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Synthesis via Chain-Growth Condensation Polymerization and Gelating Properties of a Variety of Block Copolymers of Meta- and Para-Substituted Aromatic Polyamides

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ABSTRACT: Well-defined diblock copolymers consisting of poly(*m*-benzamide)s with different *N*-alkyl groups and of poly(*m*-benzamide)s and poly(*p*-benzamide)s with different *N*-alkyl groups were synthesized by means of sequential chain-growth condensation polymerization. The polymerization of 3-(alkylamino)benzoic acid alkyl ester **1** was carried out with phenyl 4-methylbenzoate (**3**) as an initiator in the presence of 2.2 equiv of lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) as a base, followed by addition of another kind of **1** or 4-(alkylamino)benzoic acid alkyl ester **2** to the reaction mixture to yield the block copolymer. The 4-octyloxybenzyl groups on the amide nitrogen in the obtained block copolymers were removed with trifluoroacetic acid (TFA) to give block copolymers containing an *N*−H polyamide segment. These block copolymers showed gelating properties at low concentration in various solvents ranging from aromatic to aprotic polar solvents. Scanning electron microscopic (SEM) images of the CH_2Cl_2 gel revealed that the block copolymers self-assembled to form three-dimensional network structures, in which the solvent was confined to afford a gel. The gelating properties were dependent on both the orientation of the monomer substituents (meta or para) and the composition ratio of the *N*−H poly(benzamide) segment in the block copolymers.

Introduction

Para-substituted aromatic polyamides such as Kevlar and poly(*p*-benzamide) are among the toughest organic materials, because of the intermolecular hydrogen bonding between the amide bonds and the $\pi-\pi$ stacking of aromatic rings. However, these strong intermolecular interactions make the polymers insoluble in organic solvents. On the other hand, meta-substituted aromatic polyamides are more flexible and have better solubility in organic solvents than their para-substituted counterparts and have good mechanical properties. In order to produce materials having features of both para- and meta-substituted aromatic polyamides, diblock copolymers consisting of rigid poly(*p*-benzamide) and flexible poly(*m*-benzamide)[1] or poly(*m*-phenylene isophthalamide)[2−4] have been synthesized by the coupling reaction of each polyamide. Those block copolymers can form intriguing nanostructures by virtue of multiple hydrogen bondings between polymers of the same length. For example, poly(*p*-benzamide)-*b*-poly(*m*-phenylene isophthalamide) forms supramolecular assemblies in *N*,*N*-dimethylacetamide (DMAc) containing LiCl and in 96% H_2SO_4.[3,4] However, control of the molecular weight and polydispersity of these polymers has not so far been reported.

We have developed chain-growth condensation polymerization, a kind of living polymerization system in condensation polymerization, to provide condensation polymers with controlled molecular weight and low polydispersity.[5−7] In the synthesis of well-defined N-alkylated poly(*p*-benzamide)s, the aminyl anion of the monomer not only acts as a nucleophilic site, but also deactivates the acyl group by virtue of the resonance effect, resulting in suppression of self-condensation of the monomer.[8,9] Furthermore, we have demonstrated that a sequential monomer addition method can afford well-defined block copolymers consisting of poly(*p*-benzamide)s with different *N*-alkyl groups and that the use of a protecting group as the *N*-alkyl group affords poly(N-alkylated-*p*-benzamide)-*b*-poly(*p*-benzamide) by deprotection after the sequential polymerization. The latter block copolymer self-assembled to form bundle and flake structures, presumably due to hydrogen bonding between the polymer backbones.[10] However, the length of the poly(*p*-benzamide) segment in these block copolymers was limited, because *N*-(4-octyloxybenzyl) poly(*p*-benzamide), which affords poly(*p*-benzamide) upon deprotection, shows poor solubility in organic solvents. Recently, we have achieved control of the molecular weight and polydispersity of poly(*m*-benzamide)s and demonstrated that the inductive effect of the nucleophilic site on the reactivity of the electrophilic site at the meta position of the monomer is as applicable to chain-growth condensation polymerization as is the resonance effect in para-substituted monomers.[11] The obtained poly(*m*-benzamide)s having various kinds of alkyl and oligo(ethylene glycol) side chains on the nitrogen atom showed higher solubility than the corresponding poly(*p*-benzamide)s.[12,13] However, block copolymers containing these poly(*m*-benzamide)s have not been synthesized, except for preliminary synthesis of a block copolymer of *N*-octyl poly(*m*-benzamide) and *N*-octyl poly(*p*-benzamide).[11] Since *N*-alkyl and even N-unsubstituted poly(*m*-benzamide)s have higher solubility, block copolymers containing the poly(*m*-benzamide)s should not be restricted as to the chain length of the segments in the block copolymers. Furthermore, it would be intriguing to examine differences of self-assembling behavior between the block copolymer containing *N*−H poly(*m*-benzamide) and that containing the para counterpart. We herein describe the synthesis of well-defined block copolymers consisting of meta-substituted aromatic polyamides and block copolymers of meta- and para-substituted aromatic polyamides with various kinds of side chains by means of a sequential chain-growth condensation polymerization process (Scheme 1). We also found that the block copolymers containing either *N*−H poly(*m*-benzamide) or *N*−H poly(*p*-benzamide) convert their solutions in organic solvents into gels by the formation of self-assembled three-dimensional network aggregates.

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Scheme 1

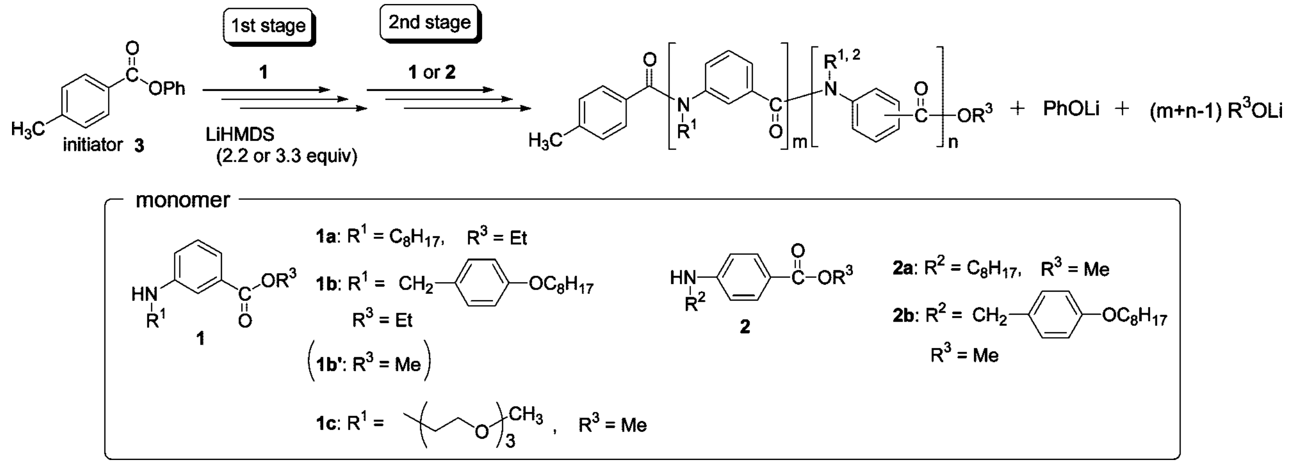


Table 1. Block Copolymerization of Various 1 with 3 by Two-Stage Polymerization[a]

entry	stage	monomer	[**1**]$_0$/[**3**]$_0$	equiv of LiHMDS	additive	M_n calcd	M_n NMR[b]	M_w/M_n[c]	DP[d]
1[e]	first	**1a**	10	2.2	LiCl[f]	2310	2640	1.10	10
	second	**1b**	10			6180	6680	1.10	10
2[g]	first	**1a**	20	3.3	LiCl[h]	4600	5090	1.07	21
	second	**1b**	10			8050	8600	1.07	10
3[i]	first	**1a**	10	3.3	LiCl[h]	2400	2710	1.10	11
	second	**1b**	20			9390	9830	1.08	21
4[e]	first	**1a**	10	2.2		2500	2660	1.08	11
	second	**1c**	10			5350	5670	1.10	11
5[e]	first	**1b′**	10	2.2		3520	3830	1.07	11
	second	**1c**	10			6580	6910	1.15	12
6[g]	first	**1b′**	20	3.3		6900	7170	1.07	21
	second	**1c**	10			10400	9940	1.08	11

[a] Two-stage polymerization of **1a** and **1b**−**c** with **3** was carried out in THF at 0 °C. [b] Determined by ^{1}H NMR. [c] Determined by GPC based on polystyrene standards (eluent, THF). [d] Degree of polymerization determined by ^{1}H NMR. [e] First stage, [**1a**]$_0$ = [**1b′**]$_0$ = 0.20 M; second stage, [**1b**]$_0$ = [**1c**]$_0$ = 0.13 M. [f] 11 equiv to **1a**. [g] First stage, [**1a**]$_0$ = [**1b′**]$_0$ = 0.20 M; second stage, [**1b**]$_0$ = [**1c**]$_0$ = 0.09 M. [h] 16.5 equiv to **1a**. [i] First stage, [**1a**]$_0$ = 0.11 M; second stage, [**1b**]$_0$ = 0.17 M.

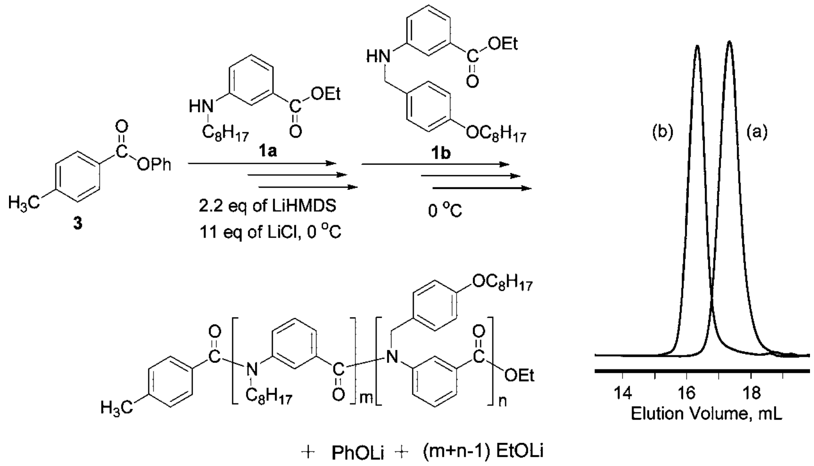


Figure 1. Two-stage block polymerization of **1a** and **1b** with **3** in THF ([**1a**]$_0$ = 0.15 M, [**1b**]$_0$ = 0.13 M) at 0 °C. GPC profiles of (a) poly**1a** as a prepolymer ([**1a**]$_0$/[**3**]$_0$ = 10.0, M_n = 3270, M_w/M_n = 1.10) and (b) poly**1a**-*b*-poly**1b** as a postpolymer ([**1b**]$_0$/[**3**]$_0$ = 10.0, M_n = 6680, M_w/M_n = 1.10).

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were obtained on JEOL ECA-600 and 500 instruments operating in the pulsed Fourier transform (FT) mode, with tetramethylsilane (TMS) as an internal standard. 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) using two Shodex KF-804 L columns and a TOSOH HLC-8220 GPC unit (eluent, solution of LiBr and phosphoric acid (20 × 10^{-3} M) in dimethylformamide (DMF); calibration, polystyrene standards) using three polystyrene gel columns (Shodex gel: 2 × GF-310 HQ and GF-510 HQ). Isolation of polyamides was carried out with a Japan Analytical Industry LC-908 recycling preparative high-performance liquid chromatography (HPLC) instrument (eluent, chloroform) fitted with two TSK-gel columns (2 × G 2000H$_{HR}$).

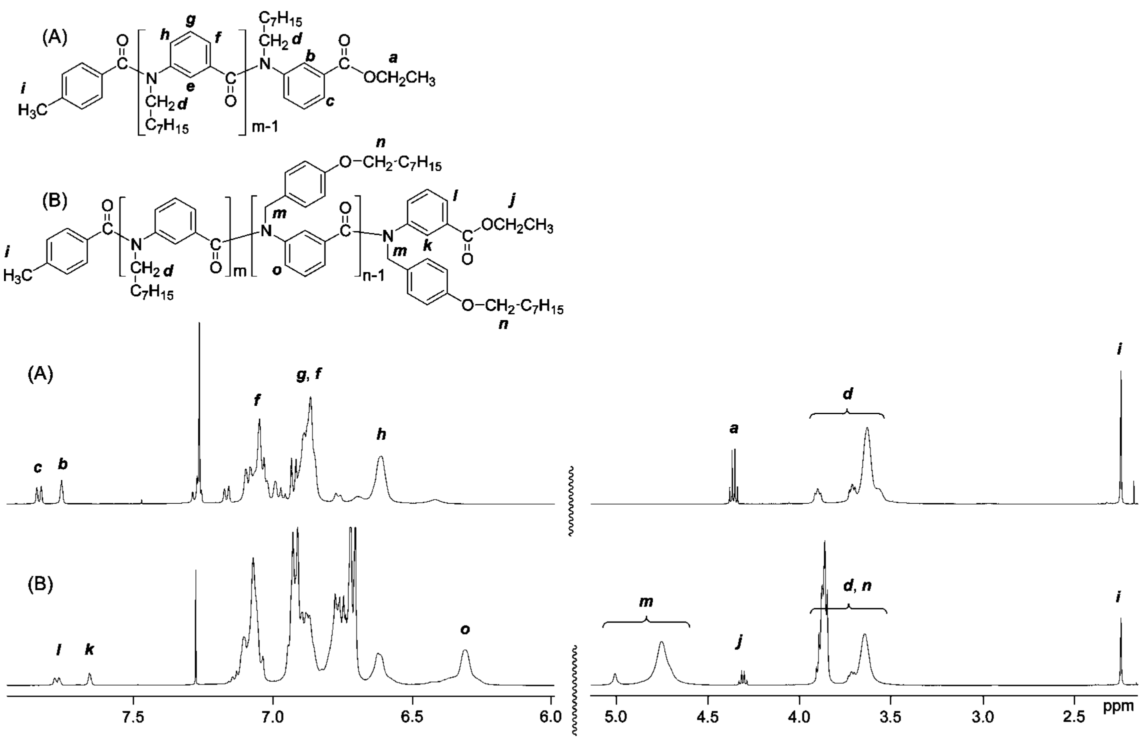


Figure 2. ^1H NMR spectra of (A) poly**1a** and (B) poly**1a**-*b*-poly**1b** in $CDCl_3$ at 25 °C.

Table 2. Block Copolymerization of Various 1 and 2 with 3 by Two-Stage Polymerization[a]

entry	stage	monomer	[monomer]$_0$/[initiator]$_0$	equiv of LiHMDS	additive	M_n calcd	M_n NMR[b]	M_w/M_n[c]	DP[d]
1[e]	first	**1a**	10	2.2	LiCl[f]	2480	2590	1.09	10
	second	**2b**	10			6100	6430	1.11	11
2[g]	first	**1a**	20	3.3	LiCl[h]	4580	5210	1.06	21
	second	**2b**	10			8010	8840	1.14	11
3[e]	first	**1b′**	10	2.2	LiCl[f]	3450	3980	1.07	11
	second	**2a**	11			6030	6300	1.09	10

[a] Two-stage polymerization of **1a**−**b′** and **2a**−**b** with **3** was carried out in THF at 0 °C. [b] Determined by ^1H NMR. [c] Determined by GPC based on polystyrene standards (eluent, THF). [d] Degree of polymerization determined by ^1H NMR. [e] First stage, $[\mathbf{1a}]_0 = [\mathbf{1b'}]_0 = 0.15$ M; second stage, $[\mathbf{2a}]_0 = [\mathbf{2b}]_0 = 0.13$ M. [f] 11 equiv to **1a** or **1b′**. [g] First stage: $[\mathbf{1a}]_0 = 0.20$ M; second stage, $[\mathbf{2b}]_0 = 0.09$ M. [h] 16.5 equiv to **1a**.

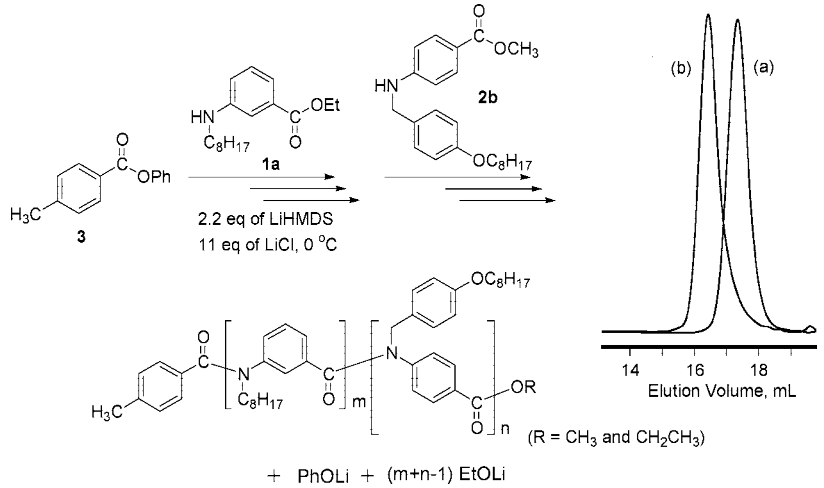


Figure 3. Two-stage polymerization of **1a** and **2b** in THF ($[\mathbf{1a}]_0 = 0.15$ M, $[\mathbf{2b}]_0 = 0.13$ M) at 0 °C. GPC profiles of (a) poly**1a** as a prepolymer ($[\mathbf{1a}]_0/[\mathbf{3}]_0 = 10.0$, $M_n = 3460$, $M_w/M_n = 1.09$) and (b) poly**1a**-*b*-poly**2b** ($[\mathbf{2b}]_0/[\mathbf{3}]_0 = 10.0$, $M_n = 6160$, $M_w/M_n = 1.11$).

Scanning electron microscopy (SEM) was carried out with a Hitachi S-4000. Samples were prepared by dropping CH_2Cl_2 gel of copolymers on a Cu grid and drying at 25 °C for 3 days.

Materials. Ethyl 3-(octylamino)benzoate (**1a**),[12] ethyl and methyl 3-(4-octyloxybenzylamino)benzoate (**1b**, **1b′**),[12] methyl 3-{2-[2-(2-methoxyethoxy)ethoxy]ethylamino}benzoate (**1c**),[13] and methyl 4-(octylamino)benzoate (**2a**)[9] were prepared according to the previously established procedures. Phenyl 4-methylbenzoate (**3**) was prepared according to the literature.[14] A solution of lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) (Aldrich; 1.0 M solu-

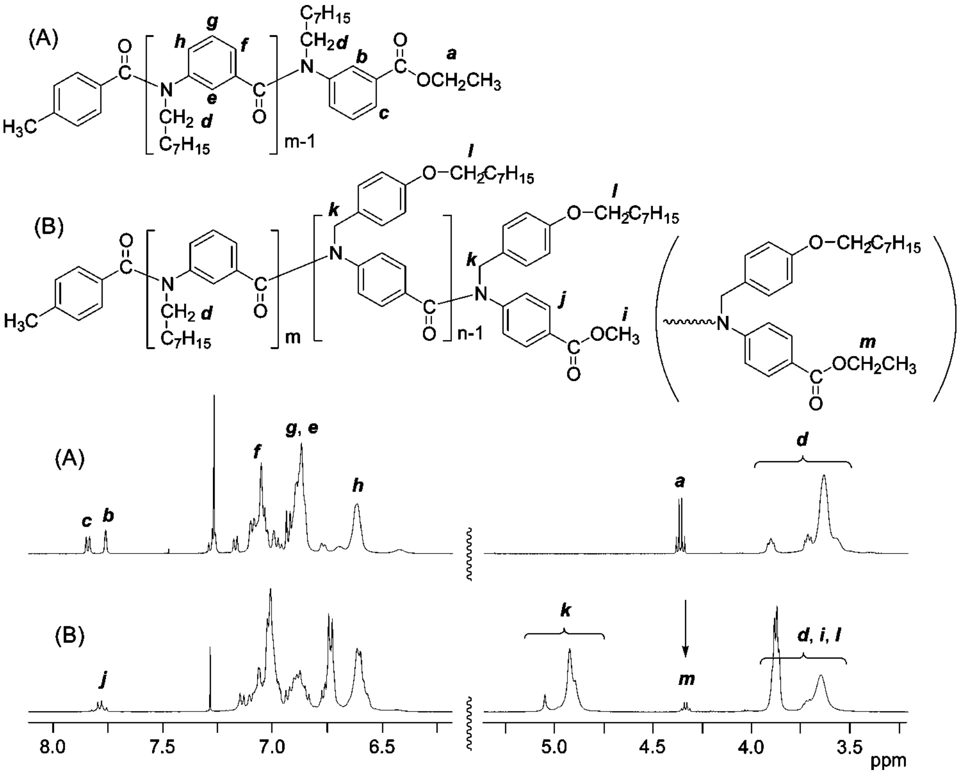
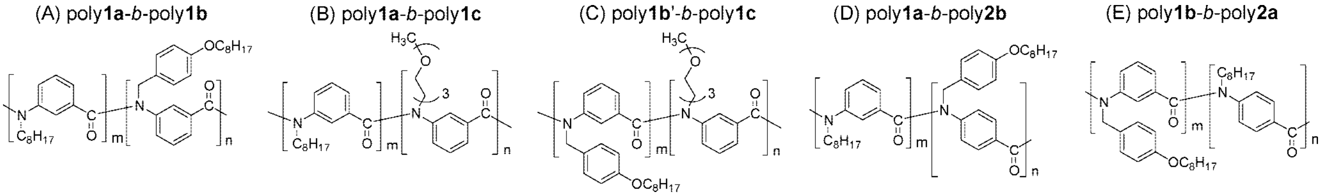


Figure 4. ^{1}H NMR spectra of (A) poly**1a** and (B) poly**1a**-*b*-poly**2b** in CDCl$_3$ at 25 °C.

Table 3. Solubility of N-Substituted Diblock Copolymers[a]



	(A)			(B)	(C)		(D)		(E)
solvent	*m* = 10 *n* = 10	*m* = 20 *n* = 10	*m* = 10 *n* = 20	*m* = 10 *n* = 10	*m* = 10 *n* = 10	*m* = 20 *n* = 10	*m* = 20 *n* = 10	*m* = 10 *n* = 10	*m* = 10 *n* = 10
hexane	−	−	−	−	−	−	−	−	−
toluene	++	++	++	++	++	++	++	++	++
ether	++	++	++	++	++	++	−	−	++
THF	++	++	++	++	++	++	++	++	++
CH_2Cl_2	++	++	++	++	++	++	++	++	++
ethyl acetate	++	++	++	++	++	++	+	−	++
acetone	++	++	++	++	++	++	−	−	++
CH_3CN	−	−	−	++	++	−	−	−	−
DMF	++	++	++	++	++	++	+	−	++
DMSO	−	+	−	++	++	−	−	−	−
ethanol	−	−	−	++	++	+	−	−	−
methanol	−	−	−	++	+	+	−	−	−
H_2O	−	−	−	−	−	−	−	−	−

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

tion in THF), dehydrated THF (Kanto), and trifluoroacetic acid (TFA) were used as received without purification.

Synthesis of Methyl 4-(4-Octyloxybenzylamino)benzoate (2b). To a solution of methyl 4-aminobenzoate (3.03 g, 20 mmol) in THF (90 mL) were added 4-octyloxybenzaldehyde (4.40 mL, 18 mmol), acetic acid (1.00 mL, 18 mmol), and sodium triacetoxyborohydride[15] (6.86 g, 32 mmol), successively. The mixture was stirred at room temperature for 7 h, and then the reaction was quenched with saturated $NaHCO_3$. The whole was extracted with ethyl acetate, and the combined organic layers were washed with brine, followed by drying over anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 5/1) to give 4.65 g of **2b** as a white solid (68%): mp 94.1−95.1 °C; IR (KBr) 3373, 2945, 2922, 1686, 1601, 1286, 1175, 827, 772, 700 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.86 (dt, J = 8.6 and 2.2 Hz, 2 H), 7.24 (d, J = 8.6 Hz, 2 H), 6.87 (dt, J = 8.6 and 2.5 Hz, 2 H), 6.58 (dt, J = 8.9 and 2.3 Hz, 2 H), 4.40 (s, 1 H), 4.29 (s, 2 H), 3.94 (t, J = 6.6 Hz, 2 H), 3.84 (s, 3 H), 1.77 (quint, J = 7.1 Hz, 2 H), 1.48−1.28 (m, 12 H), 0.89 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl$_3$)

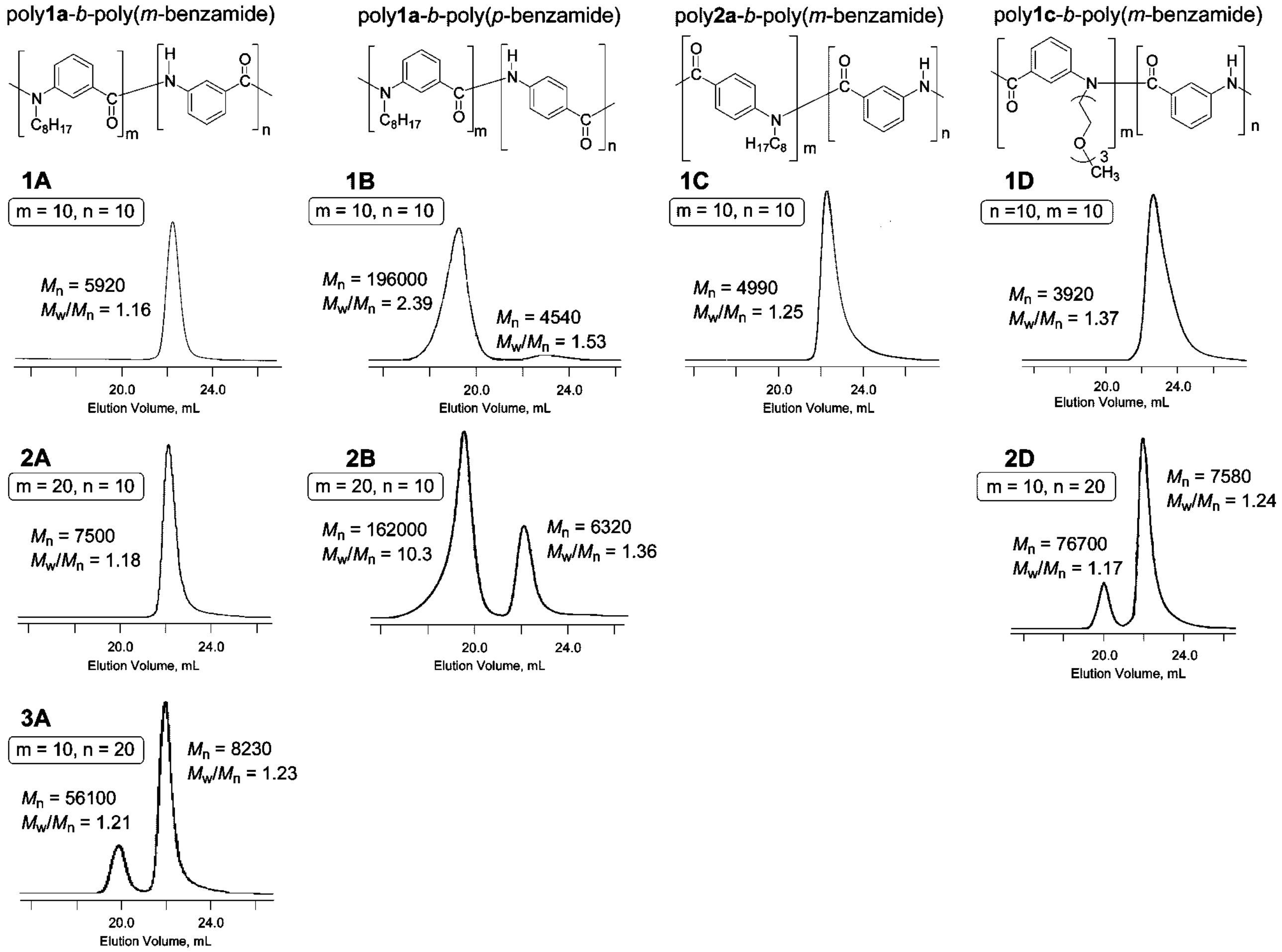


Figure 5. GPC profiles of diblock copolymers containing *N*−H poly(*m*- or *p*-benzamide) (eluent, DMF).

Figure 6. CH_2Cl_2 gel of poly**1a**-*b*-poly(*p*-benzamide) at 5 wt %.

δ 167.3, 158.6, 151.7, 131.5, 130.0, 128.7, 118.5, 114.7, 111.6, 68.0, 51.5, 47.2, 31.8, 29.3, 29.23, 29.21, 26.0, 22.6, 14.1.

Synthesis of Block Copolymers. An example of the procedure for the synthesis of poly**1a**-*b*-poly**1b** is as follows. LiCl (0.188 g, 4.4 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 (1.0 mL) and 1.0 M LiHMDS in THF (0.88 mL, 0.88 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 **3** (0.0084 g, 0.04 mmol) in dry THF (0.2 mL) under dry nitrogen, followed by a solution of **1a** (0.111 g, 0.40 mmol) in dry THF (0.5 mL) dropwise over ca. 50 min at 0 °C with stirring under dry nitrogen. The mixture was stirred at 0 °C for 20 min, then 0.2 mL of the solution was withdrawn, and the reaction was 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) = 3550, M_n (NMR) = 2550, M_w/M_n = 1.09). Right after the sampling, a solution of **1b** (1.53 g, 0.41 mmol) in dry THF (0.5 mL) was added dropwise over ca. 50 min to the reaction mixture, and the mixture was stirred at 0 °C for 20 min. The reaction was quenched with saturated NH_4Cl, followed by extraction of the mixture 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) = 7430, M_n (NMR) = 6700, M_w/M_n = 1.06). The residue was purified by preparative HPLC (eluent, chloroform) using polystyrene gel columns to give 0.18 g of the block copolymer of **1a** and **1b** as a yellow viscous oil (74%).

Synthesis of Block Copolymers Containing *N*−H Polybenzamide via Deprotection. An example of the procedure for removal of the 4-octyloxybenzyl group on poly**1a**-*b*-poly**1b** is as follows. TFA (1.0 mL) was added to a solution of poly**1a**-*b*-poly**1b** (0.0303 g, M_n = 6700) in CH_2Cl_2 (1.0 mL). The solution was stirred at room temperature for 3 days, 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 0.083 g of poly**1a**-*b*-poly(*m*-benzamide) (79%).

Results and Discussion

Synthesis of Block Copolymers of Poly(*m*-benzamide)s with Various Kinds of Side Chains. Block copolymers of meta-substituted poly(benzamide)s with various side chains were synthesized by sequential chain-growth condensation polymerization. Thus, **1a** was polymerized in the presence of **3** as an initiator ($[\mathbf{1a}]_0/[\mathbf{3}]_0 = 10$) and LiHMDS (2.2 equiv) as a base in THF at 0 °C to give a prepolymer. A fresh feed of **1b** ($[\mathbf{1b}]_0/[\mathbf{3}]_0 = 10$) was added to the prepolymer in the reaction mixture.

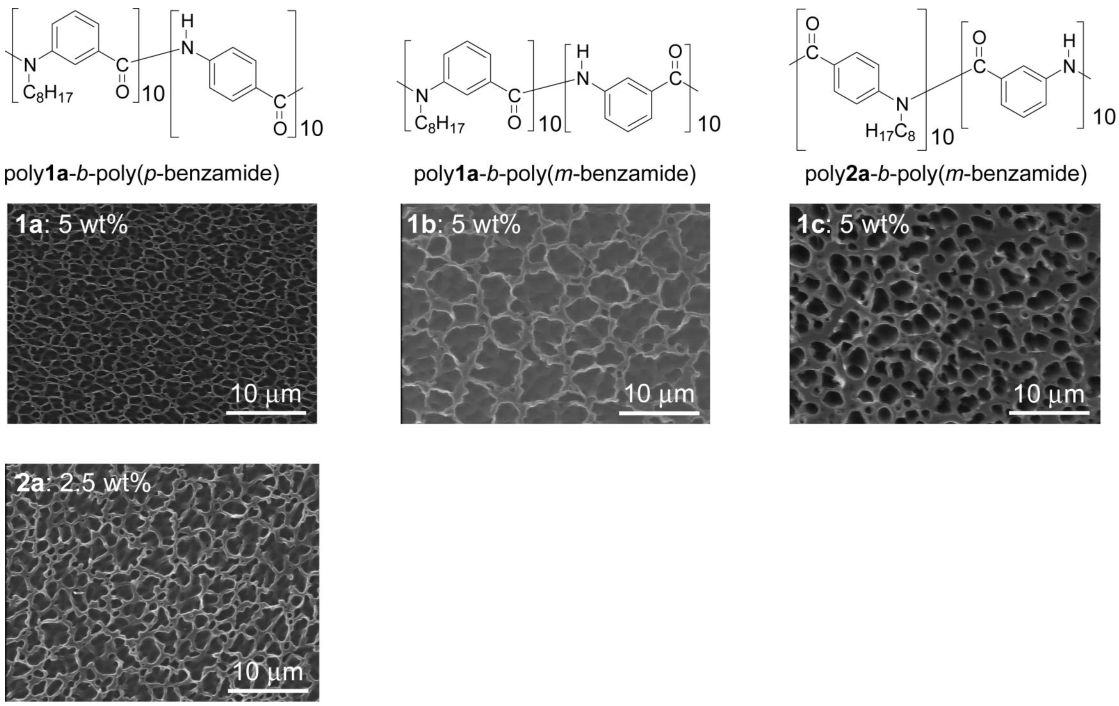
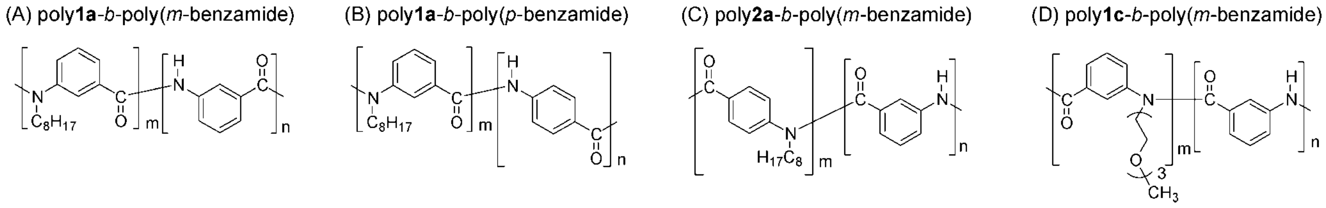


Figure 7. SEM images of (1a) dried CH_2Cl_2 gel at 5 wt % of diblock copolymer and (1b, 1c, 2a) structures formed after drying 5 or 2.5 wt % solution of diblock copolymer in CH_2Cl_2.

Table 4. Solubility and Gelating Properties of Diblock Copolymers Containing *N*−H Poly(*m*- or *p*-benzamide)[a]



	(A)			(B)		(C)	(D)	
solvent	$m = 10$ $n = 10$	$m = 20$ $n = 10$	$m = 10$ $n = 20$	$m = 10$ $n = 10$	$m = 20$ $n = 10$	$m = 10$ $n = 10$	$m = 10$ $n = 10$	$m = 10$ $n = 20$
hexane	−	−	−	−	−	−	−	−
toluene	G (10 wt %)	++	TG (10 wt %)	TG (10 wt %)	TG (10 wt %)	G (10 wt %)	−	−
ether	−	−	+	−	−	−	−	−
THF	++	++	++	G (10 wt %)	++	++	++	++
CH_2Cl_2	++	++	G (5 wt %)	G (5 wt %)	++	++	+	TG (5 wt %)
ethyl acetate	G (10 wt %)	−	TG (10 wt %)	−	+	−	−	−
acetone	−	−	++	−	−	−	−	−
CH_3CN	−	−	−	−	−	−	−	−
DMF	+	−	++	G (10 wt %)	++	G (10 wt %)	++	++
NMP	++	++	TG (10 wt %)	G (10 wt %)	++	++	++	++
DMSO	++	++	++	−	−	++	++	++
ethanol	−	−	−	−	+	−	−	−
methanol	−	−	−	−	−	−	−	−
H_2O	−	−	−	−	−	−	−	−

[a] ++, soluble at room temperature; +, soluble on heating; −, insoluble; G, gelation (determined by the tube inversion method); TG, turbid gel (determined by the tube inversion method).

The added **1b** was completely consumed. The GPC elution curve of the product was clearly shifted toward the high molecular weight region, but showed a tiny shoulder in the higher molecular weight region, implying that the chain-growth polymerization was accompanied with a low level of self-polycondensation.

In order to suppress self-polycondensation, LiCl (11.0 equiv to **1a**), which is effective for stabilization of anions,[12,16] was employed in the polymerization (Table 1, entry 1). In this case, the GPC elution curve of the product did not show the shoulder and was clearly shifted toward the higher molecular weight region, while the polydispersity remained below 1.10, indicating efficient production of the block copolymer, poly**1a**-*b*-poly**1b** (Figure 1). The terminal structures of the prepolymer and block copolymer were confirmed by ^1H NMR spectroscopy (Figure 2). In the spectrum of the prepolymer, the signal *i* of the methyl group of the initiator **3** unit and the signals of the terminal **1a** unit *a*, *b*, and *c* were observed, and the integral ratio of *i*:*a*:*b*:*c* was 3:2:1:1 (Figure 2A). In the spectrum of the block copolymer, the signals *a*, *b*, and *c* were absent, and the signals of the terminal **1b** unit *j*, *k*, and *l* were observed, as well as the signal *i* of the initiator unit. The integral ratio of *i*:*j*:*k*:*l* was also

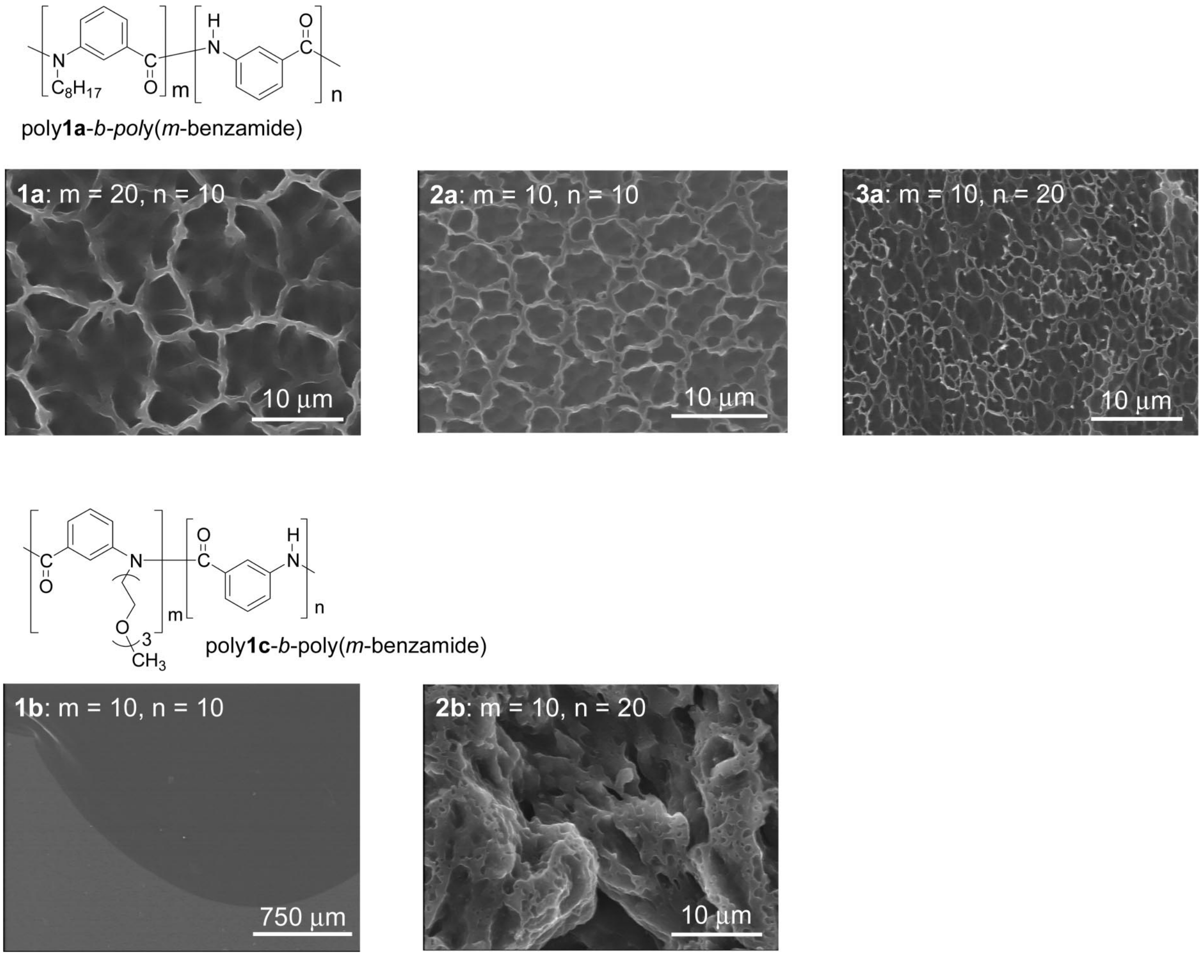


Figure 8. SEM image of (3a, 2b) dried CH_2Cl_2 gel at 5 wt % of diblock copolymer and (1a, 2a, 1b) structures formed after drying a 5 wt % solution of diblock copolymer in CH_2Cl_2.

3:2:1:1 (Figure 2B). These results indicate that one initiator molecule formed one prepolymer chain and one chain end of the prepolymer formed one block copolymer chain. Furthermore, the M_n values of the prepolymer and block copolymer estimated from these ^1H NMR spectra were in good agreement with the calculated values based on the feed molar ratio of monomers **1a** and **1b** to initiator **3** (Table 1, entry 1). Other block copolymers of **1a** and **1b** with different compositions were also synthesized in a controlled fashion (entries 2 and 3).

In the synthesis of block copolymers containing poly(*m*-benzamide) with *N*-tri(ethylene glycol) methyl ether side chain (poly**1a**-*b*-poly**1c** and poly**1b′**-*b*-poly**1c**), poly**1a** or poly**1b′** was prepared as a prepolymer, and the postpolymerization of **1c** was carried out. This is because, in the reverse order polymerization, the tri(ethylene glycol) methyl ether moiety of poly**1c** would associate with the lithium cation of LiHMDS and/or the aminyl anion of **1a** or **1b′**, to retard the polymerization of **1a** or **1b′**. The GPC profiles of the products in these block copolymerizations were clearly shifted toward the high molecular weight region, while retaining a narrow molecular weight distribution ($M_w/M_n < 1.20$), indicating successful production of the block copolymers (entries 4−6).

Synthesis of Block Copolymers of Meta- and Para-Substituted Aromatic Polyamides. In our preliminary report, we described the synthesis of poly(*N*-octyl-*m*-benzamide)-*b*-poly(*N*-octyl-*p*-benzamide) (poly**1a**-*b*-poly**2a**) as a block copolymer of meta- and para-substituted aromatic polyamides.[11] In this block copolymerization, the order of the polymerization was important: the meta-substituted monomer **1a** was polymerized first and then the para-substituted monomer **2a**. In the reverse order of polymerization, a small amount of poly**2a** prepolymer remained after the postpolymerization, because excess LiHMDS in the slow prepolymerization of **2a** reacted with the terminal ester moiety of poly**2a** to afford an amide-ended poly**2a**, which is inert for the postpolymerization of **1a**. Accordingly, other meta- and para-substituted block copolymers were synthesized here by the polymerization of the meta-substituted monomer, followed by the postpolymerization of the para-substituted monomer (Table 2). We first synthesized block copolymers of **1a** and **2b**. Thus, the polymerization of **1a** was carried out with **3** ($[\mathbf{1a}]_0/[\mathbf{3}]_0 = 10$) in the presence of 2.2 equiv of LiHMDS and 11 equiv of LiCl in THF at 0 °C. After consumption of **1a**, a fresh feed of **2b** ($[\mathbf{2b}]_0/[\mathbf{3}]_0 = 10$) was added to poly**1a** in the reaction mixture. The GPC elution curve of the postpolymer was shifted toward the higher molecular weight region from that of the prepolymer, while maintaining the unimodal and narrow shape (Figure 3). In the ^1H NMR spectrum of the postpolymer, the signals *b* and *c* of the terminal **1a** unit in the prepolymer were absent, and the signal *j* characteristic of the terminal para-substituted **2b** unit was observed. The methyl signal *i* of the terminal methoxycarbonyl group of the poly**2b** segment seems to overlap with the signals *d* and *l*, but a small methylene signal *m* assignable to the terminal ethoxycarbonyl group was also observed (Figure 4). These results from GPC and ^1H NMR indicate successful production of poly**1a**-*b*-poly**2b** (Table 2, entry 1), although some terminal methyl ester moieties were converted to ethyl ester moieties by transesterification with ethoxide, which is a byproduct eliminated in the prepolymerization of ethyl ester monomer **1a**. The polymerization at different feed ratios of **1a** and **2b** ($[\mathbf{1a}]_0/[\mathbf{3}]_0 = 20$, $[\mathbf{2b}]_0/[\mathbf{3}]_0 = 10$) also yielded the corresponding block copolymer with a defined molecular weight and a low polydispersity (entry 2). In a similar manner, a block copolymer consisting of *N*-octyloxybenzyl poly(*m*-benzamide) and *N*-octyl poly(*p*-benzamide), poly**1b′**-*b*-poly**2a**, in which the *N*-alkyl groups are reversed compared to those of poly**1a**-*b*-poly**2b**, was synthesized in a controlled fashion (entry 3).

Solubility of Block Copolymers. Solubility of the obtained copolymers is summarized in Table 3. The copolymer of the *N*-octyl and *N*-octyloxybenzyl meta-substituted polyamides, poly**1a**-*b*-poly**1b**, was soluble in less polar solvents, such as ether, and insoluble in polar solvents, such as dimethyl sulfoxide (DMSO) and acetonitrile (CH_3CN) (Table 3, A). The copolymers of meta-substituted polyamides containing the poly**1c** segment having the tri(ethylene glycol) methyl ether moiety were highly soluble in a wide range of common organic solvents (Table 3, B and C). However, the solubility of poly**1b′**-*b*-poly**1c** became similar to that of poly**1a**-*b*-poly**1b** when the poly**1b′** segment with the *N*-octyloxybenzyl group was long (Table 3, C). As for the block copolymers of meta- and para-substituted polyamides having the *N*-octyl and *N*-octyloxybenzyl groups, the block copolymer with the *N*-octyloxybenzyl group attached to the para-substituted polyamide segment had low solubility and was only soluble in toluene, THF, and CH_2Cl_2 (Table 3, D), whereas the block copolymer with the *N*-octyloxybenzyl group attached to the meta-substituted polyamide segment had a solubility similar to that of poly**1a**-*b*-poly**1b** (Table 3, E).

Removal of the *N*-Octyloxybenzyl Group on Block Copolymers: Synthesis of Block Copolymers Containing an *N*−H Poly(benzamide) Segment. The 4-octyloxybenzyl group on amide nitrogen in the obtained block copolymers was removed with TFA in CH_2Cl_2 at ambient temperature for 3 days.[10,12] The deprotection reaction of all the copolymers proceeded homogeneously, and the products were purified by reprecipitation into a large excess of hexane. In the ^{1}H NMR spectra of the products, the signal of the benzylic protons of the octyloxybenzyl group at around 4.90 ppm was absent, and a new signal due to amide N−H protons was observed at around 10.5 ppm. The FT-IR spectra of the products showed N−H stretching bands at 3290 cm^{-1}. Consequently, removal of the 4-octyloxybenzyl group took place quantitatively without scission of the amide linkage of the block copolymers.

The GPC elution curves (eluent, DMF) of the deprotected block copolymers containing an *N*−H *m*- or *p*-benzamide segment are shown in Figure 5. The block copolymers containing the *N*−H poly(*m*-benzamide) segment with DP 10 showed narrow monomodal elution curves, which were slightly shifted toward the lower molecular weight region from those of the block copolymers before deprotection (Figure 5, parts 1A, 1C, 1D, and 2A). However, the block copolymers containing a longer *N*−H poly(*m*-benzamide) segment (DP 20) showed a small peak in the higher molecular weight region, as well as the peak corresponding to the deprotected block copolymer (Figure 5, parts 3A and 2D). Furthermore, the peak in the high molecular weight region became larger in the case of the block copolymers containing an *N*−H poly(*p*-benzamide) segment (Figure 5, parts 1B and 2B). Especially, the block copolymer consisting of poly**1a** and *N*−H poly(*p*-benzamide) with the composition ratio *m*/*n* of 10/10 showed almost a single peak in the high molecular weight region (Figure 5, part 1B). The observed peaks in the high molecular weight region imply that these block copolymers were aggregated in the GPC eluent, DMF, and that the block copolymers containing *N*−H poly(*p*-benzamide) were more strongly aggregated than the block copolymers containing the meta counterpart.

Gelating Properties of Block Copolymers Containing an *N*−H Poly(benzamide) Segment. The solubility of the above block copolymers containing the *N*−H poly(benzamide) segment was tested, and we found that the block copolymers formed gels in some organic solvents (Table 4, Figure 6). We first compared the gelating properties of four kinds of block copolymers whose composition ratio *m*/*n* is 10/10. The block copolymers containing poly(*m*-benzamide)s, such as poly**1a**-*b*-poly(*m*-benzamide) and poly**2a**-*b*-poly(*m*-benzamide), formed gels in several solvents, such as toluene, ethyl acetate, and DMF, at 10 wt %. Poly**1c**-*b*-poly(*m*-benzamide) did not form a gel. On the other hand, poly**1a**-*b*-poly(*p*-benzamide) showed gelating properties at 5−10 wt % in toluene, THF, CH_2Cl_2 (Figure 6), DMF, and even *N*-methyl-2-pyrrolidone (NMP). This high gelating character may stem from the high aggregability of this block copolymer, which was shown by the observed large peak in the high molecular weight region of the GPC chromatogram (Figure 5, part 1B).

Gel formation with block copolymers of hydrophilic and hydrophobic poly(vinyl ether)s has been reported to take place by virtue of entanglement of the corona segment of micelles that are initially formed from the block copolymer.[17] On the other hand, low molecular weight gelators generally self-assemble to form long fibers in gel tissues.[18] To shed light on the origin of the gelating properties of our polyamide block copolymers, we performed SEM analysis of the dried CH_2Cl_2 gel of poly**1a**-*b*-poly(*p*-benzamide) at 5 wt %. Surprisingly, the obtained image did not show micelles or fibers but a three-dimensional network structure (Figure 7, part 1a). Although a 2.5 wt % CH_2Cl_2 solution of this block copolymer did not form a gel, the SEM image obtained after drying the solution on a glass plate showed a similar network structure, except that the network is coarser than that obtained at 5 wt % (Figure 7, part 2a). Furthermore, 5 wt % CH_2Cl_2 solution of poly**1a**-*b*-poly(*m*-benzamide) and poly**2a**-*b*-poly(*m*-benzamide), which did not contain gel, also showed a similar coarse network structure (Figure 7, parts 1b and 1c). Accordingly, the gelating properties of these block copolymers are probably dependent on the fineness of the network structures, and solvent is presumably confined within the network in the gel.

We next examined the effect of the composition ratio *m*/*n* of poly**1a**-*b*-poly(*m*-benzamide) and poly**1c**-*b*-poly(*m*-benzamide) on the gelating properties in CH_2Cl_2. When the poly**1a** segment of poly**1a**-*b*-poly(*m*-benzamide) was elongated to $m = 20$, gel was not formed. On the other hand, when the poly(*m*-benzamide) segment was elongated to $n = 20$, the CH_2Cl_2 solution formed a gel. The SEM images of three kinds of poly**1a**-*b*-poly(*m*-benzamide) with $m/n = 20/10$, 10/10, 10/20 revealed that increase of the poly**1a** segment resulted in a coarser network (Figure 8, part 1a), whereas increase of the poly(*m*-benzamide) segment resulted in a finer network (Figure 8, part 3a). This result also supports our hypothesis that the fineness of the network structure predominantly determines the gelating properties of the polyamide block copolymers. In the case of poly**1c**-*b*-poly(*m*-benzamide), gel was not formed at $m/n = 10/10$, and the SEM image did not show any assembled structures (Figure 8, part 1b). At $m/n = 10/20$, however, the block copolymer formed a turbid gel at 5 wt %, and the SEM image showed a spongelike thick network (Figure 8, part 2b), which is probably responsible for the turbidity (not transparency) of the gel.

Conclusions

We have demonstrated that well-defined *N*-alkyl poly(*m*-benzamide)-*b*-*N*−H-poly(*m*-benzamide), *N*-alkyl poly(*m*-benzamide)-*b*-*N*−H-poly(*p*-benzamide), and *N*-alkyl poly(*p*-benzamide)-*b*-*N*−H-poly(*m*-benzamide) can be synthesized by means of sequential chain-growth condensation polymerization of *N*-alkyl and *N*-octyloxybenzyl monomers, followed by removal of the octyloxybenzyl group and that these block copolymers show gelating properties. In the synthesis of block copolymers of meta- and para-substituted aromatic polyamides, the meta-substituted monomer was first polymerized in the presence of an initiator and LiHMDS as a base, and then postpolymerization of the para-substituted monomer was carried out. The octyloxybenzyl group on the amide nitrogen in the obtained block copolymers was removed with TFA to yield block copolymers containing the *N*−H polyamide segment. These block copolymers showed gelating properties at low concentration in various solvents. The SEM analysis of the dried CH_2Cl_2 gel revealed that the block copolymers self-assembled to form a three-dimensional network structure. The gelating properties are dependent on the substitution position (meta or para) and the composition ratio of the *N*−H poly(benzamide) segment in these block copolymers. Among them, the block copolymer containing *N*−H poly(*p*-benzamide) showed extensive gelating properties in solvents ranging from aromatic to aprotic polar solvents. Studies of the self-assembly process of the polyamide block copolymers to form network structures will be reported in the near future.

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