Macromolecules

Volume 28, Number 12 June 5, 1995

Severely Hindered Propagation and Termination Allowing Radical Polymerization of α-Substituted Acrylate Bearing a Bis(carbomethoxy)ethyl Group

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Received November 9, 1994; Revised Manuscript Received March 15, 1995[⊗]

ABSTRACT: Methyl α-[2,2-bis(carbomethoxy)ethyl]acrylate [M(DM)EA], which was synthesized by the reaction of methyl α-(bromomethyl)acrylate and dimethyl malonate in the presence of triethylamine at room temperature, was found to readily polymerize and copolymerize to high molecular weight, although the presence of a considerable steric hindrance was expected. The propagating polymer radical from M(DM)EA was detected and quantified by ESR spectroscopy during bulk polymerization. The absolute rate constants of propagation and termination (k_p and k_t) for M(DM)EA at 60 °C, k_p = 4.0 L/(mol s) and $k_t = (3.8-4.2) \times 10^4$ L/(mol s), which were evaluated using the concentration of the propagating radical at the steady state, are extraordinarily smaller than those for methyl methacrylate (MMA) by 2 and 3 orders of magnitude, respectively. The balance of the propagation and termination rates allows the polymer formation because the steric effect of the α-substituent suppresses the propagation and termination simultaneously. A relatively low ceiling temperature of M(DM)EA, which was estimated to be ca. 90 °C in bulk, reduced the polymerization rate at high temperatures. The steric hindrance was also observed in the copolymerization of M(DM)EA with styrene and MMA. It is concluded that M(DM)-EA is one of the polymerizable acrylates bearing an α-substituent exhibiting significant steric hindrance.

Introduction

α-Alkylacrylic esters, except for methacrylic esters, do not yield high polymers via radical polymerization because the alkyl group hinders propagation.[1] In contrast, a variety of α-(substituted methyl)acrylic esters derived directly or indirectly from the (hydroxymethyl)acrylate have recently drawn attention as polymerizable monomers bearing bulky groups.[2-15] Furthermore, several of the α-(substituted methyl)acrylates which yield no homopolymer and copolymer undergo chain transfer through the addition–fragmentation mechanism.[16,17]

Monomers bearing α-substituted methyl groups such as alkoxymethyl,[2] (fluoroalkoxy)methyl,[3,4] (acyloxy)-methyl,[5-7] fluoromethyl,[8,9] and hydroxymethyl[10-12] groups polymerize to high molecular weights. However, the α-[(alkylthio)methyl]acrylates,[16] α-(bromomethyl)acrylates,[16c,17] and some other α-(substituted methyl)-acrylates[16c] are reluctant to polymerize and copolymerize because of fast chain transfer through the addition–fragmentation mechanism. The α-(phenoxymethyl)-acrylates[13] and α-(chloromethyl)acrylates[9,14] undergo polymerization and copolymerization in competition with the addition–fragmentation, and polymers and copolymers bearing a 2-(carboalkoxy)allyl group at the ω-terminus are obtained. Among the acrylates bearing these structurally simple α-substituted methyl groups, competition between propagation and addition–fragmentation seriously affects polymerizability.

The propagating polymer radicals from the α-(substituted methyl)acrylates have been readily detected and quantified by ESR spectroscopy. Based on the absolute values of the propagation and termination rate constants (k_p and k_t) for α-(substituted methyl)acrylates,[2a,c,5,7] it has been shown that the steric hindrance due to the substituent results in a slightly smaller k_p and a considerably smaller k_t than those for methyl methacrylate (MMA). Taking into account the much smaller k_p and k_t values for itaconic esters[18,19] than those of MMA, we can expect that the absolute values of the rate constants for the polymerizable α-(substituted methyl)acrylates are variable in magnitude. Noteworthily, all the rate constants have been evaluated by the ESR method, which has made possible determination of the rate constants of wide ranges from extraor-

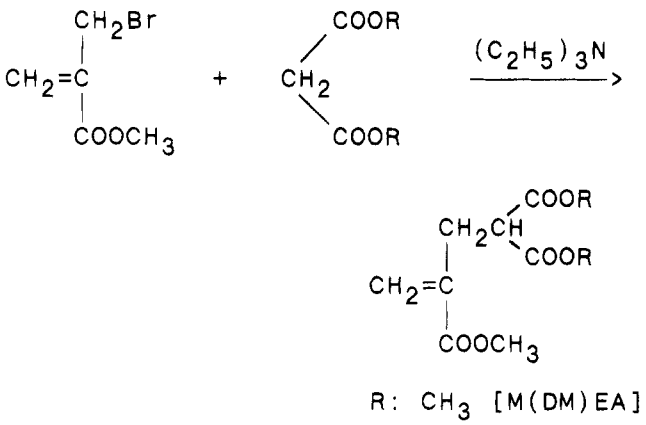
[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1995.

0024-9297/95/2228-4047$09.00/0

dinarily small values to values as large as the rate constants for MMA. The balance of slow propagation and termination allows polymer formation, and the polymerization of the α-(substituted methyl)acrylates can be called *steric hindrance assisted polymerization*.

Methyl α-[2-methyl-2-(carbomethoxy)propyl]acrylate, a MMA dimer, which can be regarded as one of the α-(substituted methyl)acrylates, is reluctant to homopolymerize in accordance with the behavior of the α-alkylacrylates,[17d,20-22] although the addition–fragmentation chain transfer of this compound occurs at an appreciable rate at 100 °C or above.[23] However, methyl α-[3-(carbomethoxy)butyl]acrylate, another MMA dimer, yields a low molecular weight polymer,[22,24,25] and methyl α-[2-(carbomethoxy)ethyl]acrylate, a dimer of methyl acrylate, readily polymerizes to high molecular weight.[22] These findings imply that the interposition of more methylene groups between the carbon–carbon double bond and the branched carbon in the α-substituent enhances polymerization. Among these types of monomers, the steric hindrance of the α-substituents predominantly suppresses polymerization. Probably, the balance of the propagation rate and termination rate shifts in the direction of lowering the polymerization ability.

In the course of a search for new α-(substituted methyl)acrylates as polymerizable monomers, we found that the reaction of methyl α-(bromomethyl)acrylate with malonic esters in the presence of a tertiary amine such as triethylamine took place smoothly to give α-[2,2-bis(carboalkoxy)ethyl]acrylic esters in high yields as described in our preliminary report.[26]



Although synthesis of methyl α-[2,2-bis(carbomethoxy)-ethyl]acrylate [M(DM)EA] has been reported,[27,28] no polymerization study except for our preliminary work has been done. The polymerization of M(DM)EA as a novel monomer bearing three carbomethoxy groups is worth studying in detail.

The present paper deals with a kinetic study of the polymerization and copolymerization of M(DM)EA by the ESR method in relation to the *steric hindrance assisted polymerization* characteristic of the hindered monomers including the α-(substituted methyl)acrylates.[7] Characterization of the polymers from M(DM)-EA and methyl α-[2,2-bis(carboethoxy)ethyl]acrylate has been described in our preliminary report.[26]

Experimental Section

Materials. M(DM)EA was prepared according to the method described in the previous paper.[26] Dimethyl ethylmalonate was synthesized from dimethyl malonate sodium salt and ethyl bromide. Styrene (St) and MMA were commercially available and were distilled under reduced pressure before use. Commercial dimethyl 2,2′-azobis(isobutyrate) (MAIB), 2,2′-azobis(isobutyronitrile) (AIBN), 2,2′-azobis(2,4-dimethylvaleronitrile) (AVN), 1,1′-azobis(cyclohexane-1-carbonitrile) (ACN), and 2,2′-azobis(2,4,4-trimethylpentane) (ATMP) as initiators were used after recrystallization. 1,3,5-Triphenylverdazyl (TPV) was synthesized as described in the literature[29] and recrystallized from methanol.

Polymerization Procedure. All polymerizations and copolymerizations were carried out in glass tubes sealed under vacuum. After polymerization for a prescribed time, the contents of the tube were poured into a large amount of *n*-hexane for the homopolymers and the copolymer with MMA, and aqueous methanol for the copolymer with St, to isolate the respective polymers and copolymers. Compositions of the copolymers were calculated from intensity ratios of the resonances corresponding to the respective monomer units in their ^{1}H NMR spectra. The monomer reactivity ratios (r_1 and r_2) were evaluated by a nonlinear least-squares procedure.[30]

Measurements. The viscosities of the polymerization mixture (η) before polymerization were determined from the flow time and the density, which were measured with an Ubbelohde viscometer and a pycnometer, respectively.

The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were determined by size-exclusion chromatography (SEC) at 38 °C using tetrahydrofuran as eluent and calibration with standard poly(St). SEC was performed by a Tosoh 8000 series high-performance liquid chromatograph equipped with columns packed with TSK gel G7000HHR, G6000HHR, G4000HHR, and G2000HHR connected in this order.

^{1}H and ^{13}C NMR spectra were recorded on a Jeol JNM A-400 spectrometer at 400 and 100 MHz, respectively. Deuteriochloroform and tetramethylsilane were used as the solvent and internal standard, respectively.

ESR spectra of the polymer radicals were taken with a Bruker ESP-300 spectrometer at the X-band (9.50 GHz) with 100-kHz field modulation at a microwave power of 10.0 mW and a modulation amplitude of 10 G. The spectra were recorded after a single scan over a magnetic field of 150 G in width centered at 3390 G divided into 1024 points. The conversion time and time constant of each point were 40.96 and 655.36 ms, respectively. A 3-mm-o.d. quartz tube containing the monomer and initiator sealed under vacuum was maintained at the polymerization temperature in the cavity. The polymer radical was also generated by irradiation with a 500-W xenon lamp (Ushio) at a distance of ca. 45 cm from the tube in the cavity. The ESR spectral intensity was obtained by double integration. Concentration of the propagating polymer radical was calibrated to the signal intensity of TPV dissolved in the monomer.

Results and Discussion

Homopolymerization. We earlier reported that conversion of M(DM)EA to the polymer ($\bar{M}_n$ = 10 000–20 000) reached 20–30% after bulk polymerization for 10 h at 60 °C.[26] The polymerization of M(DM)EA initiated with AVN (0.01 mol/L) in bulk at 30 °C gave a polymer of higher $\bar{M}_n$ (159 000) at 35.6% conversion after 76 h. It appeared that the polymerization of M(DM)EA proceeded without steric hindrance. We predicted that the balance of the propagation and termination rates for the polymerization of M(DM)EA would allow polymer formation.[26] To confirm this point, the effect of the substituent on the rates of the elementary reactions must be quantitatively considered.

Because propagation alone consumes the monomer, the overall rate of the polymerization (R_p) is expressed by the following equation:

$$R_p = k_p[M^\bullet][M] \quad (1)$$

where [M•] and [M] are the concentrations of the propagating polymer radical and the monomer, respectively. The integrated form of eq 1 may be given by eq

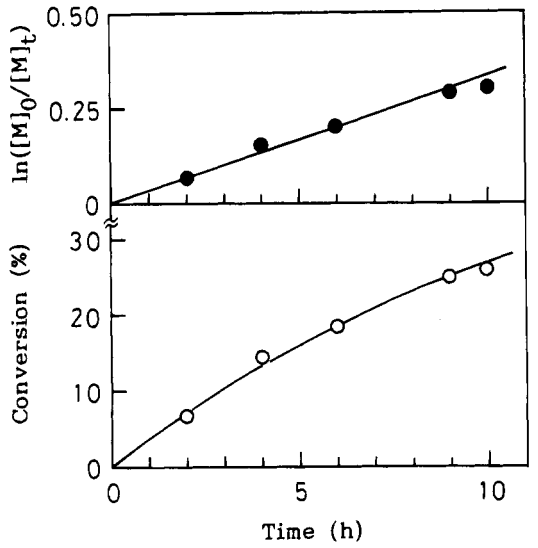


Figure 1. Time–conversion (○) and first-order kinetic plot (●) for the bulk polymerization of M(DM)EA at 60 °C: [MAIB] = 0.050 mol/L.

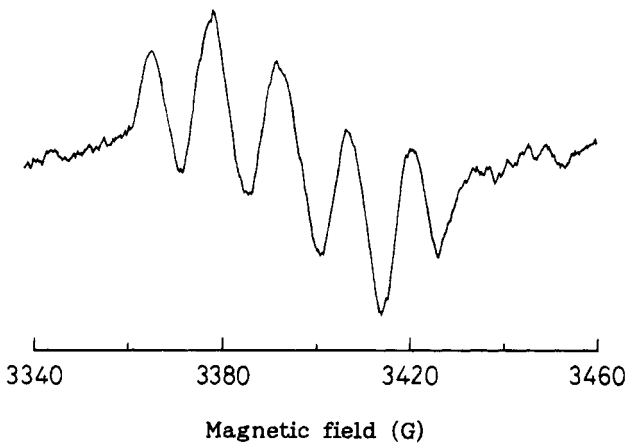


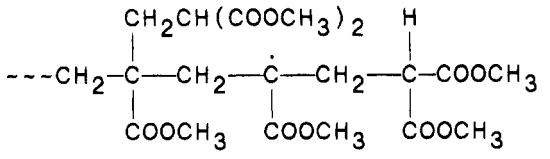
Figure 2. ESR spectrum observed during the bulk polymerization of M(DM)EA at 60 °C: [MAIB] = 0.050 mol/L.

2, and the value of $k_p[M^\bullet]$ can be calculated from this equation:

$$\ln([M]_0/[M]_t) = k_p[M^\bullet]t \quad (2)$$

Figure 1 shows a time–conversion relationship for the bulk polymerization of M(DM)EA at 60 °C under the conditions of [M(DM)EA] = 5.0 mol/L and [MAIB] = 0.050 mol/L. R_p was calculated from the monomer concentration and the slope of the first-order kinetic plot; $R_p = 4.8 \times 10^{-5}$ mol/(L s). The absolute value of k_p can be determined from eq 1 using [M•] measured by ESR spectroscopy.

The ESR spectrum of the propagating radical shown in Figure 2 was recorded after a single scan during the bulk polymerization at 60 °C. The five-line spectrum observed is interpreted by coupling with the two sets of the two β-hydrogens (a = 12–16 G) of the propagating radical **1**.



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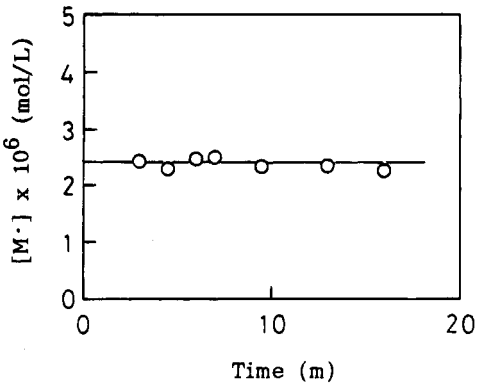
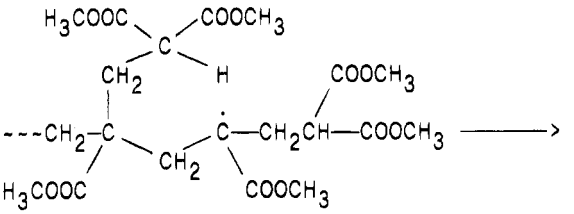
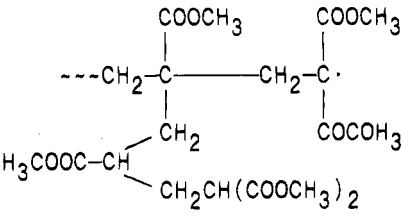


Figure 3. Change in the concentration of the propagating radical with polymerization time for the bulk polymerization of M(DM)EA at 60 °C: [MAIB] = 0.050 mol/L.

This spectrum consisting of broad lines was recorded at a high modulation amplitude, 10 G. Care was taken to avoid distortion of the line shape and saturation. Similar five-line spectra were observed during the polymerizations of other α-(substituted methyl)acrylates such as α-(alkoxymethyl)acrylates,[2a,4a] α-(acyloxymethyl)acrylates,[5,7] and dialkyl itaconates.[18,19]

An intramolecular hydrogen abstraction through a six-membered ring transition state might take place to a certain degree. However, a considerable steric congestion of the cyclic transition state comprising carbon atoms bound to large substituents would suppress the intramolecular reaction.





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If the methylenemalonic ester radical **2** was presented in a significant concentration, the radical species should be detected as a three- or four-line spectrum superimposed with the five-line spectrum for the radical **1**. However, the intensity ratio of the individual lines in Figure 2 was found to be 1:4:6:4:1, consistent with the five-line spectrum. Based on these considerations of the transition state and the intensity ratio of the ESR signals, the intramolecular hydrogen abstraction was ruled out.

Because the ESR measurement was performed at an early stage of the polymerization (<1% conversion), change in the sensitivity of the cavity with conversion was neglected. Figure 3 shows the radical concentration at different polymerization times, showing that establishment of the steady state results in constant [M•]:

$$[M^\bullet] = 2.4 \times 10^{-6} \text{ mol/L}$$

Table 1. k_p and k_t Values for the α-(Substituted methyl)acrylic Esters at 60 °C

α-substituent	ester	k_p (L/(mol s))	$k_t \times 10^{-6}$ (L/(mol s))	$k_p/k_t^{0.5} \times 10^3$ ($L^{0.5}/(mol^{0.5}\ s^{0.5})$)	ref
$CH_2CH(COOCH_3)_2$	CH_3	4.0	0.038	20	this work
CH_3	CH_3	510	42	79	31
CH_2COOCH_3	CH_3	5.2	0.36	8.7	19b
CH_2OCOCH_3	CH_3	350	2.1	240	7
$CH_2OCOCH(CH_3)_2$	CH_3	300	1.1	290	7
$CH_2OCOC(CH_3)_3$	CH_3	230	0.59	300	7
$CH_2OCOCH_2COCH_3$	C_2H_5	300	1.0	300	5a
$CH_2OCOC_6H_5$	C_2H_5	990	2.9	580	5b
$CH_2OC_4H_9$	CH_3	298	8.0	110	2a
$CH_2OCH_2C_6H_5$	CH_3	182	1.6	140	2c

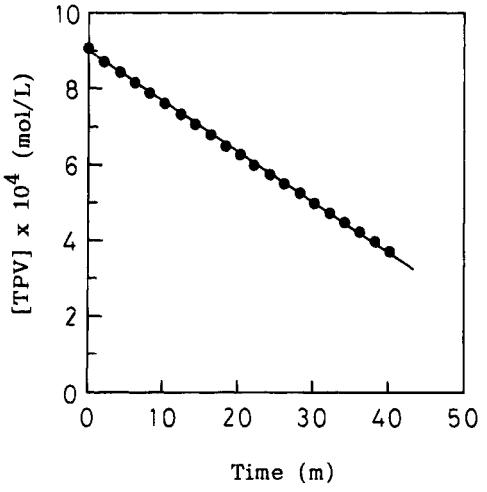


Figure 4. Consumption of TPV by reaction with the primary radical of MAIB in the bulk polymerization of M(DM)EA at 60 °C: [MAIB] = 0.050 mol/L.

By substitution of this value in eq 1, k_p is evaluated as follows:

$$k_p = \frac{4.8 \times 10^{-5}}{(2.4 \times 10^{-6})(5.0)} = 4.0\ \text{L/(mol s)}$$

Table 1 compares the k_p value of M(DM)EA with those of other α-(substituted methyl)acrylates. The k_p values of the α-(substituted methyl)acrylates at 60 °C range from an extraordinarily small value for dimethyl itaconate (k_p = 5.2 L/(mol s)[19b]) to that for ethyl α-(benzoyloxymethyl)acrylate (k_p = 990 L/(mol s)[5b]). The k_p value of M(DM)EA is the smallest among these and as small as that of dimethyl itaconate. The steric hindrance of the 2,2-bis(carbomethoxy)ethyl group is confirmed to suppress propagation leading to an extraordinarily small k_p value.

If the polymerization proceeds through the chain mechanism involving bimolecular termination, the k_t value can be calculated from eq 3 at the steady state:

$$d[M^\bullet]/dt = R_i - k_t[M^\bullet]^2 = 0 \qquad (3)$$

where R_i is the rate of initiation.

R_i was measured by the scavenger method using TPV based on the assumption that the primary radical emerging out of the cage was quantitatively trapped. The peak intensity of the ESR spectrum of TPV decreased with polymerization time in the bulk polymerization of M(DM)EA initiated with MAIB as shown in Figure 4, and R_i was evaluated from the slope of the linear relationship to be 2.2×10^{-7} mol/(L s). By substitution of $[M^\bullet] = 2.4 \times 10^{-6}$ mol/L and $R_i = 2.2 \times 10^{-7}$ mol/(L s) to eq 3, the k_t value was obtained as follows:

$$k_t = \frac{2.2 \times 10^{-7}}{(2.4 \times 10^{-6})^2} = 3.8 \times 10^4\ \text{L/(mol s)}$$

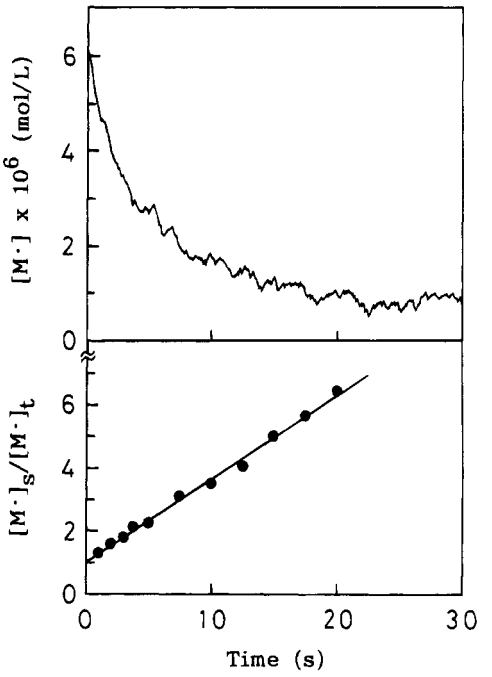


Figure 5. Decay curve of the ESR signal and the second-order plot for the bimolecular termination of the poly[M(DM)EA] radical produced by the photosensitization with ATMP at 60 °C.

Alternatively, the k_t value was determined from the decay of the propagating radical produced by UV irradiation after the interruption of the irradiation. Because no initiation with ATMP used as a sensitizer occurred in the dark at 60 °C, a decrease in the radical concentration was caused solely by mutual reaction of the polymer radical. No primary radical termination took place in the dark. Figure 5 shows the decay curve of the spectrum of the poly[M(DM)EA] radical, and k_t was evaluated from the second-order plots based on the decay curve according to eq 4:

$$[M^\bullet]_s/[M^\bullet]_t = k_t[M^\bullet]_s t + 1 \qquad (4)$$

where $[M^\bullet]_s$ denotes the concentration of the propagating radical at the steady state. This gives $k_t = 4.2 \times 10^4$ L/(mol s).

The agreement between the k_t values obtained by the different procedures indicates that the propagating radicals lose their activity through bimolecular termina-

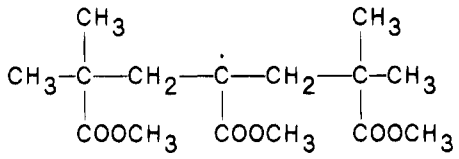
Table 2. Polymerization of MMA in the Presence of Dimethyl Ethylmalonate for 2 h at 60 °C[a]

[malonate] (mol/L)	η^b	conv/$\eta^{0.5}$ (%)	$\bar{M}_n/\eta^{0.5}$	$\bar{M}_w/\bar{M}_n$
0	1.00	15.7	99 300	2.14
0.37	1.04	15.9	105 000	2.00
1.1	1.18	15.6	100 000	2.03
1.9	1.33	15.2	105 000	2.00

[a] [MMA] = 3.0 mol/L, [AIBN] = 5.0×10^{-3} mol/L. [b] The viscosity of polymerization mixture relative to a benzene solution of MMA at 3 mol/L in the absence of the malonate at 30 °C before polymerization.

tion and that a considerable contribution of primary radical termination can be ruled out.

Although the steric hindrance of the α-substituent primarily reduces the k_t value, the specific reactivity of the radical **1** in propagation is an unexpected phenomenon based on the persistent nature of the radical from a MMA dimer **3**.[32]



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Structural analysis of poly[M(DM)EA] by ^{1}H NMR spectroscopy (400 MHz) rules out the competition of the addition–fragmentation with propagation.[26]

Noteworthy is the fact that the k_t value obtained is smaller than that for MMA by 3 orders of magnitude as shown in Table 1. A quantitative comparison of the polymerizability based on the rate constants confirms that the lower termination rather than propagation rate allows polymer formation of M(DM)EA.

The possibility of hydrogen abstraction from the α-hydrogen of the malonyl groups of M(DM)EA and poly[M(DM)EA] during polymerization of M(DM)EA was considered. To estimate the chain transfer to the malonyl compound, the polymerization of MMA in the presence of dimethyl ethylmalonate as a model compound bearing the malonyl group was carried out in benzene at 60 °C as shown in Table 2. Because the viscosity of the polymerization mixture increased with increasing concentration of dimethyl ethylmalonate, R_p and $\bar{M}_n$ of the resulting polymer must be corrected for the initial viscosity of the polymerization mixture. The $R_p/\eta^{0.5}$ and $\bar{M}_n/\eta^{0.5}$ values remained constant irrespective of the concentration of dimethyl ethylmalonate. Also, hydrogen abstraction of the poly(MMA) radical, which is sterically less hindered than the poly[M(DM)EA] radical, from dimethyl ethylmalonate did not exhibit a significant contribution. Chain transfer cannot be a major factor governing the polymerizability of M(DM)EA.

Ceiling Temperature. Although bulk polymerization afforded poly[M(DM)EA], solution polymerization of M(DM)EA (2.0 mol/L) in benzene initiated with MAIB (5.0×10^{-2} mol/L) for 10 h at 60 °C yielded no polymer. The equilibrium monomer concentration as the boundary between polymerization and no polymer formation may be higher than 2.0 mol/L at 60 °C.

When the polymerization becomes appreciably reversible at a high temperature, the ceiling temperature (T_c) can be defined as a temperature at which the rate of propagation is equal to that of depropagation. Experimentally, T_c can be determined as the temperature above which no polymer formation occurs according to eqs 5 and 6:[33a]

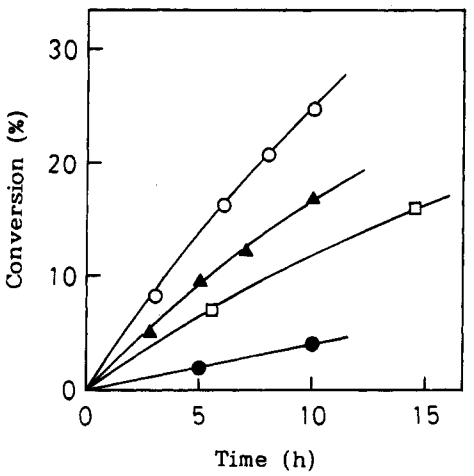

Figure 6. Time–conversion relationships for the bulk polymerization of M(DM)EA at various temperatures: [AVN] = 0.05 mol/L at 30 °C (□), [AVN] = 0.05 mol/L at 40 °C (○), [ACN] = 0.20 mol/L at 70 °C (▲), [ACN] = 0.05 mol/L at 80 °C (●).

$$\frac{d(\ln k_p'/k_t^{0.5})}{d(1/T)} = \frac{k_d E_d/R[M] - k_p E_p/R}{k_p - k_d/[M]} + \frac{E_t}{2R} \quad (5)$$

$$\lim_{T \to T_c} \frac{d(\ln k_p'/k_t^{0.5})}{d(1/T)} = \infty \quad (6)$$

where E, k, and R represent the activation energy, the rate constant, and the gas constant, respectively. Subscripts, p, t, and d denote propagation, termination, and depropagation, respectively. k_p' is the apparent propagation rate constant defined by the following equation:

$$k_p' = k_p - k_d/[M] \quad (7)$$

Previously, we determined the T_c of *o*-substituted phenyl methacrylates from the temperature dependence of the overall rate of polymerization.[33] The steric hindrance of the nuclear substituent resulted in a decrease in T_c. Among the α-substituted acrylates, methyl α-ethylacrylate, di-*n*-butyl itaconate, and methyl α-benzylacrylate have been subjected to T_c determination: T_c = 82 °C for the ethylacrylate at 8.35 mol/L,[34] T_c = 120 °C for di-*n*-butyl itaconate at 1.99 mol/L,[18a] and T_c = 67 °C for the benzylacrylate at 5 mol/L.[35] Apparently, a slight structural change in the α-substituent affects T_c greatly. Furthermore, we have shown that the polymerization of some α-(alkoxymethyl)acrylates and α-(phenoxymethyl)acrylates at 60 °C is slightly influenced by T_c.[2,13]

The steric hindrance of the α-substituent to propagation has generally been observed as a lowering of the k_p value, while the decrease in T_c appears less often. Although no quantitative correlation between T_c and the size of the α-substituent has been available, we point out that a large substituent does not always bring about a low T_c.

Figure 6 shows the time–conversion curves for the polymerization of M(DM)EA in bulk (5.0 mol/L) in the temperature range from 30 to 80 °C. Because R_i was dependent on temperature, $R_p/R_i^{0.5}$, which is equal to $k_p[M]/k_t^{0.5}$ according to the standard kinetics of radical polymerization, was employed for the comparison of the polymerizability at different temperatures as shown in

Table 3. Polymerization of M(DM)EA in Bulk at Various Temperatures

temp (°C)	initiator (mol/L)	$R_i \times 10^7$ [a] (mol/(L s))	$R_p \times 10^5$ (mol/(L s))	$R_p/R_i^{0.5}$ (mol$^{0.5}$/(L$^{0.5}$ s$^{0.5}$))	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
30	AVN (0.050)	0.18	1.8	0.13	65 700	1.78
40	AVN (0.050)	1.3	4.0	0.11	43 300	1.71
60	MAIB (0.050)	2.2	4.8	0.10	19 400	1.62
70	ACN (0.20)	3.7	2.6	0.043	9 800	1.76
80	ACN (0.050)	3.2	0.57	0.010	1 700	2.00

[a] Determined by the scavenger method using TPV.

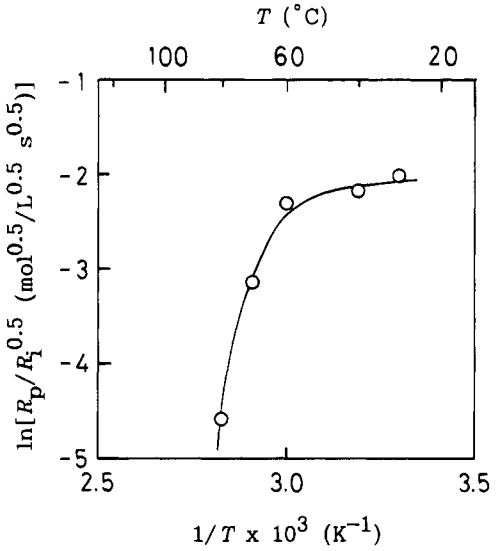

Figure 7. Plot of $\ln(R_p/R_i^{0.5})$ versus $1/T$ for the bulk polymerization of M(DM)EA.

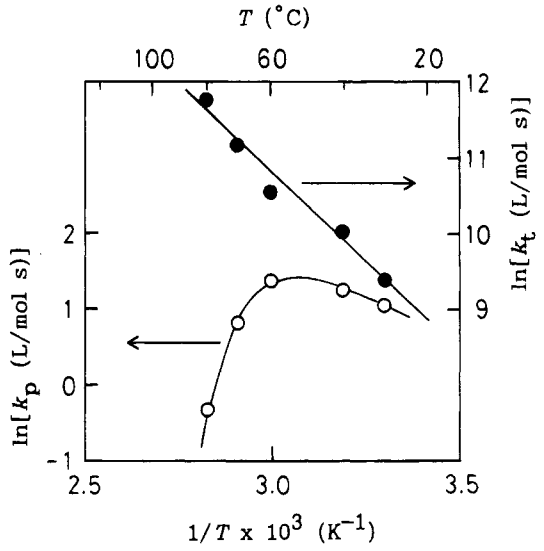

Figure 8. Plot of ln k_p and ln k_t versus $1/T$ for the bulk polymerization of M(DM)EA. The k_p values should be the k_p' values according to eq 7.

Table 4. Values of k_p and k_t at Various Temperatures[a]

temp (°C)	[M$^\bullet$] $\times 10^6$ (mol/L)	k_p[b] (L/(mol s))	$k_t \times 10^{-4}$ (L/(mol s))	$k_p/k_t^{0.5} \times 10^2$ [b] (L$^{0.5}$/(mol$^{0.5}$ s$^{0.5}$))
30	1.2	2.9	1.2	2.7
40	2.3	3.5	2.3	2.3
60	2.4	4.0	3.8	2.0
70	2.3	2.3	7.0	0.87
80	1.6	0.73	13	0.20

[a] Polymerized under the conditions shown in Table 3. [b] The k_p values should be the k_p' values according to eq 7.

Table 3. R_i's at the different temperatures were determined by the scavenger method. Figure 7 shows a plot of $\ln(R_p/R_i^{0.5})$ versus $1/T$ instead of $\ln(k_p'/k_t^{0.5})$ versus $1/T$ according to eq 5, and T_c was determined as the temperature at which the slope of the curvature became infinitely large: T_c = ca. 90 °C. This is higher than values for methyl α-ethylacrylate[34] and methyl α-benzylacrylate[35] at the same monomer concentration.

The k_p and k_t values evaluated by the ESR method as shown in Table 4 were used for the Arrhenius plots of k_p and k_t given in Figure 8. Although the plot for k_t shows a linear relationship, the plot of k_p gives a curvature resembling the plot of $\ln(R_p/R_i^{0.5})$ versus $1/T$ shown in Figure 7. The k_p values deviating from the Arrhenius relationship should be the k_p' values. The apparent E_t determined from the slope of the Arrhenius plot for k_t is 39.1 kJ/mol, which is considerably higher than those of common vinyl monomers such as St[36] and MMA.[37] Similarly, high E_t values were observed in the polymerizations of some itaconic esters.[18d] The E_t value obtained by the Arrhenius plot for $k_t\eta$ seems to be as large as those for the common monomers: E_t = 8.1 kJ/mol.

Tacticity of the Polymer. Tacticity of the polymer formed at the respective temperatures was examined using ^{13}C NMR spectroscopy. The carbonyl carbons in poly(MMA) are well-known to give tacticity information.[38,39] In a previous paper, we reported that poly[M(DM)EA] and poly[methyl α-[2,2-bis(carboethoxy)ethyl]acrylate] prepared at 60 °C gave higher isotacticity (mm = 51–56%) than radically polymerized poly(MMA) and that considerable deviations from Bernoullian statistics were observed.[26] Figure 9 shows the carbonyl region of the ^{13}C NMR spectra of the poly[M(DM)EA] prepared at 30, 60, and 80 °C in $CDCl_3$ at room temperature. Sharp peaks at 169 ppm were assignable to the resonances from the carbonyl carbon in the malonyl groups, and three peaks at 170.0, 173.5, and 176.0 ppm were considered to reflect the triad tacticity of the polymers in the same way as for poly(MMA).[38,39] The triad tacticity determined from the intensity ratio of the respective resonances is shown in Table 5. It is interesting to note that the isotacticity of poly[M(DM)EA] increased at higher temperature, although poly(MMA) is close to random propagation at higher temperature.

Copolymerizations of M(DM)EA with St and MMA. The copolymerizations of M(DM)EA (M_2) with St and MMA (M_1) were carried out using AIBN as initiator in benzene at 60 °C: $[M_1] + [M_2] = 3.0$ mol/L, [AIBN] = 5.0×10^{-3} mol/L. The R_p's for the copolymerization of St remained constant irrespective of the content of M(DM)EA in the monomer mixture as shown in Figure 10. However, the R_p's for the MMA–M(DM)EA copolymerization decreased with an increase in the M(DM)EA content. The $\bar{M}_n$'s of the respective copolymers decreased with an increase in the M(DM)EA content. These findings indicate that M(DM)EA and the poly[M(DM)EA] radical participate in the elemenatry

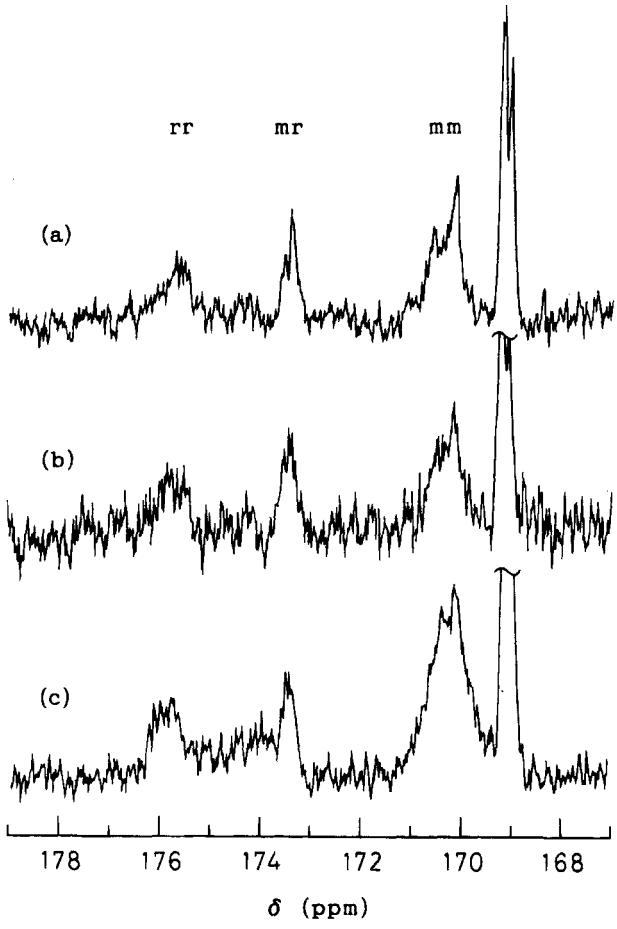

Figure 9. Expanded ^{13}C NMR spectra of poly[M(DM)EA] prepared at 30 (a), 60 (b), and 80 °C (c).

Table 5. Triad Tacticity of Poly[M(DM)EA] Prepared at Various Temperatures

	triad tacticity (%)			
temp (°C)	mm	mr	rr	$P_{m/r} + P_{r/m}$[a]
30	53	21	26	0.45
60[b]	51	23	26	0.49
80	66	14	20	0.36

[a] $P_{m/r}$ = [mr]/(2[mm] + [mr]), $P_{r/m}$ = [mr]/(2[rr] + [mr]). [b] Reference 26.

reactions of the copolymerization. In accordance with this expectation, the comonomer–copolymer composition curves shown in Figure 11 exhibit significant copolymerizabilities of M(DM)EA, and the experimental points fit the theoretical curves calculated from the terminal model. The r_1 and r_2 values were obtained as follows:

$r_1 = 0.58$ and $r_2 = 0.09$ for copolymerization with St

$r_1 = 3.70$ and

$r_2 = 0.04$ for copolymerization with MMA

For comparison of the reactivity as monomer and polymer radicals, the cross-propagation rate constants were calculated from the k_p values of the respective monomers and the r_1 and r_2 values:

$$k_{12} = k_{11}/r_1 \quad (8)$$

$$k_{21} = k_{22}/r_2 \quad (9)$$

where k_{11} and k_{22} denote the k_p of St or MMA and

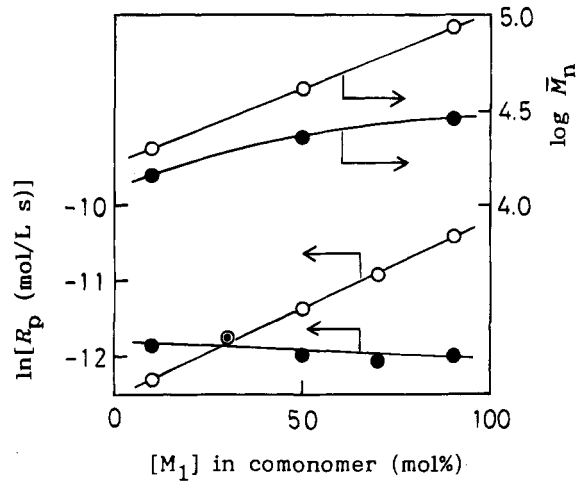

Figure 10. $\bar{M}_n$'s of copolymer and R_p for the copolymerizations of M(DM)EA (M_2) with St (●) and MMA (○) (M_1) in benzene at 60 °C: $[M_1] + [M_2] = 3.0$ mol/L, $[AIBN] = 5.0 \times 10^{-3}$ mol/L.

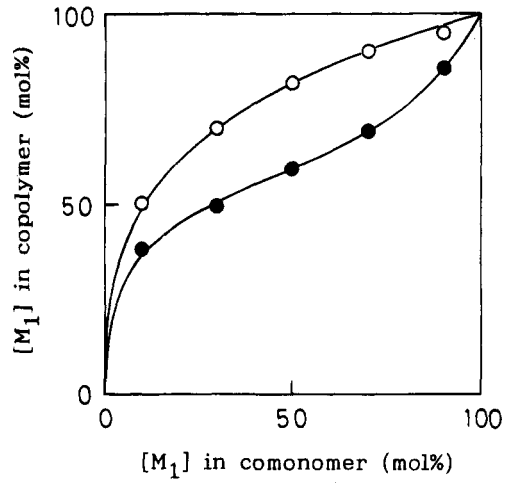

Figure 11. Comonomer–copolymer composition curves for the copolymerizations of M(DM)EA (M_2) with St (●) and MMA (○) (M_1) in benzene at 60 °C: $[M_1] + [M_2] = 3.0$ mol/L, [AIBN] = 5.0×10^{-3} mol/L.

M(DM)EA, respectively: $k_{11} = 328$ L/(mol s) for St[36] and $k_{11} = 510$ L/(mol s) for MMA.[31] According to eqs 8 and 9, the cross-propagation rate constants were obtained as follows at 60 °C:

$$\sim\sim\sim St^{\bullet} + MMA \xrightarrow{k = 630\ L/(mol\ s)} \sim\sim\sim MMA^{\bullet}$$

$$\sim\sim\sim St^{\bullet} + M(DM)EA \xrightarrow{k = 570\ L/(mol\ s)} \sim\sim\sim M(DM)EA^{\bullet}$$

M(DM)EA and MMA exhibit similar reactivities toward the poly(St) radical. Apparently, M(DM)EA reacts with the poly(St) radical without significant steric hindrance.

$$\sim\sim\sim MMA^{\bullet} + St \xrightarrow{k \approx 1100\ L/(mol\ s)} \sim\sim\sim St^{\bullet}$$

$$\sim\sim\sim M(DM)EA^{\bullet} + St \xrightarrow{k = 47\ L/(mol\ s)} \sim\sim\sim St^{\bullet}$$

The addition of St to the poly[M(DM)EA] radical is slower than that of St to the poly(MMA) radical because of the steric hindrnace of the α-substituent.

$$\sim\sim\sim MMA^{\bullet} + MMA \xrightarrow{k = 510\ L/(mol\ s)} \sim\sim\sim MMA^{\bullet}$$

$$\sim\sim\sim MMA^{\bullet} + M(DM)EA \xrightarrow{k = 140\ L/(mol\ s)} \sim\sim\sim M(DM)EA^{\bullet}$$

$$\sim\sim\sim\text{M(DM)EA}^{\bullet} + \text{MMA} \xrightarrow{k = 93\ \text{L/(mol s)}} \sim\sim\sim\text{MMA}^{\bullet}$$

$$\sim\sim\sim\text{M(DM)EA}^{\bullet} + \text{M(DM)EA} \xrightarrow{k = 4\ \text{L/(mol s)}} \sim\sim\sim\text{M(DM)EA}^{\bullet}$$

Unlike similar reactivity of M(DM)EA with MMA toward the poly(St) radical, M(DM)EA exhibits a considerably lower reactivity toward the poly(MMA) radical which is a tertiary-carbon centered radical. Furthermore, the reactivities of M(DM)EA and the poly[M(DM)EA] radical in the copolymerization of M(DM)EA with MMA were found to decrease with the steric hindrance due to the large α-substituents in comparison with values of MMA and its polymer radical. According to the cross-propagation rate constants, M(DM)EA is less reactive than MMA toward the poly(MMA) radical by a factor of 3, while a much greater decrease in reactivity of the poly[(M(DM)EA] radical toward the respective monomers is estimated.

We can deduce that the radical center of the poly[M(DM)EA] radical is more constrained than the carbon–carbon double bond of monomeric M(DM)EA particularly in the reactions with MMA and the poly(MMA) radical. The extraordinarily small k_t value for M(DM)EA is also attributed to considerable steric congestion around the radial center of the poly[M(DM)EA] radical. Because of the unusually small k_p and k_t values and relatively low T_c, M(DM)EA is one of the still-polymerizable acrylates bearing a substituent exerting the most significant steric effect observed to date.

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MA9462114