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Synthesis and Characterization of Poly(1-adamantyl methacrylate): Effects of the Adamantyl Group on Radical Polymerization Kinetics and Thermal Properties of the Polymer

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ABSTRACT: Radical polymerization of 1-adamantyl methacrylate (AdMA) and 3,5-dimethyl-1-adamantyl methacrylate (DMAdMA) with 2,2′-azobisisobutyronitrile in benzene at 60 °C was investigated kinetically. The introduction of the bulky adamantyl groups increased its polymerization rate and the molecular weight of the resulting polymer, compared with those for other methacrylates, e.g., methyl, *tert*-butyl, and cyclohexyl esters. It was ascribed to decrease in the termination rate, resulting in increase of the concentration of its propagating polymer radical at a stationary state. It was confirmed directly by observation of ESR spectra of the propagating radical and verified that the concentration of the polymer radical was ca. 10^{-6} mol/L, being higher than that for ordinary polymerization. The conformational structure of the poly(AdMA) radical was also discussed from the hyperfine coupling constants in the spectrum. Subsequently, the tacticity was examined by NMR spectroscopy and compared with those for poly(methyl methacrylate). It was revealed that the polymers bearing adamantyl esters showed extremely high glass transition temperatures, and the effect of the tacticity was also investigated. From thermogravimetric analysis in a nitrogen stream, the decomposition temperatures of these adamantyl-containing polymers were quite high in spite of the tertiary alkyl ester groups.

Introduction

Adamantane (tricyclo[3.3.1.1^{3,7}]decane) is a thermodynamically stable and highly symmetrical tricyclic hydrocarbon, which consists of fused chair-form cyclohexane rings with the same structure as a diamond lattice.[1] Some reports have been published on the synthesis of polymers that have an adamantyl moiety in their main or side chains, taking advantage of the unusual physical and chemical properties of adamantane, e.g., thermal and oxidation stabilities, low surface energy, high density, and hydrophobicity.[2] The polymerization of 1-adamantyl methacrylate (AdMA)[2b,c] has been reported but radical polymerization kinetics have not been investigated.

Recently, we found that dialkyl fumarates bearing bulky alkyl esters proceed by radical polymerization to give a less flexible poly(substituted methylene) because of a decrease in the bimolecular termination rate between polymer radicals,[3] and it was shown that polymerization reactivity,[3b] rigidity (flexibility) of the polymer chain,[4] and tacticity[5] depend strongly on the structure of the alkyl groups in the side chain. Similar effects of the ester substituents on polymerization reactivity are also expected for alkyl methacrylates (RMA) with a bulky ester substituent. For example, Kamachi et al.[6] found in 1982 by ESR that triphenylmethyl methacrylate (TPMA) has small propagation and termination rate constants in radical polymerization. It has also been reported that poly(TPMA) has an isotactic structure even in radical polymerization,[7] in contrast to the predominantly syndiotactic poly(RMA).[8] The characteristics of the polymer chain for poly(RMA) with various ester alkyl groups have been investigated from their dilute solution properties.[9]

It was also anticipated that the introduction of an adamantyl moiety would confer unique thermal properties on the polymer, e.g., glass transition temperature (T_g) and decomposition temperatures. The T_g of poly(RMA) including poly(methyl methacrylate) (poly(MMA)) has been reported,[10] and it depends strongly on tacticity.[8]

In the present work the radical polymerization of AdMA and 3,5-dimethyl-1-adamantyl methacrylate (DMAdMA) has been studied kinetically in detail, and compared with the results for other RMA (Chart I), to elucidate the relation between polymerization reactivity and flexibility of the polymer chain. Some properties of the resulting polymers containing an adamantyl moiety, i.e., tacticity and thermal properties, were also investigated.

Experimental Section

Materials. AdMA and DMAdMA were supplied from Hakusui Chemical Industries, Ltd. (Osaka, Japan), and purified by column chromatography on silica gel with *n*-hexane as eluent, followed by distillation under reduced pressure.

AdMA: bp 82 °C (0.1 mmHg); IR (neat) $\nu_{C=O}$ 1720, $\nu_{C=C}$ 1640 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 166.4, 138.1, 124.1, 80.3, 41.3, 36.2, 30.8, 18.3; ^{1}H NMR (CDCl$_3$) δ 6.00 (s, $CH_2{=}$, 1 H), 5.46 (s, $CH_2{=}$, 1 H), 2.18 (br, CH, 3 H), 2.16 (br, CH_2, 6 H), 1.89 (s, CH_3, 3 H), 1.68 (br, CH_2, 6 H).

DMAdMA: bp 90 °C (0.1 mmHg); IR (neat) $\nu_{C=O}$ 1720, $\nu_{C=C}$ 1640 cm^{-1}, ^{13}C NMR (CDCl$_3$) δ 166.5, 138.0, 124.2, 81.7, 50.5, 47.2, 42.6, 39.7, 33.8, 31.1, 29.9, 18.3; ^{1}H NMR (CDCl$_3$) δ 5.99 (s, $CH_2{=}$, 1 H), 5.46 (s, $CH_2{=}$, 1 H), 1.1–2.2 (m, adamantyl, 13 H), 1.88 (s, α-CH_3, 3 H), 0.88 (s, CH_3 (adamantyl), 6 H).

2,2′-Azobisisobutyronitrile (AIBN) and dimethyl 2,2′-azobisisobutyrate (MAIB) were recrystallized from methanol. Commerical di-*tert*-butyl peroxide (D*t*BPO) was used without further purification. Other monomers, solvents, and reagents were used after ordinary purifications.

Polymerization. Radical polymerization was carried out in a sealed glass tube in the presence of an initiator in benzene or toluene. The resulting polymer was isolated with an appropriate precipitant and dried under vacuum. The polymer yield was determined gravimetrically.

Hydrolysis and Methylation. Hydrolysis of poly(AdMA) was accomplished in concentrated H_2SO_4 at room temperature for 60 days. The resulting poly(methacrylic acid) was reprecipitated from methanol and diethyl ether; yield 77–98%. Subsequently, poly(methacrylic acid) was methylated by reflux in methanol in the presence of H_2SO_4 for 25 h and then reacted with diazomethane. The quantitative transformation to the methyl ester from poly(AdMA) was confirmed by NMR spectroscopy.

Measurements. IR spectra were recorded on a Jasco A-202 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GX-400 with CDCl$_3$ and tetramethylsilane as solvent and internal standard, respectively. The triad tacticity was determined from the peak intensities of the α-methyl proton in the ^{1}H NMR spectra

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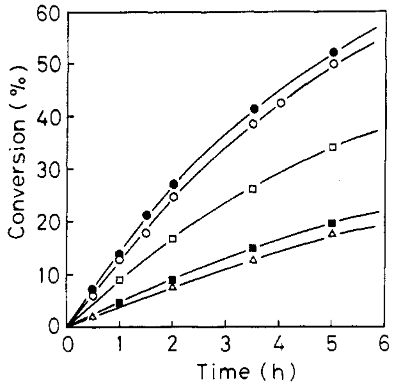
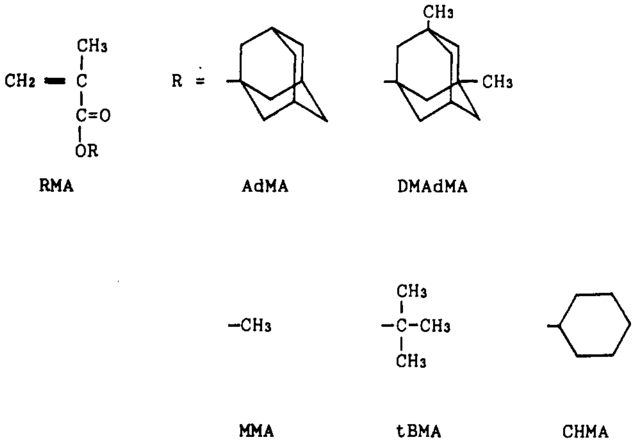


Figure 1. Time–conversion relations for radical polymerization of alkyl methacrylates in benzene at 60 °C. (○) AdMA, (●) DMAdMA, (□) CHMA, (■) tBMA, (△) MMA; [monomer] = 1 mol/L, [AIBN] = 1 × 10^{-3} mol/L.

Chart I



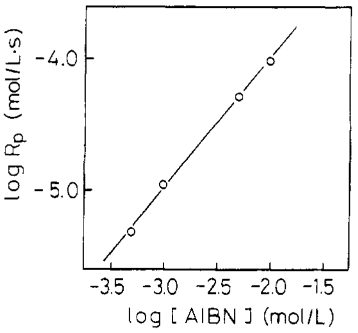


Figure 2. Dependence of the concentration of AIBN on the polymerization rate (R_p) for radical polymerization of AdMA in benzene at 60 °C. [AdMA] = 1 mol/L.

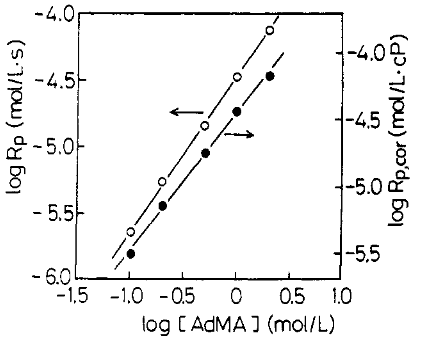


Figure 3. Dependence of the concentration of AdMA on the polymerization rate (R_p) for radical polymerization of AdMA in benzene at 60 °C. [AIBN] = 1 × 10^{-3} mol/L; (○) against R_p observed, (●) against $R_{p,cor}$ ($R_p/\eta^{0.5}$).

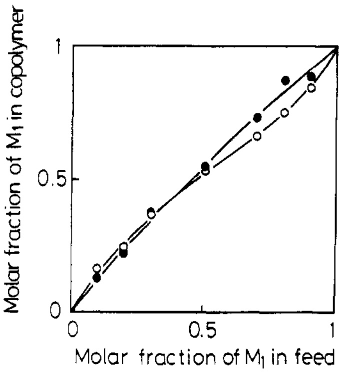


Figure 4. Comonomer–copolymer composition curves for radical copolymerization of AdMA (M_1) with St (○) or with MMA (●) (M_2) in benzene at 60 °C.

and of the carbonyl carbons in the ^{13}C NMR spectra. The measurement of ESR spectra was performed by means of Brüker ESP-300 with variable-temperature control. Gel permeation chromatography was performed with Tosoh 8000 Series GPC system equipped with TSK-gel columns (G6000HXL, G4000-HXL × 2, G2000HXL). Number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were calibrated with standard polystyrenes. The viscosities of polymerization solutions at 30 °C were determined from a flow time and a density, which were measured with an Ubbelohde viscometer and a pycnometer, respectively, by using benzene as reference. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out with ca. 1.5 mg of a polymer sample in a nitrogen stream with a heating rate of 10 °C/min.

Results and Discussion

Comparison of Polymerization Reactivity. The radical polymerization of AdMA was carried out in the presence of AIBN in benzene at 60 °C. The time–conversion relation is depicted in Figure 1, in which the results for other methacrylates (RMA) are also included for comparison. It is clear that the polymerization rate (R_p) and the number-average molecular weight of the polymer ($\bar{M}_n$) of AdMA are much higher than those for other esters, i.e., MMA, *tert*-butyl methacrylate (tBMA), and cyclohexyl methacrylate (CHMA), and they are about 3 times as large as those for MMA, as summarized in Table I. It was also found that the 3,5-dimethyl-substituted-DMAdMA had as high or higher polymerization reactivity as AdMA. It thus appears that there is a correlation between the magnitude of R_p or $\bar{M}_n$ and the bulkiness of the ester alkyl groups.

The dependence of the concentration of AIBN and AdMA on R_p was examined to clarify further the kinetics of polymerization. The plots of log R_p against log [AIBN] and log [AdMA] gave lines with slopes of 0.50 and 1.15, respectively (Figures 2 and 3). The 0.5 order with respect to the AIBN concentration indicates that bimolecular termination is preferred in the polymerization of AdMA. The reaction order of greater than unity with respect to the AdMA concentration may be interpreted as the effect of the viscosity of the polymerization medium.[11,12] It was concluded that the highly viscous solution caused a decrease of the termination rate (i.e., increase in R_p) when the monomer concentration was high, as discussed in detail later, resulting in an increase of the apparently high reaction order with respect to the AdMA concentration.

The reason for the high polymerization reactivity of AdMA is discussed below for each elementary step i.e., initiation, propagation, and termination.

Initiation. In general, R_p is defined as follows:

$$R_p = -(d[M]/dt) = k_p[M^\bullet][M] \quad (1)$$

where k_p is the propagation rate constant, and M and M•

Table I
Kinetic Data for Radical Polymerization of Alkyl Methacrylates (RMA) with AIBN in Benzene at 60 °C

monomer	[RMA], mol/L	10^3[AIBN], mol/L	$10^5 R_p$, mol/L·s	$10^{-5}\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[a]	$10^{-3}\bar{P}_n$[b]	density,[c] g/cm^3	η,[d] cP	$10^5 R_{p,cor}$,[e] mol/L·s·cP$^{0.5}$
AdMA	1.0	1.0	3.52	3.91	1.73	1.77	0.906	0.801	3.93
	2.0	1.0	7.33	11.4	2.12	5.17	0.943	1.18	6.75
	0.5	1.0	1.42	2.04	2.17	0.925	0.886	0.654	1.76
	0.2	1.0	0.550	0.731	2.00	0.331	0.875	0.592	0.715
	0.1	1.0	0.226	0.280	2.21	0.127	0.870	0.573	0.299
	1.0	10.0	9.75	1.45	2.09	0.658			
	1.0	5.0	7.15	1.85	2.41	0.839			
	1.0	0.5	2.21	5.42	2.23	2.45			
DMAdMA	1.0	1.0	3.93	4.10	1.79	1.65	0.899	0.825	4.33
CHMA	1.0	1.0	2.28	2.73	2.23	1.62	0.883	0.661	2.80
tBMA	1.0	1.0	1.28	1.29	2.06	0.907	0.867	0.581	1.68
MMA	1.0	1.0	1.10	1.04	1.76	1.03	0.874	0.550	1.48

[a] By GPC. [b] Number-average degree of polymerization. [c] Density of the polymerization solution at 30 °C. [d] Viscosity of the polymerization solution at 30 °C. [e] $R_{p,cor} = R_p/\eta^{0.5}$.

denote the monomer and the propagating polymer radical, respectively.

With the bimolecular termination step and a steady-state condition of the radical concentration, R_p, may be represented in the following equation.

$$R_p = (2fk_d/k_t)^{0.5}k_p[\mathrm{I}]^{0.5}[\mathrm{M}]^{1.0} \qquad (2)$$

where k_t is the termination rate constant, I is the initiator, and k_d and f are the rate constant and the efficiency for decomposition of the initiator, respectively.

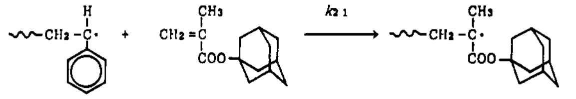
In the initiation step, k_d of AIBN is usually independent of the kind of medium, i.e., monomer or solvent.[13] The increasing viscosity of the medium may reduce the efficiency of the initiation, f, resulting in a decrease of the apparent overall initiation rate, $R_i = 2fk_d[\mathrm{I}]$. The increase in M_n or the number-average degree of polymerization ($\bar{P}_n$) also supports the conclusion that the increase in R_p is not caused by an increase in R_i, because the $\bar{P}_n$ is in reciprocal proportion to R_p if k_p and k_t are constant and chain transfers are negligible (eq 3).

$$\bar{P}_n \propto \frac{R_p}{R_t} = \frac{k_p[\mathrm{M}][\mathrm{M}^\bullet]}{k_t[\mathrm{M}^\bullet]^2} = \frac{k_p^2[\mathrm{M}]^2}{k_tR_p} \qquad (3)$$

Propagation. In propagation, the increase in k_p or [M$^\bullet$] may increase the observed R_p. It has been reported that k_p for alkyl methacrylates increase with an increase of the electron-withdrawing nature of the ester alkyl groups.[14] The negative Taft's polar constant ($\sigma^* = -0.26$)[15,16] and considerable bulkiness of the adamantyl group lead to the conclusion that the k_p value for AdMA may be no more than those for MMA and other RMA.

To investigate this problem further, copolymerizations of AdMA with styrene (St) or MMA were carried out in benzene at 60 °C. As seen in Table II, the copolymerization rate and $\bar{M}_n$ of the copolymer increased with an increase of the AdMA content in the feed. The comonomer–copolymer composition curves are depicted in Figure 4, from which monomer reactivity ratios were determined to be $r_1 = 0.62$ and $r_2 = 0.54$ for AdMA(M$_1$)–St(M$_2$) and $r_1 = 1.25$ and $r_2 = 0.79$ for AdMA(M$_1$)–MMA(M$_2$). Therefrom, Q_1 and e_1 were calculated to be 0.81 and 0.25 for AdMA, respectively.

The reactivity of AdMA toward the poly(St) radical was compared with that of MMA (eqs 4 and 5), and the ratios of the rate constants in these reactions were determined; $k_{21}/k'_{21} = (k_{21}/k_{22})/(k'_{21}/k'_{22}) = r'_2/r_2 = 1.1$, where the values reported in the literature[17] were used for calculation, $r'_1 = 0.46$ and $r'_2 = 0.57$ for MMA(M$_1$)–St(M$_2$).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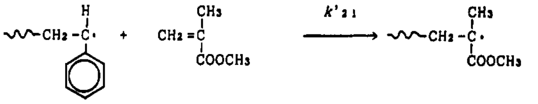
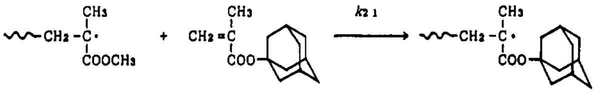

(5)

This means that AdMA shows a slightly higher reactivity toward the poly(St) radical than MMA.

When the relative reactivity of AdMA toward the poly(MMA) radical was compared similarly (eqs 6 and 7), it was found that AdMA had a 1.3-fold higher reactivity to MMA, i.e., $k_{21}/k_{22} = 1/r_2 = 1.3$. The reactivities toward the poly(AdMA) radical were similar; $k_{11}/k_{12} = r_1 = 1.25$.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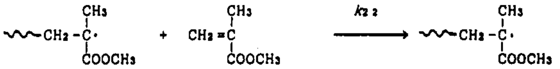
$$\sim\!\mathrm{CH_2}\!-\!\overset{\mathrm{CH_3}}{\underset{\mathrm{COOCH_3}}{\mathrm{C}}}\!\cdot \;+\; \mathrm{CH_2}\!=\!\overset{\mathrm{CH_3}}{\underset{\mathrm{COOCH_3}}{\mathrm{C}}} \xrightarrow{k_{22}} \sim\!\mathrm{CH_2}\!-\!\overset{\mathrm{CH_3}}{\underset{\mathrm{COOCH_3}}{\mathrm{C}}}\!\cdot \qquad (7)$$

Thus, the monomer reactivity of AdMA was found to be greater than that of MMA from these copolymerization data, but it is impossible to explain the high polymerization reactivity of AdMA by such a weak preference of addition reactivity. Therefore, the increase in R_p was considered to be due mainly to the high concentration of the polymer radical in eq 1, that is, the decrease in k_t.

Termination. It has been reported that k_t is affected significantly by the viscosity of the polymerization medium.[11,18,19] The results of viscosity measurements on polymerization solutions indicated a correlation between R_p and viscosity (Table I), i.e., R_p increased in highly viscous polymerization systems.

The bimolecular termination process consists of the following several steps: translational diffusion (movement of the center of gravity in a polymer chain), segmental diffusion (reorientation of a radical center), and subsequent chemical reaction between mutual polymer radicals. Because the activation energy for the last step is small, the termination rate may be controlled by diffusion steps. In radical polymerization of RMA, the segmental diffusion is more important,[20] except for the Trommsdorff effect[21] at a high conversion, and a propagation–diffusion-controlled model[22,23] in a latter stage of the polymerization.

Table II
Radical Copolymerization of AdMA(M_1) with St or MMA(M_2) in Benzene at 60 °C[a]

molar fractn of M_1 in feed	time, min	yield, %	R_p, %/h	$10^{-5}\bar{M}_n{}^b \times 10^{-5}$	$\bar{M}_w/\bar{M}_n{}^b$	fractn of M_1 in copolymer		T_g,[c] °C
						mol	wt	
				AdMA(M_1)–St(M_2)				
0.900	90	5.65	3.76	1.50	1.85	0.844	0.922	223
0.800	90	3.57	2.38	1.03	1.84	0.753	0.870	206
0.700	120	3.61	1.80	0.766	1.85	0.662	0.811	195
0.500	180	3.75	1.25	0.534	1.81	0.531	0.713	166
0.300	210	3.36	0.961	0.390	1.79	0.367	0.560	142
0.200	240	3.49	0.873	0.345	1.76	0.244	0.415	128
0.100	300	3.96	0.792	0.320	1.73	0.162	0.298	115
0	360	4.37	0.728	0.293	1.73			102
				AdMA(M_1)–MMA(M_2)				
1.000	30	5.97	11.9	3.91	1.73			nd[d]
0.900	75	13.5	10.8	3.60	2.06	0.886	0.945	nd[d]
0.800	75	11.9	9.52	3.26	1.97	0.873	0.938	230
0.700	75	8.26	6.61	1.98	2.13	0.730	0.856	216
0.500	90	9.27	6.18	1.62	2.03	0.548	0.727	190
0.300	105	9.03	5.16	1.80	1.92	0.370	0.564	165
0.200	105	8.12	4.64	1.54	1.96	0.223	0.387	150
0.100	120	8.40	4.20	1.34	1.92	0.126	0.241	139
0	120	7.59	3.80	1.04	1.76			127

[a] [comonomers] = 1.0 mol/L, [AIBN] = 1 × 10^{-3} mol/L. [b] By GPC. [c] By DSC (10 °C/min). [d] Not detected.

The rate constants for translational diffusion-controlled and segmental diffusion-controlled termination reactions are expressed in the following equations, respectively.[11]

For a translational diffusion-controlled reaction

$$k_t = \frac{8K_B T N_A}{3\eta} \tag{8}$$

and for a segmental diffusion-controlled reaction

$$k_t = \frac{4P_{AB}kT}{3\eta}\,\frac{R_E}{x_0 N_L{}^{0.5}} \tag{9}$$

Equation 8 is derived by combination of the Stokes–Einstein relation with the relation for a reaction between spherical particles by Smoluchowski,[24] where k_B is Boltzmann's constant, T is temperature, η is the viscosity of the solvent, and N_A is Avogadro's number.

Equation 9 was proposed by Benson and North,[20] where P_{AB} is a factor for the segmental diffusion constant for chain entanglement and restricted direction of approach, R_E is a transition-state separation of the chain ends, x_0 is a constant of proportionality, and N_L is some characteristic segmental length associated with segmental diffusion.

Both eqs 8 and 9 mean that k_t is proportional to the reciprocal of the viscosity, if the chain-length dependence of k_t is disregarded. Therefore R_p was corrected for the viscosity of the solution, $R_{p,cor} = R_p/\eta^{0.5}$ (last column in Table I). When the reaction order with respect to AdMA was recalculated with the corrected value, the slope of the curve became close to unity, i.e., the slope was 1.04 as shown in Figure 3. The chain-length dependence of k_t is one of the most important effects for radical polymerization,[25] but the effect of the chain length may be small. Conclusions concerning these effects seem to require more precise experimental data and absolute values of the chain length.

However, when the $R_{p,cor}$ values for various RMA monomers were compared with each other, the values for AdMA and DMAdMA were larger than the others, suggesting that the k_t of AdMA and DMAdMA are essentially reduced by the steric effect of the substituents, i.e., the mobility of the segment around the radical center.

Recently, we determined some characteristic parameters for poly(AdMA) in dilute solutions by GPC, light scattering, and viscosity measurements. From the results it was concluded that the poly(AdMA) chain is somewhat less flexible than that of poly(MMA) or any other alkyl esters.[9] The details on dilute solution properties of poly(AdMA) are described elsewhere.[26]

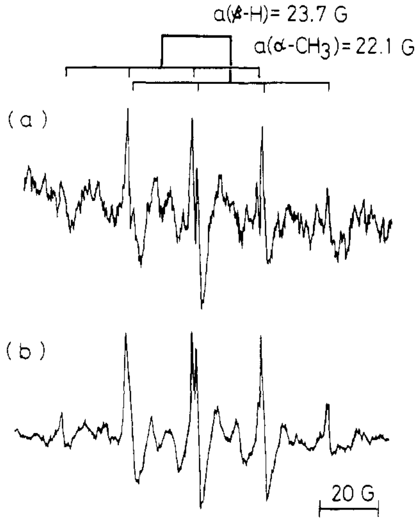

Figure 5. ESR spectra obtained from polymerization mixture. [AdMA] = 1 mol/L, [AIBN] = 0.05 mol/L in benzene; (a) at 60 °C, (b) at room temperature under UV irradiation.

ESR Study of the Propagating Radical. It seemed that a decrease in the termination rate should induce an increase in the radical concentration at the stationary state. Therefore, the direct observation of the propagating radical by ESR was attempted.

The ESR signal due to the poly(AdMA) radical is shown in Figure 5, under the usual thermal or photopolymerization conditions, i.e., [AdMA] = 1 mol/L, [AIBN] = 0.05 mol/L in benzene at 60 °C or at room temperature with UV irradiation. It is clear that both polymerizations give similar spectra. It was found that the intensity of the spectrum reached a constant value within a few seconds after UV irradiation; a rapid decay of the radical concentration was observed when the irradiation was interrupted (Figure 6). This observation under the usual polymerization conditions without any special technique or use of a designed cavity means that the polymer radical concentration is unusually high.[27,28] In fact, the concen-

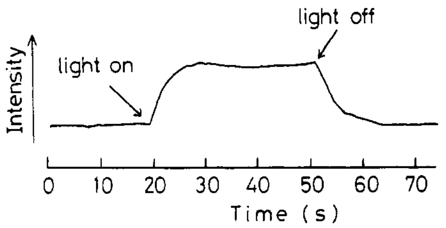

Figure 6. Change in the polymer radical concentration in polymerization of AdMA at room temperature with UV irradiation.

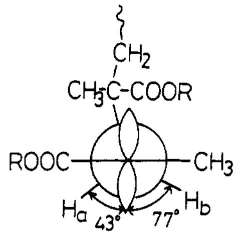

Figure 7. Projection of the speculated structure of the poly(AdMA) radical.

trations of the polymer radical for these polymerizations were evaluated to be ca. 10^{-6} mol/L by means of the solution of a stable radical of known concentration. It may be possible to determine absolute rate constants k_p and k_t by using the radical concentration at the stationary state and the posteffect. Further ESR studies on the polymerization kinetics of AdMA are now in progress.

The hyperfine splitting of the spectrum may give us information on the conformational structure of the poly(AdMA) radical.[28] The spectrum obtained for poly(AdMA) consisted of the two components, a sharp eight-line and a broad component. The intensity distribution of the eight-line spectrum was 1:3:1:3:3:1:3:1, as indicated in Figure 5. This spectrum yields the following two hyperfine splitting constants: $a_{CH_3} = 22.1$ G and $a_{\beta\text{-}H_a} = 23.7$ G. Another β-methylene proton has a small constant, as mentioned below.

The hyperfine splitting constant of the β-methylene proton is well-known to be correlated with the dihedral angle between the orbital of an unpaired electron and the carbon-to-hydrogen bond as follows:[29]

$$a = B\cos^2\theta \qquad (10)$$

When θ_a is 43° and θ_b is 77°, the hyperfine splitting constants are 23.7 and 2.2 G for H_a and H_b, respectively, where the B value was estimated to be 44.2 G from the coupling constant of the freely rotating α-methyl protons. These values agreed well with the observed values. This eight-line spectrum is considered to correspond to a five-line spectrum for the poly(MMA) radical, i.e., $\theta_a = 45°$, $\theta_b = 75°$.[30-32]

The other weak component was presumably the 13-line component due to the conformation of $\theta_a = 65°$ and $\theta_b = 55°$, which is observed for polymer radicals of other methacrylates including MMA.[6] The spectrum in Figure 5 was interpreted as resulting from the overlapping of the two conformations; the contribution of the conformation that gives the 8-line spectrum was greater than that of the 13-line.

The projections for the estimated conformations for the radical center of poly(AdMA) are depicted in Figure 7. They were ascribed to the steric hindrance of the bulky adamantyl esters between the polymer and the propagating end. The change in the conformation of the propagating end was expected to affect the structure of the resulting polymer. Indeed, the tacticity of the resulting poly(AdMA) was found to differ from that of poly(MMA) obtained under identical polymerization conditions. Poly(AdMA) was more dominantly syndiotactic, as described later, indicating steric repulsion at the growing center.

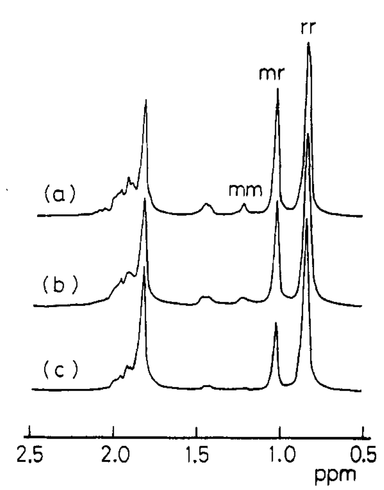

Figure 8. ^{1}H NMR spectra of poly(MMA) derived from poly(AdMA). Polymerization temperature: (a) 120 °C, (b) 60 °C, (c) 0 °C.

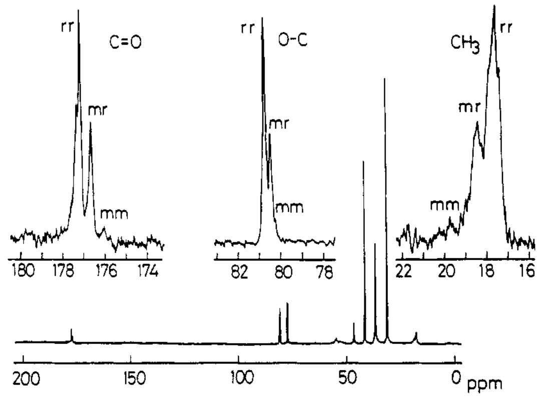

Figure 9. ^{13}C NMR spectrum of poly(AdMA) prepared for radical polymerization in benzene at 60 °C.

Solubility and Hydrolysis. Poly(AdMA) and poly(DMAdMA) were obtained as colorless powders and were soluble in benzene, chloroform, carbon tetrachloride, THF, and cyclohexanone and insoluble in dimethylformamide, acetone, methyl ethyl ketone, *n*-hexane, and methanol. A transparent film was obtained from the solution of poly(AdMA) or poly(DMAdMA), but it was very brittle.

Hydrolysis of poly(AdMA) and poly(DMAdMA) was difficult by refluxing in chloroform with an acidic catalyst, in contrast to the ease of hydrolysis of poly(tBMA), because of the sterically hindered and hydrophobic adamantyl moiety. For quantitative hydrolysis of poly(AdMA), a period of several weeks was necessary in concentrated H_2SO_4 at room temperature.

Tacticity. To investigate the tacticity of poly(AdMA), polymerization of AdMA was carried out at various temperatures. The tacticity of poly(AdMA) was obtained from the ^{1}H and ^{13}C NMR spectra.[8,33-36] Typical spectra are depicted in Figures 8 and 9. The fractions of triad tacticities, i.e., mm, mr, and rr, are summarized in Table III, in which the results for poly(MMA) are also included as comparison.

These results indicate the formation of a predominantly syndiotactic polymer. Poly(DMAdMA) was found to have a tacticity similar to that of poly(AdMA), indicating that the 3,5-dimethyl groups did not affect the manner of propagation. It was found that the fraction of syndiotactic triads increased with a decrease in the polymeri-

Table III
Tacticities of Poly(AdMA) and Poly(MMA) Obtained through Radical Polymerization in Benzene at Various Temperatures

monomer (mol/L)	initiator (mmol/L)	temp, °C	time, h	yield, %	$10^{-4}\bar{M}_n$[a]	triad fraction[b] mm	mr	rr	$P(m/r) + P(r/m)$[c]	P_m
AdMA (1)	DtBPO (1)	120[d]	2.5	38.0	14.8	0.033 (0.06)	0.349 (0.31)	0.618 (0.63)	1.06	0.207
AdMA (1)	AIBN (1)	60	2.5	38.2	33.6	0.029 (0.05)	0.300 (0.29)	0.671 (0.66)	1.02	0.179
AdMA (1)	MAIB (20)	0[d,e]	25	92.8	1.22	0.013	0.219	0.768	1.02	0.122
DMAdMA (1)	AIBN (1)	60	5	52.2	30.7	(0.04)	(0.27)	(0.69)	0.95	0.17
MMA (1)	DtBPO (5)	120[d]	5	60.8	7.17	0.051	0.403	0.546	1.07	0.252
MMA (1)	AIBN (5)	60	5	17.6	1.04	0.035	0.341	0.624	1.05	0.205
MMA (2)	AIBN (20)	30[d,e]	5	25.2	2.92	0.028	0.300	0.672	1.03	0.178
MMA (2)	AIBN (20)	0[d,e]	8	8.1	4.81	0.013	0.261	0.726	1.06	0.143

[a] By GPC. [b] From α-methyl resonances in ^{1}H NMR spectra after conversion to poly(MMA). The values in parentheses indicate those from carbonyl resonances in the ^{13}C NMR spectra of poly(AdMA). [c] $P(m/r) = [mr]/(2[mm] + [mr])$; $P(r/m) = [mr]/(2[rr] + [mr])$. [d] In toluene. [e] Under UV irradiation.

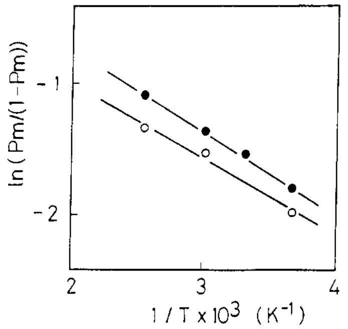

Figure 10. Temperature dependence of $P_m/(1 - P_m)$ for radical polymerization of (○) AdMA and (●) MMA.

Table IV
Differences in Activation Enthalpies and Entropies for Radical Polymerization of AdMA and MMA

monomer	$\Delta H_m^{\ddagger} - \Delta H_r^{\ddagger}$, kcal/mol	$\Delta S_m^{\ddagger} - \Delta S_r^{\ddagger}$, cal/mol·deg	ref
AdMA	1.1	0.28	this work
MMA	1.2	0.98	this work
MMA	1	1	33
MMA	0.96	0.94	37

zation temperature, identical with the tendency of polymerization of other RMA monomers, except for TPMA. From the comparison with the tacticity of poly(MMA), it is clear that poly(AdMA) is a syndiotactic, suggesting steric repulsion in propagation by the bulky adamantyl group.

The radical polymerization of AdMA was found to obey Bernoullian statistics approximately,[35,36] i.e., the sum of $P(m/r)$ and $P(r/m)$ was almost unity, where $P(m/r)$ and $P(r/m)$ represent the probabilities of racemic addition to the meso chain end and meso addition to the racemic end, respectively. Therefore, the probability of meso addition (P_m) was determined as shown in Table III.

Figure 10 shows an Arrehenius plot of the ratio of the probabilities of meso addition to the racemic one, i.e., $P_m/(1 - P_m)$. From the linear relation obtained, the differences in the activation enthalpies ($\Delta H_m^{\ddagger} - \Delta H_r^{\ddagger}$) and entropies ($\Delta S_m^{\ddagger} - \Delta S_r^{\ddagger}$) were 1.1 kcal/mol and 0.28 cal/mol·deg, respectively, for the polymerization of AdMA. The difference in the entropy change was slightly smaller than for MMA[33,37] (Table IV).

Glass Transition Temperature. The T_g values of the polymers containing adamantyl esters were determined by DSC. Poly(AdMA) showed no transition peak in the DSC thermogram below its decomposition temperature (see next section), indicating that poly(AdMA) has no thermoplasticity although it is a typical vinyl polymer. Actually it was observed that a piece of poly(AdMA) flamed up without any softening.

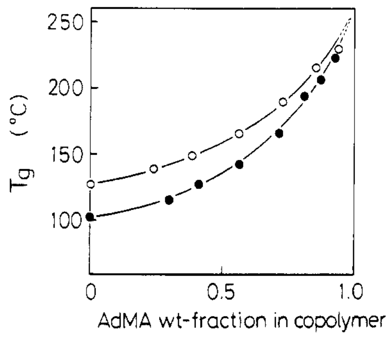

Figure 11. Dependence of the AdMA content on T_g of the copolymers with (○) MMA and (●) St.

The introduction of methyl groups into a bridgehead position of the adamantyl moiety was found to decrease T_g, e.g., the T_g of poly(DMAdMA) was 194 °C. This value is comparable to that reported by Hoagland et al. (190–196 °C).[2c] However, they reported that the introduction of the two methyl groups on the adamantane nucleus resulted in an increase of T_g, i.e., 141 °C for T_g of poly(AdMA) ($\bar{M}_n$ = 288 000), opposite to our results. Therefore, we also investigated the T_g for polyacrylates, which were prepared by radical polymerization with AIBN in benzene at 60 °C. A decrease of T_g was observed by the substitution, from 153 °C for poly(1-adamantyl acrylate) (poly(AdA)) to 105 °C for poly(3,5-dimethyl-1-adamantyl acrylate) (poly(DMAdA)),[38] supporting our conclusion that the T_g of poly(AdMA) is extremely high.

To confirm further the high T_g of poly(AdMA) over the decomposition temperature, the determination of T_g for the copolymers with MMA or St was attempted. The T_g was found to increase with increasing content of AdMA in the copolymer in both cases (Table II). Figure 11 shows T_g of the copolymers against the weight fraction of the AdMA unit in the copolymers. Extrapolation gave a higher temperature for T_g above the decomposition temperature of homopoly(AdMA).

Thus, the T_g of poly(AdMA) and poly(DMAdMA) were revealed to be higher than for any other poly(RMA) reported, e.g., 140 °C for poly(*dl*-isobornyl methacrylate),[39] 56–78 °C for poly(cycloalkyl methacrylate)s,[40] and 113 °C (118 °C)[10] for poly(tBMA).

Recently, we found that poly(AdMA) obtained by anionic polymerization with *sec*-butyllithium in toluene at -78 °C ($\bar{M}_n$ = 6300, mm = 0.88, mr = 0.10, rr = 0.02) showed a T_g at 183 °C, although that prepared in THF ($\bar{M}_n$ = 33 000, mm = 0.13, mr = 0.38, rr = 0.49) showed no T_g similarly to the polymer from radical polymerization.[38] Because a relatively low molecular weight poly(AdMA) ($\bar{M}_n$ = 8700) by radical polymerization did not

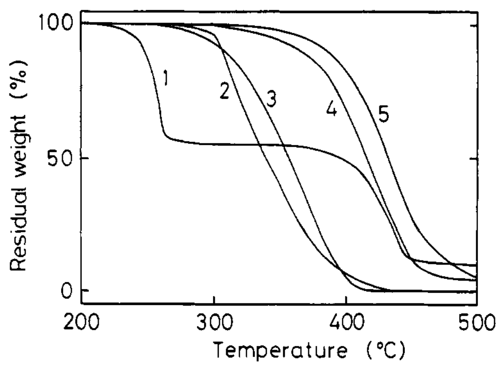

Figure 12. Thermogravimetric analysis in a nitrogen stream with a heating rate of 10 °C/min. (1) Poly(tBMA), (2) poly(AdMA), (3) poly(DMAdMA), (4) poly(DMAdA), (5) poly(AdA). Polymerization conditions: [monomer] = 1 mol/L, [AIBN] = 1 × 10^{-3} mol/L, in benzene at 60 °C.

Table V
Thermal Properties of Adamantyl-Containing Polymers^a

polymer	T_g,^{b} °C	T_{init},^{c} °C	T_{max},^{c} °C
poly(AdMA)	nd^d	254	304
poly(DMAdMA)	194	239	347
poly(AdA)	153	292	437
poly(DMAdA)	105	285	426
poly(MMA)	127 (105,^{e} 123^f)	245	296
poly(tBMA)	113 (118)^e	213	240, 447^g

^{a} Prepared by radical polymerization in benzene at 60 °C; [monomer] = 1 mol/L, [AIBN] = 1 × 10^{-3} mol/L. ^{b} By DSC (10 °C/min). ^{c} By TGA (10 °C/min). ^{d} Not detected below decomposition temperature. ^{e} Reference 10. ^{f} Reference 8. ^{g} Two-step decomposition with olefin elimination.

show any T_g, the observation of a T_g for the isotactic poly(AdMA) is not due to its low molecular weight, but to the difference in the tacticity, i.e., isotactic poly(AdMA) has a lower T_g than a syndiotactic one, agreeing well with the results for other poly(RMA). Since the tacticity of poly(DMAdMA) was similar to that of poly(AdMA), the decrease of T_g by introduction of the 3,5-dimethyl groups is probably due to free rotation of the methyl groups on the adamantyl ring and disordering of the highly symmetrical structure of the adamantyl moiety.

Thermal Decomposition. Thermal stability was investigated by thermogravimetric analysis in a nitrogen stream. The thermograms obtained, initial decomposition temperature (T_{init}), and maximum decomposition temperature (T_{max}) are shown in Figure 12 and Table V.

The polymer containing adamantyl esters exhibited a high T_{init} like that of poly(MMA), although they are tertiary alkyl esters. In general, *tert*-alkyl ester polymers are known to evolve olefins readily when they are heated to ca. 200 °C.[41] In the decomposition of adamantyl esters, the formation of a corresponding olefin, i.e., adamantene, is very unfavorable thermodynamically,[1,42] so that they showed excellent thermal stability. Poly(AdA) and poly(DMAdA) were found to have thermal stabilities higher than poly(AdMA) and poly(DMAdMA).

Conclusions

The high reactivity of AdMA in radical polymerization was interpreted as due to decrease of the termination rate, i.e., a reduction in segmental diffusion. This was directly confirmed by observation of the ESR spectra under the usual polymerization conditions. The conformations of the poly(AdMA) radical was estimated from the hyperfine coupling constant of the ESR spectrum obtained to be somewhat different from that for the poly(MMA) radical because of the steric repulsion of the adamantyl group. It was shown that poly(AdMA) prepared by radical polymerization had a more predominantly syndiotactic structure compared with poly(MMA) prepared under the same conditions. Poly(AdMA) was shown to have no thermoplasticity; i.e., poly(AdMA) by radical polymerization did not show any T_g below its decomposition temperature, although the T_g of the isotactic polymer prepared anionically decreased to 183 °C. The introduction of methyl groups into the adamantyl moiety was also observed to decrease T_g, i.e., 194 °C for poly(DMAdMA). These adamantyl-containing polymers were found to have high decomposition temperatures by TGA, because olefin elimination from the side chain did not occur in spite of their being tertiary alkyl esters.

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Registry No. AdMA, 16887-36-8; DMAdMA, 34555-75-4; St, 100-42-5; MMA, 80-62-6; AdMA (homopolymer), 28854-38-8; DMAdMA (homopolymer), 25640-24-8; (AdMA)(St) (copolymer), 133816-40-7; (AdMA)(MMA) (copolymer), 128509-51-3.