Effect of α- and β-Ester Alkyl Groups on the Propagation and Termination Rate Constants for Radical Polymerization of Dialkyl Itaconates

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ABSTRACT: Radical polymerizations of seven dialkyl itaconates (DRIs) with methyl, isopropyl, or *tert*-butyl ester groups were carried out with dimethyl 2,2′-azobis(isobutyrate) in benzene at 60 °C. The effects of the α- and β-ester alkyl substituents (see Chart I) of the DRIs on the polymerization rate (R_p) and the propagation and termination rate constants (k_p and k_t) were examined. For α-substitution R_p decreased with increasing bulkiness of the alkyl group, whereas the opposite was observed for β-substitution. Electron spin resonance (ESR) spectroscopy revealed that k_p decreases with bulkiness of the α-ester alkyl group in the order methyl > isopropyl > *tert*-butyl, with little effect observed for substitution at the β-position, whereas k_t decreases when bulkier ester alkyl groups are introduced into either the α- or β-position. The dependences of k_p and k_t on the structure of the α- and β-ester alkyl groups interpret well the polymerization reactivities of DRI.

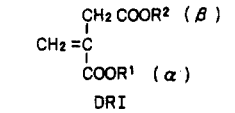
Introduction

Dialkyl itaconates (DRIs), which contain the 1,1-disubstituted ethylene structure, readily polymerize by radical polymerization,[1,2] despite a large number of examples of the failure of many other 1,1-disubstituted ethylenes to produce high polymers because of a low ceiling temperature.[3] Their polymerization reactivities depend on the structure of the ester alkyl substituents;[4,5] i.e., polymer yields and molecular weights of the polymer decrease with increasing bulkiness of the ester alkyl groups, contrary to those observed for dialkyl fumarates (DRFs), whose polymerization reactivities are enhanced by the introduction of a bulky ester alkyl group such as isopropyl or *tert*-butyl.[6] In the polymerizations of DRIs, it has been revealed that steady-state propagating radical concentrations ([P•]) are high enough to be detected by electron spin resonance (ESR) spectroscopy, and propagation and termination rate constants (k_p and k_t) have been determined.[5,7,8]

In a previous study, k_p and k_t of DRIs with various ester groups were determind by ESR spectroscopy, and the effect of the ester alkyl groups on the rate constants was discussed.[5] The observed values of k_p decreased with increasing bulkiness of the ester substituents in the order *n*-butyl ≃ isobutyl > *sec*-butyl > *tert*-butyl, and k_t was inclined to decrease with bulky ester substituents and to decrease further by the polymerization of cyclohexyl esters due to the higher viscosity of the polymerization medium.

As shown in Chart I, DRI has two ester alkyl groups, R^1 and R^2, which are named α- and β-ester alkyl groups, respectively,[1] and are expected to show different contributions in the propagation and termination reactions on account of their nonequivalency. We have studied the polymerization reactivities in the radical polymerization of α-methyl β-*tert*-butyl itaconate (MtBI), i.e., methyl 2-((*tert*-butoxycarbonyl)methyl)acrylate,[2] and α-*tert*-butyl β-methyl itaconate (tBMI), i.e., *tert*-butyl 2-((methoxycarbonyl)methyl)acrylate,[2] as well as other α-alkyl β-methyl itaconates[9] and β-monoalkyl itaconates.[10] We found a higher polymerization reactivity for MtBI than for tBMI and less dependency of the alkyl structure of the β-ester substituent on the polymerization reactivity.[2] The present study deals with the determination of k_p and k_t in the polymerization of DRIs bearing different alkyl groups, i.e., methyl, isopropyl, and *tert*-butyl, as ester alkyl groups (shown in Chart I), and the effects of each ester alkyl group on the rate constants are discussed.

Chart I



DRI

DRI	R^1 (α)	R^2 (β)
DMI	CH_3	CH_3
MiPI	CH_3	$CH(CH_3)_2$
MtBI	CH_3	$C(CH_3)_3$
iPMI	$CH(CH_3)_2$	CH_3
tBMI	$C(CH_3)_3$	CH_3
DiPI	$CH(CH_3)_2$	$CH(CH_3)_2$
DtBI	$C(CH_3)_3$	$C(CH_3)_3$

Experimental Section

Materials. Commercial dimethyl itaconate (DMI) was used after recrystallization from methanol; mp 36 °C. Di-*tert*-butyl itaconate (DtBI) and diisopropyl itaconate (DiPI) were prepared according to the method previously reported.[5] The other DRIs were synthesized according to the following methods (Scheme I).

α-Methyl β-Isopropyl Itaconate (MiPI) [Methyl 2-((Isopropoxycarbonyl)methyl)acrylate]. MiPI was synthesized as follows: itaconic anhydride (IAn) was refluxed in a slight excess of 2-propanol for 8 h, and β-monoisopropyl itaconate (miPI) was isolated by distillation under a reduced pressure, followed by recrystallization from petroleum ether. The potassium salt of miPI was reacted with methyl iodide in acetone at room temperature for 48 h. MiPI obtained was purified by distillation under a reduced pressure; bp 56 °C (1 mmHg).

α-Isopropyl β-Methyl Itaconate (iPMI) [Isopropyl 2-((Methoxycarbonyl)methyl)acrylate]. β-Monomethyl itaconate (mMI) was prepared from IAn and methanol and then recrystallized from benzene. After mMI was converted into the

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Scheme I

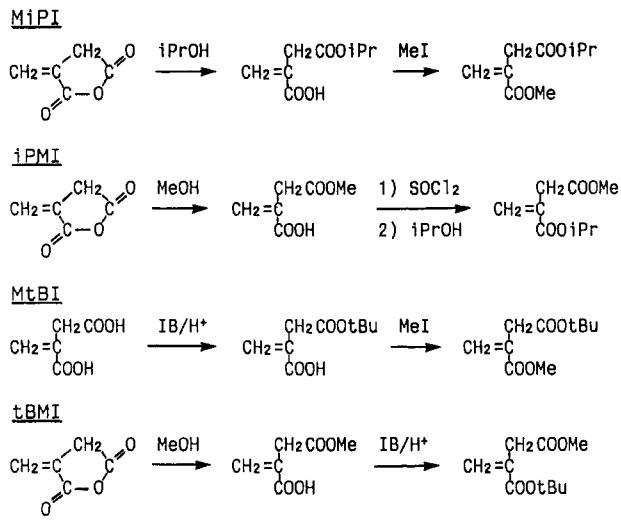


Table I. ^{1}H NMR Chemical Shifts of DRIs[a]

DRI	CH_2=C	CH_2COO	OCH_3	$OCH(CH_3)_2$	$OC(CH_3)_3$
DMI	6.33, 5.73	3.35	3.77 3.70		
MiPI	6.31, 5.69	3.30	3.77	5.02, 1.23	
MtBI	6.28, 5.66	3.25	3.77		1.44
iPMI	6.31, 5.67	3.33	3.70	5.07, 1.27	
tBMI	6.23, 5.61	3.29	3.70		1.48
DiPI	6.28, 5.65	3.29		5.01, 1.24 5.07, 1.27	
DtBI	6.19, 5.55	3.20			1.45 1.49

[a] Chemical shifts in ppm from TMS, in $CDCl_3$.

monochloride monomethyl ester with thionyl chloride in the presence of pyridine, it was reacted with 2-propanol in benzene in the presence of triethylamine at 0 °C. iPMI was distilled under a reduced pressure; bp 62 °C (1.5 mmHg).

α-Methyl β-*tert*-Butyl Itaconate (MtBI) [Methyl 2-((*tert*-Butoxycarbonyl)methyl)acrylate]. β-Mono-*tert*-butyl itaconate (mtBI) was isolated from the reaction mixture of itaconic acid with isobutene in 1,4-dioxane in the presence of a nonaqueous ion-exchange resin (Amberlyst 15) as a catalyst. mtBI was methylated in the same manner as in the synthesis of MiPI. The resulting MtBI was distilled under a reduced pressure; bp 78 °C (2 mmHg).

α-*tert*-Butyl β-Methyl Itaconate (tBMI) [*tert*-Butyl 2-((Methoxycarbonyl)methyl)acrylate]. mMI was reacted with isobutene under the same conditions as in the synthesis of mtBI. tBMI was distilled under a reduced pressure; bp 67 °C (1 mmHg).

The structure of each DRI was checked by ^{1}H NMR and ^{13}C NMR. The ^{1}H and ^{13}C NMR chemical shifts of all DRIs used in this work are listed in Tables I and II, respectively. It was confirmed that each DRI used contained only slight amounts of the other esters as shown in the NMR spectra in Figure 1; e.g., tBMI includes only a small amount of DMI, DtBI, and MtBI. The purities of the monomers were >95%.

The initiators dimethyl 2,2′-azobis(isobutyrate) (MAIB) and 2,2′-azobis(2,4,4-trimethylpentane) (ATMP) (Wako Pure Chemical Industries, Ltd., Osaka) (Chart II) were purified by recrystallization from ethanol. 1,3,5-Triphenylverdazyl (Verdazyl) was synthesized and purified as described in the literature.[11]

Polymerization Procedure. Radical polymerization of the DRIs was carried out in a sealed glass tube. 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 resulting polymer was dried under vacuum, and the conversion was determined gravimetrically.

Measurements. ESR measurements were carried out at 60 °C in a degassed sealed quartz tube by using a Bruker ESP 300 spectrometer, similarly to the procedures reported previously.[5] Typical measurement parameters were as follows: microwave frequency, 9.5 GHz; modulation frequency, 100 kHz; modulation amplitude, 0.5 or 1.0 G; conversion time, 40.96 ms; time constant, 327.68 or 655.36 ms; sweep time, 42 s; microwave power, 2.00 mW; scan number, 25 or 50. Propagating radical concentrations were determined by accumulating two scans with a 10-G modulation amplitude. A known concentration of Verdazyl was used for calibration. The change in the sensitivity of the ESR spectrometer as the polymerization proceeded was neglected because the measurements were carried out at low conversion (<2%).

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

^{1}H NMR spectra were taken with a JEOL GX-400 spectrometer with deuteriochloroform as a solvent.

Results and Discussion

Radical polymerization of DRIs was carried out with MAIB in benzene at 60 °C. The time–conversion relationships are shown in Figure 2. The rate of polymerization (R_p) which was determined from the initial slopes (less than ca. 10%) of the curves in the figure is given in Table III. The R_p decreased when the bulky substituent was introduced into α-COOR (attached directly to the carbon–carbon double bond); i.e., DMI > iPMI > tBMI. On the other hand, a bulkier β-ester alkyl group increased R_p in the following order: MtBI ≃ MiPI > DMI. Thus it has been revealed that the bulkiness of the α- and β-ester alkyl groups causes the suppression and enhancement of the R_p observed, respectively.

As reported previously,[5] in the case of the polymerization of DRI which has the same alkyl groups, the introduction of bulkier ester alkyl groups resulted in a lowering of R_p in the order primary > secondary > tertiary alkyl esters. When R_p was compared among the three DRIs in this work, DiPI showed a higher R_p than DMI in spite of the presence of a bulkier ester alkyl group at α-COOR, while DtBI bearing the bulkiest *tert*-butyl group at β-COOR had a lower R_p. This may be interpreted by the balance of the suppressions of both k_p and k_t as mentioned later.

The ESR spectra were recorded during the polymerization of DRIs. Figure 3 shows the ESR spectra obtained from the polymerization of DRIs bearing a methyl or *tert*-butyl group as an α- or β-ester alkyl. The spectrum of MtBI is very similar to that of DMI, which consists of broad five-line peaks, while the spectrum of tBMI split further as did that of DtBI. Similar results were also observed in the case of isopropyl esters; i.e., DMI and MiPI gave spectra resembling each other, and iPMI gave a spectrum similar to that of DiPI. Previously, we found that the shape of the ESR spectra observed in the DRI polymerization depended on the structure of the ester substituents. The peaks split further with an increase in the bulkiness of the ester substituents in a way similar to that depicted in Figure 3.[5] The results of this work suggest that the shape of the ESR spectra may be determined by the structure of R^1 rather than R^2.

To examine further the variation of the ESR spectra, the ESR spectra were recorded at several temperatures. Figures 4 and 5 show the ESR spectra observed in the polymerization of DMI and DiPI with MAIB or ATMP as initiator at room temperature, 60 °C, or 100 °C. The shape of the ESR spectrum of the poly(DMI) radical scarcely changed with the variation of the temperature. Contrary to this, the spectrum of the poly(DiPI) radical depended on the temperature; a more split spectrum was observed at room temperature or 60 °C, but the spectrum became a five-line spectrum similar to that of poly(DMI) radical at high temperature. These results assume that the rotation of the C–C bonds around the propagating radical center may be slow at low temperature in the case

Table II. ^{13}C NMR Chemical Shifts of DRIs[a]

DRI	$COOR^1$	$COOR^2$	$CH_2{=}C$	$CH_2{=}C$	CH_2COO	OCH_3	$OCH(CH_3)_2$	$OC(CH_3)_3$
DMI	170.98	166.46	133.59	128.39	37.33	51.97 51.87		
MiPI	170.13	166.69	134.05	128.10	38.11	51.99	68.26, 21.70	
MtBI	169.84	166.78	134.39	127.73	39.02	51.90		80.93, 27.95
iPMI	171.14	165.55	134.39	127.81	37.58	51.88	68.46, 21.66	
tBMI	171.16	165.16	135.41	127.12	37.68	51.74		81.00, 27.86
DiPI	170.10	165.55	134.56	127.43	38.03		68.26, 21.60 68.04	
DtBI	170.05	165.46	136.05	126.65	39.21			80.85, 28.01 80.71

[a] Chemical shifts in ppm from TMS, in $CDCl_3$.

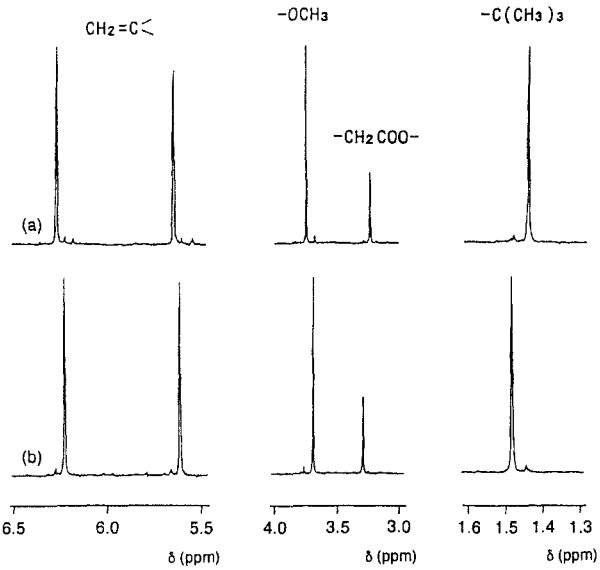
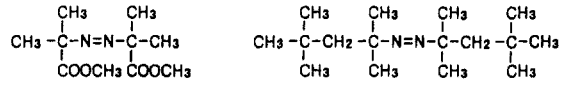
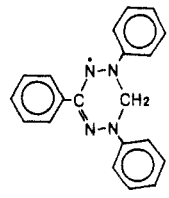


Figure 1. ^1H NMR spectra of (a) MtBI and (b) tBMI in $CDCl_3$.

Chart II



MAIB ATMP



Verdazyl

of DiPI bearing bulky substituents, and an increasing temperature allowed a rapid rotation.

From the intensity of the ESR spectra under the same polymerization conditions as shown in Table III, [P•] was determined. The polymerization systems in this work gave the same [P•] (1.5×10^{-6} M) except for DMI, which showed a lower [P•] (0.61×10^{-6} M) (Table III). These concentrations include an experimental error within ca. 10%. It is clear that these [P•] are lower than those for DiPI and DtBI. k_p can be calculated from eq 1 using R_p and [P•].

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

The k_p values obtained from eq 1 are shown in Table III. The values of k_p decreased with increasing bulkiness of the ester substituent at α-COOR in the order DMI (5.2 $M^{-1}\,s^{-1}$) > iPMI (1.9) > tBMI (0.91). On the contrary, k_p values for MtBI and MiPI, which possess bulky alkyl groups at the β-position, were nearly the same as that of DMI. It is concluded that k_p is appreciably affected by the bulkiness of the α-ester substituent to induce retardation of propagation, but not by the β-ester substitution.

k_t is calculated from eq 2, which is derived from a steady-state treatment, when the termination occurs by bimo-

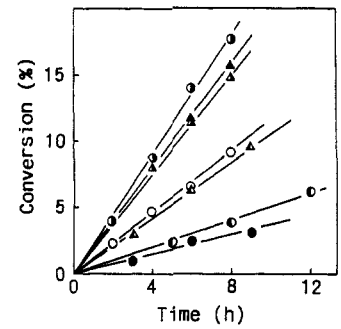


Figure 2. Time–conversion relationships for radical polymerizations of DRIs with MAIB in benzene at 60 °C ([DRI] = 1.5 M, [MAIB] = 0.02 M): (○) DMI; (▲) MiPI; (◑) MtBI; (△) iPMI; (◐) tBMI; (▲) DiPI; (●) DtBI.

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

DRI	$R_p \times 10^6$, M s^{-1}	$[P^\bullet] \times 10^6$, M	k_p,[b] $M^{-1}\,s^{-1}$	$k_d f \times 10^6$, s^{-1}	f[c]	k_t[d] $\times 10^{-4}$, $M^{-1}\,s^{-1}$
DMI	4.67	0.61	5.2	3.4	0.40	36
MiPI	7.67	1.5	3.4	3.3	0.39	6.0
MtBI	9.45	1.5	4.2	2.9	0.34	5.1
iPMI	4.45	1.5	1.9	4.0	0.48	7.0
tBMI	2.12	1.5	0.91	3.3	0.39	5.6
DiPI[e]	8.21	5.2	1.1	3.3	0.39	0.50
DtBI[e]	1.33	4.4	0.20	2.7	0.33	0.56

[a] [DRI] = 1.5 M, [MAIB] = 0.02 M. [b] Calculated from $k_p = R_p/[\mathrm{DRI}][\mathrm{P}^\bullet]$. [c] $k_d = 8.4 \times 10^{-6}\,s^{-1}$ (ref 14). [d] Calculated from $k_t = 2k_d f[\mathrm{I}]/[\mathrm{P}^\bullet]^2$. [e] Reference 5.

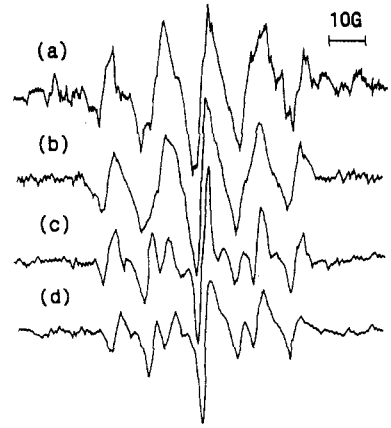


Figure 3. ESR spectra recorded during radical polymerizations of (a) DMI, (b) MtBI, (c) tBMI, and (d) DtBI ([DRI] = 1.5 M, [MAIB] = 0.02 M, in benzene at 60 °C).

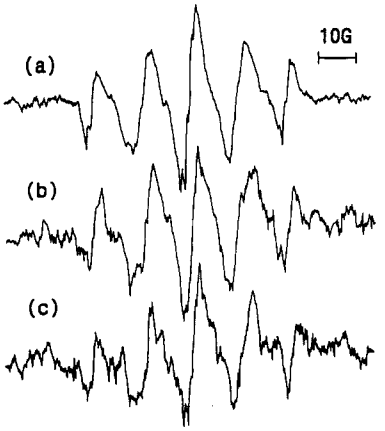


Figure 4. ESR spectra recorded during radical polymerization of DMI at various temperatures: (a) with ATMP at room temperature in toluene under UV irradiation; (b) with MAIB at 60 °C in benzene; (c) with ATMP at 100 °C in toluene.

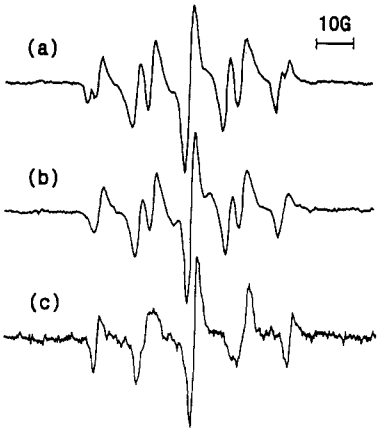


Figure 5. ESR spectra recorded during radical polymerization of DiPI at various temperatures: (a) with ATMP at room temperature in toluene under UV irradiation; (b) with MAIB at 60 °C in benzene; (c) with ATMP at 100 °C in toluene.

lecular termination.

$$2k_d f[I] = k_t[P^\cdot]^2 \quad (2)$$

where k_d and f are the decomposition rate constant and the efficiency of the initiator, respectively.

The bimolecular termination of these DRI polymerizations has already been confirmed by the fact that k_t determined according to eq 2 agreed with k_t which was determined from the decay curve of the ESR spectrum.[5] The initiation rate was determined by means of the consumption rate of Verdazyl,[12] which quantitatively traps the primary radical emerging out of the cage, monitored by the decrease in the absorbance at 720 nm in the polymerization system of DRI with MAIB. The k_t obtained are summarized in Table III.

As the bulky ester alkyl group was introduced into either α- or β-COOR, k_t decreased in the following order: DMI ≫ iPMI ≃ tBMI and DMI ≫ MiPI ≃ MtBI. Of course, when the bulky substituents were introduced into both α- and β-substituents, k_t was further lowered, i.e., in the case of DiPI and DtBI. This indicates that k_t decreases when the bulky substituent is introduced not only into α-COOR but also into β-COOR, being different from the results for k_p described above. The lowering in k_t of DRI might be caused from the suppression of bimolecular termination on the basis of the formation of less flexible polymer structure,[13] which arises by the introduction of bulky substituents to the side chain, similarly to that observed in the case of substitued polymethylenes such as poly(dialkyl fumarate)s.[6]

Conclusion

In the radical polymerization of DRI with MAIB in benzene at 60 °C, k_p decreases by the introduction of a bulky ester alkyl group at α-COOR, i.e., in the order DMI > iPMI > tBMI and DMI > DiPI > DtBI, but β-substitution hardly shows any effect. It may be concluded that the propagation is hindered by the steric effect of the bulky ester alkyl group in the α-position, which locates at a shorter distance to the reactive center (C=C bond) compared with the β-COOR.

In contrast to the results for k_p, k_t has been revealed to decrease by the introduction of bulky alkyls into either the α- or β-substituent. These results mean that the introduction of a bulky ester alkyl group into only the β-position is expected to cause an increase in R_p in the DRI polymerization, because R_p is determined by the balance between k_p and k_t. In fact, MtBI gave the highest R_p among the DRIs examined in this work. We may obtain DRI that shows a greater polymerization reactivity by the introduction of a bulkier ester alkyl group into the β-position.

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