Atom-Transfer Radical Polymerization to Synthesize Novel Liquid Crystalline Diblock Copolymers with Polystyrene and Mesogen-jacketed Liquid Crystal Polymer Segments

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Received 20 August 2001; accepted in revised form 4 December 2001

Key words: atom transfer radical polymerization, diblock copolymer, liquid crystalline behavior, mesogen-jacketed liquid crystal polymer

Abstract
The synthesis of a series of new rod-coil diblock copolymers with different molecular weights and low polydispersity was achieved by atom transfer radical polymerization. The block architecture (coil-conformation of styrene segment and rigid-rod conformation of 2,5-bis[(4-methoxyphenyl)-oxycarbonyl]styrene segment) of the diblock copolymers was experimentally confirmed by proton nuclear magnetic resonance (1H NMR) and differential scanning calorimetry (DSC). The liquid crystalline behavior of the copolymers was studied using DSC and a polarized optical microscope (POM). It was found that the liquid crystalline behavior was dependent on the molecular-weight of the rigid segment. Only those copolymers with \( M_n \) of the rigid block beyond 9,300 g/mol could form liquid crystalline phases above the glass transition temperature of the rigid block.

Introduction
Self-organization into a certain order is a common phenomenon in nature. Liquid crystalline polymers (LCPs) [1] and block copolymers [2] are two classes of synthetic materials that can readily undergo self-organization. By combining both components in a single molecular system, the competition between their self-organizing behavior offers opportunities for simultaneously creating ordered structures at many length scales in polymer systems [3] of microphase separation and liquid crystallinity, which may result in new materials with superior and unanticipated properties. Such polymers may also serve as models to provide insight into the ordering of more complicated biological systems in which multiple ordering processes are present [4]. Several review papers have been published so far on this topic [5, 6]. By definition, LC block copolymers contain at least one LC segment and may have structures that include rod-coil [7–11], side group LC (SGLC)-coil [12, 13] and other block combinations. Mesogen-jacketed liquid crystal polymers (MJLCPs) are characterized by mesogenic units laterally attached without spacers to the main chain. Consequently, the mesophase is formed by the polymer chains as a whole. For MJLCPs, the main chains are expected to take an extended conformation and behave as main-chain liquid-crystal polymers. MJLCPs can be conveniently synthesized by, say, radical chain polymerization to obtain high molecular weight, especially by controlled/living radical chain polymerization, which results in a convenient way to obtain homopolymers or copolymers with a controlled molecular weight, low polydispersity and well-defined chain-ends. All of these methods provide a convenient route to synthesize a series of novel rod-coil liquid crystalline block copolymers with a desired controlled length. Wan et al. [14, 15] were the first to synthesize a series of mesogen-jacketed liquid crystalline polymers (poly[2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene] (PMPCS)) with different molecular weights and narrow MW dispersity and a series of novel rod-coil diblock copolymers with polystyrene and PMPCS using the 2,2,6,6-tetramethyl-1-piperidinyl-oxy (TEMPO)-mediated free radical polymerization. Tu et al. [16] studied this type of copolymer, and their results showed that the copolymer chains could self-assemble into a coil-shell nanostructure when a PS-b-PMPCS dilute solution was cooled. We have earlier reported the synthesis of PMPCS by atom transfer radical polymerization (ATRP) [17]. In the present study, we synthesized this rod-coil liquid crystal diblock copolymer PS-b-PMPCS by atom transfer radical polymerization. The block architecture of the synthesized copolymers and the liquid-crystalline behavior of the copolymers are examined in this study.

** Visiting from Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan. Project supported by the National Natural Science Foundation of China (No. 20134010).
Experimental

Materials

Chlorobenzene (Acros, 99%) was purified by washing with concentrated sulfuric acid to remove residual thiophenes, followed by washing twice with water, once with 5% sodium carbonate solution, and again with water before being dried with anhydrous calcium chloride and distilled. Styrene was purified by being passed through a column with activated Al2O3 (120–160 mesh) to remove the inhibitor, stored over CaH2, and then vacuum distilled before polymerization. CuBr was prepared from CuBr2 and purified by stirring in acetic acid, washing with methanol, and then drying in vacuum. Sparteine (Sp, from Aldrich) was distilled under reduced pressure over calcium hydrate and stored under a nitrogen atmosphere at 4°C in the dark. 1-Bromoethylbenzene (BEB) was purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) was used as received. 2,5-Bis[4-methoxyphenyl]oxycarbonyl]styrene (MPCS) was synthesized using Zhang et al.’s method [18].

Preparation of PS Macro-initiators

PS-block-PMPCS was synthesized by sequential polymerization of styrene and MPCS, as shown in Scheme 1.

PS macro-initiators were prepared using a method similar to that described in references [19]. Typically, styrene (10.40 g, 100 mmol), 1-bromoethylbenzene (0.185 g, 1 mmol), CuBr (0.1435 g, 1 mmol) and Sparteine (0.4688 g, 2 mmol) were charged into a polymerization tube. After degassing with three freeze-thaw cycles, the tube was sealed off under vacuum. The reaction mixture was heated at 110°C for the required time to allow the polymerization to proceed, and was then cooled to room temperature, the PS dissolved with THF, purified by passing the solution through a column with activated Al2O3 to remove the catalyst, and precipitated from methanol and dried in a vacuum oven overnight at room temperature.

Synthesis of PS-block-PMPCS

PS-b-PMPCS diblock copolymers were synthesized by solution polymerization in chlorobenzene. Thus, in a typical solution polymerization, a polymerization tube was charged with 0.268 g of PS macro-initiator (0.02 mmol), 0.268 g of MPCS (0.66 mmol), 2.87 mg of CuBr (0.02 mmol), 9.4 mg of Sparteine (0.04 mmol) and 2.144 g of chlorobenzene, and then the system was degassed three times and the tube sealed off as before. The reaction was carried out at 90°C for 5 h, and was then cooled to room temperature. The sample was further diluted with THF, and the mixture was purified by passing the solution through a column with activated Al2O3 to remove the catalyst, and then poured into a large volume of methanol to precipitate the polymer. The precipitate was washed thoroughly with methanol and dried in a vacuum oven overnight at room temperature. The conversion of polymerization was determined gravimetrically.

Purification of Diblock Copolymers

The separation of the diblock copolymers from possible residual PS macro-initiators was carried out partly according to the previously described procedures [15]. Thus, the crude product was extracted with cyclohexane for 48 h for removal of PS. The purified product was dried in vacuum.

Apparatus and Measurements

Molecular weights \( M_n \) and polydispersity \( M_w/M_n \) were measured on a gel permeation chromatograph (Waters 150°C) equipped with three Waters Styragel columns (10^3, 10^4 and 10^5 Å) using THF as an eluent at 35°C. The column system was calibrated by a set of mono-dispersed standard polystyrenes. \(^1\)H NMR spectra were obtained on a 200 Varian NMR instrument using CDCl3 as a solvent, and tetramethyl silane as the internal standard. Thermograms were obtained using a TA DSC 2010 instrument. Polarized optical microscope observation was performed on a Leitz Laborlux 12 POL microscope with a Leitz 350 hot stage.

![Scheme 1. Synthetic route of PS-b-PMPCS.](image-url)
Table 1. GPC, DSC results and Liquid Crystallinity of PS-Br and PS-b-PMPCS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Macro-initiator</th>
<th>$M_n$ × $10^{-4}$ (g/mol)</th>
<th>PDI</th>
<th>$M_n$ × $10^{-4}$ (PMPCS block) (g/mol)</th>
<th>PMPCS content in block (%) (GPC)</th>
<th>$T_g$ (°C)/$T_g$ (°C)/ Liquid crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMPCS</td>
<td></td>
<td>4.85</td>
<td>1.31</td>
<td></td>
<td></td>
<td>121.9/121.9/Yes</td>
</tr>
<tr>
<td>PS-Br(a)</td>
<td></td>
<td>0.62</td>
<td>1.08</td>
<td></td>
<td></td>
<td>/297.5/No</td>
</tr>
<tr>
<td>PS-b-PMPCS(A)</td>
<td>a</td>
<td>1.39</td>
<td>1.09</td>
<td>0.77</td>
<td>55.4</td>
<td>101.1/122.1/No</td>
</tr>
<tr>
<td>PS-b-PMPCS(B)</td>
<td>a</td>
<td>1.55</td>
<td>1.18</td>
<td>0.93</td>
<td>60.0</td>
<td>102.9/120.5/Yes</td>
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<tr>
<td>PS-b-PMPCS(C)</td>
<td>a</td>
<td>2.24</td>
<td>1.17</td>
<td>1.62</td>
<td>72.3</td>
<td>103.5/123.2/Yes</td>
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<tr>
<td>PS-Br(b)</td>
<td></td>
<td>1.34</td>
<td>1.10</td>
<td></td>
<td></td>
<td>101.7/ /</td>
</tr>
<tr>
<td>PS-b-PMPCS(D)</td>
<td>b</td>
<td>2.12</td>
<td>1.17</td>
<td>0.78</td>
<td>36.8</td>
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<td>PS-b-PMPCS(E)</td>
<td>b</td>
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<td>1.11</td>
<td>45.3</td>
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<td>PS-b-PMPCS(F)</td>
<td>b</td>
<td>3.35</td>
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<td>2.01</td>
<td>60.0</td>
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<tr>
<td>PS-b-PMPCS(G)</td>
<td>b</td>
<td>4.77</td>
<td>1.32</td>
<td>3.43</td>
<td>71.9</td>
<td>105.4/122.7/Yes</td>
</tr>
</tbody>
</table>

Results and Discussion

A series of diblock copolymers of PS-b-PMPCS were synthesized in this work (listed in Table 1). The ‘living’/controlled free radical polymerization of styrene was carried out in bulk. The conditions were similar to those described in [19]. Two PS-Br macro-initiators with low polydispersity were obtained. The existence of end group –CHBr was proved by 1H NMR spectroscopy. Because of the high melting point of MPCS (108–109 °C), the probable low solubility of the PS-Br macro-initiator and CuBr/Sp complex in MPCS, and the relatively small amounts of the reagent used, it became difficult for the PS-Br macro-initiator and the CuBr/Sp complex to be dispersed homogeneously in the MPCS melt at the polymerization temperature. Consequently, the chain extension was carried out in chlorobenzene. In this case, CuBr/Sp complex, PS-Br macro-initiator and monomer MPCS can easily be dissolved into chlorobenzene to form a bright red transparent solution. As the polymerization proceeded, the reaction mixture remained in a homogeneous state. Eventually, the copolymers were precipitated and washed with methanol.

Figure 1 shows the GPC spectra for PS-b-PMPCS (a, b, c) and PS-Br (d). After the chain extension reaction, an increase in molecular weight was found from $M_n = 6,200 \text{ g/mol}$ with $M_w/M_n = 1.08$ to $M_n = 22,400 \text{ g/mol}$ with $M_w/M_n = 1.17$. The polydispersity index (PDI) of the copolymer was slightly higher than its predecessor, but was still lower than the theoretical limit of 1.5 for the conventional free radical polymerization.

The copolymers were each characterized by $^1$H NMR spectroscopy. Figure 2 depicts the $^1$H NMR spectra of the homopolymer PMPCS, the macro-initiator PS-Br and its related diblock copolymers, recorded in CDCl$_3$, with TMS as an internal reference. It is worth noting that the expected NMR resonance signal (around 1.60 ppm) for the main chain protons is weak in the spectrum of PMPCS. In a recent report, Armes et al. [20] examined the temperature-induced micellization of DMAEMA-block-MAA Zwitterionic copolymer using $^1$H NMR spectroscopy. They found that the intensities of DMAEMA signals decreased significantly as the hydrophobic DMAEMA block formed the micelle core at elevated temperatures. Accordingly, the above-mentioned fact may be due to reduced solvation and mobility of the main chain, the result of the ‘mesogen-jacket’ effect, which is consistent with our earlier postulation on MJLCPs [21]. The $^1$H NMR spectrum of the block copolymer displays signals at 1.0–2.0 ppm (the signal for the main chain protons of PS) and 3.0–4.0 ppm (the signals for the side chain –OCH$_3$ of PMPCS), which are characteristic of the PS and PMPCS. This complex pattern can be taken as evidence of copolymer formation. As can be seen from the block copolymer, the signals of the aromatic peak region of PS and PMPCS and CHCl$_3$ overlapped, and the signals of the aliphatic peak region of PS overlaid the weakened signals of main chain protons of PMPCS. Therefore, we cannot calculate the PMPCS content based on a comparison of the aromatic protons or aliphatic protons to –OCH$_3$ protons of PMPCS.

Figure 3 shows that the glass transition temperatures ($T_g$) of neat PMPCS and PS-Br are 121.9 °C and 97.5 °C, respectively, and two distinct glass transitions are observed in all diblock copolymers. For PS-block-PMPCS(C), the lower $T_g$
is at 103.5 °C corresponding to the glass transition of the PS block, and the second is at 123.2 °C, corresponding to that of PMPCS. This provides further evidence of two phases in the block-copolymer configuration.

The liquid-crystalline behavior of the copolymers was studied using DSC and a polarized optical microscope. The results show that only the copolymers with \( M_n \) of the rigid block beyond 9300 g/mol could form liquid crystalline phases above the glass transition temperatures of the rigid block. The birefringence did not disappear until the decomposition temperature was reached (Figure 4). Wan et al. [22] have studied the relationship between the composition and the liquid crystallinity of MPCS-co-St random copolymer. It was found that the molar content of MPCS in MPCS-co-St must be more than 79.0% to maintain liquid crystallinity. However, the mole percentages of MPCS in PS-b-PMPCS (B) and PS-b-PMPCS (E) are only 27.9 and 17.6, respectively. The significant MPCS content necessary for the two kinds of copolymers to exhibit liquid crystallinity should again suggest the rod-coil structure of the two target block copolymers. Wan et al. [15] have also synthesized diblock copolymer PS-block-PMPCS using 2,2,6,6-tetramethyl-1-piperidinyl-oxy (TEMPO)-mediated free radical polymerization. They have found that two copolymers, in which the \( M_n \) of the rigid block equals 5400 and 10800 g/mol, respectively, are thermotropic liquid crystals. In a previous paper [17], we reported on our synthesis of PMPCS with different molecular weights using ATRP. The liquid-crystalline behavior of those polymers with \( M_n \) ranging from 3800 to 17400 g/mol was studied using DSC and POM. It was found that only polymers with \( M_n \) beyond 10200 g/mol could form liquid crystalline phases. The significant difference in the PMPCS length necessary for the copolymers to exhibit liquid crystallinity might be related to the differences in the end groups (–Br for ATRP, –TEMPO for NMP) or side reactions.

In contrast to conventional side-chain liquid-crystal polymers, the molecular architecture of the mesogenic units of MJLCPs are linked to the main chain through no or only short spacers by lateral attachment. For PMPCS, only a covalent bond is used to connect the main chain and the mesogenic unit. The bonding of rigid and bulky side-groups acts as a jacket along the polymer chain, and thereby forces the main chain to take an extended or rod-like conformation. Early studies on lyotropic behavior, banded texture, and solution properties have confirmed the rod-like nature of MJLCPs [23, 24]. Tu et al. [16] have proven that these novel rod-coil diblock copolymers comprising a polystyrene block and a MJLCP block have a unique supermolecular structure and self-assembly behavior. We believe that the supermolecular structure and self-assembly behavior of this rod-coil diblock copolymer will affect the PMPCS length and its liquid crystallinity. Detailed investigations are underway.

**Conclusion**

The synthesis of a series of coil-rigid rod diblock copolymers with low polydispersity was achieved by atom transfer
radical polymerization of styrene monomers and 2,5-bis[(4-methoxyphenyl)-oxycarbonyl]styrene monomers. The block architecture of the diblock copolymers thus prepared was confirmed by $^1$H NMR and DSC studied. It was observed that all copolymers showed two distinct glass transitions, corresponding to the two phases of polystyrene having a coil-like conformation, and the two phases of poly(-2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene) having a rigid-rod conformation.

Furthermore, some of the diblock copolymers could form a liquid-crystalline phase. The liquid-crystalline behavior of the synthesized copolymers was evidenced using DSC and a polarized optical microscope. It was found that the liquid crystalline behavior was dependent on the molecular weights of the rigid-rod segment. Only those copolymers with $M_n$ of the rigid block beyond 9,300 g/mol could form liquid crystalline phases above the $T_g$ of the rigid block.

References