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Polarized Photoluminescence from Poly(*p*-phenylene−ethynylene) via a Block Copolymer Nanotemplate

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Polarized luminescent materials[1] have attracted attention for potential uses in flat panel displays[2] and other optoelectronic devices.[3] Conjugated polymers (CPs), such as poly(*p*-phenylene−vinylene) (PPV)[4] and poly(*p*-phenylene−ethynylene) (PPE)[2,5] derivatives, have been of particular interest for use as polarized emitters due to the intrinsic anisotropy of their (quasi) one-dimensional electronic structure and ability to be processed in uniaxially oriented blends by various techniques such as rubbing,[6] friction transfer,[7] tensile drawing,[4] and Langmuir−Blodgett film deposition.[8] This communication presents a new approach to achieving polarized emission from CPs, specifically PPEs, by using a block copolymer host matrix as a nanotemplate for the spatial orientation of CPs. This technique provides a means of generating large-area films for polarized photoluminescence.

Self-assembled block copolymers allow for easy access to one-, two-, and three-dimensional ordered nanostructures.[9] The different morphologies can be selected by tailoring the relative composition of each block. Furthermore, with the application of a flow field, the global orientation of a block copolymer microstructure can be directed, forming nearly single-crystal structures.[10−12] Roll cast processing is one technique that has been shown to globally orient block copolymers.[12] In this communication, we demonstrate the ability to orient a cylindrical morphology block copolymer by roll cast processing and use the resulting nanostructure as a template for the spatial and orientational ordering of a guest PPE. Sequestering the guest PPE molecules into the cylindrical microdomains of a block copolymer and globally orienting the host matrix results in the alignment of the PPEs parallel to the long axis of the cylinders. The uniaxial orientation of the PPEs within the block copolymer host gives rise to polarized absorbance and photoluminescence.

Our approach was to synthetically modify a PPE such that it would have selective miscibility to the cylinder phase of a block copolymer host. Roll cast processing preferably requires a rubbery matrix phase, and thus, we used a polystyrene−polyisoprene−polystyrene (SIS) triblock copolymer system with minority component styrene cylinders in an isoprene matrix. Consequently, we functionalized the PPE with polystyrene (PS) by grafting from a PPE macroinitiator via atom transfer radical polymerization (ATRP).[13] Grafted PPEs were synthesized as shown in Scheme 1. The diacetylene monomer with terminal hydroxyl side chains, **1**, was polymerized with the diiodide **2** under Pd(0)-catalyzed cross-coupling conditions to give the PPE backbone (**3**). The PPE was then functionalized with 2-bromoisobutyryl bromide to give the ATRP macroinitiator **4**. Subsequent ATRP polymerization of styrene gave the polystyrene grafted PPE (PPE−*g*-PS) **5**.

Scheme 1

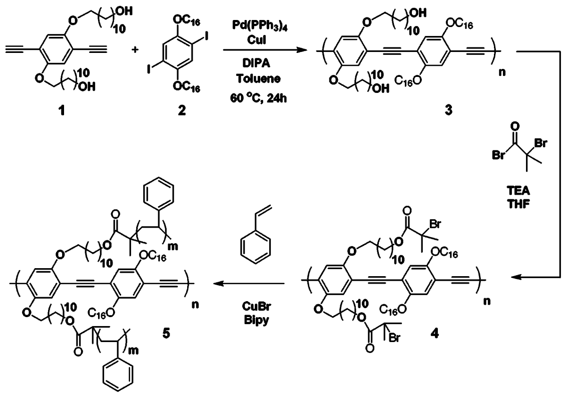

Table 1. Polymer Characterization

	GPC analysis		photophysical characterization (solid state)		
polymer	M_n	PDI	λ_{max}abs (nm)	λ_{max}em (nm)	Φ
PPE backbone (**3**)	56,000	2.59	480	495	0.10
PS grafted PPE (**5**)	80,000	1.62	445	475	0.60
cleaved PS grafts	5,600	1.17	−	−	−
PS/PI/PS	101,000	1.05	−	−	−

Table 1 contains characterization data for the synthesized polymers. The polymers were characterized by gel permeation chromatography (GPC) (Figure 1), nuclear magnetic resonance (NMR) spectroscopy, UV/vis spectroscopy, and fluorescence spectroscopy. The success of each step involved in the synthesis of the grafted polymers could be assessed through ^{1}H NMR analysis. As shown in Figure 1, the change in the chemical shift of the methylene protons adjacent to the terminal hydroxyl group on monomer **1** was monitored to verify the covalent attachment of the ATRP initiator (**4**) as well as the successful initiation of PS polymerization (**5**). Further confirmation is provided upon observation of the grafted PPEs photophysical behavior in the solid state. As expected, the PPE−*g*-PS displayed both a blue-shift and an increase in fluorescence quantum efficiency (Table 1) relative to **3** due to the presence of the PS grafts preventing aggregation of the PPE backbone.[13b] Finally, the atom transfer polymerization of styrene was assessed by measuring the polydispersity of the PS grafts (Table 1). The ester linkages of the ATRP initiator were cleaved post polymerization by treating the grafted PPE with KOH in a refluxing THF/MeOH mixture, allowing for GPC analysis of the free PS grafts.[13b]

The synthetically modified PPE was then doped into a SIS triblock copolymer (Dexco, $M_n = 101\,000$; 29% (w/w) PS) film with cylindrical morphology. The roll cast films were prepared by making 40% (w/w) solutions of polymer in cumene. The PPE−*g*-

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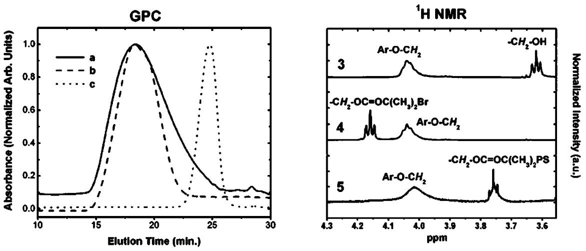

Figure 1. GPC elugrams of (a) PPE Backbone, (b) PS grafted PPE, and (c) cleaved PS grafts and ^{1}H NMR of polymers **3**, **4**, and **5**. ^{1}H NMR normalized on the aromatic methoxy proton signal.

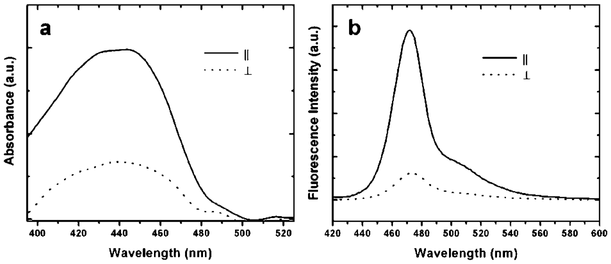

Figure 2. Polarized absorption (a) and photoluminescence (b) of a roll cast oriented film of 0.1 wt % PPE−*g*-PS doped in SIS. The spectra were obtained with polarizers oriented parallel (solid line) and perpendicular (dashed line) to the average PS cylinder orientation of the block copolymer host. It should be noted that the emission spectra in (b), measured perpendicular to the polarizers (dashed line), is corrected for instrumental polarization dependence. See Supporting Information for details.

PS dopant was blended in at a concentration of 0.1 wt % of polymer. After roll casting, the resultant films were approximately 0.04 mm thick and 6 × 16 cm^2 in area. The polystyrene cylinders were oriented in the plane of the film, and hence, the films displayed the expected mechanical anisotropy[9] due to the oriented glassy polystyrene cylinders in an elastic polyisoprene matrix. The film nanostructure was characterized by transmission electron microscopy (TEM).

Photophysical characterization of the globally oriented roll cast films was conducted. Figure 2 shows the polarized absorption and photoluminescence observed from a doped roll cast film. The measured absorbance dichroic ratio as shown in Figure 2a is 3.0 at 440 nm. The polarized emission in 2b was generated by exciting the roll cast film with 400 nm radiation normal to the plane of the film, yielding a polarization ratio of 6.4 at 472 nm. These values indicate that the transition dipoles of the guest PPE−*g*-PS are aligned parallel to the cylinder axis of the block copolymer host and thus emit polarized light with polarization parallel to the plane of the film. Furthermore, the difference in the absorbance dichroic ratio as compared to the emission polarization ratio suggests this particular materials system is able to absorb a significant fraction of unpolarized light and funnel the excitation into polarized emission. This phenomenon can be explained by intramolecular energy transfer from less aligned segments of conjugated polymer to the highly aligned, and therefore more conjugated, segments of conjugated polymer within the host cylinder domains. This rationale is supported by the fact that as the excitation wavelength is increased to 440 nm, i.e. toward the band edge, the observed polarization ratio increases to 7.3 at 472 nm.[14] The lower-energy excitation directly excites the more aligned, longer-conjugation length segments.

This materials system, combined with roll cast processing, provides advantages over other techniques for achieving polarized photoluminescence. Many of the systems and processes reported to date are not readily amenable to large-scale production.[1] In addition, the emission efficiencies of these systems are often limited by aggregation phenomena found in highly aligned parallel chains of conjugated polymer.[1] In contrast, we have demonstrated the ability to process large-area, uniform films that produce polarized photoluminescence. Furthermore, the grafted PPE, used as the optically active material, intrinsically eliminates aggregation, and thus, the aligned films have enhanced emission efficiency in the solid state.

In summary, we have demonstrated that polarized photoluminescence can be obtained from a roll cast CP-block copolymer guest/host system. Synthetic modification of an optically active PPE guest was conducted for domain-specific doping of a block copolymer host. Globally orienting the nanostructure of the host provided a template for the alignment of the guest PPE. The host/guest system gives rise to both polarized absorption and photoluminescence parallel to the cylinder axis of the host, indicative of uniaxially oriented PPEs. Our group is currently studying the effects of grafting length and film thickness on the alignment and subsequent polarized emission of the templated guest PPEs. Templating of PPEs in a block copolymer photonic crystal is also being pursued.

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Supporting Information Available: Experimental procedures, synthetic preparations for all new compounds, and roll cast film characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Grell, M.; Bradley, D. D. C. *Adv. Mater.* **1999**, *11*, 895.
(2) (a) Weder, C.; Sarwa, C.; Mantali, A.; Bastiaansen, C.; Smith, P. *Science* **1998**, *279*, 835. (b) Mantali, A.; Bastiaansen, C.; Smith, P.; Weder, C. *Nature* **1998**, *392*, 261.
(3) Granstrom, M. *Polym. Adv. Technol.* **1997**, *8*, 424.
(4) (a) Hagler, T. W.; Pakbaz, K.; Voss, K. F.; Heeger, A. J. *Phys. Rev. B* **1991**, *44*, 8652. (b) Yang, C. Y.; Heeger, A. J.; Cao, Y. *Polymer* **1999**, *41*, 4113.
(5) Arias, E.; Maillou, T.; Moggio, I.; Guillon, D.; Le Moigne, J.; Geffroy, B. *Synth. Met.* **2002**, *127*, 229.
(6) (a) Hamaguchi, M.; Yoshino, K. *Polym. Adv. Technol.* **1997**, *8*, 399. (b) Jandke, M.; Strohriegl, P.; Gmeiner, J.; Brutting, W.; Schwoerer, M. *Adv. Mater.* **1999**, *11*, 1518. (c) Bolognesi, A.; Botta, C.; Martinelli, M. *Synth. Met.* **2001**, *121*, 1279.
(7) (a) Wittmann, J. C.; Smith, P. *Nature* **1991**, *352*, 414. (b) Yoshida, Y.; Tanigaki, N.; Yase, K.; Hotta, S. *Adv. Mater.* **2000**, *12*, 1587.
(8) Cimrova, V.; Remmers, M.; Neher, D.; Wegner, G. *Adv. Mater.* **1996**, *8*, 146.
(9) Thomas, E. L.; Lescanec, R. L. *Philos. Trans. R. Soc. London, Ser. A* **1994**, *348*, 149.
(10) Folkes, M. J.; Keller, A. *Polymer* **1971**, *12*, 222.
(11) Winter, H. H.; Scott, D. B.; Gronski, W.; Okamoto, S.; Hashimoto, T. *Macromolecules* **1993**, *26*, 7236.
(12) Albalak, R. J.; Thomas, E. L. *J. Polym. Sci., Polym. Phys. Ed.* **1994**, *32*, 341.
(13) (a) Borner, H. G.; Beers, K.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. *Macromolecules* **2001**, *34*, 4375. (b) Costanzo, P. J.; Stokes, K. K. *Macromolecules* **2002**, *35*, 6804.
(14) Rose, A.; Lugmair, C. G.; Swager, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 11298.

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