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Kinetic Study of Radical Homopolymerization of Captodative Substituted Methyl α-(Acyloxy)acrylates

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ABSTRACT: Radical homopolymerizations of some captodative substituted methyl α-(acyloxy)acrylates are studied kinetically by using azo initiators at 30–60 °C. Polymerization rate and the properties of the polymer obtained are much influenced by the acyloxy substituents. Methyl α-acetoxyacrylate (MAA), which was already found to give a polymer with excellent optical properties, shows the highest reactivity and gives a high molecular weight polymer with very poor solubility. Kinetic study shows that the propagation rate constant (k_p) of the polymerization of MAA is larger than that of methyl α-(butyryloxy)acrylate (MBA) at every temperature, k_p = 255 and 114 L/mol·s at 50 °C for the polymerization of MAA and MBA, respectively. The activation energy of the overall polymerization of MAA is estimated to be E_a = 16.0 kcal/mol, smaller than that of MBA (E_a = 17.4 kcal/mol), although the energies of propagation and termination of MAA are larger than those of the bulky-substituted MBA. The mechanism of the unique polymerization of MAA is discussed based on the kinetic study, ESR spectroscopy, and the physical property measurements of the polymer obtained.

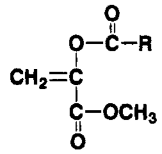
Introduction

Captodative (cd) substitution is geminal substitution with both electron-withdrawing (captive) and electron-donating (dative) groups on the same atom. In such a cd substituted compound, the odd electron on a cd substituted atom is expected to be stabilized by a synergistic polar effect (resonance stabilization).[1] This stabilization is easily understood not only by classical electronic theory[2] and ab initio theoretical calculations[3] but also by experimental results, namely, delocalization of spin over the molecule (low spin density on a cd substituted atom)[4] and a low bond energy of model cd ethanes.[5] It is often possible to observe a characteristic reactivity in free-radical organic chemistry of cd compounds. Examples are the selective peroxidation of 2,5-piperazinedione and the oxidative dimerization of indoxyl to give indigo.[6]

Viehe et al.[2] have studied the organic chemistry of small cd compounds since 1978 and found many unique reactions. In contrast to their general organic chemistry, no one had systematically studied the cd effect in polymer science. One of the reasons seems to arise from a poor radical homopolymerizability of cd monomers due to a resonance stabilization of its propagating species.[7] It has been found, however, that even cd monomers can undergo radical propagation to give homopolymers in high or moderate yields if one chooses appropriate electron-donor and -acceptor combinations in the cd substituents.[8–10] In addition, it has also been found that the cd substitution brings about unique radical polymerization compared to systems using a single electron-donor or -acceptor such as styrene and methyl methacrylate.[11] For instance, cd olefins easily undergo spontaneously polymerization without added initiator,[12] and the polymerization is much influenced by the solvents used[13] in spite of its radical mechanism.

The characteristics of general organic reactions and radical polymerizations originate from the resonance stabilization effect of the radical through spin delocalization by the cd substitutions. One can also expect a large synergistic and asymmetric polarization effect in addition to the resonance stabilization of two highly polar groups on the same atom. This polarization effect, however, has not been studied either in general organic chemistry or in the field of polymer science. Recently, we started evaluating this effect on polymerizations and found that one cd substituted olefin, i.e., methyl α-acetoxyacrylate (MAA), gave a polymer showing very high photorefraction and nonlinear second harmonic generation (SHG).[14] This suggests that the cd concept may be effective for the preparation of highly polar polymers under mild experimental conditions involving convenient radical polymerization.

In this paper, we report a kinetic study on the radical homopolymerizations of the methyl α-(acyloxy)acrylates shown below.



$CH_2{=}C(OCOR)COOCH_3$

MAA: R=CH_3
MPA: R=C_2H_5
MBA: R=n-C_3H_7
MIBA: R=iso-C_3H_7
MBzA: R=C_6H_5

Experimental Section

Materials. The (acyloxy)acrylates, other than MAA, were prepared by the reaction of methyl pyruvate with the corresponding acid chlorides such as propionyl chloride as described for (perfluorohexyl)ethyl α-acetoxyacrylate.[15] MAA was synthesized according to the method in our previous paper.[16] Bp (°C/mmHg): MAA, 64–65/8; MPA, 44–45/3; MBA, 60–61/4; MIBA, 61–62/8; MBzA, 85–86/1. ^1H NMR ($CDCl_3$, ppm): MAA, 2.20 (s, 3H), 3.77 (s, 3H), 5.44 (d, J = 1.8 Hz, 1H), 6.00 (d, J = 1.8 Hz, 1H); MPA, 1.20 (t, J = 7.2 Hz, 3H), 2.51 (q, J = 7.2 Hz, 2H), 3.80 (s, 3H), 5.50 (d, J = 1.8 Hz, 1H), 6.08 (d, J = 1.8 Hz, 1H); MBA, 1.02 (t, J = 6.6 Hz, 3H), 1.75 (m, 2H), 2.49 (t, J = 6.6 Hz, 2H), 3.80 (s, 3H), 5.45 (d, J = 1.8 Hz, 1H), 6.02 (d, J = 1.8 Hz, 1H); MIBA, 1.27 (d, J = 7.2 Hz, 6H), 2.63 (m, J = 7.2 Hz, 1H), 3.80 (s, 1H), 5.45 (d, J = 1.8 Hz, 1H), 6.05 (d, J = 1.8 Hz, 1H); MBzA, 3.80 (s, 3H), 5.45 (d, J = 1.8 Hz, 1H), 6.05 (d, J = 1.8 Hz, 1H), 7.22–8.20 (m, 5H). Anal. Calcd for $C_6H_8O_4$ (MAA): C, 50.00; H, 5.59. Found: C, 49.79; H, 5.69. Calcd for $C_7H_{10}O_4$ (MPA): C, 53.36; H, 6.37. Found: C, 53.49; H, 6.51. Calcd for $C_8H_{12}O_4$ (MBA): C, 55.81; H, 7.02. Found: C, 56.05; H, 6.96. Calcd for $C_8H_{12}O_4$ (MIBA): C, 55.81; H, 7.02. Found: C, 56.01; H, 6.95. Calcd for $C_{11}H_{10}O_4$ (MBzA): C, 64.07; H, 4.89. Found: C, 64.27; H, 4.96.

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Table 1. Polymerization of Methyl α-(Acyloxy)acrylates by AIBN in Bulk at 60 °C[a]

monomer	yield (%)	$M_n \times 10^{-5}$	M_w/M_n
MAA	69.4	>10.0	
MPA	68.7	7.91	1.79
MBA	18.2	2.88	1.78
MIBA	9.9	1.16	1.81
MBzA	62.5	2.87	2.94

[a] [AIBN] = 5.00×10^{-3} mol/L. Reaction time: 8 h.

Commercially available (Wako Chemicals) 2,2′-azobis(isobutyronitrile) (AIBN) and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) were used after recrystallization from ethanol and toluene, respectively. Methyl methacrylate (MMA) was purified by fractional distillation.

Polymerizations. Polymerizations were generally carried out in a sealed ampule with shaking at a given temperature. The ampule containing the required amounts of reagents was degassed several times by a freeze–thaw method, sealed under vacuum, and placed in a constant-temperature bath. The resulting polymer was isolated by pouring the contents of the ampule into a large amount of methanol. Time–conversion curves in the homopolymerizations of MAA and MBA in trichloroethane were determined by determining a consumption of monomer by means of gas chromatography using biphenyl as a standard.

Measurements. ESR spectra were recorded on a JEOL JES-FE2XG spectrometer operating at X-band (9.5 GHz) with a TE mode cavity. The sample for ESR measurement was prepared by degassing the reagents in an ESR cell according to a freeze–thaw method and then filling with helium. Radical concentrations were determined by means of an ESR instrument equipped with a JEOL ES-9835B computer integration system standardized with 2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO) and Mn^{2+}. Calibration curves with TEMPO were obtained in benzene solution under the same conditions as used for the polymerization system in 1,1,2-trichloroethane, i.e., the same temperature, ESR cell, instrument settings, and so on. Mn^{2+} was simultaneously employed with our samples or standard TEMPO in the same ESR cavity to check the change of experimental conditions such as the variation of the Q value with solvents and polymerization conversions and so on. Splitting constants (a) and g-values were determined according to the previous paper.[17]

^1H NMR spectra were measured on a JEOL JNM-EX400 (400 MHz) spectrometer. Number- and weight-average molecular weights (M_n and M_w) of the polymers were estimated by size exclusion chromatography using a Toyosoda HLC-802A with standard polystyrenes in dichloromethane for poly(MAA) at ambient temperature and in tetrahydrofuran for other polymers at 38 °C. Differential scanning calorimetry was used to determine glass transition temperatures with a heating rate of 10 °C/min on a Shimadzu DSC-50 under a nitrogen stream. The mean square radius of gyration, $\langle s^2\rangle^{0.5}$, was determined by the light scattering method using a Photal DLS-7000 in dichloromethane at ambient temperature.

Results and Discussion

Comparison of Polymerization Reactivity. Polymerization results for the (acyloxy)acrylates using AIBN are listed in Table 1. All acrylates are readily polymerized, and MAA shows the highest reactivity. The ^1H NMR spectrum of the (acyloxy)acrylate polymers showed broad signals around 3.0–3.5 ppm due to the methylene protons of the main chain of the polymer but no peak around 5.5 and 6.0 ppm due to the olefinic protons of the monomer, indicating the polymerization proceeded through the opening of the C=C double bond of the acrylates as expected.

It is noted that the poly(MAA) isolated is insoluble in most organic solvents including acetone, tetrahydrofuran, nitrobenzene, and dimethylformamide, only soluble in dichloromethane and nitromethane, and slightly swells in 1,1,2-trichloroethane. In contrast, all other (acyloxy)acrylate polymers are soluble in most organic solvents. A small structural change, i.e., the change from the acetoxymethyl group of poly(MAA) to the (propionyloxy)ethyl group of poly(MPA), greatly affects the solubility of the polymer. Glass transition temperatures (T_g) were determined to be 37, 44, 41, and 46 °C for the MPA, MBA, MIBA, and MBzA polymers, respectively, similar to the value of poly(MAA), T_g = 36 °C, already reported.[14] The photorefractive index (n_D) of poly(MAA), however, is much different from those of the other (acyloxy)acrylate polymers, i.e., n_D = 1.6002–1.6219 for poly(MAA) and n_D = 1.4860 for poly(MPA), suggesting a higher polarization and/or a density of poly(MAA).

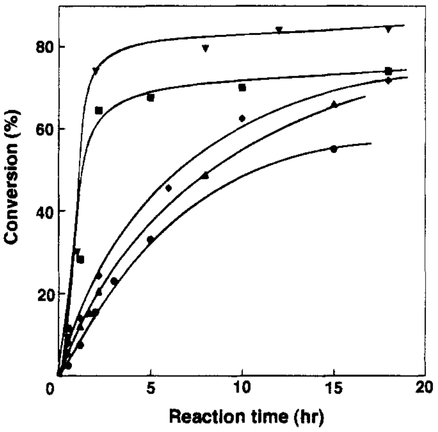


Figure 1. Time–conversion curves in the polymerizations of MAA and MMA by V-70 in bulk (▼, ■) or dichloromethane (◆, ▲, ●) at 40 °C: [V-70] = 6.7×10^{-3} mol/L, (▼) MMA, (■) MAA; (◆) [MMA] = 4.7, (▲) [MAA] = 3.9, (●) [MAA] = 3.1 mol/L.

Kinetic Study. Figure 1 shows the comparison of the radical homopolymerization conversions of MAA with that of MMA. As seen in this figure, MAA shows a high reactivity, slightly lower than that of MMA. To confirm such a high reactivity of MAA, the homopolymerization of MAA was studied kinetically in comparison with MBA. Figure 2 shows the time–conversion curves of the polymerizations of MAA and MBA, respectively, by V-70 in 1,1,2-trichloroethane at 30–60 °C. Both polymerizations proceeded homogeneously, and at every temperature, the conversion is higher for MAA than MBA. From the initial slope of these time–conversion curves, the overall polymerization rates (R_p) were determined (Table 2) with the propagation rate constant (k_p) estimated in the initial stage of the polymerizations by measuring the concentration of the polymer radical ([P*]) by means of ESR spectroscopy and using the equation[18] $R_p = k_p[P^*][\text{monomer}]$.

It is obvious that the k_p value of MAA is over twice as high as that of MBA at every temperature but only about half that of MMA.[19] On the basis of the R_p and k_p values, the activation energies of overall polymerization (E_a) and propagation (E_p) are estimated to be E_a = 16.0 and E_p = 8.5 kcal/mol for the polymerization of MAA and E_a = 17.4 and E_p = 7.3 kcal/mol for that of MBA as shown in Figures 3 and 4. The activation energies of termination (E_t) are calculated to be 11.2 and 6.0 kcal/mol for MAA and MBA, respectively, assuming $E_a = E_p + 0.5(E_d - E_t)$ and E_d (the activation energy of the initiator decomposition) = 26.2 kcal/mol.[20] The overall homopolymerization rate of MAA and high molecular weight of the polymer obtained, therefore, are considered to be partially due to a preferential suppres-

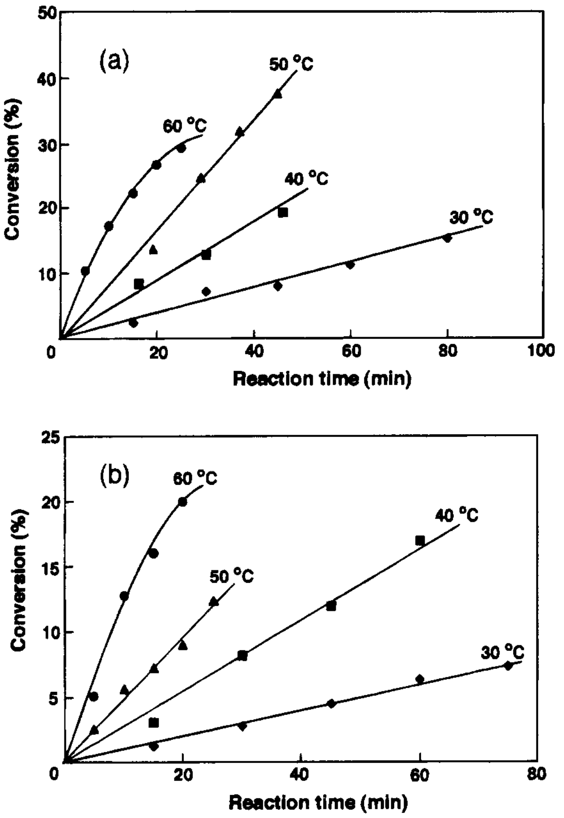


Figure 2. Time–conversion curves in the polymerizations of (a) MAA and (b) MBA by V-70 in 1,1,2-trichloroethane at 30–60 °C. [MAA] = [MBA] = 2.0 mol/L, [V-70] = 3.0×10^{-2} mol/L.

Table 2. Polymerization Parameters in the Polymerizations of MAA and MBA by V-70 in 1,1,2-Trichloroethane at 30–60 °C[a]

monomer	temp (°C)	$R_p \times 10^5$ (mol/L·s)	$[P^*] \times 10^7$ (mol/L)	k_p (L/mol·s)
MAA	30	6.25	2.78	112
	40	13.9	3.86	180
	50	27.5	5.39	255
	60	66.7	7.72	430
MBA	30	3.17	3.08	51.5
	40	8.89	5.04	80.0
	50	16.7	7.04	114
	60	43.3	11.8	184

[a] V-70: 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile), [V-70] = 3.0×10^{-2} mol/L, [monomer] = 2.0 mol/L.

sion of the termination reaction (large E_t value) rather than suppression in propagation.

ESR Spectra of Propagating Radicals. The ESR spectrum of the propagating polymer radical is changed by the acyloxy substituent of (acyloxy)acrylates as shown in Figure 5, in which the spectrum of poly(methyl methoxyacrylate), poly(MMOA), radical is also seen for comparison. From this figure, the splitting constant ($a_{\beta\text{-H}}$) due to the β-methylene protons is estimated to be 9.02 and 17.03 G (g = 2.0036) for poly(MAA) radical, 10.26 and 15.72 G (g = 2.0036) for poly(MBA) radical, and 12.75 G (g = 2.0037) for poly(MMOA) radical. That is, spectra a and b of Figure 5 clearly indicate nonequivalent β-hydrogens. It has been reported that poly(MMA)[21] and poly(vinyl acetate)[22] radicals have two stable conformers with nonequivalent β-hydrogens and one conformer with equivalent β-hydrogens, respectively. Observation of one conformer with nonequivalent β-hydrogens in the (acyloxy)acrylate polymer radicals, therefore, suggests the possible formation of a fairly stable conformer with a highly restricted rotation of the C_α–C_β bond due to the synergistic bulkiness of both the acyloxy and methoxycarbonyl substituents.

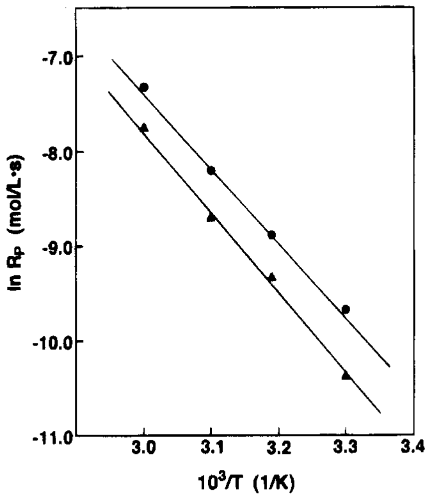


Figure 3. Dependence of the polymerization rate (R_p) on the polymerization temperature: (●) MAA, (▲) MBA.

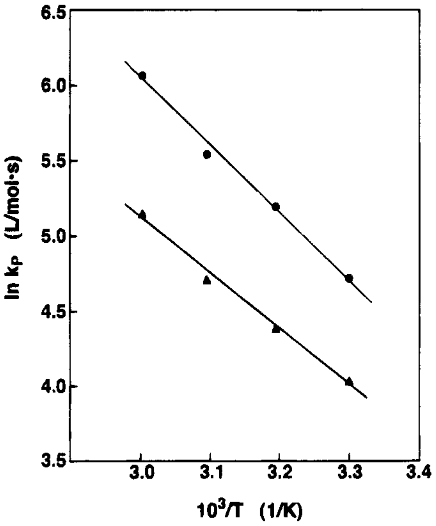


Figure 4. Dependence of the propagation rate constant (k_p) on the polymerization temperature: (●) MAA, (▲) MBA.

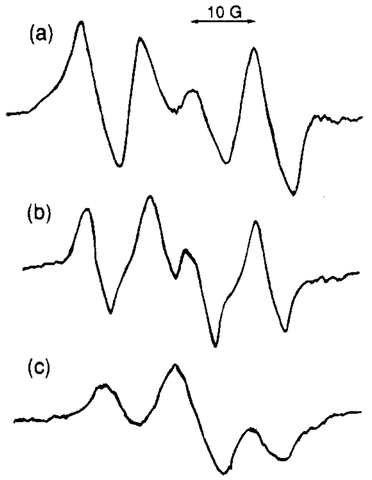


Figure 5. ESR spectra of the propagating polymer radicals generated during polymerizations of (a) MAA, (b) MBA, and (c) MMOA by V-70 in 1,1,2-trichloroethane at 40 °C. [MAA] = [MBA] = [MMOA] = 2.0 mol/L, [V-70] = 3.0×10^{-2} mol/L.

From the ESR spectral change observed in Figure 5, it is suggested that the time–average dihedral angle θ

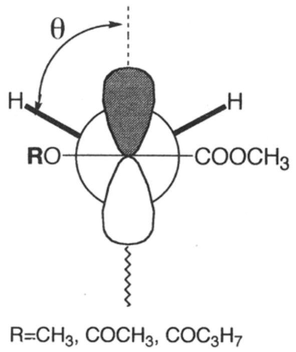
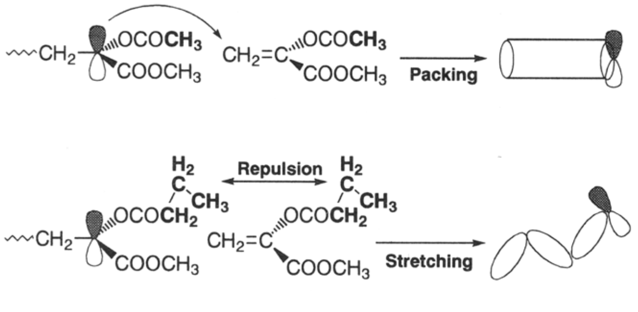


Figure 6. Conformation of radicals from MAA, MBA, and MMOA.

Scheme 1



between the β-hydrogens and the $2p_z$ orbital on the α-carbon of the propagating polymer radical varies with the acyloxy ($\theta \approx 50°$) and methoxy ($\theta = 60°$) substituents at the α-position as shown in Figure 6, and the steric hindrance of the substituents appears to increase in the order methoxy < butyryloxy ≤ acetoxy.

Mechanism of Polymerization. The results obtained from the kinetic study, ESR spectroscopy, and the physical property measurements of the polymers suggest that the MAA radical homopolymerization is unique and may proceed in mobility-restricted media such as the polymerization with ordering during propagation as shown in Scheme 1. According to this scheme, some molecular orientation occurs during the polymerization of MAA probably because of the strong dipole−dipole interaction of the monomers and polymers and of the sizes of the acetoxy and methoxycarbonyl moieties. The direction of the monomer addition toward a propagating polymer radical, therefore, may be somewhat controlled. Such a molecular orientation seems to be supported qualitatively by the fact that the refractive index is much enhanced by converting MAA monomer into the polymer, i.e., the ratio of the n_D value of the polymer to the monomer is 1.12−1.13 for MAA in contrast to other examples (1.03−1.05),[19] and that the mean square radius of gyration, $\langle s^2 \rangle^{0.5}$, of poly(MAA) is about twice (3.61×10^2 Å for $M_w = 1.75 \times 10^5$) as large as that of usual acrylate polymers.[19] The steric hindrance in the MAA polymerization is apparently similar to or larger than that in the MBA polymerization as actually observed in the ESR spectrum and larger E_p value in spite of the small size of the acetoxy moiety relative to the butyryloxy moiety.

In addition, it can be expected that the collisions of each growing polymer chain are reduced in the termination reaction of the MAA polymerization because of restricted mobility of the chain due to the ordered rigid structure. The large E_t value supports this consideration.

X-ray diffraction (Cu Kα radiation) of powdered (acyloxy)acrylate polymers showed a broad, strong line at $2\theta = 9.9°$ ($d = 8.92$ Å), 9.1° ($d = 9.71$ Å), and 8.1° ($d = 10.91$ Å) for MAA, MPA, and MBA polymers, respectively, and the densities of the polymers were 1.27 and 1.22 for poly(MAA)[14] and poly(MBA), respectively, suggesting decreased packing of the polymer chains of MPA and MBA compared with those of MAA. In addition, the mean crystallite sizes[23] (scale of crystallinity) were calculated to be 31.4, 28.5, and 27.0 Å for MAA, MPA, and MBA polymers, respectively. The crystallinity of poly(MAA), therefore, seems to be higher than that of other acrylate polymers, although these polymers seem to be poorly crystalline.[14] A more detailed study on the polymer structure is now in progress.

Conclusions

Kinetic study, ESR spectroscopy, and the physical properties of these polymers suggest that the radical homopolymerization of MAA is unique and may proceed through somewhat sterically controlled propagation and termination to give a polymer showing excellent optical properties. The captodative concept, therefore, is useful not only for the control of the polymerization reactivity but also for the preparation of highly polar polymers by applying the synergistic polarization effect. Up to now, no one has demonstrated the importance of the polarization effect of the cd concept for molecular design. Large dipole moments (μ) of the monomers (calculated by using the MOPAC AM1 program, namely, $\mu = 5.111$ D for MAA in contrast to $\mu = 2.018$ D (observed: 1.675 D)[24] for MMA) suggest the usefulness of such polarization to a polar polymer synthesis. In general, polar vinyl polymers have been prepared by anionic or radical polymerization of electron pull−pull disubstituted olefins such as vinylidene cyanide and vinylidene fluoride. Such strong electron-accepting olefins, however, are unstable and very sensitive to moisture, while cd substituted olefins are stable in general and able to polymerize even by a convenient radical methods.

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(18) This equation cannot apply to the polymerization system proceeding through a complexation or an aggregation. In the present polymerization system, some aggregation of a propagation polymer radical and/or monomers is undeniable because of their high polarity. Strictly speaking, therefore, the k_p value determined according to this equation is an apparent one. The k_p and E_p values, however, vary little even if the polymerization mechanism changes, and much more relatively, the values of kp and Ep for MAA are clearly different from those of MBA. Therefore, there is little affect on the discussion of the polymerization mechanism.

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