Preparation of Functionalized Polystyrene-*block*-polyisoprene Copolymers and Their Luminescence Properties

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Received April 26, 2001; Revised Manuscript Received November 12, 2001

ABSTRACT: A series of block copolymers functionalized with aromatic 1,3,4-oxadiazole and stilbene derivatives have been synthesized by the palladium catalyzed reaction between polystyrene-*block*-polyisoprene and different functional units. These polymers exhibited different emission properties in solution and in the solid state. In chloroform solution, they showed relatively narrow and featured emission bands while, in the solid state, the emission band was broadened and showed a significant red shift. These observations were attributed to the formation of aggregates between the luminophores. After some oxadiazole functionalized copolymers were annealed at elevated temperature, such aggregation was enhanced and there were further changes in the emission spectra. For the bifunctional copolymers, such a shift in the emission band was not significant because the presence of two different chemical species in the same block may prevent the same type of luminophores from aggregating together.

Introduction

Organic luminescent material has been the subject of growing interest in past years, particularly polymer-based materials, because of their processibility and durability. Many photoactive and electronically active compounds were blended with commercial polymers such as poly(methyl methacrylate) and polycarbonates that served as the supporting matrixes.[1,2] However, the incompatibility between the polymer and dopants may induce the crystallization of the small molecules and may also yield a material with poor strength. This problem can be overcome by attaching the functional units to the polymer main chain or side chain with covalent bonding. Nevertheless, functional polymers may still exhibit microphase separation because of the fact that functional units with similar structure tend to form aggregates. The physical properties of the functional polymers may be altered because of the presence of such aggregation. For example, it has been reported that, in some light emitting functional polymers, the emission originated from inter- and intrachain aggregate complexes.[3−5]

The aggregation effect of functional units on the physical properties of functional polymers can be studied by synthesizing functional block copolymers. Block copolymers usually exhibit unique and interesting phase separation properties in the solid state because of the thermodynamic incompatibility between different blocks.[6] Depending upon the volume fraction, block length, and chemical nature of different blocks, the degree of aggregation and the size and shape of the microdomain will be different. It has been reported that some block copolymers can self-assemble into nanoclusters[7,8] or exhibit a specific shape in the solid or in solution.[9] In our previous reports, we synthesized different block copolymers[10] that were functionalized with charge transport moieties or metal complexes. They exhibit interesting morphological behaviors, and some rhenium containing polystyrene-*block*-poly(4-vinylpyridine)s were able to form micelles in solution. The polymer morphologies were dependent on the relative block size and the solvent system used.[11] In the literature, there are several examples of incorporating fluorescence tags or other photosensitizing functional groups into block copolymers. Different polycyclic aromatic compounds such as naphthalene,[12] pyrene,[13] perylene,[14] cinnamoyl,[15] and phenanthryl[16] groups were used. By studying the fluorescence properties[17] or intramolecular energy migration process,[18] one can obtain information about the aggregation, morphology, or micelle formation in these copolymers.

In this paper, we report the synthesis of a series of polystyrene-*block*-polyisoprene (PSt-*b*-PIP) that were tagged with luminescent aromatic oxadiazole or stilbene derivatives on the polymer side chain. The functional groups were generally used as the electron transport and emission units in light emitting polymers. They were attached to the polymer side chain by a palladium catalyzed olefinic coupling reaction. The resulting functionalized block copolymers are expected to have more defined domain sizes and morphologies, and they can serve as a good model for studying the aggregation of luminophores in some light emitting polymers. Some of the polymers also exhibit electroluminescence activities. Besides, it is envisaged that an annealing process would enhance microphase separation between different domains that in turn affects the degree of aggregation. The effect of annealing on the morphologies and luminescence properties was also studied. This paper reports the results.

Experimental Section

Materials. Polystyrene-*block*-polyisoprene (PS-*b*-PIP) **1** was synthesized by the anionic polymerization in THF using *sec*-butyllithium as the initiator.[19] The molecular weight of the polymer and the polydispersity were 150 000 and 1.2, respectively (determined by gel permeation chromatography). The ratio of the PS to PIP block was 6:4. In the polyisoprene block the content of the pendant vinyl group was above 80% as determined by ^{1}H NMR spectroscopy. *p*-Bromobenzonitrile, benzoyl chloride, *p*-nitrobenzoyl chloride, benzaldehyde, *p*-nitrobenzaldehyde, biphenylcarboxylic acid, *p*-bromobenzyl bromide, 4-*tert*-butylbenzoic acid, 1-cyanonaphthalene, 9-anthraldehyde, tributylamine, triphenylphosphine, sodium azide, ammonium chloride, benzene, toluene, *N*,*N*-dimethylformamide (DMF), and pyridine were purchased from Lancaster Ltd. Tri-*o*-tolylphosphine and palladium acetate were purchased

10.1021/ma0107206 CCC: $22.00
Published on Web 12/29/2001

from Strem Chemicals. Unless otherwise specified, all the reagents were used as received.

Instruments. ^{1}H and ^{13}C NMR spectra were collected on a Bruker 300 DPX-NMR spectrometer. FTIR spectra were collected on a Bio-Rad FTS-7 FT-IR spectrometer. Mass spectrometry was performed on a high-resolution Finnigan MAT-95 mass spectrometer. UV−visible absorption spectra were recorded in a Hewlett 8452A Packard diode array spectrophotometer. The photo- and electroluminescence spectra were collected on an ORIEL MS 257 monochromator equipped with an ANDOR DV420-BV charge coupled device (CCD) detector. Thermal transition processes were studied by using a Perkin-Elmer DSC7 differential scanning calorimeter. Transmission electron microscope (TEM) photographs of the samples were recorded on a JEOL-100 electron microscope operated at 80 kV. The specimen for TEM studies was prepared by dropping a 0.5% polymer solution in dichloroethane on the surface of water, and the solvent was evaporated slowly. The thin film was then transferred to the surface of a copper grid, and then the sample was stained with osmium tetroxide prior to the TEM studies. For the fabrication of the light emitting devices, the polymer thin film was prepared by spin coating onto an ITO glass slide with a typical thickness of 80−100 nm. A layer of aluminum electrode (thickness = 100 nm) was coated on the polymer film surface by vacuum deposition under a pressure of 10^{-6} mbar. The polymer film thickness was measured with a Veeco Dektak 3ST surface profiler.

Synthesis of Substituted Aromatic Oxadiazoles 3a−f. The aromatic oxadiazoles were synthesized according to a procedure similar to that reported in the literature.[20] The synthesis of 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole (**3a**) is described as the general procedure (Scheme 1). 4-Bromophenyltetrazole (**2**; 4.26 g, 20 mmol) and benzoyl chloride (4.24 g, 30 mmol) were mixed with anhydrous pyridine (40 mL). The resulting mixture was heated under reflux under a nitrogen atmosphere for 3 days. The solution was poured into water, and the solid was filtered. The crude product was recrystallized with methanol−$CHCl_3$ and dried in a vacuum oven for 24 h. Yield: 86%. Mp: 180 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.15−8.12 (d, J = 7.8 Hz, 2 H), 8.03−8.00 (d, J = 8.4 Hz, 2 H), 7.70−7.67 (d, J = 8.4 Hz, 2 H), 7.50 (m, 3 H). ^{13}C NMR ($CDCl_3$): δ (ppm) 164.1, 163.3, 132.4, 132, 129.3, 128.5, 126.7, 125.6, 123.1, 122.5. FTIR (KBr, pellet): ν = 1601 (s, C=N), 1075 (s, C−O), 837 (s, 1,4-substituted benzene). MS (EI): m/z = 301 {M^+}.

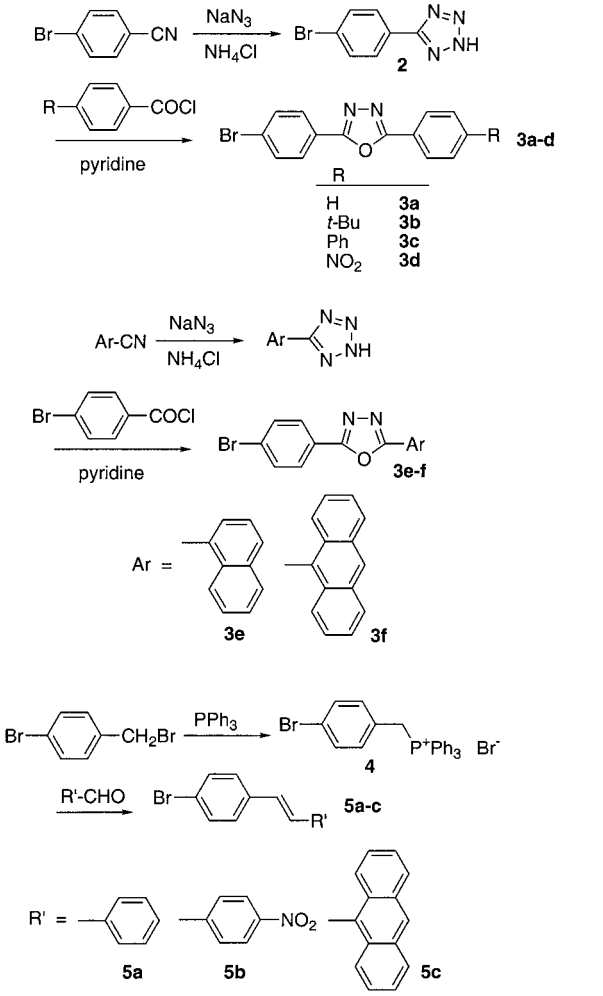
2-(4-Bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (3b). Yield: 73%. Mp: 209 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.19−8.08 (m, 4 H), 7.68 (d, J = 8.4 Hz, 2 H), 7.55 (d, J = 8.4 Hz, 2 H), 1.37 (s, CH_3, 9 H). ^{13}C NMR ($CDCl_3$): δ (ppm) 164.8, 163.7, 155.6, 132.4, 128.3, 126.8, 126.3, 126.1, 122.9, 120.9, 35.1, 31.1. FT IR (KBr, pellet): ν = 2960 (m, CH_3), 1603 (s, C=N), 1075 (s, C−O), 839 cm^{-1} (s, 1,4-substituted benzene). MS: m/z = 357 {M^+}.

2-(4-Biphenyl)-5-(4-bromophenyl)-1,3,4-oxadiazole (3c). Yield: 81%. Mp: 208 °C. ^{1}H NMR (DMSO-d_6): δ (ppm) 8.25−8.20 (d, J = 8.5 Hz, 2 H), 8.15−8.05 (d, J = 8.6 Hz, 2 H), 7.98−7.93 (d, J = 8.4 Hz, 2 H), 7.90−7.83 (d, J = 8.5 Hz, 2 H), 7.81−7.78 (d, J = 7.2 Hz, 2 H), 7.58−7.42 (m, 3 H). ^{13}C NMR (DMSO-d_6): δ (ppm) 164.7, 163.9, 144.7, 139.8, 132.4, 129, 128.4, 128.2, 127.8, 127.4, 127.2, 126.4, 122.9, 122.5. FTIR (KBr pellet): ν = 1603 (s, C=N), 1079 (s, C−O), 830 cm^{-1} (s, 1,4-substituted benzene). MS: m/z = 378 {M^+}.

2-(4-Bromophenyl)-5-(4-nitrophenyl)-1,3,4-oxadiazole (3d). Yield: 96%. Mp: 182 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.48−8.40 (d, J = 8.4 Hz, 2 H), 8.40−8.33 (d, J = 7.9 Hz, 2 H), 8.10−8.02 (d, J = 8.4 Hz, 2 H), 7.80−7.70 (d, J = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ (ppm) 164.9, 163.0, 149.7, 132.7, 129.2, 128.5, 127.8, 127.2, 124.5, 122. 2. FTIR (KBr pellet): ν = 1601 (s, C=N), 1534 (s, NO_2), 1347 (s, N−O), 1073 (s, C−O), 854 (s, C−N), 836 cm^{-1} (s, 1,4-substituted benzene). MS: m/z = 346 {M^+}.

2-(4-Bromophenyl)-5-(1-naphthyl)-1,3,4-oxadiazole (3e). Yield: 80%. Mp: 139 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.28−9.25 (d, J = 8.5 Hz, 1 H), 8.28−8.26 (d, J = 7.3 Hz, 1 H), 8.09−8.06 (d, J = 8.5 Hz, 3 H), 7.97−7.94 (d, J = 8.1 Hz, 1 H), 7.73−7.70 (m, 3 H), 7.62−7.59 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ (ppm) 164.8, 163.5, 133.9, 132.8, 132.5, 130.1, 128.7, 128.4, 128.3, 126.8, 126.5, 126.1, 124.9, 122.8, 120.3. FTIR (KBr pellet): ν = 1600 (s, C=N), 1079 (s, C−O), 830 cm^{-1} (s, 1,4-substituted benzene). MS: m/z = 352 {M^+}.

Scheme 1. Synthesis of Different Substituted Aromatic Oxadiazole and Stilbene Derivatives for the Functionalization Reaction



2-(9-Anthryl)-5-(4-bromophenyl)-1,3,4-oxadiazole (3f). Yield: 35%. Mp: 261 °C. ^{1}H NMR (DMSO-d_6): δ (ppm) 9.02 (s, 1 H), 8.35−8.25 (d, J = 8.6 Hz, 2 H), 8.15−8.00 (m, 4 H), 7.95−7.84 (d, J = 8.6 Hz, 2 H), 7.75−7.60 (m, 4 H). ^{13}C NMR (DMSO-d_6): δ (ppm) 165.6, 163.2, 133.4, 132.6, 131.6, 131.4, 129.7, 129.1, 126.8, 126.6, 125.6, 123.7, 117.3. FTIR (KBr pellet): ν = 1602 (s, C=N), 1084 (s, C−O), 843 cm^{-1} (s, 1,4-substituted benzene). MS: m/z = 402 {M^+}.

Synthesis of Stilbene Derivatives. The synthesis of 4-bromostilbene (**5a**) is described as the general procedure. 4-Bromophenyltriphenylphosphonium bromide (**4;** 0.838 g, 1.63 mmol) and benzaldehyde (0.17 g, 1.62 mmol) were dissolved in dichloromethane (6 mL). Sodium hydroxide (0.7 g, 18 mmol) dissolved in H_2O (2 mL) was added to the solution slowly with stirring. The solution was stirred at room temperature for 12 h, and the product was extracted with dichloromethane (30 mL). After the solvent was evaporated, the crude product was purified by silica gel chromatography using chloroform as the eluent. Yield: 26.1%. Mp: 139 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.53−7.50 (d, J = 7.9 Hz, 2 H), 7.50−7.47 (d, J = 8.7 Hz, 2 H), 7.39−7.36 (d, J = 8.7 Hz, 2 H), 7.35−7.29 (m, 3 H), 7.14−7.00 (d, vinylene proton, J = 16.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ (ppm) 136.9, 136.3, 131.8, 129.4, 128.7, 128.0, 127.9, 127.4, 126.5, 121.3. FTIR (KBr pellet): ν = 968 (s, CH=CH), 812 cm^{-1} (s, 1,4-substituted benzene). MS: m/z = 258 {M^+}.

Table 1. Physical Properties of the Block Copolymers Functionalized with Substituted Oxadiazole or Stilbene Derivatives

polymer	$\lambda_{max,abs}$ (nm)	T_g (°C)	$\lambda_{max,em}(CHCl_3)$ (nm)	$\lambda_{max,em}$(pristine film) (nm)	$\lambda_{max,em}$(annealed film) (nm)	completeness of functionalization (%)[a]
P3a	310	88	410, 440	520[b]	560[b]	21
P3b	310	109	410, 440	520[b]	560[b]	39
P3c	320	98	410, 440	520[b]	560[b]	32
P3d	325	103	450, 500	520[b]	560[b]	19
P3e	335	[c]	420, 445	445	445	17
P3f	255, 305, 390	[c]	490	500	510	31
P5a	320	108	450, 490	500	510	36
P5b	370	108	580[b]	590[b]	590[b]	40
P5c	255, 330, 390	101	540[b]	580, 640	580, 640	30

[a] Percentage of functionalized pendant vinyl group in the polyisoprene block, calculated from NMR spectra. [b] Broad peak was observed. [c] Not observed.

Table 2. Physical Properties of Some Block Copolymers Functionalized with Different Ratios of Oxadiazole and Stilbene Derivatives

polymer	oxadiazole	stilbene	oxadiazole to stilbene ratio (feed)[a]	oxadiazole to stilbene ratio (experimental)[b]	completeness of functionalization (%)[c]	$\lambda_{max,abs}$[d] (nm)	$\lambda_{max,em}$[d] (nm)
T1	**3d**	**5b**	12.9	8.0	53	340	580
T2	**3d**	**5b**	9.0	2.4	23	330	580
T3	**3d**	**5b**	5.8	2.0	35	340	580
T4	**3d**	**5b**	3.3	1.2	38	340	580
T5	**3d**	**5b**	1.1	0.8	33	340	580
T6	**3d**	**5c**	4.7	8.6	49	260, 330	490
T7	**3d**	**5c**	3.1	4.0	41	260, 330	490
T8	**3d**	**5c**	1.3	0.9	33	260, 330	490
T9	**3c**	**5c**	0.9	1.1	53	260, 320	530
T10	**3c**	**5c**	2.1	2.2	50	265, 320	530
T11	**3c**	**5c**	3.3	3.8	44	265, 320	530

[a] Ratio of oxadiazole to stilbene in functionalized copolymers, based on the feeding ratio. [b] Ratio of oxadiazole to stilbene in functionalized copolymers, calculated from NMR spectra. [c] Percentage of functionalized pendant vinyl group in the polyisoprene block, calculated from NMR spectra. [d] Determined in $CHCl_3$ solution.

4-Nitro-4′-bromostilbene (5b). Yield: 31%. Mp: 207 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.27−8.20 (d, J = 8.8 Hz, 2 H), 7.64−7.61 (d, J = 8.8 Hz, 2 H), 7.55−7.50 (d, J = 8.5 Hz, 2 H), 7.43−7.39 (d, J = 8.5 Hz, 3 H), 7.22−7.09 (d, vinylene proton, J = 16.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ (ppm) 147.1, 143.4, 135.2, 132.1, 132.0, 128.4, 127.0, 126.9, 124.2, 122.8. FTIR (KBr pellet): ν = 1507 (s, NO_2), 948 (s, CH═CH), 814 cm^{-1} (s, disubstituted phenylene). MS: m/z = 303 {M^+}.

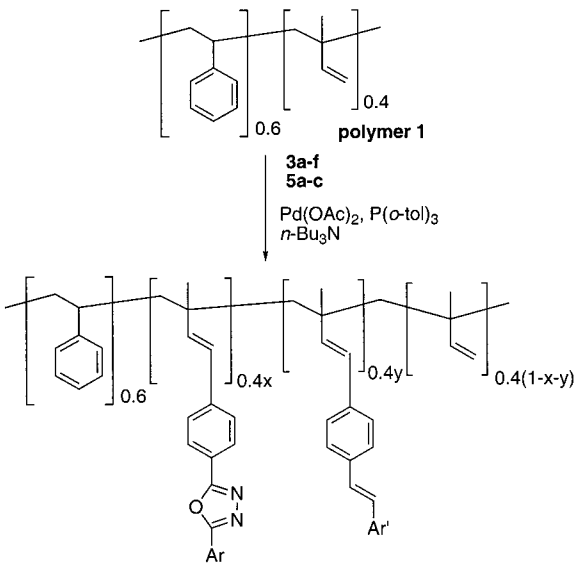
9-Anthryl-1-bromostilbene (5c). Yield: 57.4%. Mp: 167 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.42 (s, 1 H), 8.38−8.28 (m, 2 H), 8.08−7.98 (m, 2 H), 7.98−7.88 (d, vinylene proton, J = 16.5 Hz, 1 H), 7.65−7.45 (m, 8H), 6.95−6.85 (d, vinylene proton, J = 16.5 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ (ppm) 136.2, 136.0, 131.9, 131.4, 129.6, 128.7, 128.0, 126.7, 125.8, 125.7, 125.6, 125.2, 121.8. FTIR (KBr pellet): ν = 970 (s, CH═CH), 833 cm^{-1} (s, disubstituted phenylene). MS: m/z = 358 {M^+}.

Synthesis of Functionalized Copolymers. The synthesis of polymer **P3a** is described as the general procedure. A mixture of PSt-*b*-PIP copolymer (0.12 g, 0.29 mmol isoprene unit), **3a** (0.11 g, 0.38 mmol), palladium acetate (13 mg, 0.06 mmol), tri-*o*-tolylphosphine (21 mg, 0.07 mmol), and tributylamine (1.0 mL, 4.2 mmol) was heated with DMF (20 mL) at 100 °C under a nitrogen atmosphere for 3 days. The polymer was precipitated in methanol, and the product was subsequently washed with methanol in a Soxhlet extractor for 2 days. The oxadiazole and stilbene contents in the copolymers were determined by ^{1}H NMR spectroscopy, and the data are summarized in Tables 1 and 2.

Results and Discussion

Synthesis of Polymers. The functionalization of the pendant vinyl group in PSt-*b*-PIP was achieved by the palladium catalyzed Heck coupling reaction according to our previously reported procedures.[10] Compared to other functionalization methods such as hydroboration and hydrosilation, this approach enjoys the advantage that various types of functional groups are able to survive in the mild reaction conditions. We have functionalized the block copolymers with two types of functional units: aromatic oxadiazoles **3a**−**3d** and stilbenes **5a**−**5c** which bear different substituents (Scheme 1). Polymers **P3a**−**f** and **P5a**−**c** were functionalized with either oxadiazole or stilbene only (Table 1), while polymers **T1**−**11** were functionalized with both functional units with different feed ratios (Scheme 2 and Table 2). From GPC studies, there has been little change in the polydispersity of these polymers. The completeness of functionalization was examined by ^{1}H NMR spectroscopy. It was found that the degrees of function-

Scheme 2. Functionalization of Polystyrene-*block*-polyisoprene by the Palladium Catalyzed Reaction



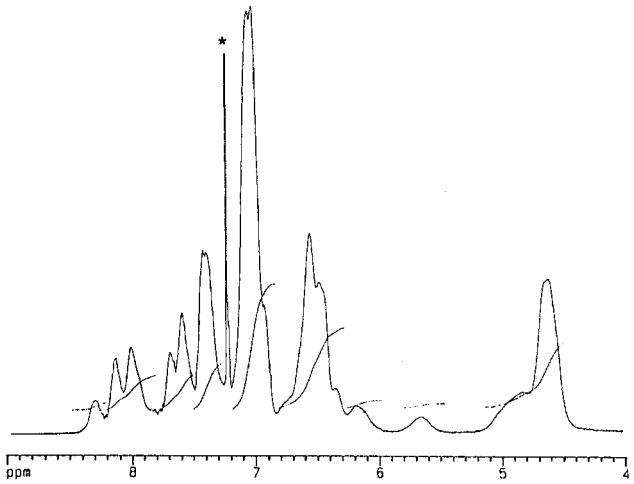


Figure 1. NMR spectrum of copolymer **T9** in $CDCl_3$.

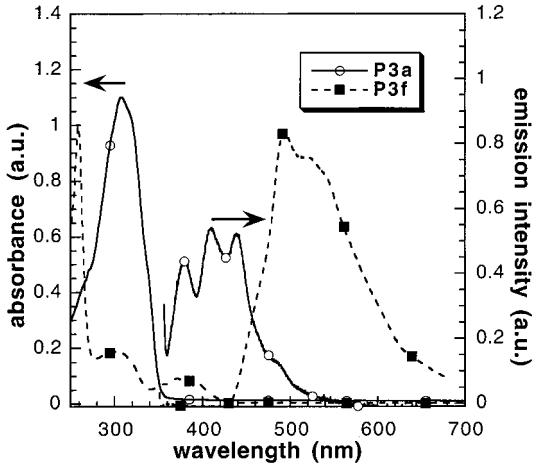


Figure 2. UV−vis absorption and emission spectra of the oxadiazole functionalized copolymers **P3a** and **P3f** in $CHCl_3$ solution.

alization in polymers **P3a**−**P5c** are approximately 20−40%. The distribution of the groups attached to the PI block should be random because there is no control of which pendant vinyl groups are preferentially functionalized. The results are summarized in Tables 1 and 2. Figure 1 shows the NMR spectrum of polymer **T11** in $CDCl_3$. The peak at 8.3 ppm is assigned to three protons in the anthracene moiety, while those at 7.9−8.1 ppm correspond to seven protons from both the oxadiazole and stilbene moieties. In addition, the peaks at 4.6−5.0 and 5.7 ppm are assigned to be the protons on the isoprene unit. From the ratio of the integration of the peaks, the amount of the oxadiazole and stilbene relative to the free isoprene units can be calculated.

Electronic Absorption Properties. The UV−vis spectral absorptions of some oxadiazole functionalized copolymers are shown in Figure 2, and the data are summarized in Table 1. In general, polymers **P3a**−**c** show strong and feature absorption bands in the range between 290 and 340 nm which is due to the $\pi-\pi^*$ transition of the conjugated oxadiazole unit. For polymers **P3d** and **P3e**, their absorption peaks show further red shift because of the presence of the electron withdrawing nitro group and the π-conjugated naphthalene moieties, respectively. For polymer **P3f**, the absorption spectrum is dominated by the absorption of the anthracene unit. The strong absorption peak at 255 nm and other smaller ones at 370−390 nm are attributed

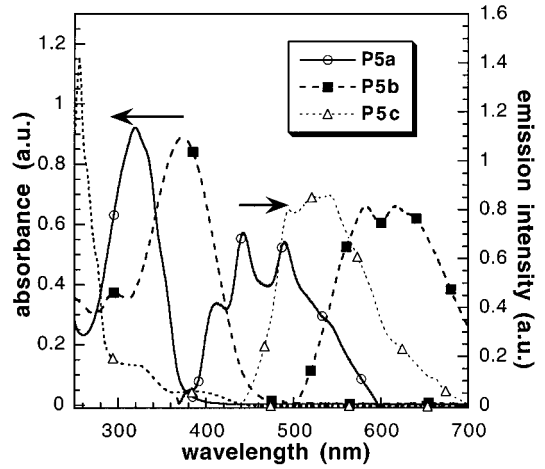


Figure 3. UV−vis absorption and emission spectra of the stilbene functionalized copolymers **P5a**−**c** in $CHCl_3$ solution.

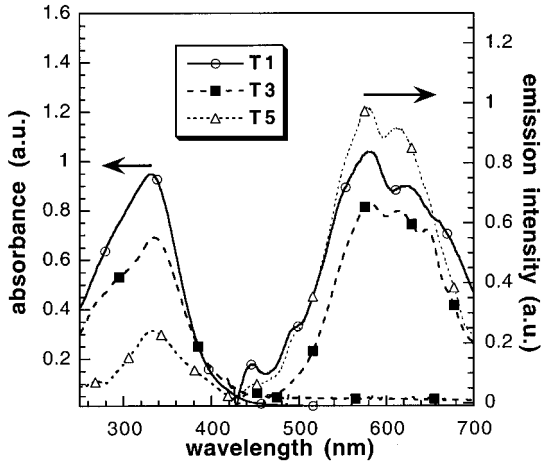


Figure 4. UV−vis absorption and emission spectra of the bifunctional copolymers **T1**, **T3**, and **T5** in $CHCl_3$ solution.

to the E_1 and E_2 ethyleneic bands of polynuclear aromatic, respectively.[21] For the stilbene functionalized copolymers (Figure 3), the absorption peaks of those polymers with nitro substituted stilbene or anthracene units (**P5b**, **P5c**) also show a remarkable red shift compared to those of the unsubstituted stilbene (**P5a**). When the copolymers were functionalized with both substituted oxadiazole and stilbene, the resulting absorption features were dependent on the ratio of the chromophores incorporated. Polymers **T1**−**T5** exhibit a broad absorption band centered at ∼330 nm, which results from the absorption of oxadiazole **3d** and stilbene **5b** (Figure 4). Figure 5 shows the absorption spectra of polymers **T9**−**11** that were functionalized with oxadiazole **3c** and stilbene **5c** in different ratios. Polymer **T9** has the highest stilbene content, and its absorption spectrum is very similar to that of polymer **P5c**. When the oxadiazole content in the copolymer was gradually increased, the peak at 320 nm corresponding to the oxadiazole absorption started to dominate. Similar trends were also observed for other series of polymers when the oxadiazole−stilbene ratios had been changed.

Photo- and Electroluminescence Properties. The photoluminescence (PL) spectra were collected in chloroform solution and in the solid state. Polymers **P3a**−**c** and **P3e** have similar luminescence properties, and peaks were observed at the vicinities of 370, 410, and 440 nm (Table 1 and Figure 2). There was no significant

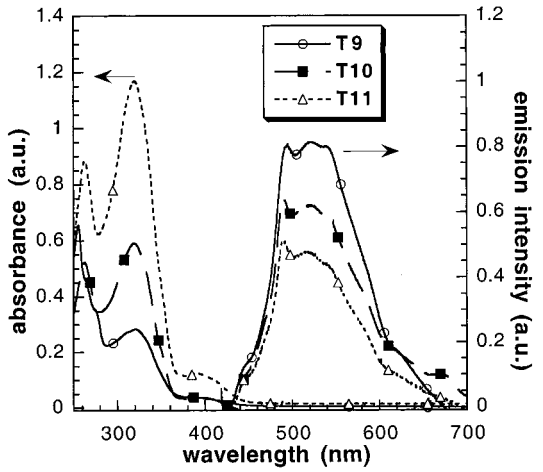


Figure 5. UV−vis absorption and emission spectra of the bifunctional copolymers **T9**−**11** in $CHCl_3$ solution.

substitution effect on the emission frequencies in solution. Polymer **P3f** shows a relatively broad emission band with a significant red shift at ~490−520 nm. This is because polycyclic aromatic hydrocarbons usually form excimers because of the proximity of different anthracene units in the pendant chain.[22] For polymer **P3d** with the nitro-substituted oxadiazole, the emission properties are of special interest. For many nitro aromatics, the existence of the n,π^* singlet states would lead to rapid singlet−triplet intersystem crossing, and the emission was from the corresponding triplet excited states.[23] For the stilbene functionalized copolymers, the position of the emission peaks for polymers **P5a**−**c** showed a gradual bathchromic shift from ~450 to 600 nm (Figure 3). Such a shift in polymers **P5b** and **P5c** to longer wavelength could be attributed to the same arguments as those for the shifts in polymers **P3d** and **P3f**. The excitation spectra of these polymers closely resemble their absorption spectra, indicating the emission originated from the excitation of the π conjugated systems. For the bifunctional copolymers, their emission bands are dominated by the emission from the stilbene moieties. The emission spectra of copolymers **T1**−**5** (Figure 4) and **T9**−**11** (Figure 5) are very similar to those of polymers **P5b** and **P5c**, respectively. They are in general dominated by the emission arising from the stilbene derivatives because of their higher quantum efficiencies.[24] We repeated the luminescence studies of these polymers in THF, which is another good solvent for both polymer blocks, and found out that the solvent had very little effect on the position of the emission bands.

When the luminescence spectra were collected in a polymer film cast on quartz plates, there were dramatic changes in the luminescence properties. Figures 6 and 7 show the emission spectra of **P3b** and **P3c** in solution and in the solid state. In chloroform solution, the width of the emission band is smaller and the peak can be resolved into vibronic fine structures. However, the emission band became broadened and shifted to lower energy in the solid state. This is due to the aggregation of luminophores in the solid state which resulted in the formation of excimers upon excitation. Such a phenomenon was commonly observed in various types of luminescent polymers.[25]

Some polymers were fabricated into single layer electroluminescence devices using indium−tin−oxide (ITO) as the anode and aluminum as the cathode. The

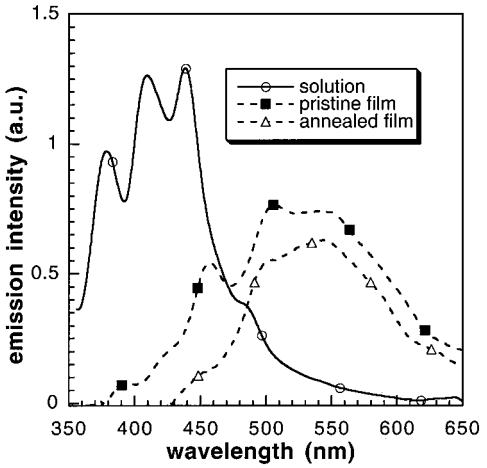


Figure 6. Emission spectra of copolymer **P3b** in $CHCl_3$ solution and in the solid state. The spectra were collected before and after annealing the polymer at 110 °C for 3 days.

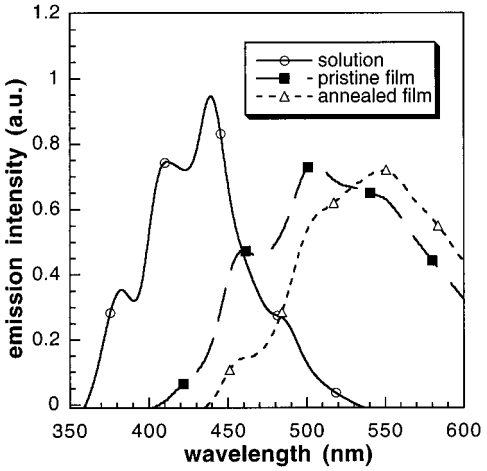


Figure 7. Emission spectra of copolymer **P3c** in $CHCl_3$ solution and in the solid state. The spectra were collected before and after annealing the polymer at 110 °C for 3 days.

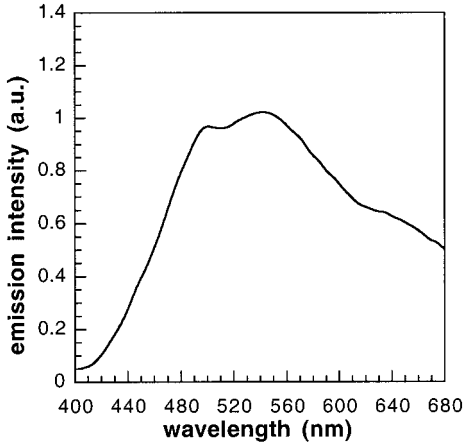


Figure 8. Electroluminescence spectrum of polymer **P3c** under a forward bias of 20 V.

devices were subjected to forward bias, and light emission was observed when the applied voltage was greater than 10 V. A typical electroluminescence spectrum of polymer **P3c** was shown in Figure 8. It closely resembles its PL spectrum, which suggests that the light emission originated from the same types of excitons. However, the lifetime of such devices was quite short (<2 min). A much more detailed study of the energy levels and

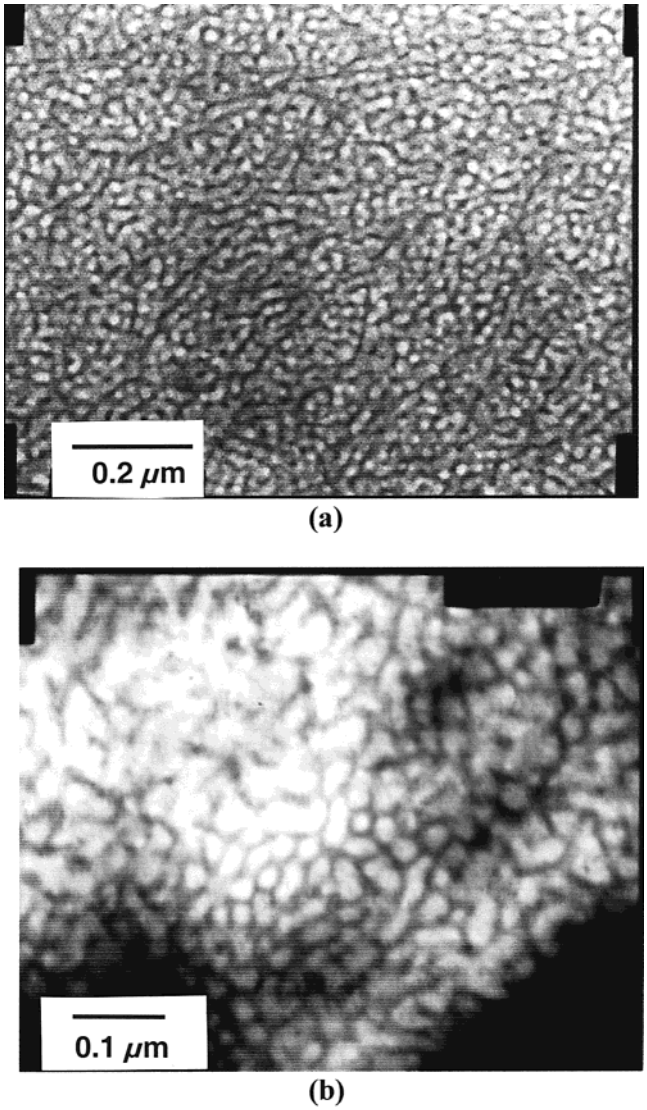


Figure 9. (a) Transmission electron micrograph of an OsO_4 stained pristine sample of polymer **P3c** (magnification = 100000×). (b) Transmission electron micrograph of an OsO_4 stained polymer **P3c** which has been annealed at 110 °C for 3 days (magnification = 150000×).

choice of electrodes is necessary in order to improve the device performance.

Effect of Annealing. In block copolymers, the microphase separation between different blocks will be enhanced after annealing at elevated temperature. Figure 9 shows the transmission electron micrograph of polymer **P3c** before and after the annealing process. The dark region corresponds to the stained polyisoprene block dispersed in a lighter matrix of polystyrene. The relative sizes of the polystyrene to the polyisoprene domain (functionalized with oxadiazole **3c**) increased after heating the polymer at 110 °C for 3 days, indicating that the polyisoprene block becomes denser due to the aggregation. The emission spectra of polymers **P3b** and **P3c** before and after annealing are shown in Figures 6 and 7. There had been very little change in film thickness before and after annealing (<3%). Compared to the case of the pristine sample, the emission peak of the annealed polymer films shifts to longer wavelength by approximately 40 nm. The emission data for the annealed samples are summarized in Table 1. It can be seen that only polymers **P3a**−**d** showed such a significant shift in the position of the emission peaks. Therefore, the effect of the polymer morphology may not be the only factor that affects the luminescence properties. When the copolymers were functionalized with both oxadiazole and stilbene moieties, the interaction between these species and their effect on the polymer morphologies became more complicated. For the bifunctional copolymers **T1**−**11**, the shift in the emission peak after annealing was not significant and was barely observable. There are two possible reasons for this observation. The first one is that the polyisoprene block is functionalized with both oxadiazole and stilbene moieties. The presence of two different chemical species in the same block may prevent the same type of luminophores from aggregating together. TEM studies also confirmed that the domain sizes of both blocks undergo little change after annealing. Alternatively, the polymer films might have achieved their optimum aggregation state immediately after the film casting process.

Conclusions

The syntheses and spectroscopic studies of some block copolymers functionalized with stilbene and aromatic oxadiazole moieties were reported. It was found that the emission properties of these functionalized copolymers were different in solids and in the solution state. Also, the emission and morphological properties were also dependent on the thermal history of the block copolymers. Due to the more defined morphology and the mocrodomain sizes, these polymers can serve as models for studying the aggregation of luminophores in light emitting polymers.

Acknowledgment. The work described in this paper was substantially supported by a grant from the Research Grant Council of the Hong Kong Special Administrative Region, China (Project No. HKU 7090/98P). Partial financial support from the Committee on Research and Conference Grant (University of Hong Kong) is also acknowledged.

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MA0107206