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Synthesis of Core Cross-Linked Star Polymers Consisting of Well-Defined Aromatic Polyamide Arms

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ABSTRACT: Homopolymer-arm, block-arm, and miktoarm star polymers consisting of poly(*N*-octyl-*m*-benzamide) and poly(*N*-H-*m*-benzamide) were synthesized by means of a core cross-linking method. Macromonomers (MM) with the styryl terminal moiety were synthesized by chain-growth condensation polymerization of 3-(alkylamino)benzoic acid esters **1** in the presence of phenyl 4-vinylbenzoate as an initiator, and copolymerization with *N*,*N*′-methylenebis(acrylamide) as a divinyl monomer in the presence of 2,2′-azobis(isobutyronitrile) at 60 °C yielded the corresponding star polymers. In the synthesis of star polymers containing poly(*N*-H-*m*-benzamide) arms, the 4-(octyloxy)benzyl group on the amide nitrogen of the obtained star polymers was removed with trifluoroacetic acid. The number of arms per molecule, determined by multiangle laser light scattering, varied in the range of 36−100 depending on the *N*-alkyl group of **1** and the molecular weight of MM. The ^{1}H NMR spectra of the star polymers in dimethyl sulfoxide revealed that the poly(*N*-octyl-*m*-benzamide) segments and arms of the block-arm and miktoarm star polymers, respectively, were compactly packed at room temperature and became extended at higher temperatures.

Introduction

Star polymers, consisting of many arms connecting to a central core, are representive of branched nanoscale materials with compact structure, globular shape, and large surface area.[1] Among a variety of synthetic approaches to star polymers, living polymerization is the most appropriate for controlled synthesis, and it can be divided into three categories: (1) living polymerization with a multifunctional initiator, (2) coupling reaction of linear living polymers with a multifunctional coupling agent, and (3) copolymerization of linear living polymers with a divinyl compound. The first and second methods can yield star polymers with a defined number of arms. In contrast, the third method is characterized by the presence of a cross-linked microgel core bearing a large, statistically distributed number (usually > 10) of arms per polymer molecule. These methods have been successfully employed in various living polymerizations, including anionic,[1,2] cationic,[3] radical polymerization,[4] and ring-opening processes.[5] However, polycondensation has not been applicable to the synthesis of well-defined star-shaped polymers because it did not proceed in a chain polymerization manner. Star-shaped condensation polymers have been prepared by copolycondensation of a star-center molecule with an AB-type monomer or with A_2 and B_2 monomers,[6] but the arm length of the polymers obtained is not controlled. Well-defined star-shaped condensation oligomers have been synthesized by the coupling reaction between a star-center molecule and monodisperse linear oligomers prepared by means of a sequential condensation procedure.[7]

We have developed chain-growth condensation polymerization, a kind of living polymerization system in the category of condensation polymerization, to provide condensation polymers with controlled molecular weight and low polydispersity.[8] In the synthesis of well-defined *N*-alkylated poly(*p*-benzamide)s, the amide anion of the monomer not only acts as a nucleophilic site but also deactivates the acyl group by virtue of the electron-donating effect, resulting in suppression of self-condensation of the monomer.[9] Recently, we also achieved control of molecular weight and polydispersity in the synthesis of poly(*m*-benzamide)s.[10] The obtained poly(*m*-benzamide)s, having alkyl and oligo(ethylene glycol) side chains on the nitrogen atom, showed higher solubility than the corresponding poly(*p*-benzamide)s.[11,12] Furthermore, we demonstrated that a sequential monomer addition method can afford well-defined block copolymers consisting of meta-substituted aromatic polyamides with different side chains and of meta- and para-substituted aromatic polyamides.[13] Taking advantage of this living polymerization nature, we have synthesized three-[14] and four-arm[15] star polyamides by using the first method mentioned above: polymerization with a multifunctional initiator. In the present study, we employed the third method to synthesize star polyamides with a large number of arms by means of radical copolymerization of well-defined styrene-terminated aromatic polyamide macromonomer (MM) and a divinyl compound (Scheme 1). A variety of MMs, including block copolymer types, were first synthesized by chain-growth condensation polymerization of monomer **1** with phenyl 4-vinylbenzoate **2** as an initiator. Octyl and 4-(octyloxy)benzyl (OOB) groups were chosen as the *N*-alkyl group of **1** because poly(*N*-octyl-*m*-benzamide) is hydrophobic and soluble in nonpolar solvents, and the OOB group can be removed with acid, leading to poly(*N*-H-*m*-benzamide), which is soluble in polar solvents. By cross-linking of these MMs with a divinyl compound, we synthesized homopolymer-type, block copolymer-type, and miktoarm star polymers, which have arms with different solubility and hydrogen-bonding ability. Furthermore, we found that the molecular geometry of block-arm and miktoarm star aromatic polyamides is thermosensitive, as in the case of star polymers composed of flexible coil polymers.[16]

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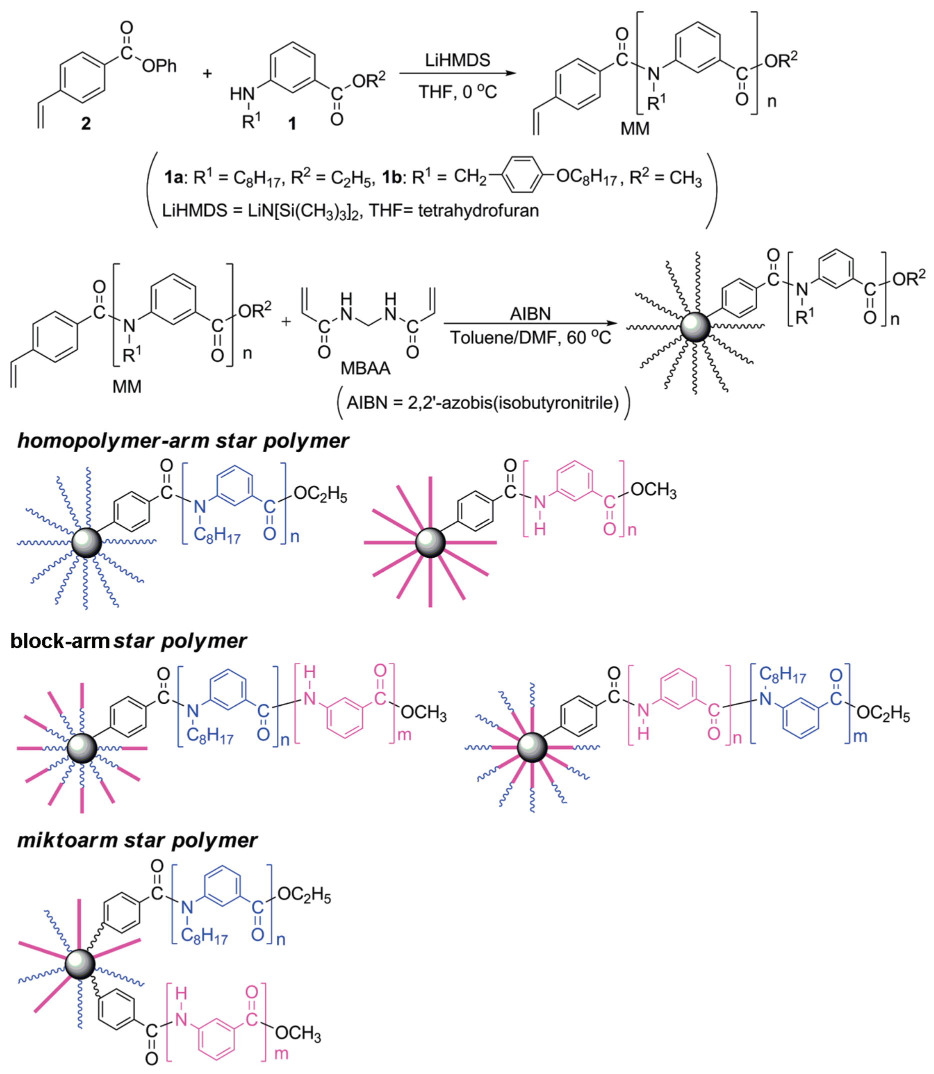
Scheme 1



Experimental Section

Measurements. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectra were obtained on JEOL ECA-600 instrument operating in the pulsed Fourier-transfer (FT) mode, using tetramethylsilane (0.00 ppm) and the midpoint of $CDCl_3$ (77.0 ppm) as internal standards for ^{1}H and ^{13}C NMR spectra, respectively. IR spectra were recorded on a JASCO FT/IR-410. The M_n and M_w/M_n values of polymers were measured with a Shodex GPC-101 gel permeation chromatography (GPC) unit (eluent: tetrahydrofuran (THF), calibration: polystyrene standards, wavelength: 256 nm) using two GPC KF-804 L columns (Shodex, exclusion limit (polystyrene): 4×10^5, particle size (μm): 7, size (mm) $\phi \times L$: 8.0×300, temperature (°C): 40, flow rate (mL/min): 1.0), and a TOSOH HLC-8220 GPC unit (eluent: solution of LiBr and phosphoric acid (20×10^{-3} M) in *N,N*-dimethylformamide (DMF), calibration: polystyrene standards, wavelength: 280 nm) using two Asahipak GF-310 HQ (Shodex, exclusion limit (pulluoan): 4×10^4, particle size (μm): 5, size (mm) $\phi \times L$: 7.5×300, temperature (°C): 40, flow rate (mL/min): 0.6) and Asahipak GF-510 HQ (Shodex, exclusion limit (pulluoan): 3×10^5, particle size (μm): 5, size (mm) $\phi \times L$: 7.5×300, temperature (°C): 40, flow rate (mL/min): 0.6). The absolute weight-average molecular weight (M_w) of the star polymers was determined by multiangle laser light scattering (MALLS) in DMF at 40 °C on a DAWN HELOES 8 instrument (Wyatt Technology, Ga–As laser, λ = 690 nm). The refractive index increment (d*n*/d*c*) was measured in DMF at 40 °C on Optilab DSP refractometer (Wyatt Technology, λ = 657 nm, *c* = 2.0 mg/mL). Isolation of polyamides was carried out with a Japan Analytical Industry LC-908 Recycling Preparative HPLC (eluent: chloroform, wavelength: 254 nm) using two TSK-gel G $2000H_{HR}$ (TOSOH, exclusion limit (polystyrene): 1×10^4, particle size (μm): 5, size (mm) $\phi \times L$: 7.8×300, room temperature, flow rate (mL/min): 7.0). The hydrodynamic radii of star polymers were measured with an ALV-6000 SLS/DLS compact goniometer (Langen). The incident beam was a He–Ne laser (λ = 632.8 nm) at 22 nW, and the scattering angle was fixed at 90°. Solutions were quickly filtered sequentially through two micropore Teflon filters (0.45 μm). A typical sampling time to obtain the time–intensity correlation function was 30 s.

Materials. Ethyl 3-(octylamino)benzoate (**1a**)[11] and methyl 3-[4-(octyloxy)benzylamino]benzoate (**1b**)[11] were prepared according to the previously established procedures. A solution of lithium 1,1,1,3,3,3-hexamethyldisilazide (Aldrich; 1.0 M solution in THF), dehydrated tetrahydrofuran (Kanto; dry THF), *N,N*′-methylenebis(acrylamide) (Aldrich), 2,2′-azobis(isobutyronitrile) (AIBN), and trifluoroacetic acid (TFA) were used as received, without purification.

Synthesis of 1,4-Divinylbenzene (DVB).[17] A mixture of terephthalaldehyde (0.264 g, 1.97 mmol), methyltriphenylphosphonium bromide (1.43 g, 4.01 mmol), and potassium carbonate (0.703 g, 5.09 mmol) in 1,4-dioxane (4 mL) and water (1 mL) was refluxed for 32 h. The mixture was then filtered, and the filtrate was evaporated. The residue was purified by column chromatography on silica gel (hexane) to give 0.112 g of DVB as a white solid (44%). IR (KBr) 3087 ($=CH_2$), 3006 ($=CH-$), 1908 ($-C_6H_4-$), 1819, 1629 ($-CH{=}CH_2$), 1558, 1509, 1400, 988, 906, 845 cm^{-1} ($-C_6H_4-$). ^{1}H NMR ($CDCl_3$): δ 7.37 (s, 4 H, $-C_6H_4-$), 6.70 (dd, J = 17.5 and 11.0 Hz, 2 H, $CH_2{=}CH-C_6H_4-$), 5.75 (d, J = 17.7 Hz, 2 H, $CH_2=$), 5.25 (d, J = 10.7 Hz, 2 H, $CH_2=$). ^{13}C NMR ($CDCl_3$): δ 137.1 ($CH_2=CH-C_6H_4-$), 136.4 ($-C_6H_4-$), 126.4 ($-C_6H_4-$), 113.7 ($CH_2=$).

Synthesis of Phenyl 4-Vinylbenzoate (2).[18] A mixture of 4-vinylbenzoic acid (5.01 g, 33.8 mmol), phenol (3.49 g, 37.1 mmol), and 4-(dimethylamino)pyridine (DMAP, 4.56 g, 37.4 mmol) in *N*,*N*-dimethylformamide (DMF, 30 mL) was stirred at 0 °C for 10 min. Into the flask was added *N*-ethyl-*N*′-(3-(dimethylamino)propyl)-carbodiimide hydrochloride (EDCI, 8.40 g, 37.4 mmol) with stirring at 0 °C. The reaction mixture was stirred at ambient temperature for 20 h, then poured into water, and extracted with ether. The combined organic layer was washed with 1 M HCl, saturated $NaHCO_3$, and saturated NaCl and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (hexane/CH_2Cl_2 = 1/1) to give 4.56 g of **2** as a white solid (53%); mp 90.8−91.2 °C (lit.[18a] 94.3−94.6 °C). IR (KBr): 2924 ($=CH_2$), 2854 ($=CH-$), 1734 ($-CO-O-$), 1647 ($-CH{=}CH_2$), 1617, 1507, 1078, 904 ($-C_6H_4-$), 689 ($-C_6H_5$), 504 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.16 (d, J = 8.5 Hz, 2 H, $-C_6H_4-$), 7.54 (d, J = 7.9 Hz, 2 H, $-C_6H_4-$), 7.43 (t, J = 7.9 Hz, 2 H, $-C({=}O)-OC_6H_5$), 7.27 (t, J = 7.6 Hz, 1 H, $-C({=}O)-OC_6H_5$), 7.22 (d, J = 8.6 Hz, 2 H, $-C({=}O)-OC_6H_5$), 6.78 (dd, J = 17.5 and 11.0 Hz, 1 H, $CH_2{=}CH-C_6H_4-$), 5.91 (d, J = 17.9 Hz, 1 H, $CH_2{=}CH-$), 5.41 (d, J = 11.0 Hz, 1 H, $CH_2{=}CH-$). ^{13}C NMR ($CDCl_3$): δ 164.9 ($-C({=}O)-OC_6H_5$), 151.0 ($-C({=}O)-OC_6H_5$), 142.6 ($CH_2{=}CH-C_6H_4-$), 135.9 ($CH_2{=}CH-$), 130.5 ($CH_2{=}CH-C_6H_4-$), 129.5 ($CH_2{=}CH-C_6H_4-$), 128.6 ($-C({=}O)-OC_6H_5$), 126.3 ($CH_2{=}CH-C_6H_4-$), 125.8 ($-C({=}O)-OC_6H_5$), 121.7 ($-C({=}O)-OC_6H_5$), 116.9 ($CH_2{=}CH-$).

Synthesis of MM. An example of the procedure for the synthesis of **MM1** is as follows. A flask, equipped with a three-way stopcock, was purged with argon and then charged with dry THF (7.2 mL) and 1.0 M LiHMDS in THF (8.0 mL, 8.0 mmol). The flask was cooled to 0 °C under an argon atmosphere with stirring for 10 min. Into the flask was added a solution of **2** (0.162 g, 0.721 mmol) in dry THF (3.6 mL) under a stream of dry nitrogen, followed by a solution of **1a** (2.00 g, 7.21 mmol) in dry THF (7.2 mL) dropwise over ca. 60 min with stirring at 0 °C under a stream of dry nitrogen. The mixture was stirred at 0 °C for 1 h, and then the reaction was quenched with saturated NH_4Cl and the whole was extracted with CH_2Cl_2. The organic layer was washed with H_2O and dried over anhydrous $MgSO_4$. Concentration in vacuo gave a crude product as a yellow viscous oil (M_n(GPC) = 2490, M_n(NMR) = 2720, M_w(MALLS) = 2170, M_w/M_n = 1.10), which was purified by preparative HPLC (eluent: chloroform) using polystyrene gel columns to give 1.62 g of **MM1a$_L$** as a slightly yellow solid (90%). IR (KBr): 2928 ($=CH_2$), 2854 ($=CH-$), 1703 ($-CO-O-$), 1609 ($-CO-N\langle$), 1478 ($-C_8H_{17}$), 1279, 1105, 750 cm^{-1} ($-C_6H_4-$). ^{1}H NMR ($CDCl_3$): δ 7.84 (d, J = 7.8 Hz, 1 H, $-C_6H_4-C({=}O)-OC_2H_5$), 7.76 (s, 1 H, $-C_6H_4-C({=}O)-OC_2H_5$), 7.19−6.54 (m, [4(n − 1) + 7] H, $CH_2{=}CH-C_6H_4-$ and $\rangle N-C_6H_4-C({=}O)-$), 5.71 (d, J = 17.4 Hz, 1 H, $CH_2{=}CH-$), 5.25 (d, J = 10.8 Hz, 1 H, $CH_2{=}CH-$), 4.36 (q, J = 7.2 Hz, 2 H, $-C({=}O)-OCH_2CH_3$), 3.99−3.34 (m, 2n H, $-C({=}O)-N(-CH_2-C_7H_{15})-$), 1.65−1.10 (m, [12$n$ + 3] H, $-C({=}O)-N(-CH_2-C_6H_{13}-CH_3)-$ and $-C({=}O)-OCH_2-CH_3$), 0.88 (t, J = 6.9 Hz, 3n H, $-C({=}O)-N(-C_7H_{15}-CH_3)-$).

An example of the procedure for the synthesis of block copolymer-type **MM2** is as follows. LiCl (1.88 g, 44.4 mmol) was placed in a round-bottomed flask, equipped with a three-way stopcock. The flask was purged with argon and then charged with dry THF (10.0 mL) and 1.0 M LiHMDS in THF (8.8 mL, 8.8 mmol). The flask was cooled to 0 °C under an argon atmosphere with stirring for 10 min. To the flask was added a solution of **2** (0.090 g, 0.40 mmol) in dry THF (2.0 mL) under a stream of dry nitrogen, followed by a solution of **1a** (1.11 g, 4.00 mmol) in dry THF (5.0 mL) dropwise over ca. 60 min with stirring at 0 °C under a stream of dry nitrogen. The mixture was stirred at 0 °C for 20 min, and then 0.2 mL of the solution was withdrawn and quenched with saturated NH_4Cl in order to measure the M_n value and M_w/M_n ratio of poly**1a** (M_n(GPC) = 3170, M_n(NMR) = 2720, M_w/M_n = 1.08). Right after the sampling, a solution of **1b** (1.48 g, 4.00 mmol) in dry THF (5.0 mL) was added dropwise over ca. 60 min to the reaction mixture, and stirring was continued at 0 °C for 20 min. The reaction was quenched with saturated NH_4Cl, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with H_2O and dried over anhydrous $MgSO_4$. Concentration in vacuo gave a crude product as a yellow viscous oil (M_n(GPC) = 6010, M_n(NMR) = 6110, M_w(MALLS) = 5420, M_w/M_n = 1.08), which was purified by preparative HPLC (eluent: chloroform) using polystyrene gel columns to give 2.07 g of **MM2** as a yellow viscous oil (88%). IR (KBr): 2926 ($=CH_2$), 2855 ($=CH-$), 1751 ($-CO-O-$), 1648 ($-CO-N\langle$), 1176, 806 ($-C_6H_4-$), 754 ($-C_6H_4-$), 703 cm^{-1} ($-C_6H_4-$). ^{1}H NMR ($CDCl_3$): δ 7.84 (d, J = 7.8 Hz, 1 H, $-C_6H_4-C({=}O)-OCH_3$), 7.76 (s, 1 H, $-C_6H_4-C({=}O)-O-CH_3$), 7.22−6.23 (m, [4n+8(m − 1)+11] H, $CH_2{=}CH-C_6H_4-$ and $\rangle N-C_6H_4-C({=}O)-$ and $-N(-CH_2-C_6H_4-OC_8H_{17})-$), 5.67 (d, J = 18.0 Hz, 1 H, $CH_2{=}CH-$), 5.21 (d, J = 10.8 Hz, 1 H, $CH_2{=}CH-$), 4.96−4.58 (m, 2 m H, $-C({=}O)-N(-CH_2-C_6H_4-OC_8H_{17})-$), 4.00−3.43 (m, [2$n$+2$m$+3] H, $-C({=}O)-N(-CH_2-C_6H_4-OCH_2-C_7H_{15})-$ and $-C({=}O)-OCH_3$), 1.79−1.70 (m, 2(n+m) H, $-C({=}O)-N(-CH_2-C_6H_4-OCH_2-CH_2-C_6H_{13})-$), 1.46−1.16 (m, 10($n$ + m) H, $-C({=}O)-N(-CH_2-C_6H_4-OC_2H_4-C_5H_{10}-CH_3)-$), 0.91−0.84 (m, 3($n$ + m) H, $-C({=}O)-N(-CH_2-C_6H_4-OC_7H_{14}-CH_3)-$).

Synthesis of Star Polymers Containing Poly(*N*-alkyl-*m*-benzamide). An example of the procedure for the synthesis of star**1** is as follows. Into a Teflon-sealed tube was added a solution of **MM1a$_L$** (M_n(NMR) = 2720, M_w(MALLS) = 2170, 0.105 g, 0.042 mmol) and *N*,*N*′-methylenebis(acrylamide) (MBAA, 0.0194 g, 0.126 mmol) in dry DMF (0.07 mL), followed by a solution of AIBN in dry toluene (0.10 mL, 0.003 mol L^{-1}; 1 mol % with respect to the vinyl group in **MM1a$_L$** and MBAA). The tube was sealed, degassed by means of three freeze−pump−thaw cycles, filled with argon, heated at 60 °C for 60 h, and cooled. A small amount of ethyl acetate was added to the tube, and the solution was poured into methanol with stirring. The precipitated polymer was collected and dried in vacuo to give 0.0897 g of star**1a$_L$** (72%).

Synthesis of Star Polymers Containing Poly(*N*-H-*m*-benzamide) by Deprotection. An example of the procedure for removal of the OOB group from star**1b** is as follows: TFA (2.0 mL) was added to a solution of star**1b** (0.0226 g, n = 10, M_w(MALLS) = 220 000, f = 53.8) in CH_2Cl_2 (2.0 mL). The solution was stirred at room temperature for 3 days and then concentrated in vacuo. The residue was again dissolved in a small amount of CH_2Cl_2, and the solution was poured into hexane with vigorous stirring. The precipitated polymer was collected and dried in vacuo to give 0.0073 g of the objective star polymer (95%).

Results and Discussion

Synthesis of MMs. Poly(*N*-octyl-*m*-benzamide) macromonomer (**MM1a**) and poly(*N*-OOB-*m*-benzamide) macromonomer (**MM1b**) were synthesized by the chain-growth condensation polymerization of ethyl 3-(octylamino)benzoate (**1a**) and methyl 3-[4-(octyloxy)benzylamino]benzoate (**1b**), respectively, in the presence of phenyl 4-vinylbenzoate (**2**) as an initiator and lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) as a base at 0 °C according to the reported procedure for the polymerization of **1a** and **1b** with phenyl 4-methylbenzoate as an initiator (Table 1).[11] The obtained MMs possessed low polydispersity as well as well-defined molecular weight based on the feed ratio of the monomer **1** to the initiator **2**. The ^{1}H NMR spectra of MMs showed that the terminal styryl moiety from **2** was attached to each polymer; self-polycondensation of **1**, without initiation reaction from **2**, did not take place. Furthermore, the styryl moiety of MMs was confirmed not to be polymerized under the conditions used for the polymerization of **1** with the base.

Block copolymer-type MM**2** was synthesized in a controlled fashion by the successive polymerization of **1a** and then **1b** in the presence of **2**, LiHMDS, and LiCl at 0 °C. MM**3** was also synthesized by polymerization in the reverse order (Scheme 2, Table 2).[13]

Synthesis of Homopolymer-Type Star Polymers with Poly(*N*-alkyl-*m*-benzamide) Arms. The radical copolymerization of MM**1a** and 1,4-divinylbenzene (DVB) as a divinyl compound was first carried out in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) at 60 °C. This polymerization afforded insoluble DVB homopolymer, implying that DVB was too reactive, compared to bulky MM**1a**, to afford the objective core cross-linked star polymer. Actually, the homopolymerization of MM**1a** under the same conditions afforded a polymer with the degree of polymerization of only 35. Styrene and DVB are much more reactive, although MM**1a** has the styryl moiety. *N*,*N*′-Methylenebis(acrylamide) (MBAA) was then used instead of DVB because MBAA is liable to copolymerize well with macromonomers having amide linkage.[19] We optimized the polymerization conditions, especially the feed ratio of MBAA to MM**1a**, in the radical copolymerization with AIBN at 60 °C and found that the copolymerization of MM**1a** with 3 equiv of MBAA in a mixed solvent of toluene and DMF ([MM**1a** + MBAA]/[toluene]/[DMF] = 100/55.3/44.7 (weight ratio)) proceeded homogeneously, and the conversion of MM**1a** and MBAA, calculated from the olefinic proton signals in the ^{1}H NMR spectrum, reached 100% in 60 h. The GPC elution curve of the main peak of the product was clearly shifted toward the high-molecular-weight region, indicating formation of star polymer via a polymer linking reaction (Figure 1b (H)). However, a small peak, the elution volume of which is almost the same as that of MM**1a**, was also observed (Figure 1b (L)). This peak is considered to be a copolymer of MM**1a** and MBAA generated before core cross-linking, as reported in the synthesis of core cross-linked star polymers.[20] The higher-molecular-weight product was fractionated by precipitation in methanol (Figure 1c), and the absolute molecular weight (M_w) and the average number of arms per molecule (*f*) of the star polymer, star**1a**$_L$, were characterized by multiangle laser light scattering (MALLS) coupled with GPC (eluent: DMF) (Table 3, entry 1). The M_w value of star**1a**$_L$ was 258×10^3 and much higher than that determined by GPC; this is consistent with the character of star polymers, which are more compact than their linear counterparts with the same molecular weight. The *f* value was calculated from the M_w values of star**1a**$_L$ and of MM**1a**$_L$ by MALLS, supposing that all

Table 1. Synthesis of Homopolymer-Type MM1s[a]

entry	1	[**1**]$_0$/[**2**]$_0$	MM				
				yield (%)	DP[b]	$M_w \times 10^3$ [c] (MALLS)	M_w/M_n [d]
1	**1a**	10	MM**1a**$_L$	90	11	2.17	1.10
2	**1a**	20	MM**1a**$_H$	93	21	4.12	1.07
3[e]	**1b**	10	MM**1b**$_L$	86	10	3.65	1.06
4[e]	**1b**	20	MM**1b**$_H$	61	20	6.22	1.10

[a] Polymerization of **1** was carried out in the presence of **2** and 1.1 equiv of LiHMDS in THF ([**1**]$_0$ = 0.28 M) at 0 °C. [b] Degree of polymerization determined by ^{1}H NMR. [c] Determined by GPC-MALLS (eluent: DMF). [d] Determined by GPC based on polystyrene standards (eluent: DMF). [e] 5 equiv of LiCl was added.

Scheme 2

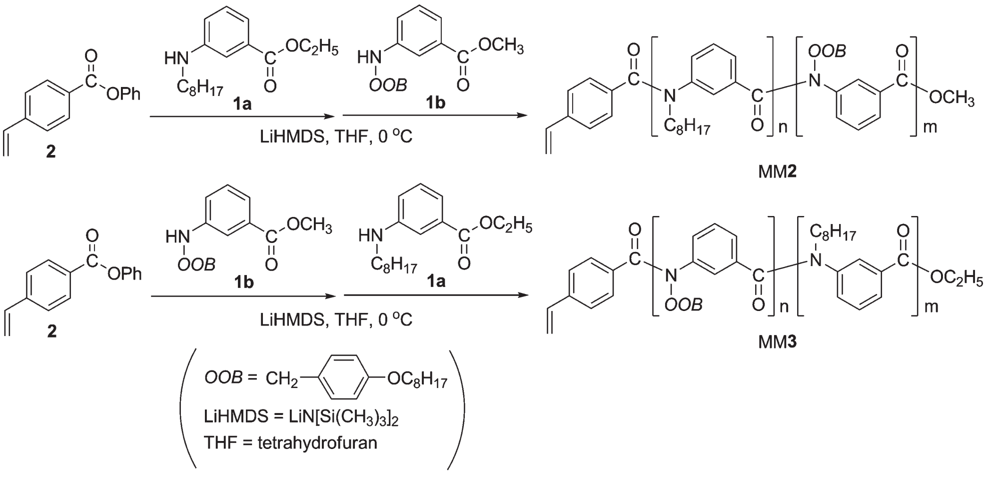


Table 2. Synthesis of Block Copolymer-Type MM2 and MM3[a]

entry	stage	monomer	[**1**]$_0$/[**2**]$_0$	MM				
					yield (%)	DP[b]	$M_w \times 10^3$ [c] (MALLS)	M_w/M_n [d]
1	first	**1a**	10			11	–[e]	–[e]
	second	**1b**	10	MM**2**	88	10	5.42	1.08
2	first	**1b**	10			11	–[e]	–[e]
	second	**1a**	10	MM**3**	91	11	5.75	1.07

[a] Two-stage polymerization of **1a** and **1b** was carried out in the presence of **2**, 2.2 equiv of LiHMDS, and 5 equiv of LiCl in THF (first stage: [**1**]$_0$ = 0.16 M, second stage: [**1**]$_0$ = 0.13 M) at 0 °C. [b] Degree of polymerization determined by ^{1}H NMR. [c] Determined by GPC-MALLS (eluent: DMF). [d] Determined by GPC based on polystyrene standards (eluent: DMF). [e] Not determined.

MBAA used for the copolymerization was incorporated into the star polymers. As a small peak was observed besides the main peak of the star polymer in the GPC elution curve (Figure 1b), a small amount of MBAA might not be incorporated into the star polymer. Therefore, the *f* value indicates the minimum average number of arms per star polymer. The calculated *f* value of star**1a**$_L$ was 100, and it is clear that star**1a**$_L$ has many polyamide arms. In a similar manner, MM**1a**$_H$ (DP = 21) was copolymerized with MBAA to yield star**1a**$_H$. The M_w value determined by MALLS was almost the same as that of star**1a**$_L$, whereas the *f* value was half that of star**1a**$_L$ (entry 2).

MM**1b**s with the poly(*N*-OOB-*m*-benzamide) chain (DP = 10 and 20) were copolymerized with MBAA under similar conditions. The polymerization proceeded homogeneously, and star polymers, star**1b**s, were isolated by precipitation in 2-propanol. The *f* value of star**1b**$_L$ was almost half that of star**1a**$_L$ (entry 3), and the *f* value of star**1b**$_H$ was smaller than that of star**1b**$_L$ (entry 4). These results are accounted for by steric hindrance of MMs: the *f* value decreases with increasing DP of MM and with increasing size of the *N*-alkyl group of MM.

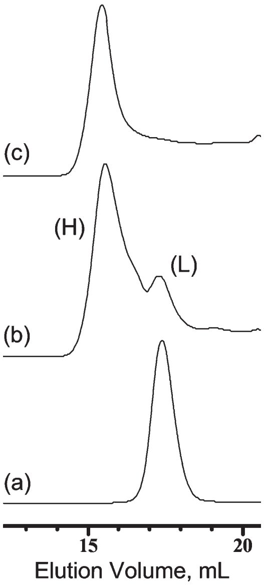


Figure 1. GPC profiles (eluent: THF) of product obtained by the copolymerization of MM**1a**$_L$ and 3 equiv of MBAA with 1 mol % of AIBN in toluene−DMF ([MM**1a** + MBAA]/[toluene]/[DMF] = 100/55.3/44.7 (weight ratio)) at 60 °C for 60 h: (a) MM**1a**$_L$, (b) crude product, (c) isolated star**1a**$_L$.

Removal of the *N*-Octyloxybenzyl Group from Star Polymer: Synthesis of Star Polymers with Poly(*N*-H-*m*-benzamide) Arms. The OOB group on the amide nitrogen of star**1b** was exposed to trifluoroacetic acid (TFA) in CH_2Cl_2 at ambient temperature for 3 days.[11,13,21] The deprotection reaction of star**1b**$_L$ proceeded homogeneously, and the products were purified by precipitation into a large excess of hexane. In the ^1H NMR spectrum of the products, the signal of the benzylic protons of the OOB group at around 4.90 ppm had disappeared, and a new signal due to amide N−H proton was observed at around 10.5 ppm (Figure 2). The FT-IR spectrum of the products showed a N−H stretching band at 3290 cm^{-1}. Consequently, removal of the OOB group proceeded quantitatively. The obtained star polymer consisting of poly(*N*-H-*m*-benzamide) was soluble in DMF, and MALLS analysis of the polymer solution in DMF indicated that the M_w value was lower than that of star**1b**$_L$ (Table 3, entry 3). In the deprotection reaction of star**1b**$_H$, slight precipitation of the products was seen, but quantitative removal of the OOB group was confirmed by the ^1H NMR and FT-IR spectra of the products purified by precipitation. However, the product was not soluble in DMF, and the M_w value was not determined by MALLS (entry 4). Longer poly(*N*-H-*m*-benzamide) arms may result in stronger hydrogen-bonding interaction between the star polymers, leading to a decrease of solubility.

Synthesis of Block-Arm Star Polymer Containing Poly(*N*-H-*m*-benzamide) Segment. The block copolymer-type MM**2** and MM**3** were copolymerized with MBAA in a similar manner to afford star**2** and star**3**, respectively, after precipitation in ethanol (Scheme 3, Table 4, entries 1 and 2). The

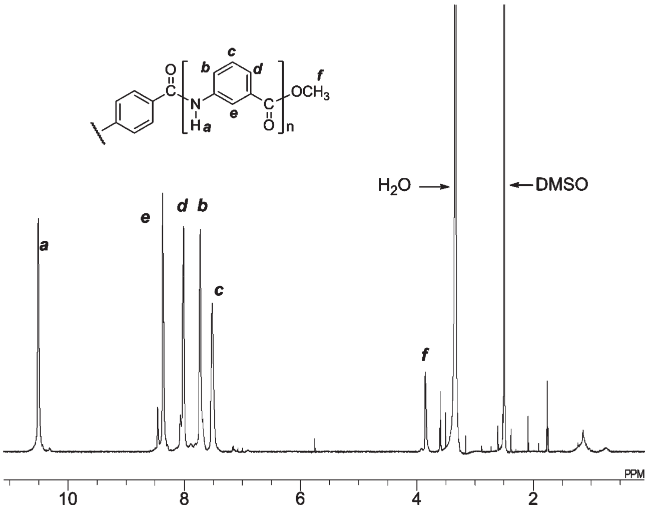


Figure 2. ^1H NMR spectrum of star polymer with poly(*N*-H-*m*-benzamide) arms in DMSO-d_6 at 23 °C.

Table 3. Synthesis of Homopolymer-Type Star Polymers[a]

				star polymer				after deprotection[g]	
				$M_w \times 10^3$				$M_w \times 10^3$	
entry	MM		yield (%)	GPC[b]	MALLS[c]	M_w/M_n[b]	*f*[d]	GPC[b]	MALLS[c]
1	MM**1a**$_L$	star**1a**$_L$	72[e]	89.4	258	1.74	100	–	–
2	MM**1a**$_H$	star**1a**$_H$	66[e]	77.2	225	1.54	50	–	–
3	MM**1b**$_L$	star**1b**$_L$	38[f]	70.1	220	1.81	54	79.2	183.7
4	MM**1b**$_H$	star**1b**$_H$	59[f]	73.6	228	1.59	36	–[h]	–[h]

[a] Copolymerization of MM and 3 equiv of MBAA was carried out with 1 mol % of AIBN in toluene−DMF ([MM**1a** + MBAA]/[toluene]/[DMF] = 100/55.3/44.7 (weight ratio)) at 60 °C for 60 h. [b] Determined by GPC based on polystyrene standards (eluent: DMF). [c] Determined by GPC-MALLS (eluent: DMF). [d] The number of arms per molecule. [e] The crude product was dissolved in a minimal amount of ether, and the solution was poured into methanol to precipitate star polymer. [f] The crude product was dissolved in a minimal amount of ethyl acetate, and the solution was poured into 2-propanol to precipitate star polymer. [g] The deprotection of star**1b** with TFA was carried out in CH_2Cl_2 at room temperature for 3 days. [h] Not determined because of insolubility of the product in DMF.

Scheme 3

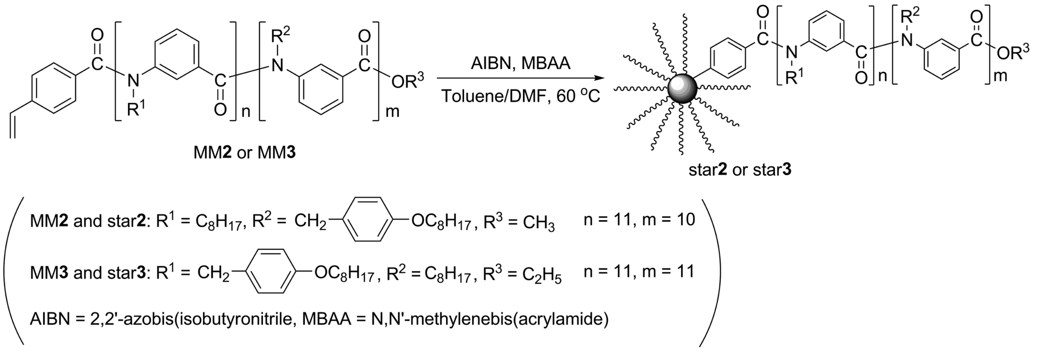
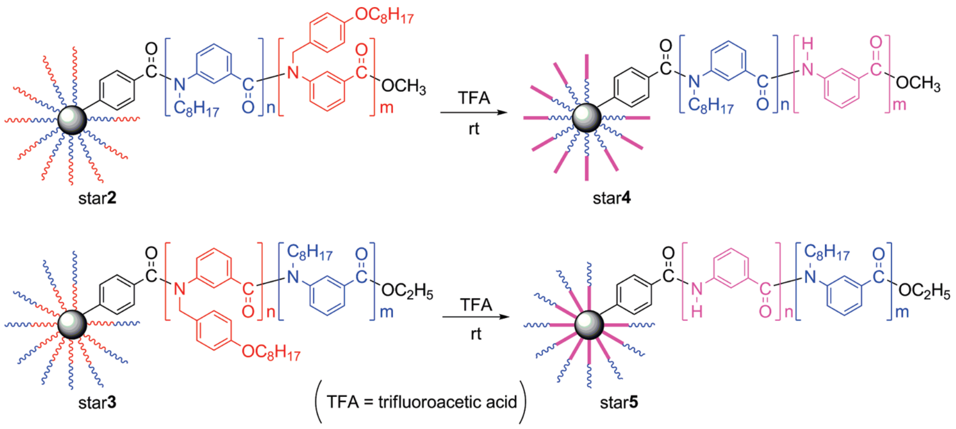


Table 4. Synthesis of Block-Arm Star Polymers and Miktoarm Star Polymer

			before deprotection					after deprotection[h]		
				$M_w \times 10^3$					$M_w \times 10^3$	
entry	MM		yield (%)	GPC[e]	MALLS[f]	M_w/M_n[e]	f[g]		GPC[e]	MALLS[f]
1[a]	**MM2**	star**2**	60[c]	95	284	1.47	49	star**4**	116	315
2[a]	**MM3**	star**3**	46[c]	115	415	1.51	67	star**5**	142	370
3[b]	**MM1a**$_L$ + **MM1b**$_L$ (feed molar ratio = 1/1)	star**6**	50[d]	61.1	164	1.67	49 (arm composition = 1/1)	star**7**	61.3	142

[a] Copolymerization of MM and 3 equiv of MBAA was carried out with 1 mol % of AIBN in toluene−DMF ([MM + MBAA]/[toluene]/[DMF] = 100/55.3/44.7 (weight ratio)) at 60 °C for 60 h. [b] Copolymerization of **MM1a**$_L$, **MM1b**$_L$, and MBAA was carried out with 1 mol % of AIBN in toluene−DMF ([MM + MBAA]/[toluene]/[DMF] = 100/55.3/44.7 (weight ratio)) at 60 °C for 60 h. [c] The crude product was dissolved in a minimal amount of ethyl acetate, and the solution was poured into ethanol to precipitate star polymer. [d] The crude product was dissolved in a minimal amount of ethyl acetate, and the solution was poured into ethanol and 2-propanol (1/1 = v/v) to precipitate star polymer. [e] Determined by GPC based on polystyrene standards (eluent: DMF). [f] Determined by GPC-MALLS (eluent: DMF). [g] The number of arms per molecule. [h] The deprotection of star polymer was carried out with TFA in CH_2Cl_2 at room temperature for 3 days.

Scheme 4



M_w and f values of star**2** with the arms of the inner poly(*N*-octyl-*m*-benzamide) segment and the outer bulky poly(*N*-OOB-*m*-benzamide) segment were lower than those of star**3** with the arms of the two segments in the reverse order. We had expected that **MM2** bearing the less bulky poly(*N*-octyl-*m*-benzamide) segment connected to the styryl moiety would have higher radical polymerizability than **MM3**, and that star**2** obtained by the cross-linking of **MM2** would possess higher M_w and f values. The reason why the opposite was the case is unclear at present.

The OOB group on the amide nitrogen of the obtained star**2** and star**3** was removed with TFA in CH_2Cl_2 at ambient temperature for 3 days (Scheme 4).[11,13,21] The deprotection reaction proceeded homogeneously to afford star**4** and star**5** containing the poly(*N*-H-*m*-benzamide) segment, respectively. The quantitative removal of the OOB group was confirmed by the ^{1}H NMR spectra of the products. The M_w value

Table 5. Solubility of Block-Arm and Miktoarm Star Polymers[a]

solvent	star**2**	star**4**	star**3**	star**5**	star**6**	star**7**
hexane	−	−	−	−	−	−
toluene	++	−	++	−	++	−
CH_2Cl_2	++	−	++	+	++	+
$CHCl_3$	++	−	++	+	++	+
ether	++	−	++	−	++	−
THF	++	−	++	−	++	++
AcOEt	++	−	++	−	++	−
acetone	++	−	++	−	++	−
CH_3CN	−	−	−	−	−	−
i-PrOH	−	−	+	−	−	−
EtOH	−	−	+	−	−	−
MeOH	−	−	−	−	−	−
DMF	++	++	++	++	++	++
DMF + LiBr	++	++	++	++	++	++
DMSO	−	++	−	−	−	++

[a] Symbols: ++, soluble at room temperature; +, soluble on heating; −, insoluble.

of star**4** became higher than that of star**2**, although the OOB group had been removed from star**2**. This higher M_w value of star**4** can probably be attributed to aggregation of star**4** by virtue of intermolecular hydrogen bonding of the outer poly(*N*-H-*m*-benzamide) segment. Dynamic light scattering (DLS) analysis of a solution of star**4** in DMF showed that the hydrodynamic radius increased with increasing concentration, again implying aggregability of star**4**. On the other hand, the M_w value of star**5** was lower than that of star**3**, as we had expected. The inner poly(*N*-H-*m*-benzamide) segment of star**5** would not support aggregation via intermolecular hydrogen bonding.

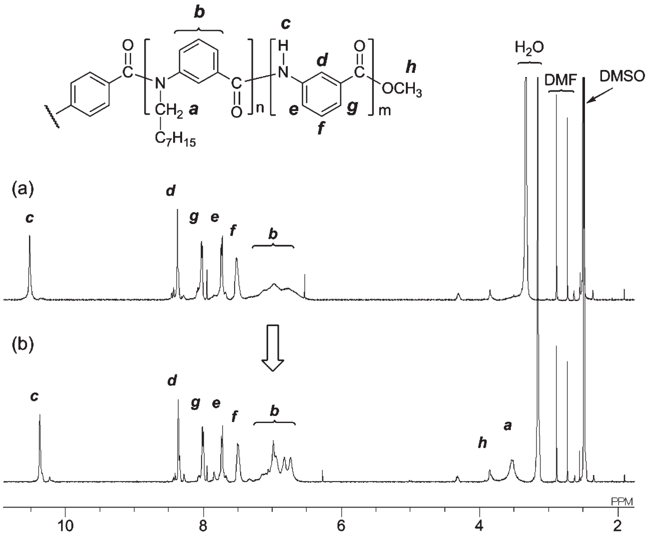


Figure 3. ^{1}H NMR spectra of star**4** in DMSO-d_6 at (a) 23 °C and (b) 60 °C.

The solubility of star**2**−star**5** is summarized in Table 5. Star**2** and star**3** before deprotection showed rather similar solubility, and they were soluble in many kinds of organic solvents, except for alcohols. After deprotection, star**4** was only soluble in polar aprotic solvents, such as DMF and dimethyl sulfoxide (DMSO), whereas star**5** was soluble in CH_2Cl_2, $CHCl_3$, and DMF and insoluble in DMSO. Therefore, the character of the external segment of the arms dominates the solubility and aggregability of the block-arm star polymers. Furthermore, in the ^{1}H NMR spectrum of star**4** in DMSO-d_6 at 23 °C, the signals **b** of the benzene ring of the poly(*N*-octyl-*m*-benzamide) segment appeared with weaker intensity than expected, but the intensity of these signals reached the expected level at 60 °C (Figure 3). This observation implies that, in DMSO at 23 °C, the inner

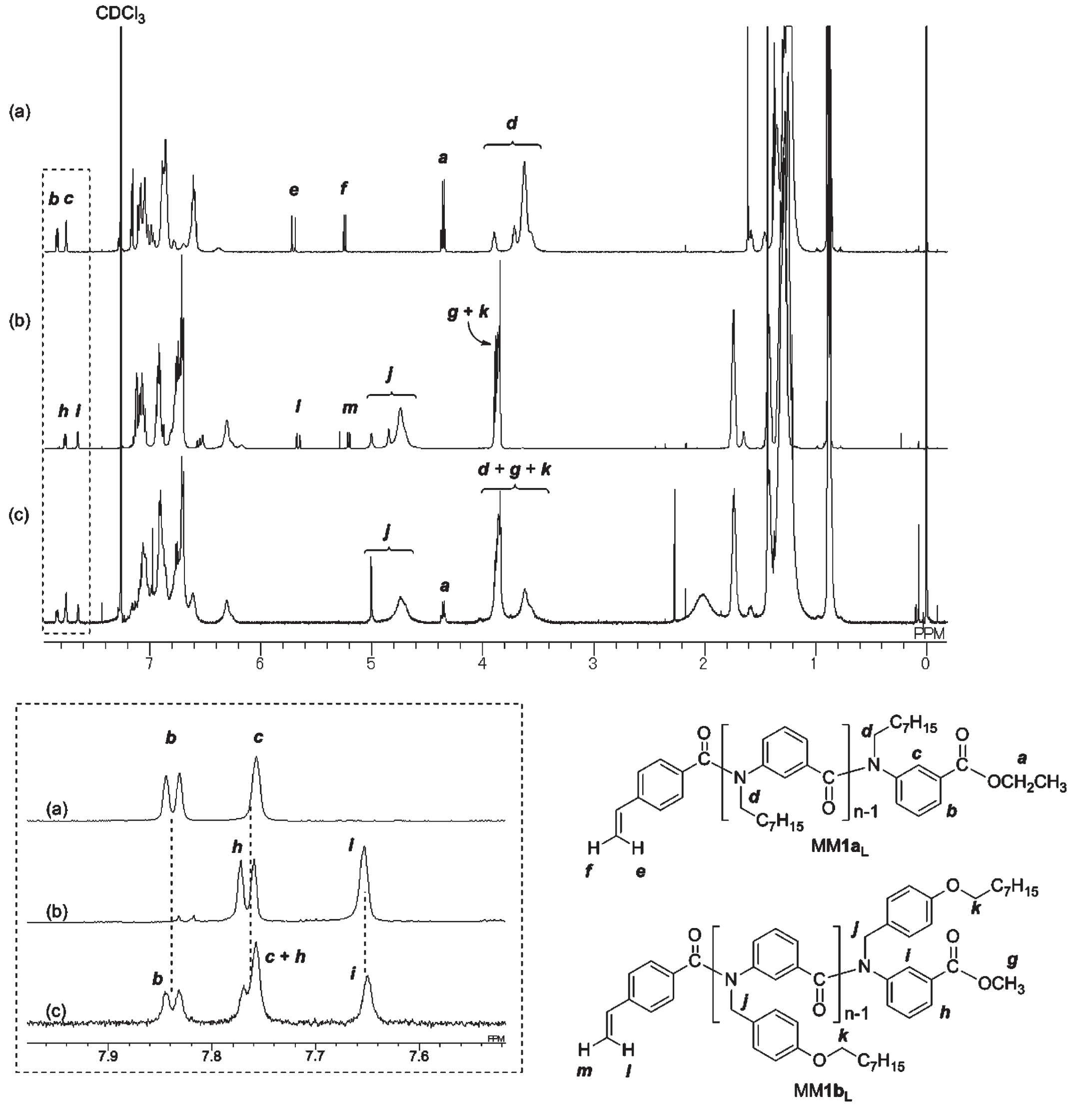
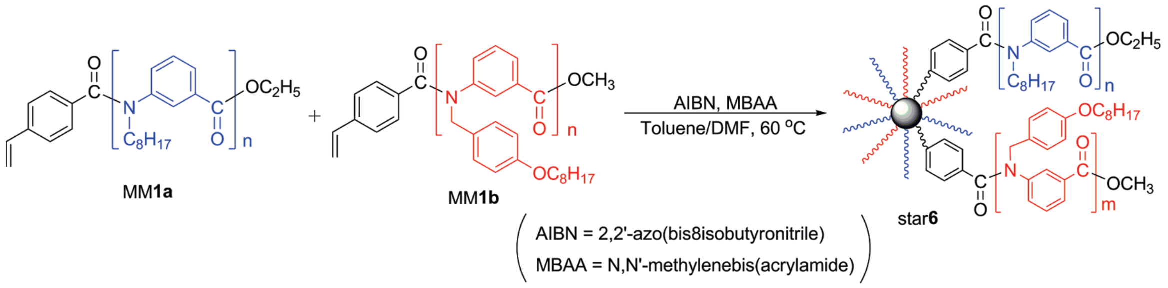
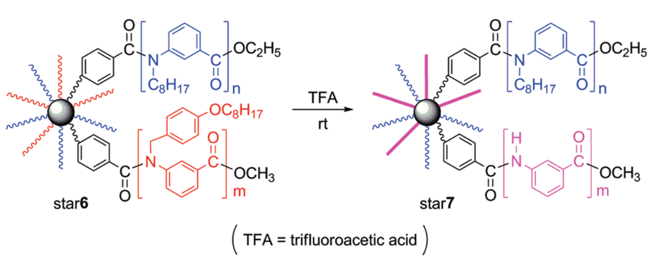


Figure 4. ^{1}H NMR spectra of (a) MM**1a**$_L$, (b) MM**1b**$_L$, and (c) star**6** in $CDCl_3$ at 23 °C.

Scheme 5



Scheme 6



poly(*N*-octyl-*m*-benzamide) segment, which is insoluble in DMSO, is packed so as to decrease the surface energy of this segment, as in the case of star polymers composed of flexible coil polymers.[16] On the other hand, this segment may be extended and solvated at 60 °C, resulting in normal intensity of the signals. This result indicates that the aromatic polyamide, which is less flexible than coil polymers, in star polymer dynamically changes the molecular geometry in response to thermal stimulation.

Synthesis of Miktoarm Star Polymer Containing Poly(*N*-H-*m*-benzamide) Arms. The miktoarm star polymer containing the poly(*N*-OOB-*m*-benzamide) arm and the poly(*N*-octyl-*m*-benzamide) arms was first prepared by the radical copolymerization of MM1a$_L$, MM1b$_L$ (1:1 molar ratio), and 3 equiv of MBAA to the macromonomers (MM1a$_L$ + MM1b$_L$) with AIBN in a mixed solvent of toluene and DMF at 60 °C (Scheme 5). The GPC elution curve of the products showed the objective star polymer, star**6**, as the main peak in the higher-molecular-weight region, and a small peak was also observed in the lower-molecular-weight region, in a manner similar to Figure 1b. Star**6** was fractionated by precipitation in a mixed solvent of ethanol and 2-propanol (1/1 = v/v), and its M_w and f values were 164 × 10^3 and 49, respectively (Table 4, entry 3). The ^{1}H NMR spectrum of star**6** showed the signals **b** and **c** of the terminal unit of the poly(*N*-octyl-*m*-benzamide) arm and the signals **h** and **i** of the terminal unit of the poly(*N*-OOB-*m*-benzamide) arm. On the basis of the integral ratio of the each terminal signal, **b**:**i**, the ratio of the two arms in star**6** was 1:1, which agreed well with the 1:1 feed ratio of MM1a$_L$ to MM1b$_L$ (Figure 4).

The protecting group on the amide nitrogen was then removed with TFA in CH_2Cl_2 at ambient temperature to afford star**7** with the poly(*N*-octyl-*m*-benzamide) and poly(*N*-H-*m*-benzamide) arms (Scheme 6, Table 4, entry 3).[11,13,21] The M_w value of star**7** became lower than that of star**6**, different from the case of the block-arm star**4**, although both star polymers have the poly(*N*-H-*m*-benzamide) segment. This result implies that aggregation of star**7** hardly occurred. We think that intermolecular hydrogen bonding between the poly(*N*-H-*m*-benzamide) arms is weakened probably because the amide linkages of the poly(*N*-octyl-*m*-benzamide) arm in star**7** would behave as hydrogen-bonding acceptors. Indeed, the hydrodynamic radius of star**7** in DMSO, measured by DLS, was constant irrespective of the concentration of star**7**, indicating that aggregation did not occur.

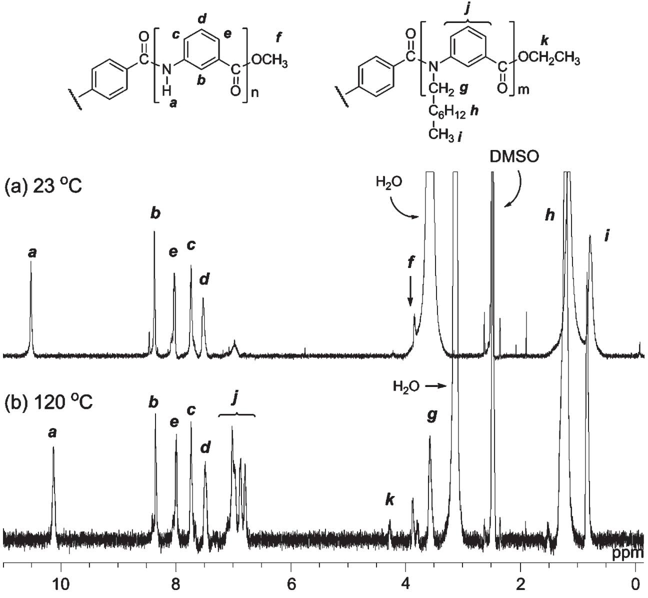


Figure 5. ^{1}H NMR spectra of star**7** in DMSO-d_6 at (a) 23 °C and (b) 120 °C.

The solubility of star**6** and star**7** is summarized in Table 5. Star**7** was not only soluble in polar aprotic solvents, such as DMF and DMSO, but also in nonpolar solvents, such as THF, CH_2Cl_2, and $CHCl_3$; it shows a sharp contrast to block-arm star**4**, which was only soluble in polar aprotic solvents. This result reflects the low aggregability of star**7**. Moreover, in the ^{1}H NMR spectrum of star**7** in DMSO-d_6 at 23 °C, the signals of the benzene ring of the poly(*N*-octyl-*m*-benzamide) arms were very weak (Figure 5a). A similar phenomenon was observed in the case of block-arm star**4**, but the intensity of the signals in the case of star**7** was much lower. However, these signals were clearly observed at 120 °C, as in the case of star**4** (Figure 5b). This result is rather unexpected but indicates that the poly(*N*-octyl-*m*-benzamide) arms in star**7** are more efficiently packed in DMSO than the inner poly(*N*-octyl-*m*-benzamide) segment of blockarm star**4**.

Conclusions

We have demonstrated that chain-growth condensation polymerization affords aromatic polyamide MMs with the terminal styryl moiety, and the radical copolymerization of MM and MBAA yields multiarmed star polymers. We synthesized homopolymer-arm, block-arm, and miktoarm star polymers by using homopolymer MM, block copolymer MM, and two kinds of MMs, respectively. All star polymers were easily isolated by precipitation. The poly(*N*-OOB-*m*-benzamide) arm and segment were converted to poly(*N*-H-*m*-benzamide) ones by treatment with TFA. In the ^{1}H NMR spectra of the block-arm star**4** and the miktoarm star**7** in DMSO at 23 °C, the signal of the poly(*N*-octyl-*m*-benzamide) moiety was weakly observed, but its intensity increased to the expected level on heating. This observation indicates that the poly(*N*-octyl-*m*-benzamide) moiety, which is insoluble in DMSO, is packed in the star polymers at 23 °C and extended at higher temperatures. It seems intriguing that semirigid aromatic polyamide arms in star polymers can dynamically change the molecular geometry in response to thermal stimulation, as in the case of star polymers composed of flexible coil polymers.

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