INVITED ARTICLE

Precise synthesis of poly(1-adamantyl methacrylate) by atom transfer radical polymerization

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1-Adamantyl methacrylate (AdMA) was polymerized using the atom transfer radical polymerization (ATRP) method with methyl α-bromoisobutyrate (MBiB), copper(I) bromide (CuBr), copper(II) bromide (CuBr$_2$) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) in toluene at 60 °C, producing well-defined poly(1-adamantyl methacrylate) (PAdMA). Simultaneous control of the molecular weight and tacticity of PAdMA was successfully achieved by the ATRP method using the MBiB/CuBr/CuBr$_2$/tris[2-(dimethylamino)ethyl]amine-initiating system in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) at −20 °C. Block copolymerization of AdMA and methyl methacrylate (MMA) was successfully achieved by the poly(methyl methacrylate) macroinitiator/CuBr$_2$/HMTETA/tin(II) 2-ethylhexanoate-initiating system based on activators generated by electron transfer (AGET) ATRP method. Differential scanning calorimetry revealed the relationship between the glass transition temperature, molecular weight and tacticity of the obtained PAdMA.
Polymer Journal (2010) **42**, 626–631; doi:10.1038/pj.2010.55; published online 30 June 2010

INTRODUCTION

Various poly(meth)acrylates bearing bulky ester groups, such as bornyl,[1] isobornyl,[1–3] adamantyl[4–7] and its derivatives,[4–6,8–11] have been synthesized to improve the thermal properties, such as the glass transition temperature and the thermal degradation temperature, of poly(methyl methacrylate) (PMMA). For example, the incorporation of adamantyl groups into polymer structures generally produces not only a high thermal stability but also an improvement in other physical and chemical properties, such as transparency to ultraviolet light, low dielectric constant, hydrophobicity, high oxidation resistance, low surface energy and high density. Although these characteristics are interesting, there are only few studies on the synthesis of poly(1-adamantyl methacrylate) (PAdMA); Otsu and colleagues[5] reported the conventional radical polymerization of 1-adamantyl methacrylate (AdMA) and its kinetic properties, and Nakahama and colleagues[4] reported the living anionic polymerization of AdMA leading to well-defined PAdMA.

Controlled/living radical polymerizations, such as nitroxide-mediated radical polymerization, atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization, have been applied to various methacrylate monomers.[12–14] The controlled/living radical polymerization of methacrylate monomers bearing bulky ester groups, such as AdMA, which guarantees the generation of well-defined macromolecular architectures such as the block copolymer, graft copolymer and star-shaped polymer on

a preparative scale, is still of great interest. In addition, we have previously reported that the simultaneous control of the molecular weight and stereochemistry[15] of PMMA was accomplished using the designed initiating system based on ATRP.[16,17] Therefore, it is interesting to expand our method to methacrylates bearing bulky group, such as AdMA.

We now report the polymerization of AdMA using the ATRP-initiating system, methyl α-bromoisobutyrate (MBiB) and copper(I) bromide (CuBr) with 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), 2,2′-bipyridyl (bpy) and tris[2-(dimethylamino)ethyl] amine (Me$_6$TREN), as shown in Scheme 1. The livingness of the ATRP of AdMA is confirmed through a kinetic investigation using the CuBr/CuBr$_2$/HMTETA-initiating system, and the stereocontrol of the ATRP of AdMA is carried out using the CuBr/CuBr$_2$/Me$_6$TREN-initiating system in a fluorinated solvent. Poly(methyl methacrylate)-*block*-poly(1-adamantyl methacrylate) (PMMA-*b*-PAdMA) was prepared by the ATRP of AdMA using the PMMA macroinitiator, PMMA-Br, as shown in Scheme 2. The effects of the molecular weight and tacticity of the well-defined PAdMAs on glass transition temperature are discussed.

MATERIALS AND METHODS
Materials
Copper(I) bromide (CuBr, 99.999%), copper(II) bromide (CuBr$_2$, 99.999%) and HMTETA (>97%) were purchased from Sigma-Aldrich Chemicals Co.

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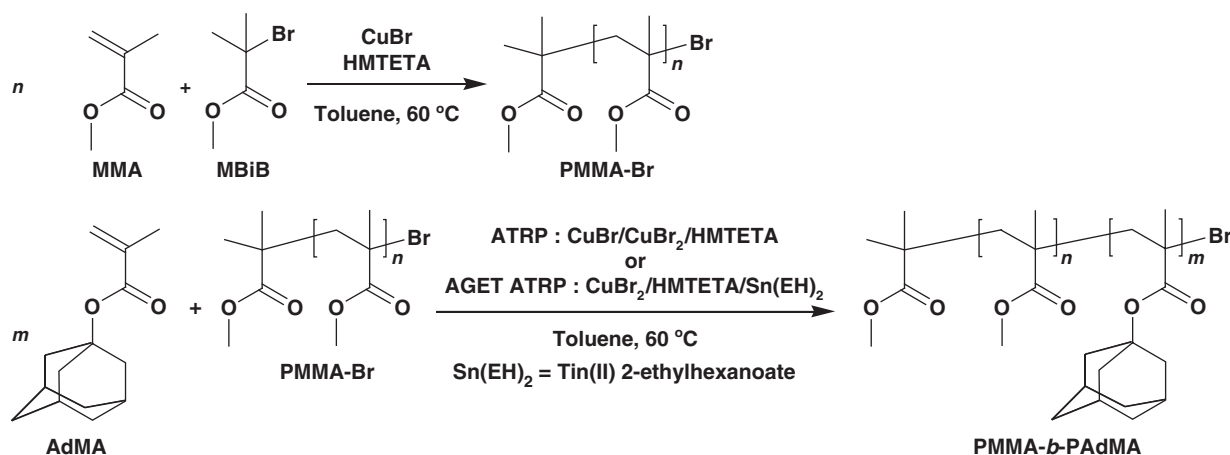Correspondence: Professor T Kakuchi, Division of Biotechnology and Macromolecular Chemistry, Graduate School of Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo 060-8628, Japan.
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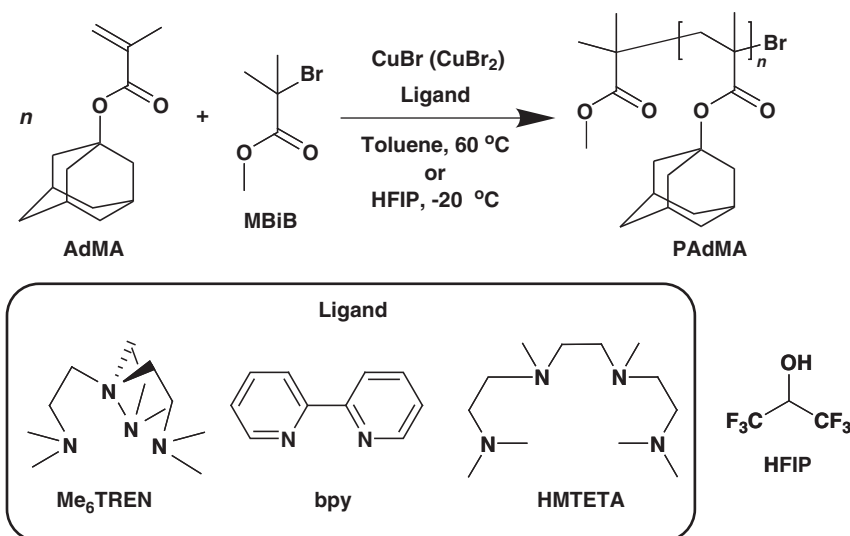
Scheme 1 ATRP of 1-Adamantyl methacrylate (AdMA).

Scheme 2 Synthesis of poly(methyl methacrylate) macroinitiator (PMMA-Br) and poly(methyl methacrylate)-*block*-poly(1-adamantyl methacrylate) (PMMA-*b*-PAdMA).

(St Louis, MO, USA) Me$_6$TREN was supplied by Mitsubishi Chemical Co. Ltd. (Tokyo, Japan) HMTETA and Me$_6$TREN were purified by distillation over CaH$_2$ under reduced pressure. AdMA was donated by Idemitsu Kosan Co. Ltd. (Tokyo, Japan) and distilled over CaH$_2$ and CuBr$_2$ under argon. bpy was purchased from Merck KGaA (Darmstadt, Germany) and purified by recrystallization from hexane. MBiB was purchased from Fluka (Buchs, Switzerland) and distilled over CaH$_2$ under argon before use. Dry toluene (>99.5%; water content, <0.001%) was purchased from Kanto Chemicals Co. Inc. (Tokyo, Japan) and was used as received. Tin(II) 2-ethylhexanoate (Sn(EH)$_2$) was purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and was used as received. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was supplied by Central Glass Co. Ltd. (Tokyo, Japan) and was distilled from CaH$_2$ under argon.

Measurements

The polymerization solution was prepared in an MBRAUN stainless steel glovebox (MBRAUN, Garching, Germany) equipped with a gas purification system (molecular sieves and copper catalyst) under a dry argon atmosphere (H$_2$O, O$_2$ <1 p.p.m.). The moisture and oxygen contents in the glovebox were monitored by MB-MO-SE 1 and MB-OX-SE 1, respectively. [1]H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL JNM-A400II (JEOL, Akishima, Japan). Size exclusion chromatography (SEC) was performed at 40 °C in chloroform (0.8 ml min^{-1}) by a Jasco GPC-900 system (Jasco, Hachioji, Japan) equipped with a Tosoh TSK$_{gel}$ GMH$_{HR}$-M column (Tosoh, Tokyo, Japan)

(linear; 7.8 mm×300 mm; pore size=16 nm; bead size=5 µm; exclusion limit-4×10^6), Shodex KF-804L columns (linear; 8 mm×300 mm; pore size=20 nm; bead size=7 µm; exclusion limit=4×10^5) and a refractive index detector. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the polymers were calculated on the basis of PMMA calibration. The monomer conversion in the polymerization was calculated from the concentration of the residual monomer in the reaction mixture, as determined by a Shimadzu GC-17A gas chromatography (GC) system (Shimadzu, Kyoto, Japan) equipped with an SGE BPX70 capillary column (SGE, Ringwood, Australia) (30 m×0.25 mm; film thickness, 0.25 µm; temperature, 120 °C) and an flame ionization detector (temperature, 120 °C) using toluene or HFIP internal standards. The inverse-gated decoupling ^{13}C NMR spectra for the tacticity analysis of PAdMA were measured using a 20% (w/v) sample in CDCl$_3$ at 55 °C with a 45° pulse angle, 7.0 s delay of the inverse-gated decoupling and 10 000 scans. The triad tacticity of a PAdMA molecule was determined from the integral values of the quaternary carbon on an adamantyl group of the polymer in the ^{13}C NMR spectrum. The glass transition temperature (T_g) of the polymers was measured by Differential scanning calorimetry (DSC) using Seiko Instruments SSC 5200 DSC 220 (Seiko, Chiba, Japan). Samples in 3–10 mg portions were first heated above their T_g at a heating rate of 10 °C min^{-1}, then cooled to −20 °C at a cooling rate of 40 °C min^{-1}. The samples were reheated to 280 °C at a heating rate of 10 °C min^{-1}. All T_g values were obtained from the second scan after removing the thermal history.

Polymerization of AdMA

A typical procedure for the polymerization is as follows: MBiB (5.88 µl, 45.4 µmol) was added to a solution of AdMA (1.00 g, 4.54 mmol), CuBr (6.5 mg, 45 µmol) and HMTETA (10.6 mg, 45.4 µmol) in toluene (3 ml) under argon. Polymerization was initiated by heating at 60 °C. After 9 h, the reaction mixture was exposed to air to quench the polymerization. The product was passed through an alumina column using toluene as the eluent to remove the copper catalyst, followed by two reprecipitations in a mixed solvent of methanol and water (1/1, v/v). The purified polymer was obtained as a white powder. The reaction yield was 0.475 g (47.1%), conversion was 57.0%, M_n was 8.3 kg mol^{-1} and M_w/M_n was 1.13. Polymerizations using the other ligands, solvent and additional CuBr$_2$ were conducted using a similar procedure.

Block copolymerization of AdMA with poly(methyl methacrylate) macroinitiator

The procedure for the preparation of the poly(methyl methacrylate) macro-initiator (PMMA-Br) in toluene at 60 °C is the same procedure used for the polymerization of AdMA. The amounts of the necessary reagents are shown as follows: MMA (22.7 g, 227 mmol), MBiB (0.294 µl, 2.27 mmol), CuBr (325 mg, 2.27 mmol), HMTETA (525 mg, 2.28 mmol) and toluene (50 ml). The PMMA macroinitiator (PMMA-Br) was obtained as a white powder. The reaction yield was 8.96 g (38.8%), conversion was 45.1%, M_n was 9.9 kg mol^{-1} and M_w/M_n was 1.15.

Block copolymerization of AdMA and MMA using the CuBr/CuBr$_2$/HMTETA catalytic system was carried out by the following procedure: a stock solution of HMTETA (5.1 mg, 22 µmol), CuBr (2.6 mg, 18 µmol) and CuBr$_2$ (0.8 mg, 4 µmol) in toluene (0.16 ml) was added to a solution of PMMA-Br (242 mg, 24.4 µmol) and AdMA (0.407 g, 1.85 mmol) in toluene (1.46 ml) under argon. Polymerization was initiated by heating at 60 °C. After 9 h, the reaction mixture was exposed to air to quench the polymerization. The subsequent purification procedure was the same as that for PAdMA. PMMA-b-PAdMA was obtained as a white powder. The reaction yield was 170.2 mg, conversion was 24.7%, M_n was 15.5 kg mol^{-1} and M_w/M_n was 1.18.

The block copolymerization of AdMA and MMA using the CuBr$_2$/HMTETA/Sn(EH)$_2$ catalytic system was carried out using the following procedures: Sn(EH)$_2$ (8.3 mg, 20.5 µmol) was added to a solution of PMMA-Br (629 mg, 62.6 µmol), AdMA (1.00 g, 4.54 mmol), CuBr$_2$ (10.2 mg, 45.7 µmol) and HMTETA (10.5 mg, 45.6 µmol) in toluene (3.00 ml) under argon to initiate polymerization by heating at 60 °C. After 2 h, the reaction mixture was exposed to air to quench the polymerization. The subsequent purification procedure was the same as that for PAdMA. PMMA-b-PAdMA was obtained as a white powder. The yield was 1.17 g, conversion was 42.4%, M_n was 18.7 kg mol^{-1} and M_w/M_n was 1.13.

RESULTS AND DISCUSSION

Atom transfer radical polymerization of 1-adamantyl methacrylate

We first carried out the polymerization of AdMA in toluene at 60 °C for 9 h using MBiB, copper(I) bromide (CuBr) and an amine ligand ($[AdMA]_0/[MBiB]_0=100/1$). The proper choice of ligand for copper is necessary to control the ATRP. Thus, three ligands, Me$_6$TREN, bpy and HMTETA, were used to optimize the polymerization conditions (Scheme 1). Table 1 summarizes the results of the polymerizations, and Figure 1 shows the SEC traces of the obtained polymers. The CuBr/Me$_6$TREN catalytic system (Table 1, run 1) produced an uncontrolled polymerization, which resulted in PAdMA having an M_n of 16.4 kg mol^{-1}, a bimodal molecular weight distribution and M_w/M_n of 2.34. Although the polymerization using the CuBr/bpy catalytic system (Table 1, run 2) produced PAdMA with a unimodal molecular weight distribution, the M_w/M_n of the obtained PAdMA was still as high as 1.35. However, polymerization using the CuBr/HMTETA catalytic system (Table 1, run 3) produced the narrow-dispersed PAdMA with an M_n of 8.3 kg mol^{-1} and an M_w/M_n of 1.13. However, the M_n value of the obtained PAdMA was lower than the theoretical

Table 1 Atom transfer radical polymerization of AdMA using the MBiB/CuBr-initiating system with Me$_6$TREN, bpy and HMTETA

Run	Ligand	$[CuBr]_0/[ligand]_0$	Time (h)	Conv. (%)[a]	M_n (kg mol^{-1}) Theo.[c]	Obsd.[b]	M_w/M_n[b]
1	Me$_6$TREN	1/1	9.0	55.1	12.3	16.4	2.37
2	bpy	1/2	9.0	55.5	12.4	18.9	1.35
3	HMTETA	1/1	9.0	57.0	12.7	8.3	1.13
4[d]	HMTETA	1/1	8.5	48.5	10.9	10.9	1.08

Solvent, toluene; temp., 60 °C; $[AdMA]_0/[MBiB]_0/[CuBr]_0=100/1/1$; $[AdMA]_0=1.14$ mol l^{-1}.
[a]Determined by GC from the concentration of the residual monomer with toluene as the internal standard.
[b]Determined by SEC using PMMA standards in CHCl$_3$.
[c]Calculated from $[AdMA]_0/[MBiB]_0 \times$ conv. $\times$ (MW of AdMA$=220.31$)+(MW of MBiB$=181.03$).
[d]0.2 equivalent of CuBr$_2$ was added to the reaction mixture.

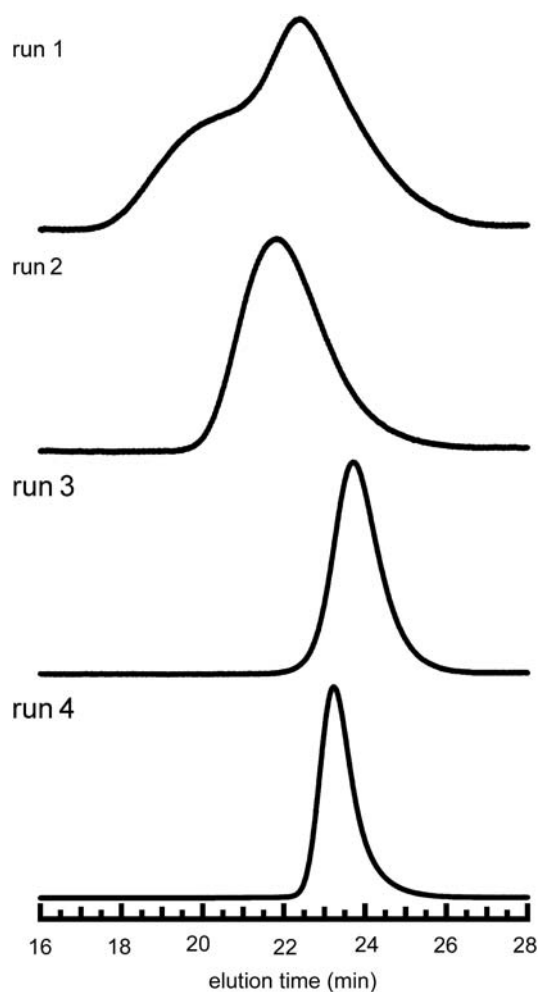**Figure 1** SEC traces of PAdMA prepared by ATRP at 60 °C in toluene using CuBr/Me$_6$TREN (run 1), CuBr/bpy (run 2), CuBr/HMTETA (run 3) and CuBr/CuBr$_2$/HMTETA (run 4) as the catalytic system.

molecular weight ($M_{n,theo.}$) of 12.7 kg mol^{-1} predicted from the monomer conversion and the initial ratio of AdMA and MBiB. Therefore, we carried out an additional AdMA polymerization using the CuBr/copper(II) bromide (CuBr$_2$)/HMTETA catalytic system in toluene at 60 °C for 8.5 h (Table 1, run 4). It is well known that the

addition of copper(II) species to an ATRP system using a copper(I) catalyst provides good control of the molecular weight.[18,19] After polymerization, the M_n value of the obtained PAdMA (10.9 kg mol^{-1}) was the same as the $M_{n,theo}$ value, and the M_w/M_n value of 1.08 was less than that of PAdMA prepared by the CuBr/HMTETA system. Thus, it was revealed that the CuBr/CuBr$_2$/HMTETA catalytic system is the most suitable for the ATRP of AdMA.

A kinetic investigation was subsequently carried out to confirm the controlled nature of the ATRP of AdMA using the CuBr/CuBr$_2$/HMTETA catalytic system in toluene at 60 °C. Figure 2a shows the relationship between the monomer conversion of the polymerization and the M_n value of the obtained PAdMA. The M_n values of the product linearly increased with the increasing conversion of AdMA, and the M_w/M_n value of 1.08–1.11 remained constant for up to at least 79% monomer conversion. Figure 2b shows the first-order kinetic plot of the polymerization. The consumption rate of AdMA with increasing polymerization time was linear with the concentration of the

Figure 2 (a) Dependence of the number-average molecular weight (M_n) and polydispersity (M_w/M_n) on monomer conversion and (b) kinetic plots for the polymerization of AdMA catalyzed by CuBr/CuBr$_2$/HMTETA in toluene at 60 °C ([AdMA]$_0$=1.14 mol l^{-1}; [AdMA]$_0$/[MBiB]$_0$/[CuBr]$_0$/CuBr$_2$]$_0$/[HMTETA]$_0$=100/1/1/0.2/1.2).

remaining monomer in the reaction mixture. In conclusion, the ATRP system for AdMA was successfully established.

Moreover, we carried out the ATRP of AdMA in HFIP, a representative fluoroalcohol, to simultaneously control the molecular weight and tacticity[15] of PAdMA (Scheme 1). The use of fluoroalcohols as the solvent for radical polymerization induces a tacticity change in the resultant polymer.[20,21] We also previously succeeded in the simultaneous control of the molecular weight and tacticity of PMMA by ATRP using HFIP.[16,17] The ATRP of AdMA in HFIP was carried out using the CuBr/CuBr$_2$/Me$_6$TREN catalytic system at 20 °C for 15 h (Supplementary Table S1, run 7) and at −20 °C for 40.5 h (Supplementary Table S1, run 11). Although the polymerization at 20 °C yielded PAdMA with a broad M_w/M_n value of 1.85, the polymerization at −20 °C produced narrow-dispersed PAdMA with a M_w/M_n ratio of 1.14 and M_n of 14.1 kg mol^{-1}. The tacticity of PAdMA prepared in toluene at 60 °C (Table 1, run 3) and in HFIP at −20 °C was compared. The triad tacticity of PAdMA can be analyzed from the resonance of the quaternary carbon in the adamantyl group appearing around 80–81 p.p.m. in the ^{13}C NMR spectrum.[5] Inverse-gated decoupling was applied to obtain the quantitative ^{13}C NMR spectra, which are shown in Supplementary Information (Supplementary Figure S1). The triad tacticity contents (*mm/mr/rr*) of PAdMA prepared in toluene and HFIP were 4/27/69 and 1/21/78, respectively. The *rr* triad contents of the PAdMA prepared in HFIP were 9% higher than that of the PAdMA prepared in toluene. Thus, the simultaneous control of the molecular weight and the tacticity of AdMA was also successfully achieved by polymerization in fluoroalcohol.

Block copolymerization of AdMA and methyl methacrylate
To use the controlled nature of the ATRP of AdMA, we first tried to prepare poly(1-adamantyl methacrylate)-*block*-poly(methyl methacrylate) (PAdMA-*b*-PMMA) from PAdMA with bromine end functionality (M_n=9.6 kg mol^{-1}, M_w/M_n=1.08), which was synthesized by the ATRP of AdMA using the MBiB/CuBr/CuBr$_2$/HMTETA-initiating system in toluene at 60 °C for 6 h (Supplementary Scheme S1). However, PAdMA could not sufficiently initiate the block copolymerization of MMA using the CuBr/CuBr$_2$/HMTETA catalytic system in toluene at 60 °C for 9 h, resulting in the mixture of PAdMA-*b*-PMMA and unreacted PAdMA, as shown in Supplementary Information (Supplementary Figure S2). This result could be caused by the low reactivity of the PAdMA radical toward MMA, which was reported by Otsu et al.[6]

Thus, we changed the synthesis strategy, as shown in Scheme 2. The PMMA macroinitiator (PMMA-Br) was prepared by the ATRP of MMA using the MBiB/CuBr/HMTETA-initiating system. The resulting PMMA-Br had an M_n value of 9.9 kg mol^{-1} and an M_w/M_n value of 1.15 (Figure 3a). The block polymerization of AdMA with PMMA-Br was then carried out using the CuBr/CuBr$_2$/HMTETA catalytic system in toluene at 60 °C under the condition of [AdMA]$_0$/[PMMA-Br]$_0$/[CuBr]$_0$/[CuBr$_2$]$_0$/[HMTETA]$_0$=76/1.0/0.74/0.16/0.90 (Table 2, run 5). Although the obtained block copolymer, PMMA-*b*-PAdMA, showed a relatively narrow and unimodal SEC trace for the M_w/M_n value of 1.18 and the observed M_n value agreed with the theoretical value, the monomer conversion of 24.7% was very low for the polymerization time of 9 h.

Given those results, we applied the AGET ATRP method[22] for the block copolymerization of AdMA with PMMA-Br (Scheme 2). Polymerization was carried out under the condition of [AdMA]$_0$/[PMMA-Br]$_0$/[CuBr$_2$]$_0$/[HMTETA]$_0$/[Sn(EH)$_2$]$_0$=73/1.0/0.73/0.73/0.33 in toluene at 60 °C (Table 2, run 6). The molecular weight of PMMA-*b*-PAdMA increased with polymerization time, as shown in Figure 3.
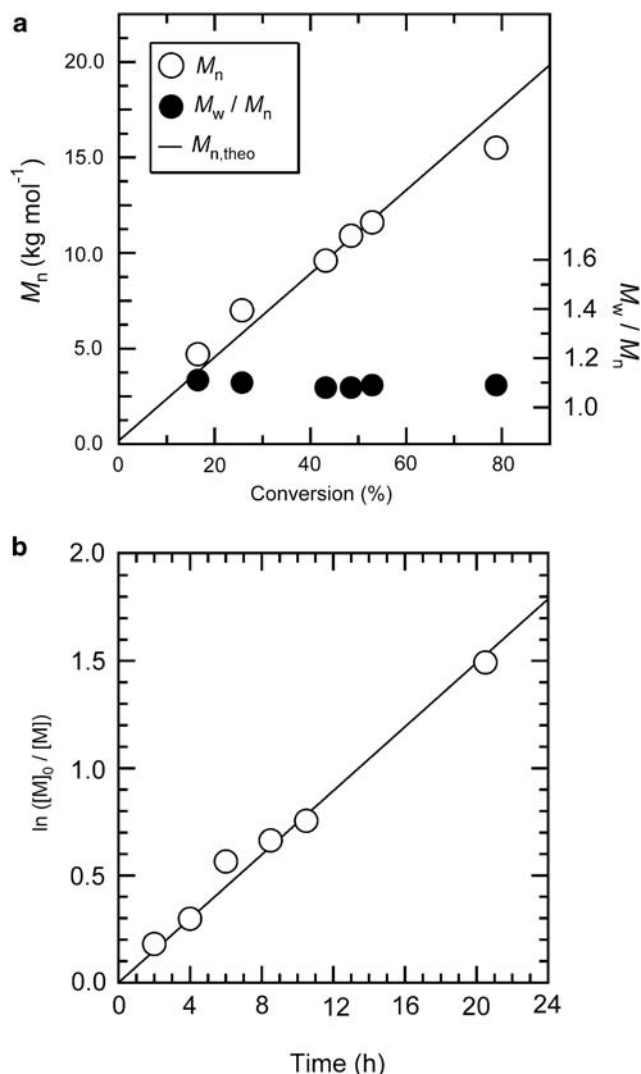
The obtained block polymers however showed bimodal SEC traces for polymerization times greater than 3 h (Figures 3d and e). However, the SEC trace of the block polymer for 2 h is unimodal and the M_w/M_n value was 1.13 (Figure 3c). The M_n value of 18.7 kg mol^{-1} agreed with the predicted value. These results indicate that the AGET ATRP method was effective for the block copolymerization of AdMA using the PMMA macroinitiator.
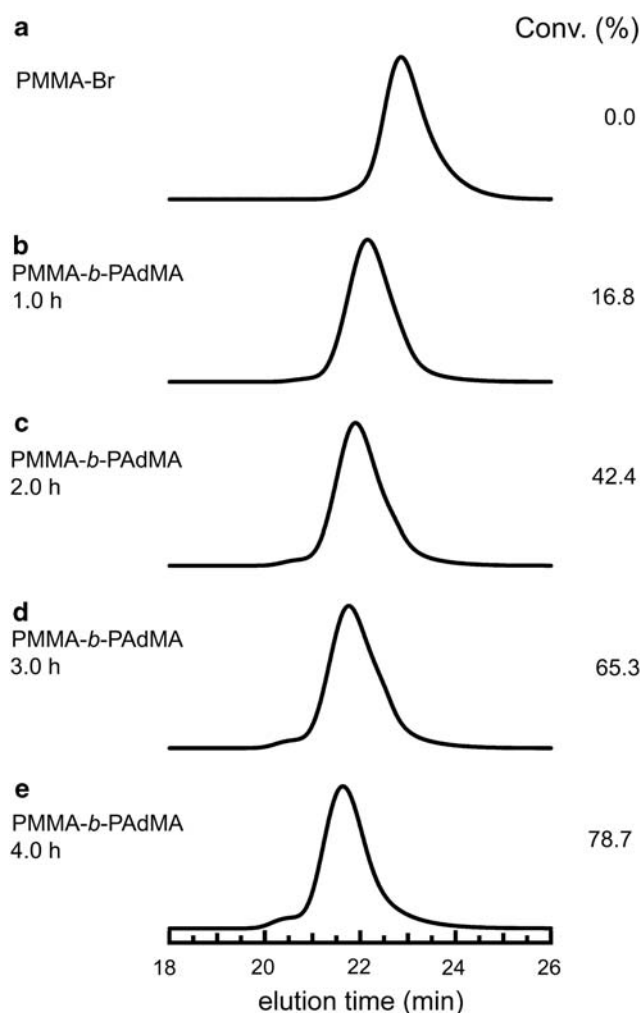

Figure 3 SEC traces of the (**a**) PMMA macroinitiator (PMMA-Br) and PMMA-*b*-PAdMA obtained by the AGET ATRP of AdMA using PMMA-Br in toluene at 60 °C after (**b**) 1 h, (**c**) 2 h, (**d**) 3 h and (**e**) 4 h ([AdMA]$_0$/[PMMA-Br]$_0$/[CuBr$_2$]$_0$/[HMTETA]$_0$/[Sn(EH)$_2$]$_0$=73/1.0/0.73/0.73/0.33).

Molecular weight and tacticity effect on the thermal properties of PAdMA

The thermal properties of polymers containing the adamantyl group were intensively investigated from the viewpoint of high thermal stability. We first investigated the relationship between the glass transition temperature (T_g) of PAdMA and its molecular weight. The T_g of each polymer was measured by DSC. Figure 4 shows the change in T_g of PAdMA with increasing M_n, and the representative DSC trace is shown in Supplementary Information (Supplementary Figure S3). The T_g value varied within the range of 200–244 °C, with an increase in molecular weight from 4.6 to 32.1 kg mol^{-1}. Although the previously reported PAdMA showed no glass transition in almost all cases,[4–6] all the PAdMAs prepared by ATRP in this study showed glass transitions, presumably because of the low molecular weights obtained. The effect of tacticity on the T_g of PAdMA was investigated next. PAdMA with a 69% *rr* triad content (M_n=14.5 kg mol^{-1}, M_w/M_n=1.12) showed a T_g of 230 °C. However, PAdMA with a 78% *rr* triad content (M_n=14.1 kg mol^{-1}, M_w/M_n=1.14) showed a T_g of 243 °C. Although these two polymers had narrow molecular weight distributions and almost the same molecular weight, the difference in their glass transition temperatures was large. This result indicates that the T_g of PAdMA increases with the increasing *rr* triad contents, corresponding to the results reported by Otsu *et al*.[5] The relationship between tacticity and the T_g of PAdMA was the same as the relationship for PMMA.[23]

Conclusions

The controlled/living polymerization system for AdMA was successfully established by the ATRP method using CuBr/CuBr$_2$/HMTETA.
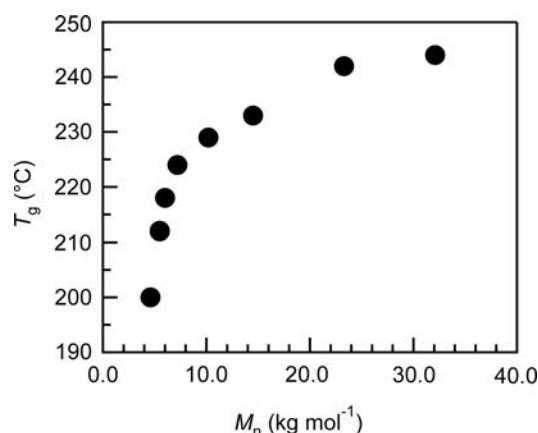

Figure 4 Dependence of the glass transition temperature (T_g) on the M_n of PAdMA (*mm*/*mr*/*rr*=4/27/69).

Table 2 Synthesis of PMMA-*b*-PAdMA by block polymerization of AdMA using the PMMA macroinitiator (PMMA-Br) in toluene at 60 °C

| | | | | M_n (kg mol^{-1}) | | |
Run	Initiating system and reaction condition (molar ratio)	Time (h)	Conv. (%)[a]	Theo.[c]	Obsd.[b]	M_w/M_n[b]
5	[AdMA]$_0$/[PMMA-Br]$_0$/[CuBr]$_0$/[CuBr$_2$]$_0$/[HMTETA]$_0$ (76/1.0/0.74/0.16/0.90)[d]	9.0	24.7	14.0	15.5	1.18
6	[AdMA]$_0$/[PMMA-Br]$_0$/[CuBr$_2$]$_0$/[HMTETA]$_0$/[Sn(EH)$_2$]$_0$ (73/1.0/0.73/0.73/0.33)[e]	2.0	42.4	16.7	18.7	1.13

PMMA-Br; M_n=9.9 kg mol^{-1} and M_w/M_n=1.15.
[a]Determined by GC from the concentration of residual monomer with toluene as the internal standard.
[b]Determined by SEC using PMMA standards in CHCl$_3$.
[c]Calculated from [AdMA]$_0$/[PMMA-Br]$_0$×conv.×(M.W. of AdMA=220.31)+(M.W. of PMMA-Br=9900).
[d][AdMA]$_0$=1.14 mol l^{-1}.
[e][AdMA]$_0$=1.51 mol l^{-1}.

The simultaneous control of the tacticity and molecular weight of PAdMA was achieved by ATRP conducted in HFIP at low temperature using the CuBr/CuBr$_2$/Me$_6$TREN catalytic system. In addition, the block copolymerization of AdMA with MMA proceeded reasonably using the PMMA macroinitiator/CuBr$_2$/HMTETA/Sn(EH)$_2$-initiating system based on the AGET ATRP method. The dependence of the glass transition temperature of PAdMA on molecular weight and tacticity was clearly revealed by DSC analyses.

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