Controlled Homeotropic and Homogeneous Orientations for Nanoscale Phase-separated Domain of Light-emitting Amphiphilic Block Copolymer Bearing a 2,5-Diarylthiazole Moiety

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An amphiphilic block copolymer composed of poly(ethylene oxide) and poly(methacrylate ester) bearing a donor–acceptor-type 2,5-diarylthiazole in the side chain is prepared by atom-transfer radical polymerization. The precursor 2,5-diarylthiazole monomer is prepared by transition-metal-catalyzed CH arylation reactions. A thin film of the block copolymer formed by spin coating exhibited nanoscale phase separation with homeotropically oriented domains, while a film formed by the friction transfer method showed domains with homogeneous orientation confirmed by AFM. Spectroscopic studies of the film, utilizing the luminescent characteristics of 2,5-diarylthiazole, showed polarized light emission as a result of the liquid crystalline ordering.

We have recently shown that controlled CH arylation of thiazole leads to a facile synthesis of 2,5-diarylated thiazoles. It was also found that 2,5-diarylthiazole derivatives bearing donor–acceptor-type substituents show strong photoluminescent and liquid crystalline characteristics.[1–3] These findings prompted us to investigate introduction of the photoluminescent 2,5-diarylthiazole moiety into the side chains of polymers to enable formation of a functional organic thin film.

On the other hand, we have also been studying the characteristics of amphiphilic block copolymers composed of hydrophilic poly(ethylene oxide) and hydrophobic poly(methacrylate) segments. We have found that liquid crystal copolymers bearing a pendant azobenzene in the hydrophobic part show remarkable nanoscale phase-separation.[4] Recently, our interest has centered on the synthesis of amphiphilic block copolymers bearing a pendant 2,5-diarylthiazole, the liquid crystalline characteristics of which should induce orientation of a thin film of the polymers and lead to remarkable light emission. We herein report preliminary results on the preparation of light-emitting amphiphilic block-copolymers with controlled molecular weight and molecular weight distribution, and present characterization data for a thin film of the copolymers, which indicates ordered nanoscale phase separation.

Preparation of a monomer bearing a 2,5-diarylthiazole moiety **1** (Chart 1) in a methacrylate side chain was carried out by tandem CH arylation, a method which we published recently,[1] using a palladium/copper catalyst system and a palladium catalyst in the presence of AgF. The block copolymer **3** was then synthesized by atom-transfer radical polymerization (ATRP)[4] using an α-bromo ester of poly(ethylene oxide) composed of 114 monomer units as the macroinitiator **2** and a complex of 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) and CuCl. The polymerization of **1** took place at 80 °C for 24 h in a living manner with a monomer/macroinitiator ratio of (9:1–48:1). Under the reaction conditions, the corresponding block copolymer was obtained with $M_n = 9800$–28500 and $M_w/M_n = 1.08$–1.10 (Scheme 1).[5]

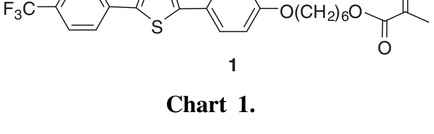

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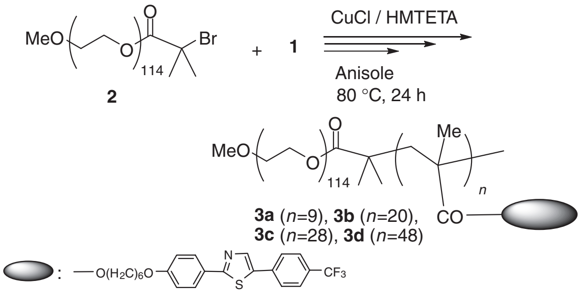
Chart 1.

UV–vis absorption and luminescence measurements were carried out on the corresponding homopolymer, which was formed from **1** by radical polymerization employing AIBN as an initiator. The polymer showed λ_{max} values of 338 nm (absorption) and 416 nm (luminescence; $\Phi = 0.19$). The results suggest that the spectroscopic characteristics of the low molecular weight 2,5-diarylthiazoles are maintained in the side-chained copolymer.[1] Further characterization of the amphiphilic block copolymer **3** were carried out on **3d**, which had a monomer/initiator ratio of 48:1. DSC analysis of polymer **3d** revealed endothermic peaks at 36, 146, and 255 °C upon heating, assigned to phase transition of the PEO domain, transition of the methacrylate domain to a liquid crystalline phase, and transition to an isotropic phase, respectively.[5] Polarizing microscope observations also suggested the formation of a smectic phase at 248 °C. Other polymers having different monomer/initiator ratios (9:1–48:1) also showed similar behavior.[5]

We then envisaged the formation of a thin film of the block copolymer **3d**. The film was fabricated on a silicon wafer by spin-coating a chloroform solution of **3d**. The spectroscopic characteristics of the film were similar to those in the corresponding homopolymer solution of the diarylthiazole. Nanoscale phase separation of oriented domains was observed upon annealing of the thin film at 180 °C for 24 h. UV–vis absorption



Scheme 1.

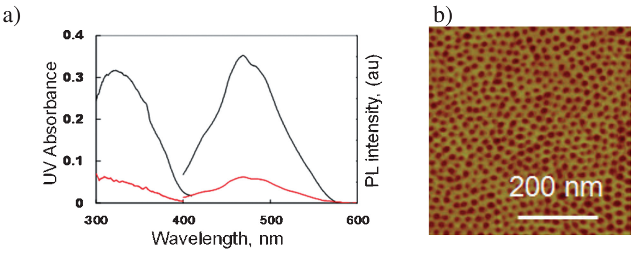


Figure 1. a) UV–vis (left) and luminescence (right) spectra of **3d** in a thin film before (black) and after (red) annealing at 180 °C for 24 h. b) AFM image (phase mode) of the thin film of **3d**.

and luminescence spectra of the film, were lower in intensity after annealing, as shown in Figure 1a. The absorption and luminescence spectra, with $\lambda_{\max}$ values at 319 and 487 nm, respectively, reduced in intensity, suggesting that homeotropic orientation of the liquid crystalline mesogen had occurred. AFM analysis also indicated nanoscale phase separation, as shown in Figure 1b, with the sample exhibiting a regular dotted structure, with the dots 18 nm in diameter (PEO domain as the dark region) separated by 26 nm on average. The structure suggests hexagonal-packed cylinders of homeotropically aligned liquid crystals, which would be induced by the orientation of the liquid crystalline mesogen moiety.[5,6] This is the first time to the best of our knowledge that the orientation of a hydrophobic domain bearing a photoluminescent chromophore has been identified.

We have recently reported that we were able to form a thin film with homogeneous orientation of the amphiphilic block copolymer bearing an azobenzene moiety when the thin film was fabricated by spin coating on the rubbing polyimide plate. The homogeneous orientation was observed along the rubbing direction.[7] Encouraged by which, we attempted a similar preparation for **3d** in the present work. However, such alignment was not observed in the 2,5-diarylthiazole pendant block copolymers.

Homogeneous orientation of the photoluminescent 2,5-diarylthiazole domain was found to be possible using a friction transfer technique, in which a thin film is formed from a pellet of the block copolymer.[8] Figure 2a shows an AFM image of a film formed by the friction transfer method, which shows nanoscale phase separation with homogeneous orientation of the diarylthiazole domain suggesting the PEO domain as the dark region and the thiazole pendant hydrophobic domain as the light region, respectively. In sharp contrast to films of main-chain-type liquid crystalline polymers formed by friction transfer, which have orientation parallel to the drawing direction,[8d] films of the side-chain-type polymer **3d**, which have not been previously examined, showed orientation perpendicular to the drawing direction.

Also worthy of note is the observation that polarized luminescence is induced as a result of the homogeneous orientation. As shown in the luminescence spectra acquired under polarized excitation at 330 nm (Figure 2b), the ratio of parallel/perpendicular intensities was found to be 1/13. The result supports perpendicular alignment of thiazole mesogen toward the friction drawing, whereas alignment of the azobenzene moiety was parallel to the rubbing direction.

In summary, amphiphilic block copolymer bearing a 2,5-diarylthiazole moiety in the side chain was synthesized by palladium-catalyzed CH arylation reactions and atom-transfer living radical polymerization protocols. A thin film of the polymer exhibited homogeneous and homeotropic orientations were successfully obtained for thin films of the polymer with nanoscale phase separation. The homogeneous orientation observed in the thin film, which was generated by the friction transfer method, was found to induce remarkable polarized light emission.[9]

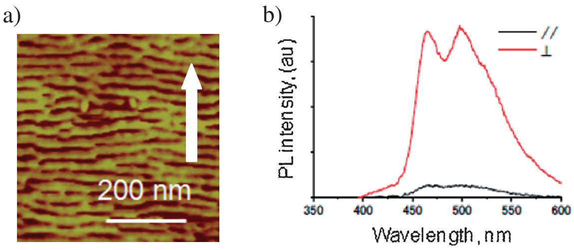


Figure 2. a) AFM image (phase mode) of the thin film of **3d** prepared by the friction transfer method. The arrow shows the drawing direction. b) Luminescence spectra of the thin film with perpendicular (upper) and parallel (lower) polarized light (excitation wavelength: 330 nm).

This work was partially supported by a Grant-in-Aid for Scientific Research in Priority Area, Advanced Molecular Transformation of Carbon Resources, by Ministry of Education, Culture, Sports, Science and Technology, Japan.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) February 2, 2008; doi:10.1246/cl.2008.272