monomers. The exceptionally high viscosities (η) of DCHMI and DCHI may also be responsible for the low k_t; e.g., η of DCHI (67.1 cP at 30 °C) is much higher than those of other DRIs: 2.81, 3.49, 3.78, 4.63, 4.70, and 7.48 cP for DEI, DiPI, DnBI, DiBI, DsBI, and DtBI, respectively. The viscosity of the polymerization medium is known to affect significantly the bimolecular termination process.[15,16]

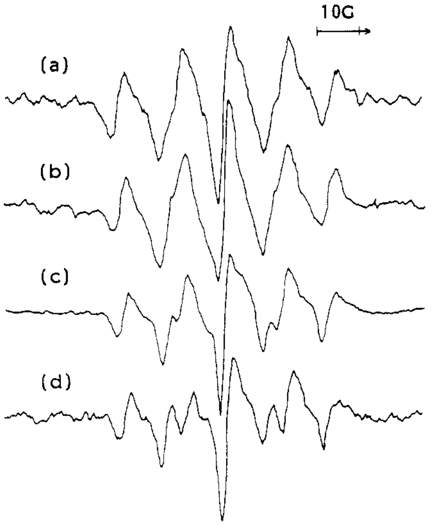


Figure 2. ESR spectra recorded during radical polymerizations of (a) DnBI, (b) DiBI, (c) DsBI, and (d) DtBI with MAIB in benzene at 60 °C ([DRI] = 1.5 M, [MAIB] = 0.02 M).

ESR Spectra of the Propagating Radicals. The ESR spectra were recorded during the radical polymerizations of DRIs with MAIB in benzene at 60 °C. Figure 2 depicts the ESR spectra of four butyl esters. All monomers gave a five-line spectrum, splitting further with increasing bulkiness of the ester substituents. These spectra are basically the same as those obtained by Kamachi et al.[8b] and Sato et al.[9] The variation in the ESR spectra obtained for primary, secondary, and tertiary substituent groups may be due to a change in the conformation of the propagating radicals which depends on the steric effect of the ester substituents. Kamachi et al.[8b] have already reported the simulation of the five-line spectrum with a small shoulder peak, which was observed in the photopolymerization of DnBI with benzoyl peroxide in bulk at low temperature, by means of the following hyperfine splitting constants: 14.1 G for two β-protons and 10.1 G for the other two β-protons. The four spectra shown in Figure 2 were also simulated similarly, i.e., a triplet of triplets due to the two sets of two protons having slightly different splitting constants.

Determination of Propagation Rate Constant. The k_p can be calculated from eq 1 using R_p and the propagating radical concentration ([P•]). By using a solution of known

$$k_p = R_p/[\mathrm{P}^\bullet][\mathrm{DRI}] \tag{1}$$

concentration of Verdazyl as a stable radical, [P•] for the polymerization systems of DRI was determined. As shown

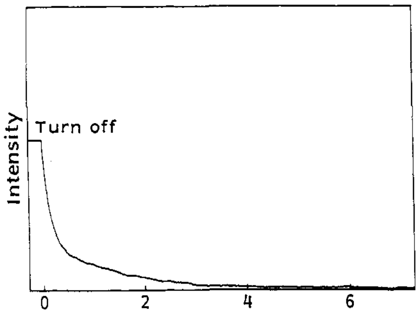


Figure 3. Decay curve of poly(DCHI) radical after interception of UV irradiation in benzene at 60 °C ([DCHI] = 1.5 M, [ATMP] = 0.02 M).

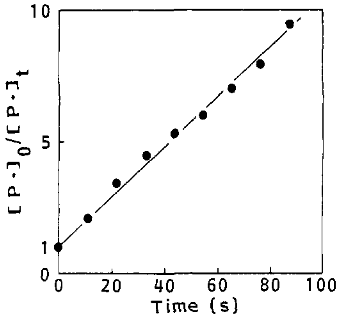


Figure 4. Second-order plot for termination of poly(DCHI) radical after interception of UV irradiation in benzene at 60 °C ([DCHI] = 1.5 M, [ATMP] = 0.02 M).

in Table I, [P•] values were (1.3–8.2) × 10^{-6} M, being 10–100 times higher than those of usual vinyl polymerization (10^{-7}–10^{-9} M). Subsequently, k_p was calculated from eq 1, and the results are given in Table I. The values obtained are much smaller than those for usual vinyl monomers, indicating that the steric effect of the two substituents on DRI contributes appreciably to the propagation reaction.

When the k_p values of the DRIs were compared, it was found that DRIs bearing primary alkyl groups have similar k_p, while k_p values for DRIs with secondary or tertiary alkyl groups, especially for DtBI, decrease. These results indicate that k_p is greatly affected by the structure of the ester substituents in DRI polymerization.

Determination of Termination Rate Constant. The k_t was determined by analysis of either a non-steady state or a steady state. The former method was performed by carrying out the radical polymerization of DRI in an ESR tube using ATMP as an initiator under UV irradiation. k_t was determined from a decay of the propagating radical after the UV irradiation was interrupted, because ATMP scarcely decomposes at 60 °C. Figures 3 and 4 show the decay curve of the propagating poly(DCHI) radical at 60 °C and the second-order plot, respectively. The k_t determined from the second-order plot of the radical concentration was 1.8 × 10^3 M^{-1} s^{-1}.

On the other hand, the steady-state method for the calculation of k_t involves eq 2, which has been derived from a steady state of the radical concentration.

$$2k_d f[I] = k_t[P^\bullet]^2 \qquad (2)$$

where k_d and f are the decomposition rate constant and the efficiency of the initiator, respectively. The initiation rate was determined by means of the primary radical trapping method with Verdazyl,[18] i.e., by a decrease in the absorbance at 720 nm in the polymerization of DRI with MAIB in the presence of Verdazyl, assuming that primary radicals emerging out of the cage are quantitatively trapped by Verdazyl. From these experimental values, $k_d f$[I] and [P•], k_t for DCHI was calculated to be 1.4 × 10^3 M^{-1} s^{-1}. It is clear that values for k_t obtained from the two different methods match, indicating that bimolecular termination occurs mainly and that eq 2 is valid for the polymerization of DRI with MAIB at 60 °C.

In Table I, k_t values for the other DRIs determined by the steady-state method are summarized. The values for k_t were smaller than those for the usual vinyl monomers, indicating that the rigidity of the propagating poly(DRI) chain may affect the rate of bimolecular termination similar to DRF polymerization. Such a small k_t supports the easy observation of the propagating radicals in DRI polymerization by ESR spectroscopy.

Among the DRIs examined in this study, k_t values show a tendency to decrease with increasing bulkiness of the ester substituents. A significant decrease in k_t in secondary and tertiary alkyl esters was observed. This may be due to the suppression of the termination reaction with increase in the rigidity of the polymer chain by the introduction of the bulky ester substituents in the side chain. However, DCHMI and DCHI, which have primary and secondary alkyl ester substituents, respectively, have remarkably low k_t values in comparison with other DRIs, because they have higher viscosity than other DRIs as described above.

Conclusion

The k_p and k_t values of DRI polymerization calculated in this study have been found to be much lower than those for ordinary vinyl polymerization. The high polymerization reactivity of DRIs may arise from the consequence that the k_t are small enough to compensate for the low k_p. These results are similar to that for DRF polymerization; i.e., the propagation reaction is retarded by the steric effect of the two substituents while bimolecular termination is more retarded by the rigidity of the polymer chain.

The relationships between R_p and the rate constants were examined. It has been established that R_p for DRI polymerization is dominated by both k_p and k_t. Although DRIs bearing primary ester substituents have similar k_p values, k_t for DEI is much larger than those for other DRIs, leading to the low R_p for DEI.

The secondary and tertiary esters except for DCHI, i.e., DiPI, DsBI, and DtBI, have much lower k_p values than the primary esters. Especially, k_p for DtBI is the lowest among all DRIs examined in this study. The low k_p values for DRIs with secondary and tertiary ester substituents are responsible for their low R_p.

On the other hand, in the case where the polymerization medium has a high viscosity, i.e., in the polymerizations of DCHMI and DCHI, high R_p values were obtained due to the low k_t.

References and Notes

(1) (a) Otsu, T.; Ito, O.; Toyoda, N.; Mori, S. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 725. (b) Otsu, T.; Toyoda, N. *Polym. Bull.* **1984**, *11*, 453. (c) Otsu, T.; Yasuhara, T.; Shiraishi, K.; Mori, S. *Polym. Bull.* **1984**, *12*, 449. (d) Otsu, T.; Yasuhara, T.; Matsumoto, A. *J. Macromol. Sci., Chem.* **1988**, *A25*, 537.

(2) (a) Otsu, T.; Matsumoto, A.; Kubota, T.; Mori, S. *Polym. Bull.* **1990**, *23*, 43. (b) Matsumoto, A.; Kubota, T.; Otsu, T. *Macromolecules* **1990**, *23*, 4508.

(3) (a) Otsu, T.; Watanabe, H.; Yang, J.-Z.; Yoshioka, M.; Matsumoto, A. *Makromol. Chem., Macromol. Symp.*, in press. (b) Otsu, T.; Watanabe, H., to be published.

(4) Nagai, S.; Uno, T.; Yoshida, K. *Kobunshi Kagaku* **1958**, *15*, 550.

(5) Marvel, C. S.; Shepherd, T. H. *J. Org. Chem.* **1959**, *24*, 599.

(6) Berger, K. C.; Meyerhoff, G. *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; p II/67.

(7) Bresler, S. E.; Kazbekov, E. N.; Fomichev, V. N.; Shadrin, V. N. *Makromol. Chem.* **1972**, *157*, 167.
(8) (a) Kamachi, M.; Kohno, M.; Kuwae, Y.; Nozakura, S. *Polym. J.* **1982**, *14*, 749. (b) Kamachi, M. *Adv. Polym. Sci.* **1987**, *82*, 207.
(9) (a) Sato, T.; Inui, S.; Tanaka, H.; Ota, T.; Kamachi, M.; Tanaka, K. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 637. (b) Sato, T.; Morita, N.; Tanaka, H.; Ota, T. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2497. (c) Sato, T.; Morino, K.; Tanaka, H.; Ota, T. *Makromol. Chem.* **1987**, *188*, 2951.
(10) Garrett, R. W.; Hill, D. J. T.; O'Donnell, J. H.; Pomery, P. J.; Winzor, C. L. *Polym. Bull.* **1989**, *22*, 661.
(11) Zhu, S.; Tian, S.; Hamielec, A. E. *Macromolecules* **1990**, *23*, 1144.
(12) Yamada, B.; Kageoka, M.; Otsu, T. *Macromolecules* **1991**, *24*, 5234.
(13) (a) Otsu, T.; Yamada, B.; Ishikawa, T. *Macromolecules* **1991**, *24*, 415. (b) Yamada, B.; Yoshikawa, E.; Miura, H.; Shiraishi, K.; Otsu, T. *Polymer* **1991**, *32*, 1892. (c) Yoshioka, M.; Matsumoto, A.; Otsu, T. *Polym. J.* **1991**, *23*, 1249. (d) Yoshioka, M.; Otsu, T. *Macromolecules* **1992**, *25*, 559. (e) Yamada, B.; Yoshikawa, E.; Miura, H.; Otsu, T. *Polym. Bull.* **1991**, *26*, 543.
(14) Kuhn, R.; Trischmann, H. *Monatsh. Chem.* **1964**, *95*, 457.
(15) North, A. M. *Reactivity, Mechanism and Structure in Polymer Chemistry*; Jenkins, A. D., Ledwith, A., Eds.; Wiley: New York, 1974; Chapter 5.
(16) Mita, I.; Horie, K. *J. Macromol. Sci., Rev.* **1987**, *C27*, 91.
(17) Otsu, T.; Yamada, B. *J. Macromol. Sci., Chem.* **1969**, *A3*, 187.
(18) Bartlett, P. D.; Funahashi, T. *J. Am. Chem. Soc.* **1962**, *84*, 2596.

Registry No. DEI, 2409-52-1; D*i*PI, 53720-10-8; D*n*BI, 2155-60-4; D*i*BI, 56525-14-5; D*s*BI, 56525-15-6; D*t*BI, 7398-94-9; DCHI, 72414-34-7; DCHMI, 15700-62-6.