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## **Abstract**

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## **Keywords**

Chemistry

## **Disciplines**

Metallurgy

## **Comments**

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# Development of a Versatile Methodology for the Synthesis of Poly(2,5-benzophenone) Containing Coil–Rod–Coil Triblock Copolymers

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**ABSTRACT:** A short, simple, versatile methodology was developed for the synthesis of poly(2,5-benzophenone) containing coil–rod–coil triblock copolymers. After a model study, poly(2,5-benzophenone) macroinitiators were synthesized via end-capping poly(2,5-dichlorobenzophenone) synthesized by Ni(0)-catalyzed polymerization and functionalization of the chain ends utilizing phase transfer chlorination. Varying molecular weights of polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene were synthesized using the macroinitiators in the atom transfer radical polymerization of styrene. The materials were characterized by gel permeation chromatography, nuclear magnetic resonance, differential scanning calorimetry, and transmission electron microscopy. Applications were explored through dynamic mechanical analysis and the construction of a distributed junction photovoltaic device.

## Introduction

Rod–coil and coil–rod–coil block copolymers are a unique and interesting class of new materials. The combination of the flexible random coil segments with rigid-rod blocks gives rise to many potential applications in optoelectronic devices, nanopatterning, and mechanical reinforcing agents. The utility of these materials arises from the block copolymer architecture. The inherent incompatibility resulting from entropic factors between the rigid-rod-like block and the flexible random coil block leads to phase separation at much lower molecular weights than coil–coil systems.<sup>1</sup> The flexible coil-like blocks also increase the solubility and processability of the copolymer over that of the rodlike homopolymer. Rod–coil block copolymers containing materials such as oligophenylenevinylene (OPV),<sup>2,3</sup> oligophenyleneethylene (OPE),<sup>4</sup> and poly-*p*-phenylene (PPP)<sup>5</sup> have been synthesized. Additionally, coil–rod–coil triblock copolymer architectures containing aromatic heterocyclic rigid rod materials such as poly(benzobisthiazole) have been reported.<sup>6–9</sup>

Ordered, phase-separated structures with dimensions as small as 10 nm have been constructed. The ability to pattern materials such as PPV, PPE, and PPP on nanometer scales leads to potential utility in the electronics industry. For example, coil–rod–coil block copolymers have exhibited narrowed emission spectra over that of the rod homopolymer due to isolated domains of the optically active material.<sup>8,10</sup> Furthermore, the high modulus of the rigid backbones has been exploited through the use of these materials to construct nanocomposites.<sup>11</sup>

Narrow overall polydispersity is generally considered a prerequisite for the formation of ordered structures from most block copolymers consisting of two coil blocks.

However, the importance of polydispersity in systems containing a polydisperse rod block has never fully been explored. Because of the incompatibility of the rod block in the random coil phase, phase separation is expected, but the degree of control of the resulting morphology is not known.<sup>1</sup>

The primary challenge in working with rod–coil block copolymers lies in the synthesis of rods with controlled polydispersity and controlled functionality at the chain end. The difficulties arise from the long stepwise syntheses necessary to build functionalized rods of useful molecular weight. Poly(ethylene oxide)-*b*-poly(phenylenevinylene)-*b*-poly(ethylene oxide) is a good example.<sup>2</sup> This material, containing monodisperse rod and coil blocks, exhibits interesting self-assembly in solution but requires seven separate synthetic steps to produce triblock copolymers containing PPV eightmers. When not a requirement for the desired application, the removal of the narrow polydispersity constraint upon the rod block expands the possible synthetic pathways. By the addition of molecules monofunctional with respect to the polymerization conditions, chain end functionalized rodlike polymers can be synthesized in a single step. Polymerization methods such as this eliminate the necessity for long, laborious, stepwise synthetic methods. The resulting materials can be converted to the desired block copolymers by grafting or by using them as macroinitiators. The rod material of interest in our research is poly(2,5-benzophenone). The benefits of this polymer include good thermal properties, excellent mechanical properties, and conductivity when doped.<sup>12</sup> In addition, many functional polymeric materials may be designed via functionalized monomers, functionalization of the polymer, or the addition of end-capping agents to the polymerization.<sup>13,14</sup> As such, this would be a valuable material to incorporate into coil–rod–coil copolymers if a feasible synthetic strategy could be designed.

Herein, we describe the details of a short, simple, versatile synthetic methodology to produce coil–rod–coil triblock copolymers. As an example material, we have synthesized polystyrene-*b*-poly(2,5-benzophenone)-

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*b*-polystyrene containing a polydisperse rigid-rod block and monodisperse coil blocks. Rigid poly(2,5-benzophenone) blocks of varying molecular weight were synthesized by end-capping the polymer formed by the Ni(0)-catalyzed polymerization of 2,5-dichlorobenzophenone with a monochloro end-capping agent. The end-capping agent was chosen after a model study to determine a simple and quantitative route to chlorinate the chain ends postpolymerization. The rigid-rod materials were used then as macroinitiators for the atom transfer radical polymerization (ATRP) of styrene to construct triblock copolymers. The phase separation behavior of the resulting triblock materials was examined by transmission electron microscopy (TEM). In addition, potential applications of these materials were explored. The mechanical properties were analyzed by dynamic mechanical analysis (DMA), and a distributed junction photovoltaic device was constructed after sulfonation of the polystyrene block.

## Experimental Section

**Materials.** All materials were purchased from Aldrich and used without further purification unless otherwise noted. *N,N*-Dimethylacetamide and anisole were dried over CaH<sub>2</sub> (Fisher) and distilled under reduced pressure. Styrene was passed over basic alumina and distilled under reduced pressure. Triphenylphosphine was recrystallized from cyclohexane. 2,2'-Bipyridine and 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbipy) were recrystallized from ethanol. The commercial bleach, Chlorox, was titrated with concentrated hydrochloric acid to pH 8.5 immediately prior to use.

**2,5-Dichlorobenzophenone.** The synthesis of 2,5-dichlorobenzophenone has been described previously.<sup>15</sup>

**4-Chloro-4'-alkylbenzophenone.** Aluminum chloride (1 equiv) was added to a stirring solution of 4-chlorobenzoyl chloride (1.1 equiv) and toluene (or cumene) (1 equiv) in nitromethane at 0 °C. The solution was allowed to warm to room temperature and stir for 24 h. The solution was then precipitated on ice and allowed to stir overnight. The off-white powder was filtered, dissolved in ethanol, treated with activated carbon, and filtered. The resulting white crystals were recrystallized twice more from ethanol. 4-Chloro-4'-methylbenzophenone (96% yield). <sup>1</sup>H NMR: δ = 2.45 (s, 3H), 7.29 (d, 2H, *J* = 8.4 Hz), 7.45 (d, 2H, *J* = 8.4 Hz), 7.69 (d, 2H, *J* = 8.4 Hz), 7.74 (d, 2H, *J* = 8.4 Hz). <sup>13</sup>C NMR: δ = 21.9 (CH<sub>3</sub>), 128.8 (CH), 129.3 (CH), 130.4 (CH), 131.6 (CH), 134.8 (q-C), 136.5 (q-C), 138.8 (q-C), 143.8 (q-C), 195.5 (CO). Anal. Calcd for C<sub>14</sub>H<sub>11</sub>OCl: C, 72.89; H, 4.82. Found: C, 72.76; H, 4.94. 4-Chloro-4'-isopropylbenzophenone (74% yield). <sup>1</sup>H NMR: δ = 1.29 (d, 6H, *J* = 6.9 Hz), 2.99 (septet, 1H, *J* = 6.9 Hz), 7.34 (d, 2H, *J* = 8.4), 7.45 (d, 2H, *J* = 8.1 Hz), 7.74 (m, 4H, *J* = 8.1, 8.4 Hz). <sup>13</sup>C NMR: δ = 23.7 (CH<sub>3</sub>), 34.3 (CH), 126.5 (CH), 128.5 (CH), 130.3 (CH), 131.4 (CH), 134.9 (q-C), 136.2 (q-C), 138.6 (q-C), 154.3 (q-C), 195.2 (CO). Anal. Calcd for C<sub>16</sub>H<sub>15</sub>OCl: C, 74.26; H, 5.85. Found: C, 74.31; H, 5.82.

**4-Chloro-4'-(chloromethyl)benzophenone and 4-Chloro-4'-(chlorodimethylmethyl)benzophenone.** 4-Chloro-4'-methylbenzophenone (11 mmol) or 4-chloro-4'-isopropylbenzophenone (10 mmol) was dissolved in 3 mL of methylene chloride. Bleach (Chlorox, pH adjusted to 8.5, 2 equiv in hypochlorite) and benzyltriethylammonium chloride (4 equiv) were added, and the mixture was stirred at 1000 rpm for 24 h. Five mL of methylene chloride was added, and the aqueous layer was removed. The methylene chloride solution was washed twice with water. The methylene chloride was then removed, yielding white crystals. 4-Chloro-4'-(chlorodimethylmethyl)benzophenone (100% yield). <sup>1</sup>H NMR: δ = 2.08 (s, 6H), 7.46 (d, 2H, *J* = 8.7 Hz), 7.70 (d, 2H, *J* = 8.7 Hz), 7.76 (m, 4H, *J* = 8.7, 8.7 Hz). <sup>13</sup>C NMR: δ = 34.4 (CH<sub>3</sub>), 69.0 (q-C), 125.9 (CH), 128.8 (CH), 130.2 (CH), 131.7 (CH), 135.9 (q-C), 136.5 (q-C), 139.2 (q-C), 151.0 (q-C), 195.1 (CO). Anal. Calcd for C<sub>16</sub>H<sub>14</sub>OCl<sub>2</sub>: C, 65.54; H, 4.82. Found: C, 64.85; H, 5.08.

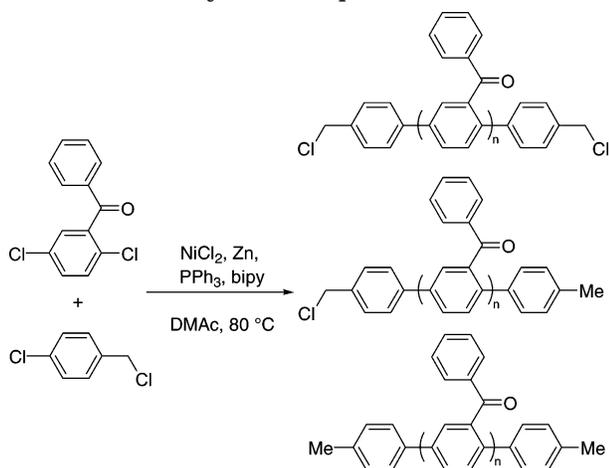
**4'-Isopropylbenzophenone-Capped Poly(2,5-benzophenone).** Under an inert atmosphere, NiCl<sub>2</sub> (0.1 equiv), Zn (3.1 equiv), PPh<sub>3</sub> (0.4 equiv), and bipyridine (0.1 equiv) were weighed and added to a flask equipped with an overhead stirrer. DMAc (10 equiv) was added, and the mixture was stirred and heated at 80 °C until a deep red color was observed. Varying ratios of 2,5-dichlorobenzophenone and end-capping agent, 4-chloro-4'-isopropylbenzophenone, were added (1 equiv total). Reactions were stirred and heated until no change in color or viscosity was observed. The polymer was precipitated into a 4:1 methanol:hydrochloric acid solution to remove excess zinc. The polymers were then washed with sodium bicarbonate solution and water and dried under vacuum. <sup>1</sup>H NMR: δ = 1.25 (broad singlet, chain end CH<sub>3</sub>), 3.0 (broad singlet, chain end CH), 6.7–8.2 (broad multiplet, aryl backbone CHs). <sup>13</sup>C NMR: δ = 23.7 (CH<sub>3</sub>), 34.3 (CH), 126.3 (CH), 126.8 (CH), 127.3 (CH), 128.1 (CH), 128.7 (CH), 130.0 (CH), 130.1 (CH), 130.3 (CH), 132.1 (CH), 132.9 (CH), 135.3 (q-C), 136.8 (q-C), 137.1 (q-C), 138.6 (q-C), 139.1 (q-C), 141.2 (q-C), 143.9 (q-C), 154.0 (q-C), 195.8 (CO), 198.2 (CO). Anal. Calcd for C<sub>162</sub>H<sub>110</sub>O<sub>12</sub>: C, 86.52; H, 4.94. Found: C, 86.07; H, 5.32.

**Chain End Chlorination of 4'-Isopropylbenzophenone-Capped Poly(2,5-benzophenone).** The procedure was followed as with the chlorination of 2,5-dichloro-4'-isopropylbenzophenone, except that after 24 h the reaction mixture was precipitated into acidic methanol, filtered, and washed with water. The yellow powder was then reprecipitated from chloroform into acidic methanol. The resulting material was a pale yellow powder. <sup>1</sup>H NMR: δ = 2.05 (chain end CH<sub>3</sub>), 6.9–8.1 (broad multiplet, aryl backbone). <sup>13</sup>C NMR: δ = 34.1 (CH<sub>3</sub>), 67.5 (q-C), 125.6 (CH), 126.9 (CH), 127.5 (CH), 128.1 (CH), 130.0 (CH), 130.1 (CH), 130.3 (CH), 130.7 (CH), 131.1 (CH), 133.0 (q-C), 136.9 (q-C), 137.0 (q-C), 138.1 (q-C), 138.8 (q-C), 139.6 (q-C), 141.2 (q-C), 143.5 (q-C), 150.4 (q-C), 196.7 (CO), 198.6 (CO). Anal. Calcd for C<sub>162</sub>H<sub>108</sub>O<sub>12</sub>Cl<sub>2</sub>: C, 81.00; H, 4.50. Found: C, 81.86; H, 4.65.

**Polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene.** Chain end chlorinated 4'-isopropylbenzophenone-capped poly(2,5-benzophenone) (1 equiv in chain ends), CuCl (1 equiv), and Cu (0.1 equiv) were added to a Schlenk flask under an inert atmosphere. The flask was sealed with a septum. Styrene was added via syringe along with anisole (1 mL of solvent/1 mL of monomer) and pentamethyldiethyltriethylamine (PMDETA) (2 equiv). The reaction was heated and stirred at 110 °C for 24 h. After the time period, THF was added, and the solution was precipitated into stirring acidic methanol, filtered, and reprecipitated from chloroform into acidic methanol. The resulting material was a pale yellow powder. <sup>1</sup>H NMR: δ = 1.48 (polystyrene (PS) backbone CH<sub>2</sub>), 2.26 (PS backbone CH), 6.63 (broad, PS phenyl), 7.13 (broad, PS phenyl), 7.43 (broad, polybenzophenone (PB)), 7.74 (broad, PB). <sup>13</sup>C NMR: δ = 42.02 (PS backbone), 44.37 (PS backbone), 125.65 (PS phenyl), 126.74 (PB), 127.71 (PS phenyl), 128.00 (PS phenyl), 129.03 (PB), 129.85 (PB), 130.32 (PB), 130.71 (PB), 132.84 (PB), 137.29 (PB), 139.25 (PB), 145.39 (PS phenyl), 145.71 (PB), 146.11 (PB), 197.35 (PB).

**Sulfonated Polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene.** Fuming sulfuric acid (5 mL) was added dropwise to stirring polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene (0.5 g) dissolved in methylene chloride (5 mL). The reaction was allowed to stir for approximately 5 min until the lower methylene chloride layer was clear and colorless. The layers were separated, and the aqueous layer was neutralized with 3 M NaOH. The sodium salt of the sulfonated copolymer was precipitated from water into stirring methanol. <sup>1</sup>H NMR: δ = 1.5 (broad multiplet), 6.7 (broad singlet), 7.6 (broad singlet). <sup>13</sup>C NMR: δ = 20.1 (sulfonated PS backbone CH<sub>2</sub>), 23.4 (sulfonated PS backbone CH), 133.3 (sulfonated PS phenyl CH), 135.3 (sulfonated PS phenyl CH), 150.3 (sulfonated PS phenyl q-C), 158.3.

**Characterization.** Molecular weights, relative to narrow polystyrene standards, were measured using a Waters gel permeation chromatography (GPC) system consisting of a Waters 510 pump, a Waters 717 autosampler, a Wyatt Optilab DSP refractometer, and a Wyatt Dawn EOS light scattering

**Scheme 1. Synthesis of Benzyl Chloride-Terminated Poly(2,5-benzophenone)**


detector. The measurements were taken at 40 °C with THF as the mobile phase on four columns (Polymer labs PLgel 100, 500,  $1 \times 10^4$ , and  $1 \times 10^5$  Å). Glass transitions were determined at the inflection point of the endotherm with a Perkin-Elmer Pyris 1 differential scanning calorimetry system (DSC) with a heating rate of 10 °C/min. Transmission electron microscopy (TEM) was performed on a 1200EX JEOL STEM with a 120 kV accelerating potential and a Philips CM30 STEM with a 100 kV accelerating potential. Dynamic mechanical analysis (DMA) measurements were conducted on a Perkin-Elmer DMA 7e in a three-point bending mode with a 100 mN static force and a 110 mN dynamic force. Photovoltaics were constructed by casting a thin polymer film upon an indium tin oxide-coated 2 in.  $\times$  2 in. glass plate by controlled solvent evaporation over a period of 2 days. The polymer-coated plates were then immersed for 1 h in a sodium dispersion in mineral oil. The plates were then rinsed with dry hexanes and dried, and then a second ITO-coated glass plate was placed over the polymer film. Rudimentary evaluation of the devices was accomplished by measuring the voltage and current developed across the two ITO electrodes in the dark and when exposed to full sunlight.

**Results and Discussion**

The goal of this work was to develop a simple, versatile methodology for the synthesis of poly(2,5-benzophenone) containing coil-rod-coil triblock copolymers. The utilization of end-capping agents yielded chain-end-functionalized rod materials in a single step, avoiding the necessity of time-intensive multistep methods. These rodlike materials can be used as macroinitiators or grafted with other chain-end-functionalized polymers. Previously, our group explored the end-capping of poly(2,5-benzophenone)s by addition of molecules that are monofunctional with respect to the Ni(0) coupling reaction.<sup>10</sup> The monofunctional end-caps can be chosen so that they contain a functionality, not reactive in Ni(0) coupling but reactive under other conditions. In this work it was chosen to end-cap the polymers with molecules containing functionalities that can act as initiating sites in atom transfer radical polymerization (ATRP). Functionalities that act as ATRP initiators are known to be reactive under a variety of Ni-catalyzed coupling conditions. Despite this likely incompatibility, it was desired to utilize the simplest possible synthetic route. Therefore, *p*-chlorobenzyl chloride was explored as a potential end-capping agent (Scheme 1). Addition of this compound yields poly(2,5-benzophenone)s with limited chain-end functionalization due to reduction of the benzyl halide in the

Ni(0) coupling reaction. These polybenzophenones will be referred to as Mibenzyl (macroinitiator with benzyl chloride end-caps). End-capping agent mole fractions of 0.2, 0.1, and 0.05 were employed. The molecular weights obtained were  $3.1 \times 10^3$  g/mol with a polydispersity index (PDI) of 1.9,  $3.5 \times 10^3$  g/mol with a PDI of 2.1, and  $3.9 \times 10^3$  g/mol with a PDI of 2.4. While the molecular weight differences are not large, numerous experiments at specific mole fractions of end-capping agent gave consistent results.

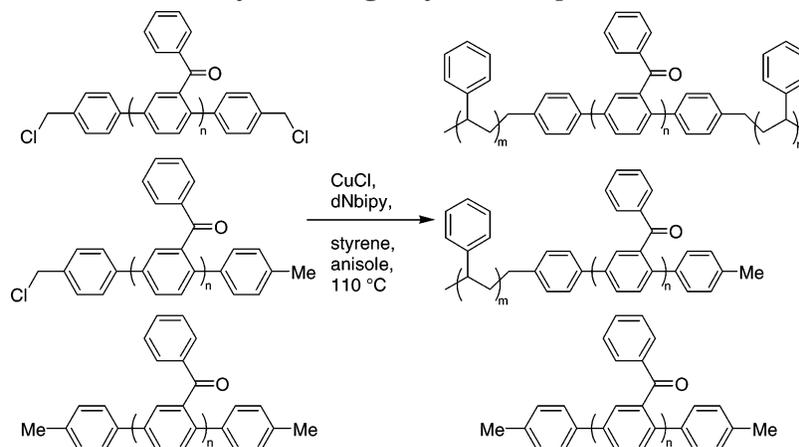
Although macroinitiators with quantitatively chlorinated chain ends could not be synthesized in this manner, these materials were utilized to explore the reaction conditions and the feasibility of the method (Scheme 2). Because of the limited solubility of poly(2,5-benzophenone) in common solvents, polymerizations were run in two suitable solvents, *N,N*-dimethylacetamide (DMAc) and anisole. The results of these polymerizations are summarized in Table 1. Although the Mibenzyl series lacked quantitatively functionalized chain ends, triblocks of varying molecular weights were synthesized. With DMAc as solvent, reaction times of 48 h were necessary to achieve high yields. When anisole was used as a solvent, 96% yield was achieved in 14 h. This behavior is most likely due to solvent-induced changes in the catalyst structure.<sup>16</sup>

The triblock materials from both solvents had bimodal distributions due to the macroinitiator lacking benzyl halide chain ends. The incorporation of the poly(2,5-benzophenone) into the triblock copolymer was confirmed by extracting the samples with ethyl acetate. Poly(2,5-benzophenone) is not soluble in ethyl acetate, while the diblock and triblock copolymers are soluble. This mixture was added to ethyl acetate and centrifuged, and the clear solution was removed. The soluble material was precipitated into methanol and isolated. <sup>1</sup>H NMR of this material confirmed the incorporation of the poly(2,5-benzophenone) into the triblock copolymer with broad signals at 7.35 and 7.7 ppm. Furthermore, GPC of the material recovered from solution was monomodal with a number-average molecular weight of  $100.1 \times 10^3$  g/mol and PDI of 1.4. The GPC trace of the polymer prior to fractionation was bimodal with an  $\langle M_n \rangle$  of  $115.7 \times 10^3$  g/mol and a PDI of 1.6.

To synthesize macroinitiator with quantitatively functionalized chain ends, the reduction of the benzyl chloride in the Ni(0) coupling reaction had to be overcome. To accomplish this, an end-capping system with good compatibility to the Ni(0) coupling reaction was designed. Aryl chloride-containing species with a benzylic carbon, which could be chlorinated postpolymerization, were investigated. The end-capping agents chosen were 4-chloro-4'-alkylbenzophenones. These benzophenone derivatives are structurally similar to the monomer, giving them reactivities close to that of the monomer. End-capping was attempted with *p*-chlorotoluene but resulted in materials with broad multimodal molecular weight distributions. This result in the presence of *p*-chlorotoluene was most likely due to differences in reactivity, which will be discussed later.

A simple, selective chlorination route is also necessary to functionalize the chain ends postpolymerization. Phase-transfer chlorination is a simple high yield route to chlorination of benzylic carbons. It has previously been shown that bleach and benzyltriethylammonium chloride can effectively chlorinate benzylic carbons in both small molecules and macromolecules.<sup>17,18</sup> When

## Scheme 2. ATRP of Styrene Using Poly(2,5-benzophenone) Macroinitiator



**Table 1. Polymerization Results and Conditions for the ATRP of Styrene Using the Benzyl Chloride End-Functionalized Macroinitiator<sup>a</sup>**

sample	M/I <sup>b</sup>	time (h)	solvent	$\langle M_n \rangle \times 10^{-3}$ (g/mol) <sup>c</sup>	PDI <sup>c</sup>	% yield <sup>d</sup>
TB1	60	48	DMAc	32.5	1.5	74
TB2	80	48	DMAc	115.7	1.6	92
TB3	80	14	anisole	85.9	1.6	96

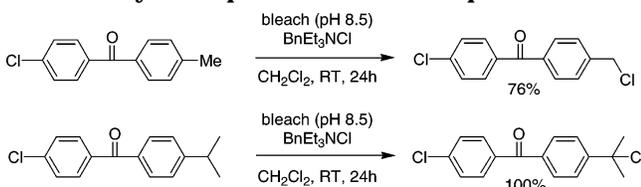
<sup>a</sup> Polymerization conditions:  $3.1 \times 10^3$  g/mol macroinitiator, 2 equiv of dNbipy, 110 °C. <sup>b</sup> M/I = mol monomer/mol initiator (theoretical number of chain ends). <sup>c</sup> Data obtained by GPC. <sup>d</sup> Determined by mass recovered.

**Table 2. Conditions and Results of the Phase Transfer Chlorination of 4-Alkylbenzophenone Derivatives**

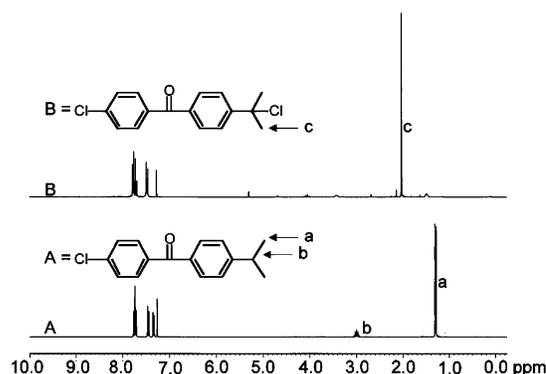
substrate	time (h)	bleach equiv	BnEt <sub>3</sub> NCl equiv	temp (°C)	% yield <sup>a</sup>
Me	8	2	2	RT	41
	4	8	2	RT	37
	8	8	2	RT	41
	24	8	2	RT	47
	24	8	2	40	39
	4 <sup>b</sup>	8	2	80	5
<i>i</i> -Pr	24	2	4	RT	76
	24	2	4	RT	100

<sup>a</sup> Determined by <sup>1</sup>H NMR. <sup>b</sup> Reaction mixture turned black.

**Scheme 3. Phase Transfer Chlorination of Alkylbenzophenone Model Compounds**



4-chloro-4'-methylbenzophenone was reacted using the conditions described in the literature (2 equiv of bleach and 2 equiv of benzyltriethylammonium chloride), a yield of only 41% was obtained (Table 2). Increasing the amount of bleach and varying the time from 4 to 24 h at room temperature only increased the yield to 47%. Higher temperatures were also ineffective, with 40 °C giving a yield of 39% in 24 h. When the temperature was increased to 80 °C, a yield of only 5% was observed at 4 h. However, when 4 equiv of benzyltriethylammonium chloride was utilized with 2 equiv of bleach, the yield increased to 76%. Unfortunately, further increase in the amount of ammonium salt did not lead to increased yields with the methyl derivative. It is known that the phase transfer chlorination reaction exhibits a

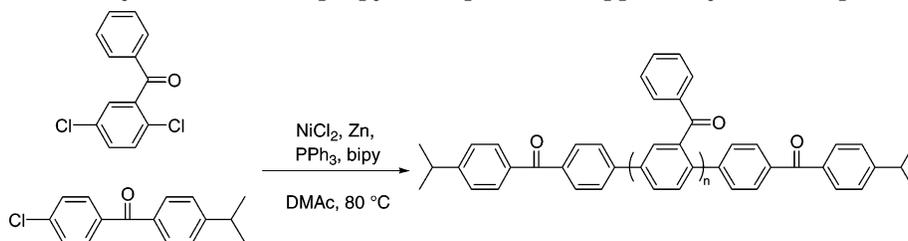


**Figure 1.** <sup>1</sup>H NMR of 4-chloro-4'-isopropylbenzophenone before and after chlorination.

significant negative  $\rho^+$  value, and thus the presence of electron-withdrawing groups, such as a carbonyl in the para position, slows the chlorination reaction.<sup>17</sup> To increase the rate of chlorination, electron density must be added to the benzylic carbon. It was found that 4-chloro-4'-isopropylbenzophenone could be quantitatively chlorinated under the best reaction conditions for the methyl derivative (Scheme 3). The addition of the methyl substituents on the benzylic carbon increases the electron density at the reaction site enough to overcome the electron-withdrawing effect of the carbonyl. The reaction can be easily followed by <sup>1</sup>H NMR before and after chlorination (Figure 1). Prior to chlorination, the methyls of the isopropyl group have a shift of  $\delta$  1.3 ppm. After chlorination, the peak was shifted downfield to  $\delta$  2.0 ppm due to the chlorine atom in the benzylic position.

4-Chloro-4'-isopropylbenzophenone was utilized as an end-capping agent in the Ni(0)-catalyzed polymerization of 2,5-dichlorobenzophenone (Scheme 4). These materials will be referred to as MIiso (macroinitiator with isopropylbenzophenone end-caps). Varying the feed ratio from 0.2 to 0.025 mole fraction end-capping agent yielded polymers with molecular weights ranging from  $1.7 \times 10^3$  to  $3.3 \times 10^3$  g/mol (Table 3). Once again, although the variation in molecular weights is not large, repeated experiments consistently gave these molecular weights. The incorporation of the end-capping agent was observed by <sup>1</sup>H NMR (Figure 2). With increasing mole fraction of end-capping agent in the feed, an increase in the signal arising from the methyl of the isopropyl group ( $\delta$  1.3 ppm) was observed. Attempts with lower amounts of end-capping agent in the feed led to broad

## Scheme 4. Synthesis of 4'-Isopropylbenzophenone-Capped Poly(2,5-benzophenone)

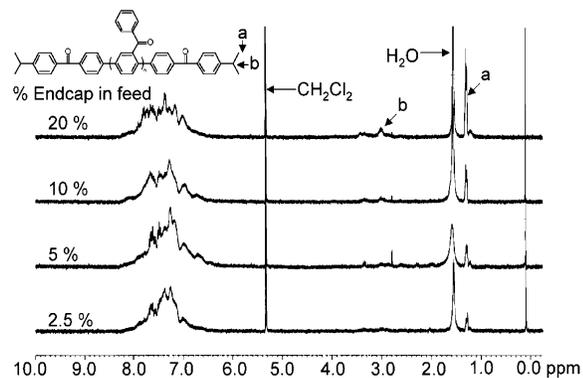


**Table 3. Molecular Weight Data for Isopropylbenzophenone-Capped Poly(2,5-benzophenone)s**

sample	end-cap feed <sup>a</sup> (mole fraction)	$\langle M_n \rangle \times 10^{-3}$ (g/mol) <sup>b</sup>	PDI <sup>b</sup>
MI1	0.2	1.7	1.7
MI2	0.1	2.4	1.8
MI3	0.05	2.9	2.1
MI4	0.025	3.3	2.1

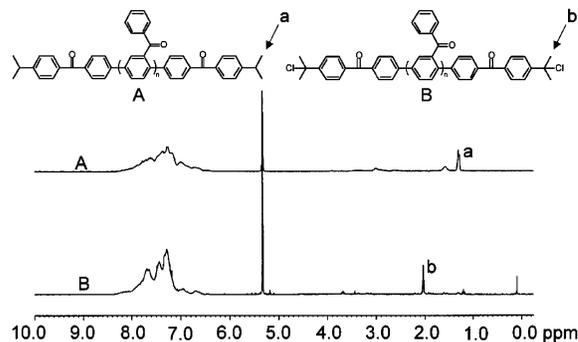
<sup>a</sup> End-cap feed = mol end-cap/(mol end-cap + mol monomer).

<sup>b</sup> Data determined by GPC.



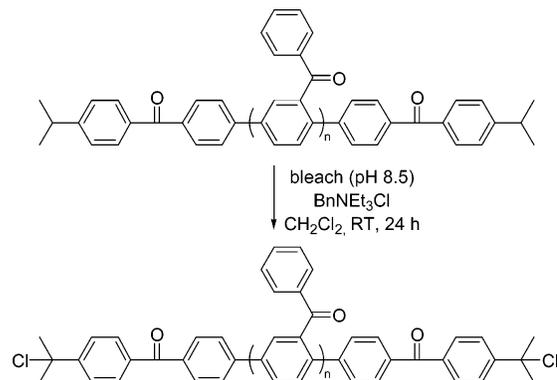
**Figure 2.** <sup>1</sup>H NMR 4'-isopropylbenzophenone-functionalized benzophenones resulting from varying feed ratios of monomer and end-capping agent.

multimodal molecular weight distributions and poor molecular weight control. The loss of control with end-cap amounts less than 2.5% is presumably due to side reactions such as the reduction of aryl chlorides and reduction of ketones.<sup>13,19</sup> It is also interesting to note the difference in molecular weights of the MIbenzyl series compared to the MIiso series (Table 3). With the same feed ratio of monomer and end-capping agent, the materials end-capped with chlorobenzyl chloride are higher molecular weight. At 0.2 mole fraction end-capping agent, a molecular weight of  $3.1 \times 10^3$  g/mol was achieved in the MIbenzyl series. At the same mole fraction of end-capping agent in the MIiso series, the resulting material had a molecular weight of  $1.7 \times 10^3$  g/mol. Similar results were observed for the other end-capping agent feed ratios. Percec et al. have observed a diminished reactivity to Ni(0)-catalyzed coupling of monomers with electron-donating substituents ortho to the leaving group.<sup>20</sup> Monomers with electron-withdrawing groups ortho to the reactive site show an increased reactivity. The same effect would be expected for substituents in the para position. Indeed, this is observed in the reactivities of the end-capping agents. Because of a diminished reactivity, chlorobenzyl chloride reacts with monomer at a slower rate than monomer reacts with itself, leading to higher molecular weights. The benzophenone end-capping agent is structurally similar to the monomer and therefore reacts with monomer at



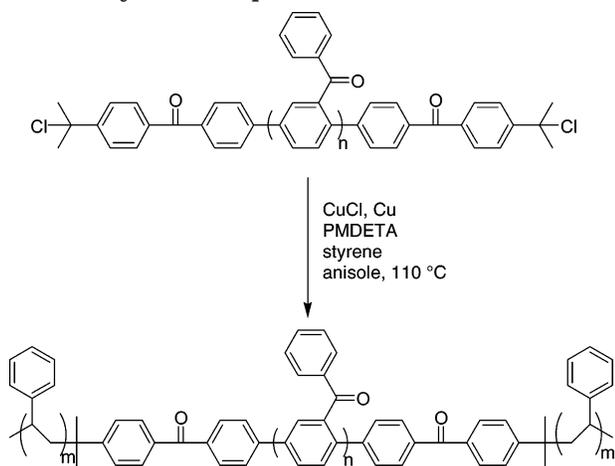
**Figure 3.** <sup>1</sup>H NMR of 4'-isopropylbenzophenone chain-end-functionalized poly(2,5-benzophenone) before and after chlorination.

## Scheme 5. Phase Transfer Chlorination of 4'-Isopropylbenzophenone-Capped Poly(2,5-benzophenone)



or near the same rate that monomer reacts with monomer. The electron-withdrawing capability of the end-capping agents also provides insight into the difficulty in the use of *p*-chlorotoluene as an end-capping agent in Ni(0)-catalyzed coupling. Of the three end-capping agents considered here, *p*-chlorotoluene is the most deactivated to Ni(0) coupling. The differences between the reactivities of the benzophenone monomer and the *p*-chlorotoluene end-capping agent lead to poor control of the chain end functionality.

Utilizing the conditions determined in the model chlorination study, it was possible to chlorinate the chain ends of poly(2,5-benzophenone) terminated with 4'-isopropylbenzophenone functionalities (Scheme 5). The chlorination reaction proceeded in quantitative yield and was followed by <sup>1</sup>H NMR. As shown in Figure 3, prior to chlorination, the methyls of the isopropyl are observed as a broad doublet at  $\delta$  1.3 ppm. After chlorination, the signal is shifted to  $\delta$  2.0 ppm due to the presence of the chlorine atom at the benzylic position.

**Scheme 6. ATRP of Styrene Using Poly(2,5-benzophenone) Macroinitiator****Table 4. Variation of Triblock Copolymer Weight by Use of the Monomer to Initiator Ratio<sup>a</sup>**

sample	MI $\langle M_n \rangle \times 10^{-3}$ (g/mol) <sup>b</sup>	PDI <sup>b</sup>	M/I <sup>c</sup>	TB $\langle M_n \rangle \times 10^{-3}$ (g/mol) <sup>d</sup>	PDI <sup>d</sup>
TB1	1.7	1.69	39	7.9	1.4
TB2	1.7	1.69	78	12.9	1.4
TB3	1.7	1.69	157	19.0	1.9
TB4 <sup>e</sup>	2.4	1.82	314	42.0	1.5

<sup>a</sup> Polymerization conditions = isopropyl functionalized macroinitiator, PMDETA, anisole, 110 °C, 24 h. <sup>b</sup> Data determined by GPC for the polybenzophenone macroinitiator. <sup>c</sup> M/I = moles monomer/moles chain ends of macroinitiator. <sup>d</sup> Data determined by GPC for triblock copolymer. <sup>e</sup> 48 h reaction.

These macroinitiators were used in the ATRP of styrene (Scheme 6). It was found that under optimized conditions clean and efficient initiation of styrene yielded triblock copolymers. DMAc again proved to be an ineffective solvent, while the reaction in anisole with PMDETA as the ligand gave good yields of the triblock copolymer. Variation of the monomer-to-initiator ratio was utilized to synthesize polystyrene blocks of varying molecular weight (Table 4). As the monomer-to-initiator ratio was increased from 39 to 157, polymers of increasing molecular weight were synthesized. For large monomer-to-initiator ratios (approximately >150), it was necessary to increase the reaction time in order to reach high conversions. It also was found that yields less than 75% were desirable due to increased viscosity at higher conversions that led to broad multimodal molecular weight distributions. Increasing the amount of solvent reduced the rate early in the reaction, preventing high yields from being obtained.

Differential scanning calorimetry of these materials showed two glass transition temperatures for triblock copolymers with rod blocks greater than  $1.7 \times 10^3$  g/mol (Table 5). Furthermore, the transitions observed were characteristic of the transitions of the two homopolymers, indicating that there is little blending of the two phases. For copolymers with rod blocks of  $1.7 \times 10^3$  g/mol, the only glass transition observed was for polystyrene.

To elucidate the morphologies formed, TEM studies were undertaken. Thin films were cast from toluene upon a water surface and picked up onto carbon-coated grids. The films were then annealed at 180 °C for 48 h and stained with RuO<sub>4</sub> vapor. To identify the components upon staining, thin films of the two materials were immersed in a 5% solution of RuO<sub>4</sub>. After immer-

**Table 5. Glass Transition Temperatures of Macroinitiators and Triblock Copolymers**

MI $\langle M_n \rangle \times 10^{-3}$ (g/mol) <sup>a</sup>	MI $T_g^b$	TB $\langle M_n \rangle \times 10^{-3}$ (g/mol) <sup>c</sup>	PDI <sup>c</sup>	$T_g$ PS block <sup>b</sup>	$T_g$ PB block <sup>b</sup>
1.7	139	7.9	1.4	103	
		12.9	1.4	106	
2.4	149	8.0	1.6	103	155
		42.2	1.5	101	154
2.8	159	23.8	1.2	102	158
		34.6	1.7	110	152
3.3	158	34.6	1.5	105	151
		36.0	1.2	100	147

<sup>a</sup> Data determined by GPC for the macroinitiator. <sup>b</sup> Glass transition determined by DSC; MI = macroinitiator, PS = polystyrene, PB = polybenzophenone. <sup>c</sup> Data determined by GPC for the triblock copolymer.

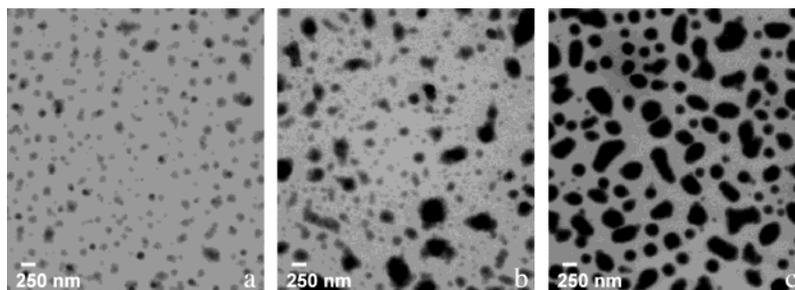
sion, the poly(2,5-benzophenone) film was stained to a greater extent than the polystyrene film. Polystyrene and polybenzophenone were also confirmed to be immiscible. The two materials were blended and analyzed by TEM. Before and after annealing at 180 °C for 48 h, two phases were observed.

Representative TEM micrographs are shown in Figures 4–6 for triblocks containing varying lengths of rod block and coil block. Rod blocks of molecular weight  $1.7 \times 10^3$  g/mol led to the formation of a random distribution of spheroids of relatively uniform size (~50 nm) at 7.3 vol % (Figure 4). As the rod block volume was increased to 11.7% and then 19.4%, larger more size disperse spheroids were formed. The series containing rod blocks of  $2.4 \times 10^3$  g/mol exhibited a similar trend with the average size of the polybenzophenone domains increasing with increasing volume fraction. Analysis of the triblock materials containing  $2.7 \times 10^3$  g/mol rod blocks showed polybenzophenone spheroids at 10% rod block, but upon increasing the volume fraction to 15.7%, a highly disordered morphology was formed (Figure 5). Unlike the previous examples, rod blocks of  $3.3 \times 10^3$  g/mol led to the formation of more disordered phases at lower rod volume fractions with 9.2 vol % forming size disperse spheroids (Figure 6).

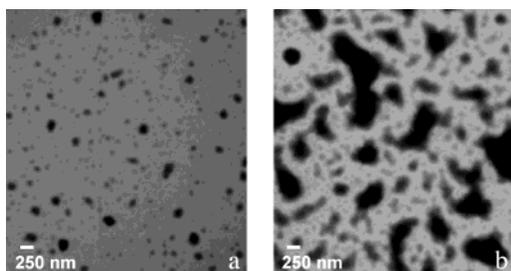
Although not highly ordered, clear phase separation was observed in all examples. Overall, volume fractions of less than 10% led to the formation of polybenzophenone spheroids of relatively uniform size. Larger volume fractions formed spheroids, but the size of the phases varied greatly. Upon increasing the rod size and or the volume fraction, more disordered, but phase-separated, structures were observed (Figures 5b and 6b). As shown in the  $1.7 \times 10^3$  g/mol series, the potential for formation of more ordered structures at higher rod volume fractions still exists (Figure 4b,c). Increasing the volume fraction from 11.7% rod to 19.4% rod led to a decrease in the variation of the spheroid size.

The overall polydispersity of these materials varied from 1.2 to 1.9. This variation seemed to have little effect upon the resulting morphologies. In fact, the copolymer in Figure 5b has an overall polydispersity of 1.3, while the material in Figure 4a has an overall polydispersity of 1.9. The material with the larger polydispersity exhibited a higher degree of order. The polydispersity of the rod block also seemed to have little effect upon the phase separation. The rod block polydispersity in Figure 4a was 1.7 and in Figure 6a was 2.1. Both materials exhibited similar morphologies of relatively uniform spheroids.

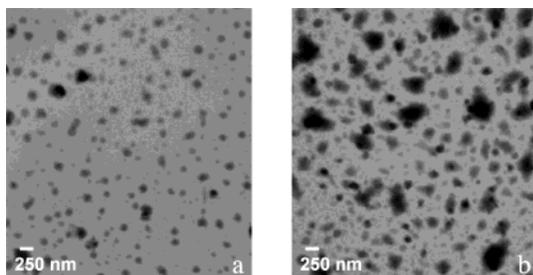
$\chi N$  values were determined from solubility parameters according to Sperling,<sup>21</sup> and the data were plotted



**Figure 4.** TEM micrographs of polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene with  $1.7 \times 10^3$  g/mol rod blocks: (a) 7.3 vol % rod block; (b) 11.7 vol % rod block; (c) 19.4 vol % rod block.



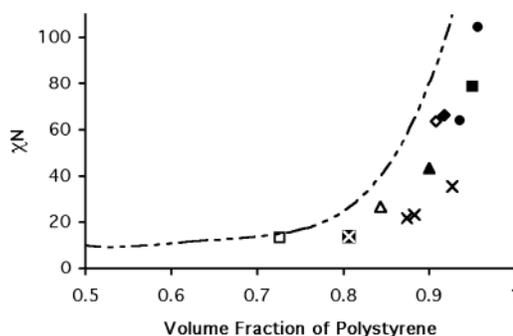
**Figure 5.** TEM micrographs of polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene with  $2.7 \times 10^3$  g/mol rod blocks: (a) 10.0 vol % rod block; (b) 15.7 vol % rod block.



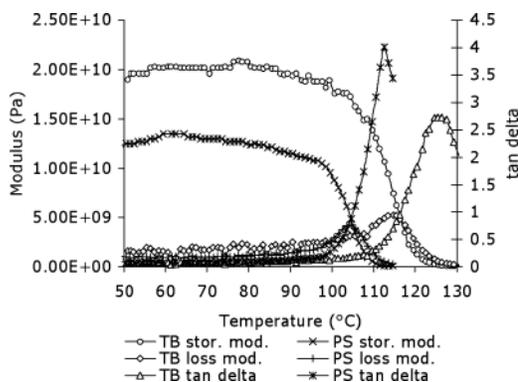
**Figure 6.** TEM micrographs of polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene with  $3.3 \times 10^3$  g/mol rod block: (a) 8.3 vol % rod block; (b) 9.2 vol % rod block.

to give a partial phase separation diagram (Figure 7). All block copolymers presented here exhibit phase separation and lay outside the spinodal known for coil-coil systems. This decreased miscibility correlates well with what is predicted by theory, with the rod block driving the system toward phase separation by limiting the number of chain conformations the coil block can adopt when the two are blended. It is also interesting to note that all materials presented here exhibit phase separation at relatively small rod volume fractions. This fact is contrary to what has been predicted by theoretical models, which have shown the spinodal of the rod-coil systems shifting toward higher rod volume fractions compared to coil-coil systems.<sup>22,23</sup> It is, however, necessary to present a complete phase separation diagram before definitive conclusions can be drawn.

Simple synthetic routes to a wide variety of these materials create the potential for their use in mechanical and electronic applications. As an example of this class of materials utility to enhance mechanical properties, dynamic mechanical analysis was performed on the triblock copolymers. When compared to similar molecular weight polystyrene, the triblock copolymer ( $\langle M_n \rangle = 55.7 \times 10^3$  g/mol, PDI 1.9, 4.4 vol % rod block) exhibited a large increase in storage modulus ( $\sim 50\%$ ) as well as a 15 °C increase in the tan delta maximum (Figure 8). Furthermore, the maximum value of the tan



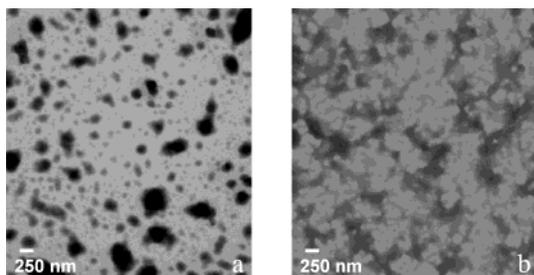
**Figure 7.** Partial phase separation diagram for polystyrene-*b*-poly(2,5-benzophenone)-*p*-polystyrene: Filled points: uniform spheroids, 50 nm and smaller. Unfilled points: large size disperse spheroids.  $\blacklozenge$ ,  $3.3 \times 10^3$  g/mol rod block;  $\blacktriangle$ ,  $2.9 \times 10^3$  g/mol rod block;  $\bullet$ ,  $2.7 \times 10^3$  g/mol rod block;  $\blacksquare$ ,  $2.4 \times 10^3$  g/mol rod block;  $\times$ ,  $1.7 \times 10^3$  g/mol rod block. Dashed line represents the spinodal for coil-coil block copolymer systems.



**Figure 8.** DMA results of polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene and polystyrene.

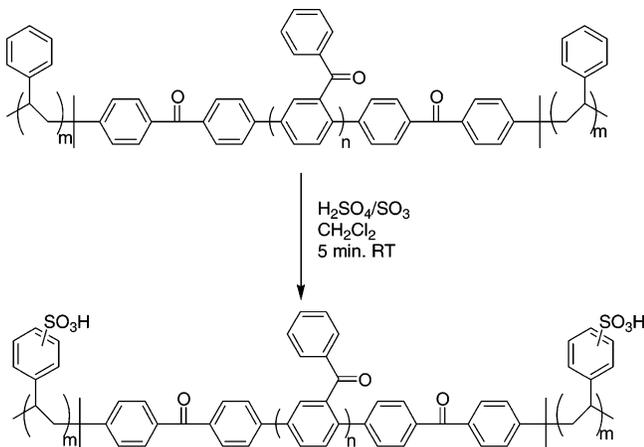
delta was decreased over that of neat polystyrene, indicating increased elastic properties. This level of improvement in the mechanical properties is not typically achieved in polymer composites at loading levels less than 10%, although nanocomposite materials have shown similar properties at low loading levels.<sup>24</sup> While these polystyrene-based materials are only examples and are unlikely to be used in such mechanical roles, triblocks of materials such as Nylon or polyesters have this potential. Utilizing the end-capping methodology presented here, the rod blocks could be functionalized to initiate the polymerization of monomers such as lactones or incorporated into the triblock copolymer via grafting with other chain-end-functionalized materials.

The phase-separated morphology exhibited here has, in addition to use in mechanical applications, the potential to be utilized in the electronics industry to exploit the conductive backbone of the polybenzophenone. One such application is construction of dis-



**Figure 9.** TEM micrographs of polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene before (a) and after sulfonation (b).

**Scheme 7. Synthesis of Sulfonated Polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene**



tributed junction photovoltaics. The key feature to these materials is a two-phase system with dimensions on the scale of tens to hundreds of nanometers. One phase should exhibit good electron mobility and the other good hole mobility. Coil-rod-coil block copolymer systems are excellent candidates for such applications due to the conjugated rod block and the phase separation at the submicrometer length scale. As an example synthesis of these materials for such an application, polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene was reacted with fuming sulfuric acid (Scheme 7). The resulting material was soluble in all polar organic solvents, such as THF, methanol, and water. Upon extraction of the polymer solution with NaOH, the resulting sodium salt was only soluble in water. The triblock copolymer functionalized with sodium sulfonate groups exhibited one  $T_g$  at 255 °C. No transition due to poly(2,5-benzophenone) was observed. Sulfonation of the poly(2,5-benzophenone) block is unlikely under the conditions used as no sulfonation of poly(2,5-benzophenone) homopolymer was observed under the same reaction conditions.

TEM studies of the resulting sulfonated materials showed a two-phase morphology, different from that of the nonsulfonated triblock copolymer (Figure 9). While the polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene copolymer exhibited a spheroidal morphology, the sulfonated derivative exhibited a much more disordered morphology. The dimensions of the two phases are near 200 nm.

The sulfonated block copolymer was dissolved in water and cast upon indium tin oxide (ITO)-coated 2 in.  $\times$  2 in. glass plates. The films (approximately 250 nm in thickness) were slowly dried over a period of 2 days and then submerged in a bath of sodium dispersed in mineral oil for 1 h. In an inert atmosphere, the glass plates were washed with dry hexanes, and then a second

ITO-coated glass slide was placed over the polymer film. When the device was exposed to full sunlight, a stable voltage of 250 mV and current density of 0.39 A/cm<sup>2</sup> were observed. Presently, extensive characterization of the current-voltage properties of the devices is being conducted.

## Conclusions

A method for the synthesis of coil-rod-coil triblock copolymers was demonstrated by the synthesis of polystyrene-*b*-poly(2,5-benzophenone)-*b*-polystyrene. Poly(2,5-benzophenone) macroinitiators were synthesized utilizing 4-chloro-4'-isopropylbenzophenone as an end-capping agent followed by phase transfer chlorination to quantitatively chlorinate the chain ends. Differing molecular weights of triblock copolymer were synthesized in anisole with PMDETA as the ligand by varying the monomer-to-initiator ratio. All triblock materials synthesized exhibited phase separation with rod volume fractions smaller than 10% producing a morphology consisting of relatively uniform sized poly(2,5-benzophenone) spheroids. Furthermore, all materials phase separated at volume fractions much smaller than more traditional coil-coil systems. Potential applications of this class of materials were also demonstrated. DMA analysis showed the triblock copolymers exhibited improved mechanical performance over that of neat polystyrene. It was also shown that through a simple modification an architecture could be designed to exploit the conjugated rod block in photovoltaic applications. Photovoltaic devices built utilizing the sulfonated triblock copolymer exhibited a voltage of 250 mV and a current density of 0.39 A/cm<sup>2</sup> in sunlight. Currently, efforts are underway to synthesize high molecular weight poly(2,5-benzophenone) macroinitiators. In addition, differing end-capping agents and methods of chain end functionalization are being explored.

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