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Rigid−Flexible Alternating Block Copolymers That Contain Poly(*p*-phenylene) Units of Defined Length as the Rigid Blocks

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Since the discovery that poly(*p*-phenylene) conducts electricity when doped with oxidizing or reducing agents,[1] a great deal of research has gone into the study of this material and its derivatives.[2−5] Other interesting and important properties that poly(phenylene)s exhibit include liquid crystallinity[6] and photo- and electroluminescence.[7] Unfortunately, the rigid conjugated backbone largely responsible for these properties also renders underivatized poly(*p*-phenylene) insoluble and infusible. Consequently, it cannot be processed, and straightforward syntheses result in only oligomeric materials.[8] One strategy used to combat this problem has been to stitch solubilizing side chains onto the polymer backbone.[9] However, this can disrupt the conjugation and alter the sought-after properties.[10] Another approach is to incorporate flexible solubilizing groups between blocks of the rigid, conjugated material.[11−14] This alternating rigid−flexible block copolymer strategy is well-established in the synthesis of main-chain liquid crystalline polyesters[15] and poly(urethane)-based thermoplastic elastomeric materials.[16] In this communication, we present the synthesis, characterization, and initial materials properties investigations on soluble rigid−flexible block copolymers composed of conjugated poly(*p*-phenylene) segments[17] as the rigid blocks.

In 1992, Kantor described the synthesis and properties of all-hydrocarbon main-chain liquid crystalline polymers composed of biphenyl mesogens alternating with poly(methylene) flexible spacers (eq 1 of Scheme 1).[18] Unfortunately, the molecular weights of the materials were limited to 6000 g/mol, and it is possible that the low molecular weights had a significant effect on the materials properties.[19] These low molecular weights could have been due to either the inefficiency of the polymerization reaction or the insolubility of the materials produced. Also, although the authors presented thorough investigations on the effects of the length of the flexible segment on the liquid crystalline properties, the effects of the length of the rigid segment were not studied.

Our approach to these problems was to use a Suzuki coupling[20] methodology to synthesize the alternating rigid−flexible block copolymers (eq 2). This reaction is extremely efficient, and it has been successfully applied to numerous polymerization systems.[2,4,5] Furthermore, with the appropriate choice of dibromide and diboronic acid monomers, the length of the rigid block can be systematically varied from three phenyl rings on up. To address the solubility issue, we used oligomers of poly(ethylene glycol) for the flexible blocks. In their work with main-chain liquid crystalline polyesters, Meurisse[21] and Lenz[22] had success at solubilizing rigid aromatic mesogens with oligo(ethylene glycol) flexible segments. Considering that poly(ethylene glycol) is soluble in a variety of solvents, we believed that it would be more efficient at solubilizing the materials than the polymethylene spacers.

The poly(ethylene glycol) spacer and part of the polyphenylene blocks were incorporated into the dibromide macromonomers (eq 3). In this fashion, macromonomers **1** and **2** were conveniently synthesized from commercially available phenols and the ditosylate of poly(ethylene glycol) (MW = 1000 g/mol). They were purified by chromatography and recrystallization, and characterized by NMR, elemental analysis, and MALDI-TOF mass spectrometry.

Polymerizations (eq 2) between **1**−**2** and diboronic esters **3**−**4** were performed under optimized Suzuki coupling polymerization conditions[23] to form polymers **5**−**8**. The resulting data on molecular weight and yields are presented in Table 1. All except **8**, consisting of rigid blocks with six para-linked phenyl rings, were soluble in chloroform, allowing for characterization by NMR and GPC. The number-averaged molecular weights for the polymers are above 10 000 g/mol, high enough for these materials to form films, and exhibit uniform spectroscopic properties. These somewhat lower than expected values appear to be due to a small amount contamination of the dibromide monomers with monofunctional chains (as determined by ^{13}C NMR),[24] caused by incomplete tosylation in the first step. Despite this, the measured degrees of polymerization are not far from those observed in other Suzuki coupling polymerizations performed on aryl bromide monomers.[25] A ^{13}C NMR spectrum of polymer **7** is presented in Figure 1. The expected five resonances for the quaternary carbons are clearly present, while the methine resonances converge into four signals. Thus, this spectrum indicates the regular all-para repeat unit provided by the Suzuki coupling methodology. Similar analyses on spectra for polymers **5** and **6** lead us to conclude that we have successfully synthesized soluble polymers containing exactly three, four, or five para-linked phenyl rings without the use of solubilizing side chains.

The synthetic strategy outlined in this paper is very general. The only factor preventing the synthesis of materials with greater than five benzene rings in the rigid block is solubility, which appears to end with six rings for this system. However, any telechelic oligomer with primary alcohol end groups can be utilized as a solubilizing flexible block. Furthermore, this strategy should also be applicable to other palladium-mediated couplings, which can lead to soluble materials incorporating defined and controlled lengths of different conjugated polymers.

The materials show interesting thermal behavior as shown in their DSC traces. The thermatograms for polymers **5** and **7** are presented in Figure 2. In general, all of the samples exhibit an apparent glass transition at −50 °C and an exothermic peak between −5 and −10 °C. The fact that these are relatively constant for all of the polymers suggests that these are due to phenomena in the PEG segments. (Parent poly(ethylene glycol) has a T_g and T_m of −41 and 66 °C, respectively.[26]) Thermal transitions also occur at higher temperatures, and these do vary with the length of the rigid block (shifting toward higher temperatures with increasing numbers

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Scheme 1

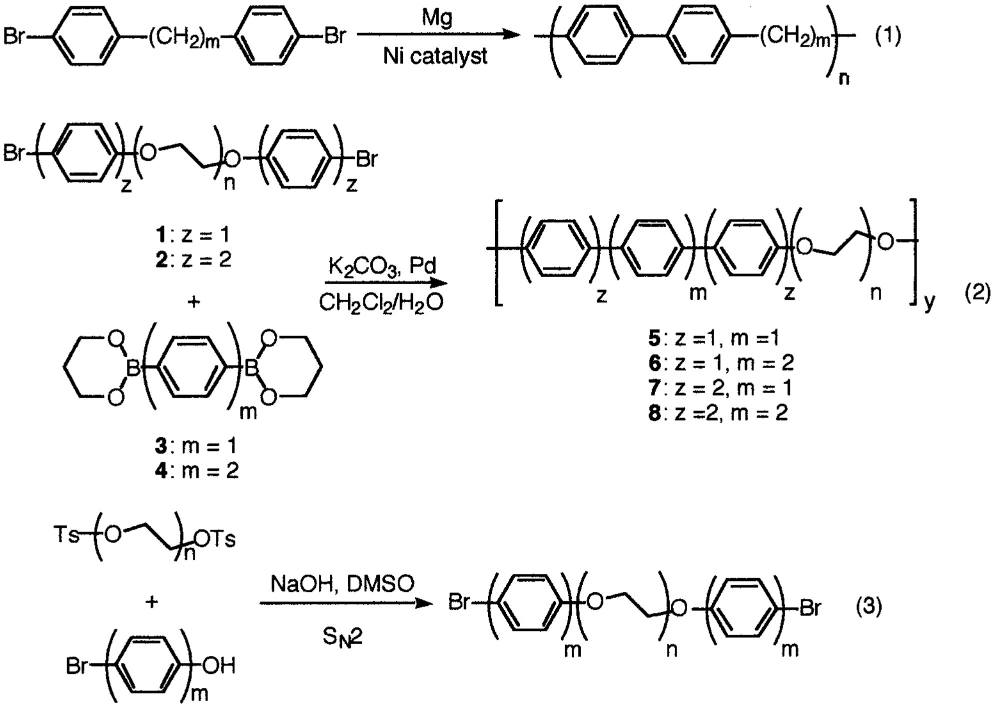

Table 1. Polymer Yields and Molecular Weight Data

entry	monomers	polymer	rings[a]	% yield[b]	M_n[c]	M_w[c]	DP[d]
1	**1** + **3**	**5**	3	80 (57)	19 600	45 200	31
2	**1** + **4**	**6**	4	95 (77)	11 200	32 600	17
3	**2** + **3**	**7**	5	79 (64)	19 300	49 900	27
4	**2** + **4**	**8**	6	80 (78)	*e*	*e*	*e*

[a] Number of phenyl rings in polymer repeat unit. [b] Isolated yield; purified yield after multiple precipitations in parentheses. [c] Molecular weights were determined by GPC in chloroform relative to polystyrene standards. [d] Number-averaged degree of polymerization. [e] Material was not soluble enough for GPC characterization.

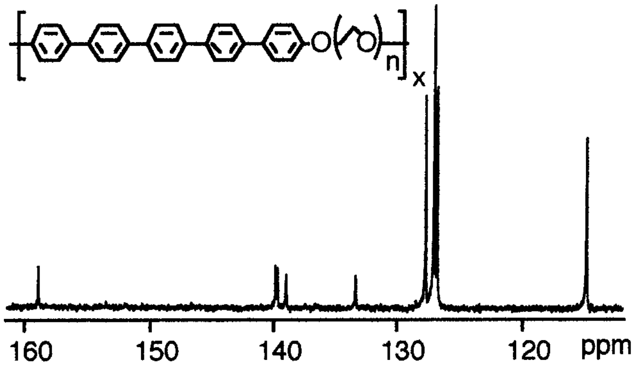

Figure 1. Aromatic region of the ^{13}C NMR spectrum of polymer **7**.

of phenyl rings), suggesting that they are due to melting phenomena of the polyphenylene regions. The fact that these two distinct regimes exist suggests the possibility of microphase separation between poly(ethylene glycol)-rich regions and poly(*p*-phenylene)-rich regions of the bulk polymer samples. Jenekhe found evidence for such behavior with certain compositions of similar rigid–flexible alternating block copolymers.[13] Polymer **6** exhibited only one high-temperature transition at 148 °C; polymer **8** showed no obvious polyphenylene transitions below its point of decomposition. Polymer **5** was also studied by polarizing optical microscopy. Above 81 °C, the material was clearly isotropic and liquid. Birefringence became visible as the sample was cooled to 78 °C, and the material no longer flowed once it reached 76 °C. The fact that two polyphenylene transitions are apparent in the cooling cycle of the DSC curve suggests that a mesophase may exist between 76 and 81 °C. However, we were unable to characterize the phase any further using microscopy, as the crystalline regions were too small (on the order of 1–10 μm). TGA analysis (N_2) indicated that these materials all decompose cleanly at around 380 °C to yield 2.5–23% char, increasing with the number of phenyl rings in the rigid blocks.

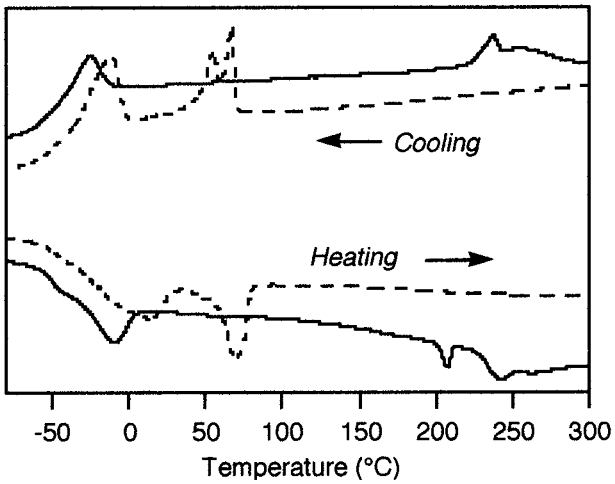

Figure 2. DSC curves (10 °C/min, second heating/cooling cycles) for polymer **5** (dashed line) and polymer **7** (solid line), normalized to the same sample mass. Endothermic peaks point down.

Also of interest are the light-emitting properties of these materials. Jenekhe showed that in the solid state conjugated materials form intermolecular aggregates or excimers, and that film luminescence of these materials is produced by these aggregates with significantly

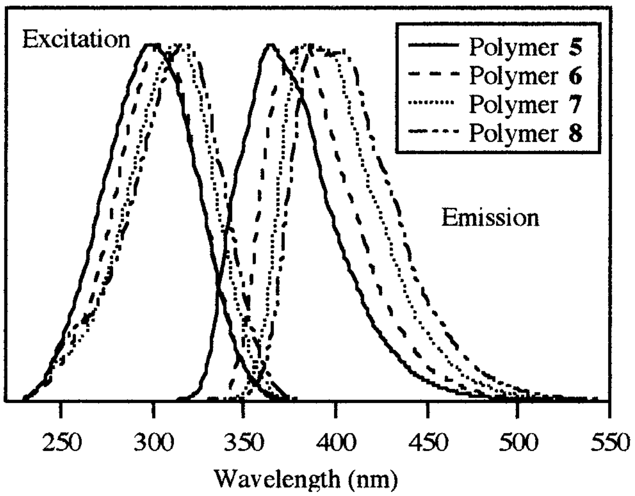

Figure 3. Fluorescence spectra for dilute chloroform solutions of polymers **5**−**8**. Emission spectra were obtained at or near the excitation maxima (295, 305, 313, and 317 nm for **5**, **6**, **7**, and **8**, respectively).

reduced quantum efficiency.[27] Furthermore, excimers have been cited as the cause of dramatic red shifts in solid-state emission (relative to solution).[28] In other work, Jenekhe,[29] and more recently Sun,[30] have shown that alternating block copolymer designs similar to the system presented here can be effective at preventing excimer formation in the solid state. Absorption and emission fluorescence spectra (chloroform solution) for our rigid−flexible alternating block copolymers are presented in Figure 3. All of the polymers emit strongly in the blue region of the visible spectrum. The absorption and emission spectra are shifted to the red as the length of the poly(*p*-phenylene) block is increased, in line with what has been seen with the parent oligophenylenes.[31] In the solid state, the emission for polymer **7** is slightly red-shifted (though still well within the blue) relative to the solution spectrum ($\lambda_{\max} = 385$ nm in solution vs 415 nm as a film), suggesting that excimer formation is occurring. This is still short of that of parent poly(*p*-phenylene) (450 nm) in the solid state,[7] indicating that five benzene rings do not yet approach the limiting conjugation length for the underivatized material. The emissive properties of these materials may render them as viable candidates for applications in flat panel displays.

In summary, we have synthesized and characterized soluble alternating rigid−flexible block copolymers with poly(*p*-phenylene) units of defined length as the rigid blocks. The weight-averaged molecular weights of these materials are as high as 49 900 g/mol, as determined by GPC. The polymers show interesting thermal properties, in that several transitions are observed by DSC. The materials fluoresce strongly in the blue region of the spectrum, both in solution and in the solid state. The synthetic strategy outlined in this paper is very general; it should be applicable to a variety of solubilizing flexible blocks and rigid conjugated blocks. These investigations are currently under way, as well as further studies on the materials properties of these polymers; the results will be presented upon completion.

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Supporting Information Available: Experimental methods for monomer synthesis and polymerization reactions; spectroscopic and analytical data of monomers **1**−**4** and polymers **5**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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