Block Conjugated Copolymers: Toward Quantum-Well Nanostructures for Exploring Spatial Confinement Effects on Electronic, Optoelectronic, and Optical Phenomena

X. Linda Chen and Samson A. Jenekhe*

Department of Chemical Engineering and Center for Photoinduced Charge Transfer, University of Rochester, Rochester, New York 14627-0166

ABSTRACT: An ABA triblock conjugated copolymer, poly(2,5-benzoxazole)-*block*-poly(benzobisthiazole-2,6-diyl-1,4-phenylene)-*block*-poly(2,5-benzoxazole), **1**, was synthesized, characterized, and used to demonstrate spatial confinement effects on the electronic structure and the optical and optoelectronic properties of block copolymers. Optical absorption, photoluminescence, and photoluminescence excitation spectra of thin films of the triblock copolymer evidence spatial confinement of excitons as well as *microphase separation*. Efficient energy transfer via interchain and intrachain mechanisms was observed in the triblock conjugated copolymer. The results suggest that microphase separation in bulk block conjugated copolymers can significantly modify the spatial modulation and confinement dimensionalities expected in isolated block copolymer chains.

Block conjugated copolymers are expected to exhibit novel electronic, optoelectronic, and optical properties not found in conjugated homopolymers, random copolymers, and alternating copolymers.[1−8] A possible origin of the expected novel features of *block conjugated copolymers* is the quantum confinement phenomenon which arises in nanostructured semiconductor quantum-well structures.[6,9,10] If the conjugated homopolymers $(-A-)_n$ and $(-B-)_m$ are characterized by highest occupied molecular orbital−lowest unoccupied molecular orbital (HOMO−LUMO) or $\pi−\pi^*$ energy gaps E_g^A and E_g^B, respectively, where $E_g^A > E_g^B$, the related ABA triblock copolymer chain would represent a *quantum-well structure* in which the B block forms a square potential well and the large-gap A blocks form electron potential energy barriers of height $\Delta E_g = E_g^A - E_g^B$. Similarly, an $(AB)_n$ multiblock conjugated copolymer chain would represent a quasi zero-dimensional quantum-well structure or *superlattice structure* with a periodic electron potential modulation ΔE_g along the chain. There have been many theoretical studies predicting *electronic localization phenomena* and *quantum size effects* in block conjugated copolymers[1−5] but very few experimental investigations have been reported.[6−8] In fact, the few experimental studies to date have been on copolymers $(-A_xB_y-)_n$ where the segment lengths are so short ($x = 2-3$, $y = 2-6$) that the materials are not really *block* copolymers and thus could not clearly test the predicted spatial confinement effects.[6−8]

In this paper, we report preliminary results of experimental studies exploring quantum-well structures in block conjugated copolymers and the associated spatial confinement effects on electronic, optoelectronic, and optical properties. An ABA triblock copolymer, poly(2,5-benzoxazole)-*block*-poly(benzobisthiazole-2,6-diyl-1,4-phenylene)-*block*-poly(2,5-benzoxazole), **1**, was synthesized, characterized, and investigated by optical absorption, photoluminescence (PL), and photoluminescence excitation (PLE) spectroscopies as well as by time-resolved PL decay dynamics. The results show clear evidence of spatial confinement of excitons in the different blocks. However, we also show that *mi-*

crophase separation in the bulk block conjugated copolymer significantly modifies the modulation and confinement dimensionalities expected at the single-chain level.
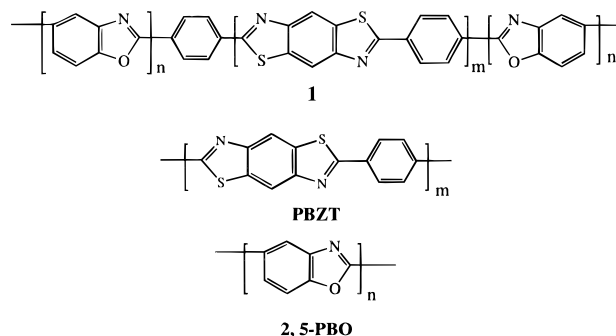
The ABA triblock copolymer **1** consists of a poly(benzobisthiazole-2,6-diyl-1,4-phenylene) (PBZT) middle block and poly(2,5-benzoxazole) (2,5-PBO) outer blocks. The electronic structure, redox, and optical and nonlinear optical properties as well as photoluminescence (PL) and photoconductivity of the PBZT homopolymer have been extensively investigated in our laboratory.[11−13] The electroactive and photoactive properties of the 2,5-PBO homopolymer have not been reported. The optical absorption maxima in the homopolymers PBZT and 2,5-PBO are 438 and 467 nm and 340 and 355 nm, respectively. The corresponding HOMO−LUMO energy gaps based on absorption band edges are $E_g^B = 2.48$ eV (PBZT) and $E_g^A = 3.24$ eV (2,5-PBO). Thus, the PBZT segment of the triblock **1** chain is expected to form a quantum well, while the 2,5-PBO blocks form electron potential barriers with $\Delta E_g = 0.76$ eV.

Triblock **1** was synthesized by combining the known literature methods for the homopolymers.[11b,14] Carboxylic acid-terminated PBZT block (HOOC−B_m−COOH) was synthesized by reacting 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) with excess terephthalic acid (TA) in poly(phosphoric acid) (PPA). The $A_nB_mA_n$ triblock was obtained by copolymerizing HOOC−B_m−COOH with 3-amino-4-hydroxybenzoic acid (AHBA) in PPA. The block lengths *m* and *n* were controlled through the stoichiometric ratios of TA to
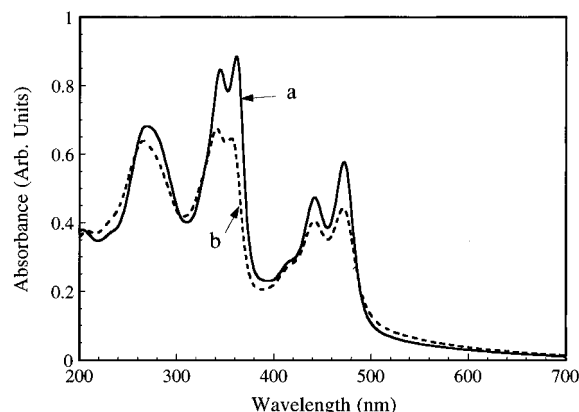
Figure 1. Optical absorption spectra of thin films of (a) triblock **1** and (b) a physical blend of identical composition of 2,5-PBO (81.6 mol %)/PBZT.

Figure 2. PL emission spectra of thin films excited at 340 nm: (a) triblock; (b) 2,5-PBO/PBZT (18.4 mol %) blend; (c) triblock (1 wt %)/PMMA blend.

DABDT and AHBA to HOOC−B_m−COOH. The particular triblock investigated here has the average composition $A_{20}B_9A_{20}$, where A and B are the 2,5-PBO and PBZT repeat units, respectively. From the known X-ray diffraction data for the homopolymers,[15,16] the PBZT repeat unit length is 1.25 nm and the 2,5-PBO repeat unit length is 1.16 nm. Thus, this symmetric triblock sample has a middle block of 11 nm and two outer blocks of about 23 nm each. Thin films of the triblock and homopolymers were prepared by spin coating of solutions in formic acid/methanesulfonic acid or nitromethane/GaCl₃.[11,12] The methods and equipment used in the photophysical characterization have previously been described.[11,12,17]

The synthetic approach outlined above ensured that the desired triblock copolymer structure was obtained. Various spectroscopic and other characterizations have confirmed the proposed triblock structure and composition. Thermogravimetric analysis (TGA) of the triblock showed a single onset of decomposition in N₂ (665 °C) that was different from either homopolymer, 650 °C for 2,5-PBO and ∼700 °C for PBZT. The intrinsic viscosity of **1** in methanesulfonic acid (MSA) at 30 °C was 2.3 dL/g, which is higher than either the starting HOOC−B₉−COOH (0.8 dL/g) or a 2,5-PBO homopolymer with a degree of polymerization of 60 (1.7 dL/g). ¹H NMR of the triblock in deuterated nitromethane containing AlCl₃ gave four proton resonances, in accord with the proposed structure and composition.[18]

Figure 1a shows the optical absorption spectrum of a thin film of the triblock copolymer. A highly structured electronic absorption in the UV−visible region is observed: a vibrationally resolved absorption band in the 400−500 nm region with λ_{max} of 440 and 470 nm which is characteristic of the B block (PBZT) and a vibrationally resolved band in the 240−380 nm region with λ_{max} of 270, 344, and 360 nm which is due to the A blocks (2,5-PBO). The optical absorption of a physical mixture of 2,5-PBO with PBZT (18.4 mol %) is shown in Figure 1b, indicating that the absorption spectrum of the triblock is a superposition of those of the homopolymers. The main difference between the triblock and the physical blend is the rather sharp vibronic structures of the triblock absorption spectrum. Observation of optical absorption bands characteristic of the homopolymers in the electronic absorption of the triblock is an important evidence that excitons produced on triblock chains are split and confined into two distinct spatial regions with different energy levels. Such a spatial confinement effect as evidenced by distinct segment
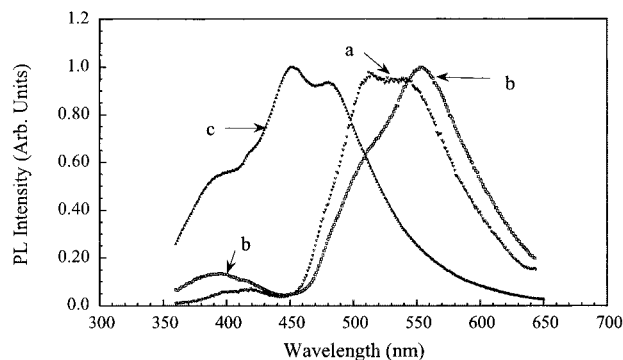
absorption bands is similar in nature to the well-known phenomenon of two separate glass or melting temperatures in microphase-separated block flexible-coil copolymers.[19] Also, we point out that spatial confinement of excitons as observed here (Figure 1) for a block conjugated copolymer has not been observed in numerous conjugated random or alternating copolymers that have been reported.[17]

Figure 2a shows the PL emission spectrum of a thin film of the triblock when the absorption band of the 2,5-PBO block was excited at 340 nm. A broad PL emission band in the 460−640 nm region and centered at ∼510−544 nm is observed and assigned to the emission from the PBZT block. This assignment was made because similar PL emission spectra were obtained when the PBZT segment absorption band was excited at 440 and 460 nm, where the 2,5-PBO block does not absorb. The PL emission spectrum of the triblock is also very similar to that of the PBZT homopolymer (not shown), which is broad (460−640 nm), featureless, and centered at ∼560 nm. There is only a very weak emission in the triblock PL spectrum near 400 nm where the 2,5-PBO block emits. The nearly complete quenching of emission from the higher energy 2,5-PBO blocks indicates that the lower energy PBZT block acts as a quantum well which traps excitons and acts as a radiative recombination center. This also means that there is efficient energy transfer from the 2,5-PBO blocks to the middle PBZT block.

The similarity of the triblock emission spectrum to that of the PBZT homopolymer thin film, which is known to luminesce via excimer-forming aggregates,[12] suggests that microphase separation has occurred in the triblock copolymer. Additional photophysical evidence of microphase separation in the block copolymer was obtained through comparisons with a physical 2,5-PBO/PBZT (18.4 mol %) blend (Figure 2b) and with an isolated triblock chain (1 wt %) in the matrix of inert poly(methyl methacrylate) (PMMA) (Figure 2c). The PL emission spectrum of the physical blend was slightly red shifted from that of the triblock but nearly identical with that of the PBZT homopolymer. This means that the PBZT/2,5-PBO blend is phase separated and that the emitting PBZT domains in the blend are larger or more like the PBZT homopolymer than in the copolymer. It is also noteworthy that quenching of the 2,5-PBO PL emission near 400 nm is not as complete as in the triblock. Hence, energy transfer in the blend is not as efficient as in the triblock. The PL spectrum of the isolated triblock chain shown in Figure 2c exhibits a band with vibronic structure at 451 and 480 nm which is due to the isolated PBZT block and a shoulder at ∼400
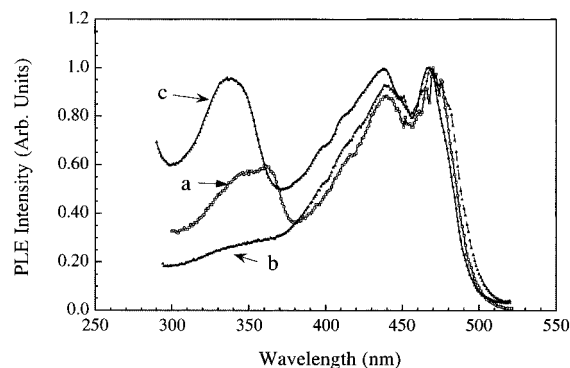
Figure 3. PL excitation spectra of thin films whose emission at 540 nm is monitored: (a) triblock; (b) 2,5-PBO/PBZT (18.4 mol %) blend; (c) triblock (1 wt %)/PMMA blend.
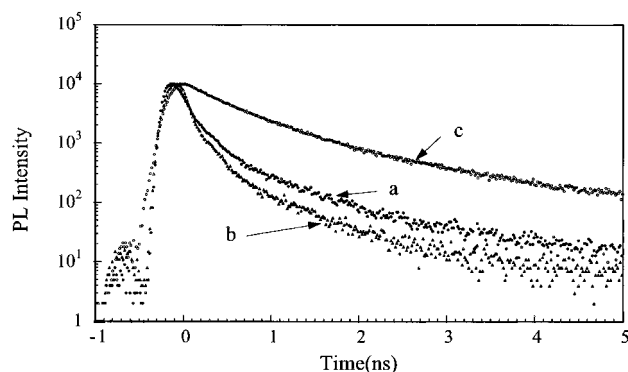

Figure 4. PL decay dynamics of thin films excited at 350 nm and monitored at 540 nm: (a) triblock; (b) 2,5-PBO/PBZT (18.4 mol %) blend; (c) triblock (1 wt %)/PMMA blend (monitored at 480 nm).
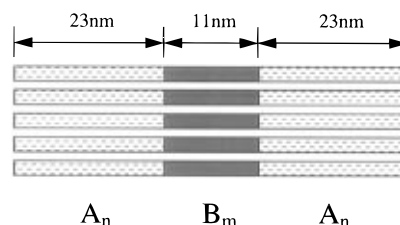

Figure 5. Schematic illustration of microphase-separated triblock and estimated sizes.

nm that is attributed to the 2,5-PBO blocks. The large blue shift of the PL spectrum of isolated triblock chains in PMMA compared to that of the pure triblock (Figure 2) means that the luminescence from the microphase-separated triblock is from excimer-forming aggregates or microdomains. The relatively high intensity of the 400 nm band of the PL emission spectrum of the isolated triblock chains in PMMA (Figure 2c) suggests that interchain energy transfer is an important mechanism of 2,5-PBO block PL quenching in the triblock thin film.

Figure 3 shows the photoluminescence excitation (PLE) spectra (normalized at 470 nm) corresponding to the PL emission spectra of Figure 2. These excitation spectra were obtained by monitoring the emission of thin films of triblock, 2,5-PBO/PBZT blend, and triblock/PMMA blend at 540 nm, where there is negligible emission from the 2,5-PBO chromophore. The PLE spectrum of the triblock (Figure 3a) shows features similar to the absorption spectrum in Figure 1a. Most importantly, the presence of the large 340−360 nm band due to 2,5-PBO block absorption reveals that the 540 nm emission from the PBZT block has a significant component in excitation energy transfer from the 2,5-PBO block. Due to the negligible emission of 2,5-PBO homopolymer at 540 nm and its lower PL quantum efficiency than PBZT homopolymer, the PLE spectrum of the blend (Figure 3b) shows that the blend emission at 540 nm comes from PBZT. Comparison of the PLE spectra of the copolymer and blend suggests that intrachain energy migration from the 2,5-PBO blocks to the lower energy PBZT block is a significant photophysical process in the triblock copolymer. Efficient *intrachain energy migration* in the block copolymer was further evidenced by the PLE spectrum of the isolated triblock chains (1 wt %) in PMMA (Figure 3c), where *interchain* energy transfer was ruled out. These excitation spectra and the previously discussed emission spectra provide additional evidence of the chemical connectivity of the segments of the triblock copolymer.

The time-resolved PL decay dynamics of the triblock, 2,5-PBO/PBZT blend, and the triblock dispersed in PMMA are shown in Figure 4. The PL of the isolated triblock chains in PMMA decays slowest, having biexponential lifetimes of 0.58 and 2.26 ns with amplitudes of 71 and 29%, respectively. The biexponential lifetimes for the triblock copolymer (0.23 ns, 73%; 0.9 ns, 27%) and blend (0.14 ns, 84%; 0.9 ns, 16%) were considerably shorter. The observed fast PL decay dynamics of the copolymer and blend are similar to those of the PBZT homopolymer.[12] These results further confirm the microphase separation of the triblock and phase separation of the physical blend. Figure 5 shows a schematic

illustration of the microphase-separated triblock conjugated copolymer **1** and our estimates of the relevant sizes of the nanostructures based on the X-ray diffraction data of the homopolymers. Possible deviation of the crystalline structure and morphology of the block copolymer from the homopolymers is unknown but will be investigated in the future.

Although all the results presented here together show clear evidence of spatial confinement of excitons within the lower energy segment of a symmetric triblock conjugated copolymer, we have not yet observed any new energy levels in the absorption or emission spectra that could be attributed to quantum mechanical behavior[6,9,10] of such confined nanostructures. Among the possible reasons for not observing such quantum size effects are the following. Microphase separation of the triblock copolymer has the effect of changing the confinement dimensionality as illustrated in Figure 5. Theoretical studies to date[1−5] have not taken account of the possibility and consequence of microphase separation on quantum size effects in block conjugated copolymer quantum-well and superlattice structures. It may also be that the composition of the triblock, the block length, and the spread in block length of the lower energy segment that forms the quantum well are not optimum for observing the quantum-well energy levels.[1] Quantum size effects in multiple quantum wells, of which the ABA triblock is a model, are generally more difficult to observe as optical transitions than superlattices[9,10] of which multiblock copolymers would be models. Our ongoing work is aimed at addressing these issues as well as the synthesis and investigation of various block conjugated copolymer quantum-well structures.

In summary, an ABA triblock conjugated copolymer, poly(2,5-benzoxazole)-*block*-poly(benzobisthiazole-2,6-diyl-1,4-phenylene)-*block*-poly(2,5-benzoxazole), was synthesized, characterized, and used to demonstrate spatial confinement effects on the electronic structure and the optical and optoelectronic properties of block copoly-

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(18) The solubility of the triblock in $CD_3NO_2/AlCl_3$ allowed us to obtain ^{1}H NMR spectra to confirm the proposed structure and composition. The spectra of the 2,5-PBO and PBZT homopolymers were also obtained for comparison. The protons of the PBZT block appear as a singlet at 9.4 ppm, assigned to the benzobisthiazole ring system, and a singlet at 8.7–8.8 ppm, assigned to the 1,4-phenylene protons. The protons of the 2,5-PBO blocks appear as a singlet at 9.2 and a doublet at 9.0 ppm, which are assigned to the protons *ortho* and *para* to the oxazole nitrogen, respectively. The proton *meta* to the oxazole nitrogen appears as a doublet between 8.7 and 8.8 ppm, thus overlapping with the *p*-phenylene protons of the PBZT block. The fact that the ^{1}H NMR spectrum of the triblock is a superposition of those of the PBZT and 2,5-PBO homopolymers indicates that **1** is a true block copolymer. Integration of the proton resonances was in excellent agreement with the proposed composition.

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