Synthesis of Well-Defined Rod-Coil Block Copolymers Containing Trifluoromethylated Poly(phenylene oxide)s by Chain-Growth Condensation Polymerization and Atom Transfer Radical Polymerization

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ABSTRACT: Well-defined trifluoromethylated poly(phenylene oxide)s were synthesized via nucleophilic aromatic substitution (S_NAr) reaction by a chain-growth polymerization manner. Polymerization of potassium 4-fluoro-3-(trifluoromethyl)phenolate in the presence of an appropriate initiator yielded polymers with molecular weights of ~4000 and polydispersity indices of <1.2, which were characterized by ¹H nuclear magnetic resonance spectroscopy and gel permeation chromatography. Initiating sites for atom transfer radical polymerization (ATRP) were introduced at the either side of chain ends of the poly(phenylene ox-

ide), and used for ATRP of styrene and methyl methacrylate, yielding well-defined rod-coil block copolymers. Differential scanning calorimetry study indicated that the well-defined trifluoromethylated poly(phenylene oxide)s showed high crystallinity and were immiscible with polystyrene. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1049–1057, 2010

KEYWORDS: atom transfer radical polymerization; block copolymers; chain-growth condensation polymerization; poly(phenylene oxide)

INTRODUCTION Macromolecules with well-defined structures have been of recent interests, partly because they can be a basic building block for nanostructured organic materials. For example, self-assembled pattern of diblock copolymer thin films has been utilized for nanopatterning in an attempt to overcome the resolution limit of traditional photolithographic technique.¹ Much of diblock copolymer studies have been focused on the diblock copolymers obtained by living or controlled chain polymerization of two different kinds of vinyl monomers.² Recently, rod-coil block copolymers consisting of condensation and addition blocks have been studied, but most of them do not have a precisely defined condensation block mainly because of synthetic difficulties.³ However, a recent development of chain-growth condensation polymerization (CGCP) has opened an easy access for rod-coil block copolymers containing condensation and addition blocks.4

Poly(phenylene oxide), composed of phenyl rings and ether linkages, is a high-performance condensation polymer with excellent physical properties and finds applications in many areas.⁵ A variety of materials including the blend of poly-(phenylene oxide)s and styrenic polymers are commercially available due to the high miscibility between two kinds of polymers.⁶ By using the CGCP technique, well-defined poly-(phenylene oxide)s with narrow polydispersities have been synthesized.⁷ In addition, use of orthogonal initiators for CGCP and atom transfer radical polymerization (ATRP)⁸ has produced well-defined rod-coil block copolymers, which is expected to show interesting self-assembly behaviors due to the large incompatibility between the rod and the coil segments.⁹

An interesting class of poly(phenylene oxide)s is a fluorinecontaining poly(phenylene oxide), promising material for optoelectronic applications. The introduction of fluorine is important because it provides low optical loss, birefringence, dielectric constant, and moisture absorption.¹⁰ Previously we have found that a trifluoromethyl group at the *ortho* position of the leaving group (i.e., F or NO₂) facilitates a nucleophilic aromatic substitution (S_NAr) reaction, and we synthesized a number of poly(phenylene oxide)s containing trifluoromethyl groups which show excellent optical properties.¹¹ Here, we report the synthesis of well-defined poly(phenylene oxide)s by using a phenoxide monomer containing the trifluoromethyl group with appropriate initiators for CGCP. Also, synthesis of rod-coil block copolymers containing trifluoromethylated poly(phenylene oxide) block is presented.

EXPERIMENTAL

Materials

4-Fluoro-3-(trifluoromethyl)phenol (Fluorochem), 4-fluoro-3-(trifluoromethyl)aniline (Aldrich), 4-nitro-3-(trifluoromethyl)benzonitrile (**2**, Aldrich), 2-bromoisobutyryl bromide (Aldrich), and 2,2'-bipyridine (bpy, Aldrich) were used as received. Phenol was distilled under reduced pressure. 2-

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Nitrobenzotrifluoride (3) was recrystallized from methanol/ hexane. Dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) were stirred in the presence of calcium hydride overnight and then distilled under reduced pressure. Methyl methacrylate (MMA) and Styrene (Aldrich) was passed through a column filled with neutral alumina, stirred in the presence of calcium hydride overnight, and then distilled under reduced pressure before use. Copper(I) chloride (CuCl) was washed with glacial acetic acid and absolute ethanol, and dried in vacuo. 4,4'-Di-(5-nonyl)-2,2'-bipyridine (dnbpy) was synthesized as reported previously. Methanol (HPLC grade), dichloromethane (HPLC grade), tetrahydrofuran (THF, HPLC grade), cyclohexane (HPLC grade), and anisole (anhydrous grade) were used without further purification. Polystyrene standards were purchased from Senshu Scientific. Other commercially available reagent grade chemicals were used without further purification.

Potassium 4-Fluoro-3-(trifluoromethyl)phenoxide) (1)

4-Fluoro-3-(trifluoromethyl)phenol (14.1 g, 78.3 mmol) was stirred in methanol (30 mL) in a 250 mL flask. Potassium hydroxide (4.26 g, 76.0 mmol) dissolved in methanol (70 mL) was slowly added to the flask at 0 °C, and the mixture was stirred at room temperature for an additional hour. After excess solvent was evaporated, oil-like product was poured into dichloromethane. The white powder was filtered, washed with dichloromethane, and dried *in vacuo* (13.9 g, 81% yield). m.p. 73–75 °C.

¹H NMR (400.13 MHz, DMSO- d_6 , 25 °C, ppm): 6.67 (t, J = 10.6 Hz, 1H), 6.20–6.10 (2H). ¹³C NMR (100.62 MHz, DMSO- d_6 , ppm): 167.97, 144.59 (d, J = 229.5 Hz), 124.00 (dq, J = 271.6 Hz, J = 1.5 Hz), 121.85 (d, J = 6.0 Hz), 116.32 (d, J = 19.7 Hz), 115.76 (dq, J = 29.9 Hz, J = 12.4 Hz), 113.10 (dq, J = 3.9 Hz, J = 1.6 Hz).

4'-Hydroxy-4-fluoro-3-(trifluoromethyl)azobenzene) (4)

4-Fluoro-3-(trifluoromethyl)aniline (5.07 g, 28.3 mmol) and 50 mL of 2 N HCl (aq) was placed in a 100 mL flask. The mixture was stirred at 0 °C while sodium nitrite (2.34 g, 33.9 mmol) in distilled water (10 mL) was added slowly. The mixture became homogenous, which was indicative of the formation of diazonium salt. Then, aqueous sodium phenoxide solution, prepared by dissolving phenol (3.19 g, 33.9 mmol) and sodium hydroxide (2.72 g, 67.9 mmol) in distilled water (10 mL) was slowly added to the flask. The reaction mixture was stirred at room temperature for additional 2 h. The resulting precipitate was filtered, washed with distilled water, and dried in vacuo. After the precipitate was added into ethyl acetate (200 mL), insoluble compound was filtered. Excess solvent in the filtrate was evaporated to give orange-colored product which was further purified by silica column chromatography using ethyl acetate/n-hexane (1/8) as an eluent, and then recrystallized from dichloromethane/cyclohexane (6.90 g, 86% yield). m.p. 121-122 °C.

¹H NMR (400.13 MHz, tetrahydrofuran- d_8 , 50 °C, ppm): 8.92 (s, 1H), 8.15 (dd, J = 6.73 Hz, J = 2.37 Hz, 1H), 8.14–8.09 (m, 1H), 7.87–7.82 (m, 2H), 7.45 (t, J = 9.44 Hz, 1H), 6.92–6.87 (m, 2H). ¹³C NMR (100.62 MHz, tetrahydrofuran- d_8 , 50

°C, ppm): 162.66, 161.21 (qd, J = 258.9 Hz, J = 2.1 Hz), 150.13 (d, J = 3.6 Hz), 147.01, 128.91 (d, J = 9.1 Hz), 126.09 (q, J = 34.4 Hz), 123.65 (dq, J = 272.3 Hz, J = 1.2Hz), 121.84 (dq, J = 4.6 Hz, J = 2.0 Hz), 119.61 (dq, J = 33.3Hz, J = 13.9 Hz), 118.60 (d, J = 22.3 Hz), 116.68. EI HRMS (m/z): calcd for C₁₃H₈F₄N₂O, 284.0573; found, 284.0572 [M]⁺.

Syntheses of Poly(phenylene oxide)s via CGCP (CF3PPO3 and CF3PPO4)

All the polymerizations were carried out under dry argon atmosphere. A typical polymerization procedure was exemplified with the synthesis of CF3PPO3. A dried, 100 mL three-necked flask was equipped with a mechanical stirrer and a Dean-Stark trap connected to a water-cooled condenser. 1 (3.02 g, 13.9 mmol), 3 (0.177 g, 0.924 mmol), and DMSO (55 mL) were added to the flask. The polymerization mixture was stirred at 120 °C. To investigate the polymerization kinetics, small portion of the reaction mixture was taken via syringe (previously purged with argon) under dry argon atmosphere at a certain time interval. For the NMR measurement, each crude mixture was added to tetrahydrofuran- d_8 . For the GPC measurement, each crude mixture was added to tetrahydrofuran and passed through a 0.2 μ m filter before injection. After the polymerization was complete, the solution was poured into vigorously stirred distilled water. The resulting polymer was filtered, washed with distilled water, and dried in vacuo.

Using the aforementioned procedure, CF3PPO4 was synthesized from 1 (2.14 g, 9.79 mmol), 4 (0.186 g, 0.653 mmol), and DMSO (40 mL).

Synthesis of the Macroinitiator CF3PPO3Br

A 100 mL three-necked flask was equipped with a Dean-Stark trap connected to a water-cooled condenser. **CF3PP03** (1.50 g, 0.577 mmol), 4-aminophenol (0.252 g, 2.31 mmol), K_2CO_3 (0.399 g, 2.89 mmol), DMF (35 mL), and benzene (18 mL) were added to the flask. The reaction mixture was heated to 140 °C for 24 h at which the benzene was brought to reflux. After the reaction was complete, the solution was poured into vigorously stirred distilled water. The product was filtered, washed with distilled water and methanol repeatedly, and dried *in vacuo*.

The amine-terminated **CF3PPO3** (0.800 g, 0.295 mmol) was added into a dried 50 mL flask with triethylamine (0.120 g, 1.18 mmol) and THF (20 mL). 2-Bromoisobutyryl bromide (0.272 g, 1.18 mmol) in THF (3 mL) was slowly added to the flask at room temperature. Then, the mixture was stirred at 60 °C for 24 h. After the reaction was complete, the solution was poured into vigorously stirred distilled water. The resulting **CF3PPO3Br** was filtered, washed with distilled water and methanol repeatedly, and dried *in vacuo*. **CF3PPO3Br** was further purified by the reprecipitation in methanol.

Synthesis of the Macroinitiator CF3PPO4Br

CF3PPO4 (0.600 g, 0.240 mmol) was added into a dried 50 mL flask with triethylamine (0.0971 g, 0.960 mmol) and



SCHEME 1 Self-polymerization of the monomer 1.

THF (15 mL). 2-Bromoisobutyryl bromide (0.221 g, 0.960 mmol) in THF (2 mL) was slowly added to the flask at room temperature. Then, the mixture was stirred at 60 °C for 24 h. After the reaction was complete, the solution was poured into vigorously stirred distilled water. The product was filtered, washed with distilled water and methanol repeatedly, and dried *in vacuo*. **CF3PPO4Br** was further purified by the reprecipitation in methanol.

Synthesis of CF3PPO-b-PMMA

A typical polymerization procedure was exemplified with the ATRP of MMA from CF3PPO3Br macroinitiator (Table 2, Entry 1). CuCl (0.0139 g, 0.140 mmol), bpy (0.0437 g, 0.280 mmol), and MMA (3.50 g, 35.0 mmol) was placed in a dried Schlenk flask under dry argon atmosphere. The mixture was diluted with anisole (3.7 mL), stirred until it became homogeneous, and then degassed by "freeze-pump-thaw" cycles. After deoxygenated anisole solution of the CF3PPO3Br macroinitiator (0.200 g, 0.0700 mmol) was added to the flask via gastight syringe under dry argon atmosphere, three more "freeze-pump-thaw" cycles were performed. Then, the flask was immersed in an oil bath thermostatted at 90 $^\circ$ C. At a proper monomer conversion below 50%, the polymerization mixture was cooled to room temperature and diluted with THF. After the solution was passed through a small column of alumina and a 0.2 μ m filter, it was poured into *n*-hexane. The resulting precipitate was filtered, washed with *n*hexane, and dried in vacuo. Reprecipitation in hot methanol yielded the desired CF3PPO-b-PMMA block copolymer.

Synthesis of CF3PPO-b-PS

A typical polymerization procedure was exemplified with the ATRP of styrene from CF3PPO4Br macroinitiator (Table 2, Entry 4). CuCl (0.0374 g, 0.377 mmol), dnbpy (0.308 g, 0.755 mmol), and styrene (3.93 g, 37.7 mmol) was placed in a dried Schlenk flask under dry argon atmosphere. The mixture was diluted with anisole (4.3 mL), stirred until it became homogeneous, and then degassed by "freeze-pumpthaw" cycles. After deoxygenated anisole solution of the CF3PPO4Br macroinitiator (0.200 g, 0.0755 mmol) was added to the flask via gastight syringe under dry argon atmosphere, three more "freeze-pump-thaw" cycles were performed. Then, the flask was immersed in an oil bath thermostatted at 110 °C. At a proper monomer conversion below 50%, the polymerization mixture was cooled to room temperature and diluted with THF. After the solution was passed through a small column of alumina and a 0.2 μ m filter, it was poured into methanol. The resulting precipitate was filtered, washed with methanol, and dried in vacuo. The polymeric mixture was stirred in cyclohexane overnight. Filtration of insoluble precipitates and evaporation of the filtrate yielded the desired CF3PPO-b-PS block copolymer.

Characterization

¹H NMR and ¹³C NMR spectra of the synthesized compounds were recorded on a Bruker Fourier Transform AVANCE 400 (400.13 MHz for ¹H and 100.62 MHz for ¹³C) spectrometer. Chemical shift of NMR was reported in part per million (ppm) using residual proton resonance of solvent as internal reference. Splitting patterns designated as s (singlet), d (doublet), q (quartet), dd (doublet of doublet), dq (doublet of quartet), gd (quartet of doublet), m (multiplet), and br (broaden). Electron impact high-resolution mass (EI HRMS) spectra of the synthesized compounds were obtained with a Micromass Autospec Ultima mass spectrometer. Gel Permeation Chromatography (GPC) traces were obtained with Viscotek T60A equipped with UV detector and packing column (PLgel 10 μ m MIXED-B) using tetrahydrofuran as an eluent at 35 °C. Number (M_n) and weight (M_w) average molecular weights of the polymers were calculated on the basis of polystyrene standards. Differential scanning calorimetry (DSC) analyses were performed on a TA Q100 instrument. Melting (T_m) and/or glass (T_g) transition temperatures of the synthesized compounds were obtained with the DSC instrument at a heating rate of 5 $^{\circ}$ C/min in N₂.

RESULTS AND DISCUSSION

Synthesis of Well-Defined Poly(phenylene oxide)s

For the synthesis of well-defined poly(phenylene oxide)s containing trifluoromethyl groups via S_NAr reaction, potassium 4-fluoro-3-(trifluoromethyl)phenolate (1) was chosen as an appropriate AB' type monomer. Because the reactivity of the fluorine is suppressed by the electron-rich phenoxide group at the *para* position of the phenyl ring, self-polymerization of the monomer 1 does not proceed below 140 °C in DMSO or *N*,*N*-DMF. However, once the phenoxide group is transformed into ethereal oxygen, the fluorine is activated by the trifluoromethyl group at *ortho* position and polymerization proceeds (Scheme 1).

On the basis of the previous results, CGCP of the monomer **1** was investigated using different B type initiators shown in Scheme 2 and 3. Polymerization was conducted in DMSO at a total concentration of 5 wt %. The ratio between the monomer ([M]) and the initiator ([I]) was 15, and the reaction temperature was 120 °C to avoid self-polymerization of the monomer.

Initiators for CGCP should react with the monomers at temperatures where self-polymerization does not occur. 4-Nitro-3-(trifluoromethyl)benzonitrile (2) was selected as an initiator because it possesses a nitro leaving group strongly activated by the trifluoromethyl group as well as the nitrile



SCHEME 2 CGCP of the monomer **1** in the existence of initiators **2** and **3**.



FIGURE 1 (a) Evolution of GPC traces for polymerization of the monomer **1** in the existence of **3** in DMSO. Total concentration was 5 wt % and [**1**]/[**3**] was 15. (b) Number-average molecular weight M_n (circles) and PDI (M_w/M_n , triangles) as a function of overall monomer conversion. Theoretical M_n (line) was calculated from the conversion. (c) $\ln([M]_0/[M])$ versus time plot (circles). The line was obtained by linear regression.

group. However, GPC analysis of the polymer CF3PPO2 synthesized by the polymerization of **1** in the presence of the initiator 2 showed trimodal molecular weight distribution, indicating that the polymerization did not proceed in a controlled manner. The origin of the poor controllability was attributed to a transetherification reaction at the ether linkage between the initiator 2 and the repeating unit. The transetherification is likely to occur because the ether linkage is strongly activated by the trifluoromethyl group and the nitrile group as well. It will produce a polymer terminated with a phenoxide group which can grow further via a step-growth manner or which can form a macrocycle via intramolecular cyclization. These side reactions disturb the controlled polymerization behavior, resulting in the trimodal molecular weight distribution as suggested by the previous study.7(b)

Because 2-nitrobenzotrifluoride (3) contains a fluorine leaving group solely activated by the trifluoromethyl group, the synthesized polymer is expected to show higher tolerance towards the transetherification reaction when 3 is used as an initiator. Figure 1(a) shows the evolution of the GPC traces of the polymer CF3PPO3 synthesized by polymerization of the monomer 1 with the initiator 3. GPC analysis reveals that the molecular weight increases linearly with conversion and the experimental values are close to the theoretical ones, assuming quantitative initiation. The molecular weight distributions decrease with conversion, and at the end of the reaction, are relatively narrow [Fig. 1(b)]. In addition, the plot of $\ln([M]_0/[M])$ versus time is linear indicating a constant number of propagating species throughout the reaction [Fig. 1(c)]. These data support that the polymerization proceeds in a controlled chain-growth manner.¹²

Multifunctional initiators have an advantage in introducing useful functionalities into the polymer chains.¹³ In this regard, a multifunctional initiator **4** was synthesized by diazotization of 4-fluoro-3-(trifluoromethyl)aniline followed by coupling with phenol (Scheme 3). The initiator **4** contains

a fluorine leaving group (B') activated by the trifluoromethyl group at *ortho* position of the phenyl ring for CGCP. Also, the initiator contains a phenolic hydroxyl group on the other side which can be used for post-modification of the synthesized polymer. The azobenzene group in the middle of the olecule acts not only as a bridge between two functionalities but as a stimuli-responsive moiety via photoisomerization.¹⁴

Polymerization of the monomer **1** in the presence of the initiator **4** was conducted under the same condition for the polymerization with the initiator **3** (Scheme 3). The polymerization proceeds in a controlled chain-growth manner illustrated by the linear increase of the molecular weight with conversion which well matches the theoretical values, narrow PDIs throughout the polymerization, and the linear plot of $\ln([M]_0/[M])$ versus time (Fig. 2). It is interesting to observe that the phenolic hydroxyl group did not participate in the polymerization results of the synthesized polymers.

Figure 3 shows ¹H NMR spectra of **CF3PPO3** and **CF3PPO4** in THF- d_8 . All protons in the initiator and the repeating units are clearly visible. Especially, ¹H NMR spectrum of **CF3PPO4** shows a peak at 8.8 ppm corresponding to the phenolic proton confirming that the phenolic hydroxyl group remains in the polymer [Fig. 3(b)].



SCHEME 3 Synthesis of azobenzene-containing multifunctional initiator **4** and CGCP of the monomer **1** using **4**.



FIGURE 2 (a) Number-average molecular weight M_n (circles) and PDI (M_w/M_n , triangles) as a function of overall monomer conversion for polymerization of the monomer **1** with **4** in DMSO at 120 °C. Total concentration was 5 wt % and [**1**]/[**4**] was 15. Theoretical M_n (line) was calculated from the conversion. (b) $\ln([M]_0/[M])$ versus time plot (circles). The line was obtained by linear regression.

The CGCP of 1 was also attempted at an increased feed ratio relative to **3** ([1]/[3] = 30) in DMSO at 120 °C. However, the mixture became heterogeneous at the last stage of polymerization. The ¹H NMR spectrum indicated that the monomer conversion was about 80% (theoretically calculated $M_{\rm n}$ of the polymer = $\sim 4 \times 10^3$). The GPC trace showed a peak which was accompanied by a small shoulder in higher molecular weight region [Fig. 4(a), 72 h]. The continued polymerization of the heterogeneous mixture was not controllable. The shoulder peak intensified, and not only the main peak but also the shoulder peak shifted toward higher molecular weight region [Fig. 4(a), 96 h]. These polymerization behaviors implied the growths of polymer chains in two different phases, that is, one from the solution phase and the other from the precipitated solid phase. It was believed that the rigid, rod-like poly(phenylene oxide) had a limited solubility in DMSO above certain molecular weight. The poly-(phenylene oxide) showed a good solubility in THF, and was also soluble in anisole and DMF on heating. The synthesis of high molecular weight poly(phenylene oxide) was also attempted in DMF considering its better solubility in DMF than in DMSO. The molecular weight could be increased to $\sim 4 \times 10^3$ with maintaining narrow PDI of 1.14 [Fig. 4(b), 96 h]. However, the polymerization could not be complete within reasonable time (monomer conversion: $\sim 80\%$ for

 TABLE 1 CGCP of the Monomer 1 in the Presence of Different Initiators

Entry	Initiator	<i>M</i> _n ^a	<i>M</i> _w ^a	PDI
CF3PPO1	None	2.0×10^3	4.0×10^3	2.0
CF3PPO3	3	2.6×10^3	2.8×10^3	1.09
CF3PPO4	4	2.5×10^3	2.9×10^3	1.14

^a Determined by GPC using polystyrene standards (THF).

96 h) because of the polymer solubility issues and slow polymerization kinetics.

Block Copolymerization by ATRP

For the synthesis of rod-coil block copolymers, atom transfer radical polymerization (ATRP) was considered because introduction of an ATRP initiator into the synthesized poly(phenylene oxide)s can be readily achieved. Scheme 4 shows synthetic routes for the poly(phenylene oxide)s bearing ATRP initiating sites.



FIGURE 3 ¹H NMR spectra of (a) CF3PPO3 and (b) CF3PPO4 (400 MHz, THF- d_8 , 50 °C).



FIGURE 4 (a) Evolution of GPC traces for polymerization of the monomer 1 in the existence of 3 (a) in DMSO and (b) in DMF. Total concentration was 5 wt % and [1]/[3] was 30.

CF3PPO3, which contains a fluorine leaving group at the chain end, was reacted with 4-aminophenol via S_NAr reaction using potassium carbonate as a base. When the reaction was conducted in DMF at 140 °C, amine-terminated **CF3PPO3** was exclusively produced presumably because the amine group was not reactive enough as a nucleophile compared to the phenoxide ions in the given reaction condition. A slightly shifted but unimodal GPC trace was observed after the reaction, suggesting no side reaction such as transetherification occurred (data not shown). Subsequent amide formation between the amine-terminated **CF3PPO3** and 2-bromoisobutyryl bromide in the presence of triethylamine produced **CF3PPO3** bearing an ATRP initiator at the chain end **(CF3PPO3Br)**.

For **CF3PPO4**, which contains a phenolic hydroxyl group, introduction of an ATRP initiator was simply achieved by esterification of **CF3PPO4** with 2-bromoisobutyryl bromide. The reaction produced **CF3PPO4Br** bearing an ATRP initiator at the chain end. ¹H NMR spectra of **CF3PPO3Br** and **CF3PPO4Br** in THF- d_8 are shown in Figure 5.

To demonstrate the feasibility of block copolymerization, ATRP of methyl methacrylate (MMA) and styrene was con-



FIGURE 5 ¹H NMR spectra of (a) **CF3PPO3Br** and (b) **CF3PPO4Br** (400 MHz, THF- d_8 , 50 °C).

ducted using **CF3PPO3Br** and **CF3PPO4Br** macroinitiators. Scheme 5 shows the structures and synthetic schemes of the resulting CF3PPO-*b*-PMMA and CF3PPO-*b*-PS copolymers. Table 2 summarizes the ATRP conditions and the characterization results for the block copolymers. To monitor the polymerization behavior, some of the polymerization mixture was taken during ATRP, and analyzed by NMR and GPC. The feed ratio of monomer to macroinitiator was 500. The polymerization was stopped at a monomer conversion of <50% to avoid radical-radical coupling reactions.

Reaction conditions for ATRP of MMA^{15} and styrene¹⁶ have been well developed in previous studies. We utilized halogen exchange system (R-Br/CuCl) to facilitate faster initiation than propagation.¹⁷ ATRP of MMA was conducted at 90 °C in the presence of CuCl and 2,2'-bipyridine (bpy) in 50% (v/v) of anisole as a solvent. When one equivalent of CuCl/bpy



SCHEME 4 Synthesis of ATRP macroinitiators CF3PPO3Br and CF3PPO4Br containing poly(phenylene oxide) CF3PPO3 and CF3PPO4, respectively.



SCHEME 5 Synthesis of block copolymers consisting of poly(phenylene oxide)s via ATRP.

complex relative to the macroinitiator CF3PPOBr used, polymerization proceeded slowly. GPC analysis showed that some portion of the macroinitiator did not participate in the polymerization although the growing CF3PPO-b-PMMA maintained narrow molecular weight distributions during the polymerization. When the amount of the catalyst increased to two equivalents, polymerization proceeded more rapidly, and it was possible to obtain a block copolymer with high molecular weight (entry 1). Unreacted macroinitiators still remained after the polymerization, but they were readily removed by reprecipitation of the crude product in hot methanol, yielding a pure block copolymer with narrow polydispersity [Fig. 6(a)]. The molar ratio of two kinds of repeating units, MMA to PPO, in the block copolymer was determined as 15:1 by ¹H NMR. Given the GPC data (total $M_{\rm n}$ of the block copolymer: $\sim 1.8 \times 10^4$), it was estimated that PMMA block has $M_{\rm n}$ of \sim 1.6 \times 10⁴. **CF3PPO4Br** also successfully produced a high molecular weight CF3PPO-b-PMMA copolymer with narrow polydispersity using the same ATRP condition (entry 2).

For the synthesis of CF3PPO-*b*-PS copolymer from **CF3PPO3Br** or **CF3PPO4Br**, we used CuCl/4,4'-di-(5-nonyl)-2,2'-bipyridine (dnbpy) catalyst system which has been known to induce the well-controlled, homogeneous ATRP of styrene.¹⁶ Excess amount of catalyst is required because of

the slow polymerization rate in anisole at 110 °C. When the ATRP of styrene was carried out in the presence of CF3PPO3Br using 5 equivalent of CuCl/dnbpy complex, the polymerization mixture became viscous after 36 h. The GPC analyses indicated that the CF3PPO-b-PS copolymer had a high molecular weight, but relatively broad molecular weight distribution (entry 3). Furthermore, significant amount of CF3PPO3Br macroinitiator was remained without initiation. **CF3PPO3Br** might not be suitable in the controlled polymerization of styrene presumably because of the amide bond next to the initiating site. It has been reported that the amide type ATRP initiators generally have poor efficiency and can produce polymers with high polydispersities.¹⁸ When CF3PPO4Br was used as a macroinitiator, high molecular weight block copolymer was obtained as well as the molecular weight distribution was narrow [entry 4 and Fig. 6(b)]. The block copolymer was extracted with cyclohexane to remove any unreacted macroinitiators. The molar ratio of styrene to phenylene oxide in the block copolymer was determined as 14:1 by ¹H NMR (estimated $M_{\rm n}$ of PS block: 1.7×10^4).

Thermal Properties of the Polymers and Miscibility Between the Blocks

DSC studies were carried out to evaluation thermal transitions of the synthesized polymers and miscibility between the blocks. DSC thermograms of **CF3PPO3** and block

TABLE 2 ATRP of Vinyl Monomers from the Po	oly(phenylene oxide) Macroinitiators
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Entry	Monomer	Initiator	Catalyst	[M]:[l]:[Cu]:[ligand]	<i>M</i> _n ^a	<i>M</i> _w ^a	PDI ^a
1 ^b	MMA	CF3PPO3Br	CuCl/bpy ^c	500:1:2:4	1.8×10^4	2.2×10^4	1.20
2 ^b		CF3PPO4Br	CuCl/bpy ^c	500:1:2:4	1.6×10^4	1.8×10^4	1.17
3 ^d	Styrene	CF3PPO3Br	CuCl/dnbpy ^e	500:1:5:10	2.2×10^4	2.9×10^4	1.35
4 ^d		CF3PPO4Br	CuCl/dnbpy ^e	500:1:5:10	1.9×10^4	2.3×10^4	1.24

^a Determined by GPC using polystyrene standards (THF).

 $^{\rm b}$ Polymerization was carried out in 50% (v/v) of anisole at 90 °C for 1 h and the resulting polymer was purified by reprecipitation in hot methanol.

^c Bipyridine.

 $^{\rm d}$ Polymerization was carried out in 50% (v/v) of anisole at 110 $^\circ \rm C$ for 36 h and the resulting polymer was purified by extraction with cyclohexane.

e 4,4'-Di-(5-nonyl)-2,2'-bipyridine.



FIGURE 6 THF-GPC chromatograms of (a) CF3PPO-*b*-PMMA (Table 2, Entry 1) and (b) CF3PPO-*b*-PS (Table 2, Entry 4) measured by UV detector at the flow rate of 1 mL/min.

copolymers consisting of the **CF3PPO** segment are shown in Figure 7. **CF3PPO3** shows a large endothermal transition at 220 °C which was assigned as melting transition [Fig. 7(a)]. In contrast to the previously reported amorphous poly(phenylene oxide) containing trifluoromethyl group which shows a glass transition at 108 °C,^{V11(c)} the well-defined architecture achieved by CGCP might attribute to the highly crystalline nature of **CF3PPO3**.^{7(b)} CF3PPO-*b*-PMMA in which PMMA has much higher molecular weight showed only one



FIGURE 7 DSC thermograms of (a) **CF3PPO3**, (b) CF3PPO-*b*-PMMA (2.6–13.1 k), and (c) CF3PPO-*b*-PS (2.5–5.6 k). Thermograms were recorded during the second heating cycle at the heating rate of 5 $^{\circ}$ C/min under nitrogen.

glass transition corresponding to that of PMMA, indicating that both blocks are miscible [Fig. 7(b)]. However, CF3PPO*b*-PS showed two thermal transitions corresponding to the glass transition of polystyrene block and the melting transition of **CF3PPO** block, respectively [Fig. 7(c)]. This tendency is clearly different from the conventional PPOTM, which is completely miscible with polystyrene regardless of molecular weight and composition.

CONCLUSIONS

Well-defined poly(phenylene oxide)s containing trifluoromethyl groups were synthesized via CGCP. By using the appropriate polymerization conditions such as initiator and reaction temperature, trifluoromethylated poly(phenylene oxide)s with desired molecular weights and narrow molecular weight distribution were readily obtained. Furthermore, block copolymers consisting of poly(phenylene oxide)s were synthesized by introducing initiators for ATRP at the chain end. Subsequent ATRP of styrene or methyl methacrylate produced well-defined block copolymers. Thermal transitions of synthesized poly (phenylene oxide)s and their block copolymers suggest that the poly(phenylene oxide)s are highly crystalline due to the welldefined architecture and they are immiscible with polystyrene.

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