ORIGINAL ARTICLE

Synthesis of well-defined 3-arm and 6-arm poly(acrylic acid)s via ATRP of methyl acrylate and hydrolyses of 3-arm and 6-arm poly(methyl acrylate)s

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Three-arm poly(methyl acrylate)s (3-arm PMAs) and 6-arm PMAs were synthesized via atom transfer radical polymerization (ATRP) with 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene and hexakis(bromomethyl)benzene as the initiators, CuBr as the catalyst and tris [2-(dimethylamino) ethyl] amine (Me$_6$TREN) as the ligand in 2-propanol. The representative arm numbers, weight-average molecular weights (M_ws) and polydispersity indices (PDIs) were 2.65, 3.70×10^4 and 1.21, respectively, for 3-arm PMAs and 4.85, 9.60×10^4 and 1.54, respectively, for 6-arm PMAs. The effect of [Br of initiators]:[CuBr]:[Me6TREN] in feed on the arm number was investigated. The addition of slightly excess molar amounts of CuBr and Me$_6$TREN to Br of the initiators was important to generate sufficient arm numbers and low PDIs. In particular, excess molar amounts of Me$_6$TREN in the feed maintained the low PDIs of the 6-arm PMAs. It was because of not only the low reactivity of the benzyl bromide-based initiator but also the bulky exclusion volume near the initiators. To convert the PMAs to poly(acrylic acid)s (PAAs), basic hydrolysis was conducted. The maximum degrees of hydrolysis of the 3-arm and 6-arm polymers were ca. 72 mol%. However, the products were well dispersed in water as well as PAA because of the coverage of the polymers by PAA. Thermal decomposition curves determined by thermogravimetric analysis (TGA) of the 3-arm and 6-arm PAAs corresponded well to that of PAA.

INTRODUCTION

Star polymers have been focused on for their specific structures. Owing to difficulties in controlling the arm lengths and arm numbers of these polymers,[1] they have been synthesized by many different methods, including a combination of several techniques such as core-first[1–3] or arm-first[4,5] methods, and living radical,[6] cationic[7,8] or anionic[9–12] polymerization. The main benefit of the arm-first method is that well-defined arms can be used to synthesize the polymers. For this method, divinylbenzene is often used for the formation of cores.[5] The number of arms in star polymers synthesized via the arm-first method can be precisely controlled during synthesis, and 8-, 12- and 18-arm polymers have been synthesized without the use of divinylbenzene.[11,12] The synthesis of a star polymer with 31 arms has been reported; however, the core part of this polymer consisted of oligomers and did not contain small molecules.[10] Most of them were conducted using anionic polymerization.

The core-first method enables control over the arm numbers through the reaction points of the initiator. An important feature of this method is to initiate all the reaction points. Purification of polymers via core-first method is easier than those generated using the arm-first method. The polymers generated via the core-first method require removal of the monomer, whereas those produced via the arm-first method require removal of the polymeric arms. In the case of polymers with a low number of arms, a special technique is necessary for separating the product and unreacted polymeric arms. Well-defined star polymers are often synthesized via living radical polymerization, such as atom transfer radical polymerization (ATRP),[3] nitroxide-mediated polymerization (NMP),[13] and reversible addition-fragmentation chain transfer polymerization.[14] Of these polymerization techniques, ATRP is the most frequently used and does not require specific techniques or equipment.

Star polymers have been reported as effective materials for all-solid-state lithium batteries.[15] Thus, methods to produce such industrially usable star polymers are in demand. Synthetic methods to generate well-defined star poly(methacrylate)s have been reported.[16] In general, the arms are analyzed by separating them from the core. Most star polymers via ATRP were synthesized with initiators that contained ester groups. The synthesis of star poly(acrylic acid) (PAA) is rarely reported because the arms can be separated from the core in the presence of a strong base. PAA has been reported to be an effective material for use in batteries.[17,18] Star PAA is expected to be a good material for such applications. In this study, we aimed to synthesize 3-arm and 6-arm PAAs via ATRP of methyl acrylate (MA) and subsequent hydrolysis with 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (BTB)
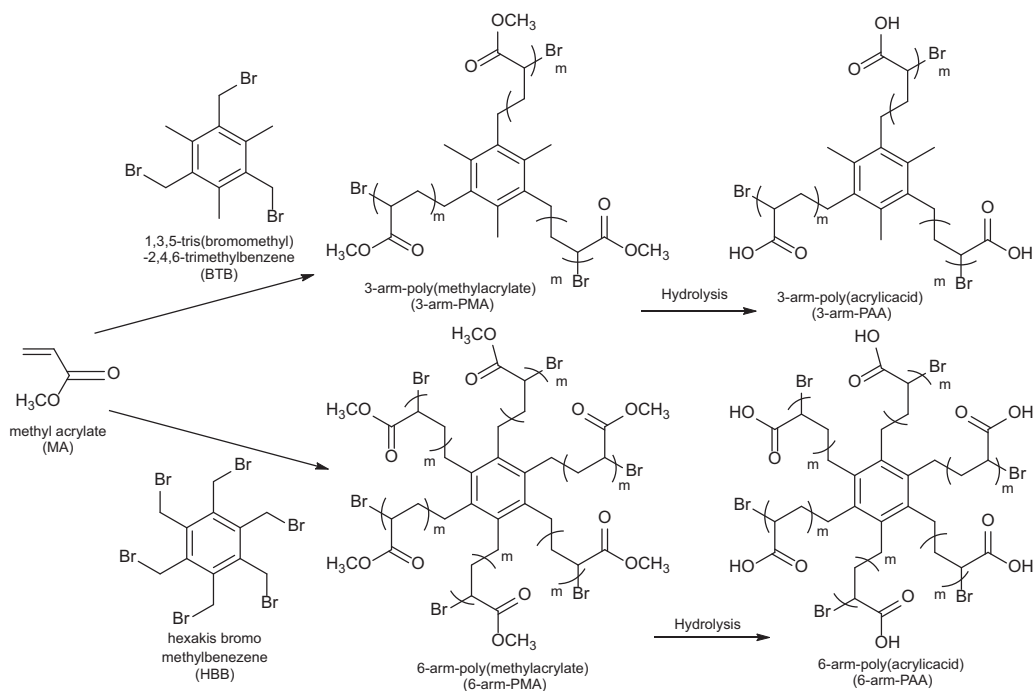
Scheme 1 Chemical structures and synthetic procedures for the generation of 3-arm and 6-arm poly(acrylic acid)s.

and hexakis bromomethylbenzene (HBB) as the initiators, containing 3 and 6 reaction groups, respectively. The synthetic procedure is shown in Scheme 1. First, star poly(methyl acrylate)s (PMAs) are synthesized via the core-first method with BTB and HBB. It is impossible to polymerize acrylic acid (AA) via ATRP. Therefore, the PMAs are synthesized and hydrolyzed in this work. The arms synthesized with BTB or HBB will not be separated from the core by hydrolysis or under strong basic conditions. Therefore, these polymers are hydrolyzed to be the PAAs.

The number of arms is an important factor for star polymers. The specific properties of star polymers, such as the drastically lower solution viscosity of a star polymer solution than that of a linear polymer solution with the same polymer concentration and the same molecular weights, are observed for star polymers when arm numbers are more than three. If all the Br groups are reacted, 3-arm and 6-arm star polymers are obtained. However, taking steric hindrance into account, it is difficult to initiate all the groups. In addition, it is difficult for the catalyst to attack the reaction sites. Two different ligands, tris[2-(dimethylamino) ethyl]amine (Me$_6$TREN) and 2,2'-bipyridyl (bpy), were chosen to initiate all the Br groups in this work. The synthesis of star polymers with BTB has been previously reported.[19,20] Detail arm synthesis of star polymers with HBB has also been reported.[21] Even though spacers were introduced to the initiator to account for steric hindrance, the arm number was found to be less than six. Various conditions were investigated to determine the factors that were effective for sufficient arm numbers in this work. To discuss the different properties derived from the molecular structures, dynamic light scattering (DLS) and thermogravimetric analysis (TGA) were used.

EXPERIMENTAL PROCEDURE
Materials
Me$_6$TREN was synthesized based on published procedures.[22] The reaction yield (66.0 vol%) and purity (91.9 mol%) were determined by proton nuclear

magnetic resonance (^{1}H-NMR). MA (TCI, Tokyo, Japan, >99.0%) and *tert*-butyl acrylate (TCI, >98.0%) were distilled under vacuum before use. BTB (TCI, >98.0%), 2-propanol (TCI, >99.5%), HBB (TCI, >98.0%), tris-2-aminoethylamine (TCI, 99%), acetic acid (Kanto, Tokyo, Japan, 99.50%), acetone (Kanto, >99.0%), dichloromethane (Kanto, >99.0%), ethyl acetate (Kanto, >99.3%), hexane (Kanto, >95.0%), magnesium sulfate (Kanto, 95%), methanol (MeOH, Kanto, 99.50%), nitric acid 1.38 (conc. HNO$_3$, Kanto, 60–61%), potassium hydroxide (KOH, Kanto, 85.50%), sodium hydroxide (NaOH, Kanto, >95.0%), toluene (Kanto, >99.0%), copper bromide (I) (CuBr, Wako, Osaka, Japan, 95%), dimethyl sulfoxide (DMSO, Kanto, Tokyo, Japan, >98.0%), 1-methyl-2-pyrrolidone (NMP, TCI, >99.0%), 18-crown-6 (Sigma-Aldrich, St Louis, MO, USA, 99%), chloroform-D1 with TMS 1 vol% (CDCl$_3$, Merck, Darmstadt, Germany, >99.5% D), methyl sulfoxide-d6 for NMR (d-DMSO, Acros organic, Geel, Belgium, 0.03% TMS, 99.9 atom% D) and (trimethylsilyl)diazomethane solution (2.0 M in diethyl ether, Sigma-Aldrich) were used as received. Linear PAA, which was synthesized via free radical polymerization, was used as a reference for the analyses. Linear PMA was synthesized through methyl esterification of linear PAA with a (trimethylsilyl)diazomethane solution ($M_w = 1.97 \times 10^5$, polydispersity index (PDI) = 4.95).

Synthesis of 3-arm and 6-arm PMAs
The conditions and results of the reactions are listed in Tables 1,2,3. The representative formulation of 6-arm-1 is as follows: MA (2 ml, 2.22 mmol), 2-propanol (0.25 ml), Me$_6$TREN (0.024 ml, 89.7 μmol) and HBB (9.5 mg, 14.9 μmol) were loaded in a vessel purged with nitrogen. CuBr (12.8 mg, 89.7 μmol) was added and the vessel was closed immediately. Polymerization was performed for 2.5 h at 52 °C with a shaker (TAITEC, Personal H-10) at 60 r.p.m. To stop the polymerization reaction, a drop of acetic acid was added to the solution, and the mixture was mixed well. The polymer was precipitated with methanol and dried under reduced pressure at room temperature. In the case of 3-arm-poly(methyl acrylate), BTB was used as an initiator instead of HBB.

6-arm-1: Yield: 15.3 wt%, M_w: 9.6×10^4, PDI: 1.54. ^{1}H-NMR: δ = 1.50–1.93 (2H, –CH$_2$–), 1.76–2.03 (1H, –CHCO–), 3.56–3.72 (3H, –OCH$_3$), 4.00–4.20 (1H, –CHBrCO–), and 4.70 p.p.m. (2H, –CH$_2$-Br) (solvent: chloroform-D1). Arm number of 6-arm-1, 4.85, was determined by ^{1}H-NMR using the

Table 1 Synthesis of 3-arm and 6-arm poly(methyl acrylate)s

	MA (ml)	Initiator	Ligand	MC^a (mol ml^{-1})	[MA]:[EA]:[Br of initiator]:[CuBr]: [ligand]	Temp. (°C)	Time (h)	Yield (wt%)	M_w^b (10^4)	PDI^c	IE^d (mol%)	AN^e	DP^f/ arm	M_n^g /arm (10^3)	M_n^f (10^4)	Remark
3-arm-1	2	BTB	Me$_6$TREN	987	494:0:1:1:1	52	2	45.7	3.70	1.21	87.5	2.62	69.1	5.95	1.56	
6-arm-1	2	HBB	Me$_6$TREN	987	247:0:1:1:1	52	2.5	15.3	9.60	1.54	80.8	4.85	7.15	0.615	0.298	
6-arm-bpy	2	HBB	bpy	987	247:0:1:1:2	52	2.5	trace	2.21	3.38	31.5	1.89	13.3	1.14	0.216	
6-arm-h.t.	2	HBB	Me$_6$TREN	987	247:0:1:1:1	98	1	37.7	7.80	1.78	—					Gelled
6-arm-dil	1	HBB	Me$_6$TREN	493	371:342:1:1:1	52	2.5	9.95	3.99	1.32	92.2	5.5	36.9	3.17	1.75	

Abbreviations: AN, arm number; bpy, 2,2'-dipyridyl; BTB, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene; DP, degree of polymerization; EA, ethyl acetate; HBB, hexakisbromomethylbenzene; IE, initiator efficiency; MA, methyl acrylate; MC, monomer concentration; Me$_6$TREN, tris[2-(dimethylamino)ethyl]amine; M_n, number-average molecular weight; M_w, weight-average molecular weight; PDI, polydispersity index.
Under reduced pressure. 2-Propanol is used as the solvent.
^{a}2-Propanol was used as the solvent except for ethyl acetate.
$^b M_w$ determined by gel permeation chromatography GPC with polystyrene PS standards.
^{c}PDI (M_w/M_n) determined by GPC with PS standards.
^{d}IE determined by proton nuclear magnetic resonance (^{1}H ^{1}H-NMR).
^{e}AN determined by ^{1}H-NMR.
^{f}DP determined by ^{1}H-NMR.
$^g M_n$ determined by ^{1}H-NMR.

Table 2 Synthesis of 3-arm and 6-arm poly(methyl acrylate)s via ATRP with different initiation systems in the feed

	MA (ml)	Initiator	[MA]:[Br of initiator]:[CuBr]: [Me$_6$TREN]	Time (h)	Yield (wt%)	M_w^a (10^4)	PDI^b	IE^c (mol%)	AN^d	DP^e/ arm	M_n^f/arm (10^3)	M_n^f (10^4)
3-arm-1^g	2	BTB	494:1:1.00:1.00	2	45.7	3.70	1.21	87.5	2.62	69.2	5.95	1.56
3-arm-2	2	BTB	494:1:1.16:1.16	2.5	3.6	2.30	1.16	80.7	2.42	187	16.1	3.89
3-arm-3	2	BTB	494:1:1.33:1.33	2.5	21.9	7.04	1.41	97.6	2.93	72.2	6.21	1.82
3-arm-4	2	BTB	494:1:1.67:1.67	2.5	9.2	3.82	4.12	54.1	1.62	127	10.9	1.77
6-arm-1^g	2	HBB	247:1:1.00:1.00	2.5	15.3	9.60	1.54	80.8	4.85	7.15	0.615	0.298
6-arm-2	2	HBB	247:1:0.92:0.92	6	12.4	6.73	1.30	26.5	1.59	975	83.9	13.3
6-arm-3	2	HBB	247:1:1.16:1.16	2.5	2.3	4.88	1.67	96.1	5.76	87.7	7.55	4.35
6-arm-4	2	HBB	247:1:1.33:1.33	2.5	5.6	7.16	1.54	84.1	5.04	176	15.2	7.66
6-arm-5	2	HBB	247:1:1.50:1.50	2.5	25.9	2.71	1.54	100.0	6.00	104	8.92	5.35
6-arm-6	2	HBB	247:1:1.67:1.67	2.5	7.6	7.60	1.47	100.0	6.00	193	16.6	9.98
6-arm-7	2	HBB	247:1:2.00:2.00	2.5	4.7	4.36	1.54	71.1	4.27	113	9.72	4.15

Abbreviations: AN, arm number; ATRP, atom transfer radical polymerization; BTB, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene; DP, degree of polymerization; HBB, hexakisbromomethylbenzene; IE, initiator efficiency; MA, methyl acrylate; Me$_6$TREN, tris[2-(dimethylamino)ethyl]amine; M_n, number-average molecular weight; M_w, weight-average molecular weight; PDI, polydispersity index.
Under reduced pressure at 52 °C. 2-Propanol is used as the solvent. Monomer concentration was set to 98.7 mol l^{-1}.
$^a M_w$ determined by gel permeation chromatography (GPC) with polystyrene (PS) standards.
^{b}PDI (M_w/M_n) determined by GPC with PS standards.
^{c}IE determined by proton nuclear magnetic resonance (^{1}H-NMR).
^{d}AN determined by ^{1}H-NMR.
^{e}DP determined by ^{1}H-NMR.
$^f M_n$ determined by ^{1}H-NMR.
^{g}Original data are shown in Table 1.

integral ratio of the peaks from –CHBrCO and –CH$_2$-Br using Equation (1).

$$Arm\ number = \frac{(Area\ of\ -CHBrCO-)}{(Area\ of\ -CHBrCO-) + (Area\ of\ -CH_2Br) \times 2} \times (the\ number\ of\ reaction\ points) \quad (1)$$

DP/arm: 7.15, M_n/arm: 6.15×10^2 and M_n: 2.98×10^3 were also determined by ^{1}H-NMR using the integral ratio of the peaks from –CHBrCO, –CH$_2$-Br and –OCH$_3$.

Synthesis of 3-arm and 6-arm PAAs (3PAA and 6PAA)

Synthesis of 3-arm and 6-arm PAAs (3PAA and 6PAA, respectively) were conducted via hydrolysis with a base and a transesterification reaction. 3-arm-5 (10 g, 166.2 mmol of –COOCH$_3$) was completely dissolved in toluene (29.1 ml), and 15.9 M KOH aqueous (29.1 ml, KOH content 26.0 g, 463.4 mmol) was added dropwise to the solution with vigorous stirring. Hexane (15 ml) was gradually added, and the solution was stirred for 3 days. The pH of the solution was set to 3 with conc. HNO$_3$ (58.1 ml). 6-arm-13

(10 g, 166.2 mmol of -COOCH$_3$) was completely dissolved in toluene (41.5 ml), and 11.2 M KOH aqueous (41.5 ml, KOH content 26.1 g, 465.2 mmol) was added dropwise to the solution with vigorous stirring. Hexane (15 ml) was gradually added, and the solution was stirred for 3 days. The pH of the solution was set to 3 with conc. HNO$_3$ (29.0 ml). To remove the salt, the solution was dialyzed for 5 days at 25 °C against 20 l of distilled water using a cellulose tube (EIDIA, Tokyo, Japan, UC-36-32-100, pore size 50 Å) until the electroconductivity of the matrix water reached 0.06 mS cm^{-1}. The polymer solution was concentrated using an evaporator (EYELA, Tokyo, Japan, NN-1100) and dried under vacuum at 40 °C. 3PAA-1: Yield: 46.9 wt%, degree of hydrolysis: 72.1 mol%. 6-PAA1: Yield: 63.8 wt%, degree of hydrolysis: 71.9 mol% ^{1}H-NMR: δ = 1.30–2.22 (2H, –CH$_2$–), (1H, –CHCO–), 3.56–3.72 (3H, –OCH$_3$), and 12.2 ppm (1H, –COOH) (solvent: d-DMSO).

Characterizations

The molecular weight and the molecular weight distribution of the products were assessed by gel permeation chromatography using tetrahydrofuran as an eluent. Gel permeation chromatography measurements of the polymers were performed using high-performance liquid chromatography (Hitachi, Tokyo,

Table 3 Synthesis of 6-arm poly(methyl acrylate)s with different molar ratios of CuBr and Me$_6$TREN

	MA (ml)	[MA]: [Br of initiator]: [CuBr]:[Me$_6$TREN][a]	Time (h)	Yield (wt%)	M_w[b] (10^4)	PDI[c]	IE[d] (mol%)	AN[e]	DP[f] /arm	M_n[g] /arm (10^3)	M_n[g] (10^4)
6-arm-1[h]	2	247:1:1.00:1.00	2.5	15.3	9.60	1.54	80.8	4.85	7	0.615	0.298
6-arm-3[i]	2	247:1:1.17:1.17	2.5	2.3	4.88	1.67	96.1	5.76	88	7.55	4.35
6-arm-5[i]	2	247:1:1.50:1.50	2.5	25.9	2.71	1.54	100.0	6.00	193	16.6	9.98
6-arm-8	2	247:1:2.00:2.00	2.5	4.7	4.36	1.54	71.1	4.27	113	9.72	4.15
6-arm-9	2	247:1:1.50:1.17	2.5	8.6	7.11	1.77	80.8	4.85	242	20.9	10.11
6-arm-10	2	247:1:2.00:1.17	2.5	4.1	5.96	1.89	41.9	2.51	536	46.1	11.59
6-arm-11	2	247:1:1.17:1.50	2.5	11.7	6.82	1.59	96.5	5.79	68	5.85	3.39
6-arm-12	2	247:1:1.17:2.00	2.5	5.7	2.87	1.42	100.0	6.00	456	39.2	23.5
3-arm-5	20	444:1:1.17:2.00	2	53.4	3.86	1.25	100	3.00	281	24.1	7.25
6-arm-13	100	372:1:1.09:1.63	6	42.9	15.7	1.33	100	6.00	610	52.5	31.5

Abbreviations: AN, arm number; DP, degree of polymerization; IE, initiator efficiency; MA, methyl acrylate; Me$_6$TREN, tris[2-(dimethylamino)ethyl]amine; M_n, number-average molecular weight; M_w, weight-average molecular weight; PDI, polydispersity index.
Under reduced pressure at 52 °C. 2-Propanol is used as the solvent. Monomer concentration was set to 98.7 mol l^{-1}.
[a]Hexakisbromomethylbenzene was used as the initiator except for 3arm-5. 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene was used as the initiator of 3-arm-5.
[b]M_w determined by gel permeation chromatography (GPC) with polystyrene (PS) standards.
[c]PDI (M_w/M_n) determined by GPC with PS standards.
[d]IE determined by proton nuclear magnetic resonance (^{1}H-NMR).
[e]AN determined by ^{1}H-NMR.
[f]DP determined by ^{1}H-NMR.
[g]M_n determined by ^{1}H-NMR.
[h]Original data are shown in Table 1.
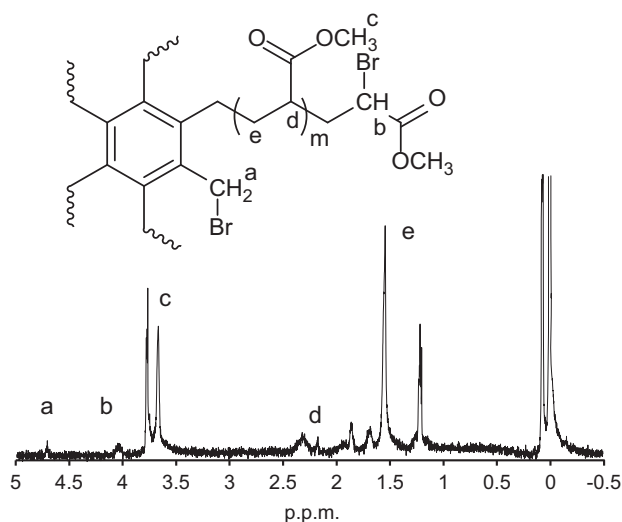[i]Original data are shown in Table 2.

Figure 1 Proton nuclear magnetic resonance (^{1}H-NMR) spectra of 6-arm-1 (solvent (sol): d-DMSO). d-DMSO, methyl sulfoxide-d6 for NMR.

Japan, column oven: CO8020, pump: L-7100, degasser: JASCO, Tokyo, Japan, DG2080-53, column: TSK gel G5000HHR) equipped with double detectors (refractive index detector: L-2490, UV detector: TOSOH UV-8011 at 256 nm). The flow rate was fixed at 1.0 ml min^{-1}. The molecular weights were determined with polystyrene standards.

^{1}H-NMR measurements were carried out using a ^{1}H-NMR spectrometer (JEOL, Tokyo, Japan, GLX-400, 400 MHz) at room temperature. CDCl$_3$ and d-DMSO were used as solvents. Typically, 32 scans were averaged per spectrum.

Attenuated total reflection Fourier transform-infrared spectroscopy (ATR FT-IR) was conducted using an FTIR spectrometer (FT-IR 4100, Jasco) equipped with an attenuated total reflection (ATR PRO450-S, Jasco) detector. A ZnSe prism (Jasco) was used to collect the spectral data. The wavenumber resolution was 2 cm^{-1} and 80 scans were accumulated for each spectrum.

DLS was performed using a DLS-8000PNA (Otsuka Electronics, Osaka, Japan, control unit: LS-81, pump controller: LS-82) at an angle of 90 ° at 25 °C. The wavelength of the laser was 632.8 nm. Water, DMSO and NMP were used as solvents. The polymer concentration was set to ca. 3 wt%. Before the

measurements, the solutions were ultrasonicated with an ultrasonic cleaner (AS-ONE, Vs-F100) at 50 kHz for 10 min at 25 °C. Typically, 100 scans were accumulated for each spectrum. The nonnegative least squares method was used for analysis.

TGA was performed using a TGA-50 (Shimadzu, Kyoto, Japan) instrument. Approximately 10 mg of the polymer was placed in a platinum pan and heated under a flow of nitrogen (20 ml min^{-1}). The thermal program was set as follows: the polymers were heated at 20 °C per min from room temperature to 120 °C and held for 1.5 h. After cooling at 20 °C per min and bringing the temperature down to 80 °C, the samples were reheated at a rate of 10 °C per min to 800 °C.

RESULTS AND DISCUSSION

To synthesize the star PMAs with 3 and 6 arms, MA was polymerized with BTB and HBB via ATRP, respectively. The conditions and results are listed in Tables 1–3.

The M_w and PDI of 6-arm-1, which were determined by gel permeation chromatography with polystyrene standards, were 9.60×10^4 and 1.54, respectively. A single peak was detected for all the polymers. This result indicated that the polymerization proceeded homogeneously.

The arm number of the product was determined by ^{1}H-NMR. Figure 1 shows the ^{1}H-NMR spectra of 6-arm-1. The –CH_2– and –CH– peaks were observed in a range from 1.00 to 2.50 p.p.m. The CH group next to the Br group (B) of the polymerized sequence was observed at 4.00 and 4.25 p.p.m., whereas the –CH_2– group next to the Br of HBB (A) was observed at 4.70 p.p.m. Taking account of the areas of peaks A and B, the initiation efficiency of the Br group was determined to be 80.8%; that is, the arm number of 6-arm-1 was 4.85 ($= 6 \times 0.808$). The arm numbers of the other polymers were also analyzed and are listed in Tables 1,2,3.

First, the types of the initiator, ligand, polymerization temperature and monomer concentration were studied as factors that determined initiation efficiencies. The conditions and results are listed in Table 1. For the reaction to initiate quantitatively, the propagation rate should be slower than the initiation rate. To obtain a polymer with a quantitative arm number, the Br groups of the initiator should be attacked by the catalyst and the ligand. Propagated MA chains tend to
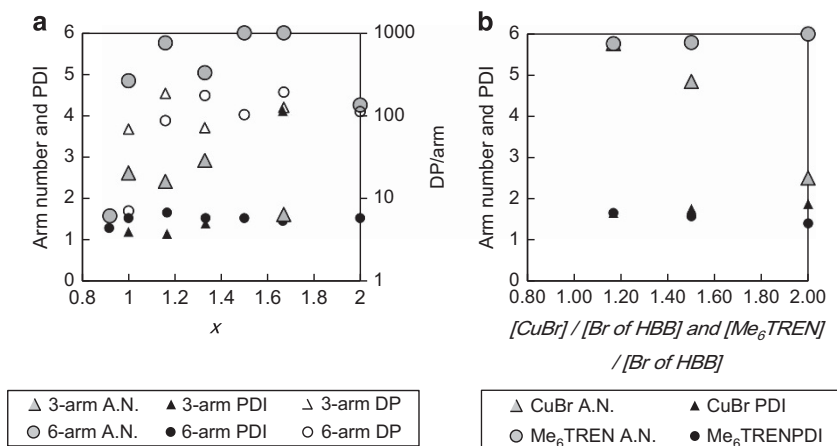
Figure 2 Arm numbers and polydispersity index (PDI) plots of 3-arm and 6-arm poly(methyl acrylate)s (PMAs) containing DP/arm plots against x ($x=$ [CuBr]/ [Br of initiator]$=$[Me$_6$TREN]/[Br of initiator]) (**a**). Arm number and PDI plot of 6-arm PMA against [CuBr]/[Br of initiator] and [Me$_6$TREN]/[Br of initiator] ([CuBr]/[Br of initiator]$\neq$[Me$_6$TREN]/[Br of initiator]) (**b**). DP, degree of polymerization; Me$_6$TREN, tris[2-(dimethylamino) ethyl]amine.

Table 4 Synthesis of 3-arm and 6-arm PAAs

	PMA		Toluene	KOH	Water	HNO$_3$	Yield	Degree of hydrolysis[a]
	Type	(g)	(ml)	(g)	(ml)	(ml)	(wt%)	(mol%)
3PAA-1	3-arm-5	10.0	29.1	26.0	29.1	58.1	46.9	72.1
6PAA-1	6-arm-13	10.0	41.5	26.1	41.5	29.0	63.8	71.9

Abbreviations: PAA, poly(acrylic acid); PMA, poly(methyl acrylate).
[a]Determined by proton nuclear magnetic resonance (^{1}H-NMR).

prohibit the initiation of the Br groups of the initiator. Higher initiation rates compared with propagation rates were expected because of the use of a ligand with a low reactivity, high polymerization temperature and low monomer concentration.[23,24] Polymers were obtained under all the reaction conditions. To determine the arm numbers by NMR with peaks derived from the end groups, the polymerization reactions were stopped in the early stages. In the case of the 6-arm series, the colors of reaction solutions changed from purple to green after 1 h, indicating initiation of the polymerization reaction, whereas the reacting solution of the 3-arm series remained green from the initiation stage. HBB took a longer time to initiate. The initiation efficiency of 6-arm-1 (80.8%) was lower than that of 3-arm-1 (87.5%). This difference can be explained from the viewpoint of a steric effect. The more crowded Br group of HBB compared with BTB caused low initiation efficiencies. Queffele introduced a spacer between the Br group and the benzene ring for ATRP.[22] The high initiation efficiency of this work indicates that HBB worked as an ATRP initiator without a spacer between the benzene Br groups for increasing its initiation efficiency.

In the case of 6-arm-bpy, a low yield of the polymer with a wide PDI and low arm number was obtained. Bpy was not suitable for synthesizing 3-arm and 6-arm polymers. Bpy with low molecular weight was expected to provide smooth initiation. However, the low activity of bpy reduced both the propagation and initiation rates.[25] The generation of long arms could not be confirmed for 6-arm-bpy from ^{1}H-NMR analysis. It was impossible to improve the initiation efficiency by increasing the reaction time.

Next, the effect of changing the reaction temperature was investigated. The polymerization reaction was completed and a gel was

formed after 1 h at 98 °C, whereas the reaction took more than 2.5 h at 52 °C; this effect was because of the propagation rate being accelerated at 98 °C. These observations indicate that as the propagation rate was increased, the cyclization of the arms occurred. Abraham et al.[26] reported cyclization of arms by radical transfer of active functional groups during the late stages of polymerization reactions. A fast initiation rate was expected at 98 °C; however, the propagation rate was also accelerated. It was difficult to synthesize the 6-arm polymer at 98 °C. It was impossible to determine the initiation efficiency because of gelation of the final product.

The effects of changing monomer concentrations were also investigated. We expected quantitative arm numbers by decreasing the propagation rate, the result of a decrease in monomer concentration. The monomer concentration of 6-arm-dil was half of that of 6-arm-1. To avoid a change in the initiation rate, ethyl acetate, which has a similar chemical structure to MA, was chosen as the solvent. The initiation efficiency was improved from 80.8 mol% (6-arm-1) to 92.2 mol% (6-arm-dil) by diluting the monomer.

Next, the feed ratio of CuBr and Me$_6$TREN to the Br groups was examined to improve initiation efficiencies. The feed of ATRP was determined with consideration of the coordination number and reactivity of the materials. In the case of the combination of R-Br, CuBr and Me$_6$TREN, ATRP is often conducted with equimolar amounts of these reagents. However, the Br groups of BTB and HBB are less reactive than common initiators, such as 2-bromopropionate, not only because of the structure of benzyl bromide but also because of steric hindrance. To quantitatively obtain 3-arm and 6-arm polymers with BTB and HBB via ATRP, [CuBr] and [Me$_6$TREN] are required to exceed [Br of the initiator]. Therefore, the ATRP reaction was conducted in the feeds. The conditions and results are listed in Table 2. To increase the possibility of collision between the Br groups, catalyst and ligand, the molar ratio of CuBr and Me$_6$TREN to the Br groups was set from 1.17 to 2.00. To simplify the reaction conditions, an equimolar amount of Me$_6$TREN to CuBr was loaded. The arm number and PDI are plotted against the feed in Figure 2a. Here, the molar ratios of CuBr and Me$_6$TREN to the Br groups are defined as x. In both cases for the 3-arm and 6-arm polymers, the arm numbers increased with increases in x and reached quantitative values when x exceeded 1.33. The arm numbers were 2.93 and 6.00 for BTB at $x=1.33$ and HBB at $x=1.50$, respectively. The excess feed of CuBr and Me$_6$TREN was found to greatly improve the arm numbers. The
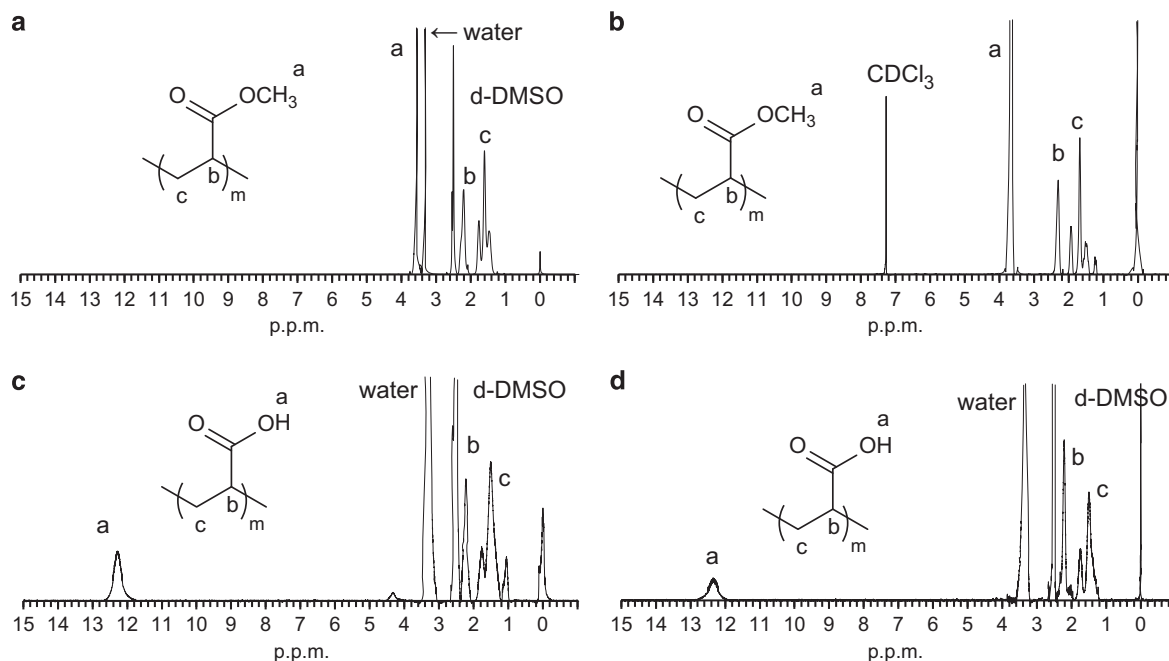
Figure 3 Proton nuclear magnetic resonance (^{1}H-NMR) spectra of 3-arm-5 (**a**), 6-arm-13 (**b**), 3PAA-1 (**c**) and 6PAA-1 (**d**). d-DMSO (**a**, **b**, **d**) and CDCl$_3$ (**c**) were used as solvents. d-DMSO, methyl sulfoxide-d6 for NMR; PAA, poly(acrylic acid).

Table 5 Solubility of the polymers

	Water	DMSO	NMP
3-arm-5	−	+ +	+ +
6-arm-13	−	+ +	+ +
3PAA-1	+ + +	+ +	+
6PAA-1	+ + +	+ +	+

Abbreviations: DMSO, dimethyl sulfoxide; NMP, nitroxide-mediated polymerization; PAA, poly (acrylic acid).
The symbols are explained as follows: + + +, freely soluble; + +, soluble by ultrasonication; +, partially soluble; −, insoluble.

3-arm series reached quantitative arm numbers at x values lower than those for the 6-arm series. However, too much feed of CuBr and Me$_6$TREN reduced the arm numbers and increased PDIs. These results indicate that the range of x for the 6-arm series is wider than that of the 3-arm series. The wide range of HBB can be explained through steric effects. It was more difficult for CuBr and Me$_6$TREN to attack to HBB than BTB. The high local density of Br in HBB reduced its reactivity. Because of the low reactivity of HBB, the excess molar ratio of CuBr and Me$_6$TREN to Br did not affect the arm number. To generate a homogeneous product and increase the possibility of collision between Br, CuBr and Me$_6$TREN, HBB required a larger amount of CuBr and Me$_6$TREN than BTB.

We also investigated the arm numbers of 6-arm at $x = 0.92$. The arm number was only 1.59 even though the reaction time was 6 h. The long reaction time did not affect the arm number. This observation was reasonable because the propagation had a higher priority than initiation. The Br of chain end was more reactive than the Br of HBB. Therefore, the polymerization reaction proceeded similarly the linear polymer.

Next, the DP/arm is discussed. Figure 2a shows the DP/arm plot against the amount of feed. The feed ratio of [CuBr] and [Me$_6$TREN] to [Br of initiator], x, was the main factor that influenced DP/arm

because the polymerization time remained constant. The DP/arm values of the 3-arm and 6-arm polymers ranged from 70 to 200, except for 6-arm-1 that had a value of 7.15 ($x = 1$). According to Equation (2) reported by Matyjaszewski et al.,[27] the molar ratio of the initiator/copper (II) halide complex ([In]/[Cu(II)X]) influenced the propagation rate.

$$R_p = k_{app}[\text{M}] = k_p[\text{P}^\bullet][\text{M}] = k_p K_{eq}[\text{In}]\frac{[Cu(\text{I})]}{[Cu(\text{II})X]}[\text{M}] \quad (2)$$

In this equation, R_p: propagation rate, k_{app}: rate coefficient appearance, [M]: monomer concentration, kp: rate coefficient of propagation, [P$^\bullet$]: polymer concentration, k_{eq}: equilibrium constant, [In]: initiator concentration, [Cu(I): concentration of active copper (I) catalyst and [Cu(II)X]: concentration of copper (II) halide complex. In this work, the DP/arm will be proportional to R_p because x is inversely proportional to [In]/[Cu(II)X]. Therefore, the value of DP/arm decreased with an increase in x. However, DP/arm remained almost constant (Figure 2a). Theoretically, excess [CuBr] and [Me$_6$TREN] to [Br of initiator] prevents propagation of the reaction. The constant of DP/arm indicated that the excess feed ratio of [CuBr] and [Me$_6$TREN] to [Br of the initiator] did not influence the polymerization process in this work. This result was because of the low reactivity of Br in the initiators and demonstrates that a slight excess of [CuBr] and [Me$_6$TREN] to [Br of the initiator] is required. It was found that a slight excess of [CuBr] and [Me$_6$TREN] to [Br of the initiator] was effective in activating the initiation site without disturbing the propagation step.

The molar ratios of CuBr and Me$_6$TREN against Br were changed independently. The conditions and results are listed in Table 3. The arm number and PDI plots against the feed are shown in Figure 2b. First, only [CuBr] was changed. The molar ratio of CuBr to the Br groups is defined as y, and the molar ratio of Me$_6$TREN to the Br groups was set to 1.17. Consequently, the arm number drastically decreased from 5.76 to 2.51, and the PDI broadened from 1.67 to 1.89 with an increase in CuBr.
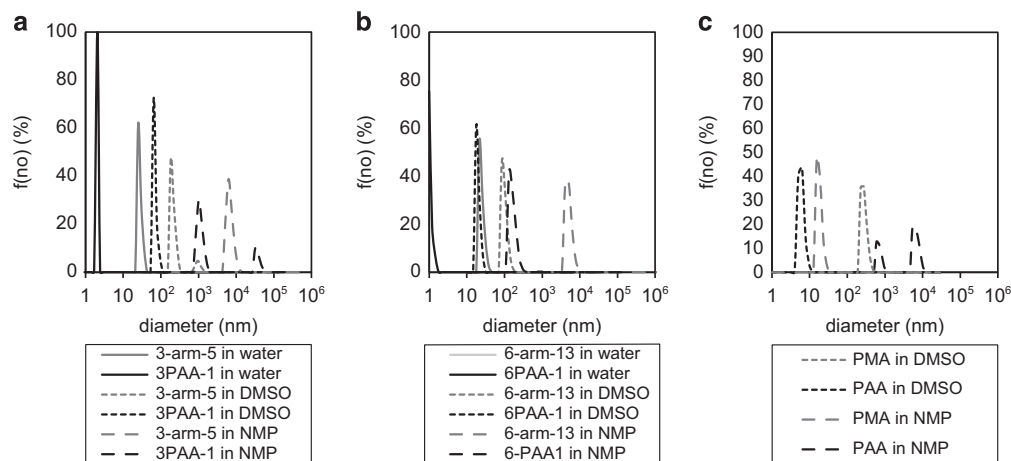
Figure 4 Dynamic light scattering (DLS) curves of the polymers 3-arm-5, 3PAA-1 (**a**) 6-arm-13, 6PAA-1 (**b**) PMA and PAA (**c**) in water, DMSO and NMP. DMSO, dimethyl sulfoxide; NMP, nitroxide-mediated polymerization; PAA, poly(acrylic acid); PMA, poly(methyl acrylate).
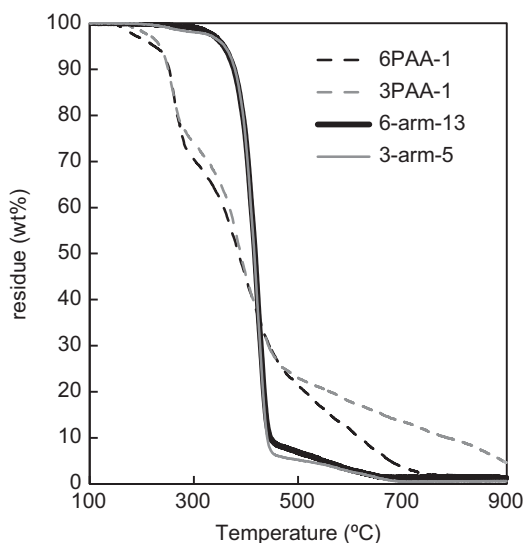

Figure 5 Thermogravimetric analysis (TGA) curves of 6PAA-1, 3PAA-1, 6-arm-13 and 3-arm-5. PAA, poly(acrylic acid).

Next, only the [Me$_6$TREN] was changed. The molar ratio of Me$_6$TREN to the Br groups was defined as z, and the molar ratio of CuBr to Br groups was set to 1.17. In contrast, the arm numbers were kept constant. In addition, the PDI decreased from 1.67 to 1.42. The excess CuBr disturbed the ATRP reaction. It was found that Me$_6$TREN was the main cause of the steric effect. The steric effect of Me$_6$TREN was overcome by increasing the Me$_6$TREN molar ratio to HBB rather than altering the molar ratio of CuBr. Consequently, the steric effect needed to be resolved to obtain quantitative arm numbers with BTB and HBB. To increase the possibility of collision between the Br groups of HBB, CuBr and Me$_6$TREN, a slight excess of [CuBr] and [Me$_6$TREN] compared with [Br of the initiators] was required. Especially, an excess [Me$_6$TREN] improved the arm numbers.

To obtain 3-arm and 6-arm PAAs, hydrolysis reactions were carried out. The conditions and results are listed in Table 4. The polymers dissolved in toluene formed emulsion droplets in aqueous KOH. The reaction solvent became clear because the hydrolyzed polymers transferred from toluene to the water phase. The hydrolysis reactions were also conducted under other conditions. Basic hydrolyses were conducted in aqueous, mixture of methanol and water and in the

presence of a phase transfer catalyst, 18-crown-6. Acid hydrolysis of 6-arm poly(*tert*-butyl acrylate) was conducted following a published procedure.[28,29] However, the degree of hydrolysis obtained under these conditions was very low. The degree of hydrolysis using the first method was the highest of all the tested conditions. The degrees of hydrolysis of the reactions were measured by ATR FT-IR and ^{1}H-NMR. ATR FT-IR spectra of 3PAA-1 and 6PAA-1 indicated that the polymers were partially hydrolyzed. A broad peak at 3300 cm^{-1} that represented -OH stretching and hydrogen bonds appeared and a strong peak at 2960 cm^{-1} that indicated -CH$_3$ vibrations vanished.

Figure 3 shows the ^{1}H-NMR spectra of 3-arm and 6-arm polymers. Before hydrolysis, -CH$_3$ peaks were observed at 3.45 p.p.m. After hydrolysis, –COOH peaks appeared at 12.5 p.p.m. It was impossible to determine the degree of hydrolysis through the reduction of the methyl peaks that overlapped with the larger water peaks. Therefore, the degree of hydrolysis was determined from the area ratio of the backbone to the –COOH peaks. The maximum degrees of hydrolysis were 72.1 and 71.9 mol% for 3PAA-1 and 6PAA-1, respectively, indicating that the hydrolysis reactions were not complete. The 3-arm PMA was slightly easier to be hydrolyzed. In general, PMA was completely hydrolyzed under these reaction conditions.[30] The 3-arm and 6-arm PMAs were hardly hydrolyzed compared with conventional linear PMA. This observation can be explained with the steric effect. The OH$^-$ anions could not attack the inner polymers because the polymer structure was too dense. The hydrolysis reaction proceeded only near the surface of the polymer. As the binder of LIB, these polymers were sufficiently hydrolyzed. No further hydrolysis would occur with OH$^-$ anions generated from LiOH that is weaker base than OH$^-$ anions that originated from KOH. Thus, it will be possible to use the polymers as 3-arm and 6-arm PAAs for LIB materials.

To investigate the solubility of the PAA star polymers, 1 g l^{-1} polymer solutions were prepared. Water, NMP and DMSO were used as solvents. The results of this experiment are listed in Table 5. The solubility of the 3-arm and 6-arm polymers in water was drastically changed by hydrolysis. 3PAA-1 and 6PAA-1 were freely dissolved in water, whereas 3-arm-5 and 6-arm-13 were insoluble in water. These observations also confirm successful hydrolysis reactions. Again, the degrees of hydrolysis were 72.1 and 71.9 mol% for 3PAA-1 and 6PAA-1, respectively. The gradient hydrolysis reaction from the surface to the insides of molecules resulted in good water solubility. All the polymers dissolved well in DMSO. This result is reasonable

because DMSO is a good solvent for both PAA and PMA. 3PAA-1 and 6PAA-1 could partially dissolve in NMP, whereas 3-arm-5 and 6-arm-13 could fully dissolve. The low solubility of the PAA star polymers in NMP demonstrated that the hydrophilicity of PAA was too strong. This result is interesting because NMP is a good solvent for linear PAA and linear PMA.

Next, DLS measurements were carried out for the solutions used for the solubility tests. The solvents used were water, DMSO and NMP. The DLS curves are shown in Figure 4. In all the solvents, the hydrodynamic diameters (D_hs) of the 3-arm and 6-arm polymers decreased as a result of hydrolysis. In particular, the D_hs in water of 3-arm-5 (27.6 nm) and 6-arm-13 (24.7 nm) shifted to 2.2 and 1.1 nm, respectively, because of hydrolysis. Both 3-arm-5 and 6-arm-13 were found to aggregate in water, and both 3PAA-1 and 6PAA-1 were dispersed as single molecules. The D_hs of the 3-arm and 6-arm polymers changed in DMSO and NMP, whereas DMSO and NMP were shown to be good solvents for PMA and PAA. In DMSO, the D_hs of 3-arm-5 (208.7 nm) and 6-arm-13 (108.1 nm) drastically decreased to 69.3 and 19.7 nm by hydrolysis, respectively. In NMP, the D_hs of 3-arm-5 (6852.4 nm) and 6-arm-13 (164.5 nm) shifted to 1117.4 and 164.5 nm by hydrolysis, respectively. The DLS data indicated that linear PMA and PAA with large molecular weights had the largest D_h areas in DMSO and NMP. DMSO and NMP were good solvents for PAA and PMA. This result indicated that the aggregation of the 3-arm and 6-arm PMAs and PAAs in DMSO and NMP was not because of their molecular architectures but their large molecular weights.

TGA was carried out for the polymers, and Figure 5 shows the TGA curves. The curves of the hydrolyzed products were clearly different from those of the PMA star polymers. Both 3PAA-1 and 6PAA-1 decomposed in 4 steps at 150, 250, 350 and 450 °C, whereas PMA star polymers started to decompose at 300 °C in a single step. The curves of the PMA star polymers were in good agreement with linear PMA.[31] Decomposition of the PMA star polymers at 300–450 °C was because of random scission of the main chains. The curves of 3PAA-1 and 6PAA-1 were also in good agreement with that of linear PAA.[32,33] In the cases of 3PAA-1 and 6PAA-1, water was lost at 100 °C. Decomposition of these polymers at 250–300 °C revealed the formation of a PAA anhydride ring. Decomposition of the anhydride ring started at 350 °C. Formation of these anhydride rings indicated the presence of continuous COOH groups. The main chain started to decompose when the temperature exceeded 450 °C. Therefore, 3PAA-1 and 6PAA-1 cam be considered as PAAs.

CONCLUSIONS

The 3-arm and 6-arm PAAs were synthesized via ATRP of MA and subsequent hydrolysis of the 3-arm and 6-arm PMAs. BTB and HBB were used as initiators of the ATRP. It was difficult for all the Br groups to react because of steric hindrance; however, excess molar amounts of CuBr and Me$_6$TREN to Br of the initiators enabled initiation of all the Br groups by increasing the possibility of collision against the sterically hindered groups. Feed control improved the reactivity of the initiators with plural groups without spacers. Excess molar amounts of catalysts and ligands compared with initiating groups did not disturb the propagation steps. The denser initiation groups had lower reactivity with the catalysts and ligands. The feed amount of the ligand was a more important factor than the amount of CuBr in the formation of dormant species because of the large molecular sizes of the ligands and low reactivity of the Br groups. Adjusting the feed amount of Me$_6$TREN rather than that of CuBr was effective for obtaining high initiation efficiencies and low PDIs. By controlling the feed, star polymers with well-defined arm numbers

were synthesized via ATRP using initiators with dense initiation groups without spacers.

Hydrolysis reactions of the 3-arm and 6-arm PMAs were conducted to prepare 3-arm and 6-arm PAAs. However, the maximum degree of hydrolysis was ca. 70% that was caused by the dense inner molecules. A strong base or acid was essential for effective hydrolysis of the polymers. The PMAs were too dense to be hydrolyzed completely, and this was especially true for the inner molecules. The 3-arm and 6-arm PAAs had similar solubility in water and thermal decomposition into PAA. The polymers behaved like PAA, even though they were not completely hydrolyzed. This result was because of the full hydrolysis of the outer molecules. The properties of star polymers depended on their surfaces, in the case of polymers with highly dense inner molecules. These polymers can be considered as 3-arm and 6-arm PAAs with well-defined arm numbers.

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