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Enhancement of Luminescence in Polymer Nanocomposites

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The light-emitting properties of polymers are currently of wide interest[1–10] following the report[1] that conjugated polymers can be used to fabricate light-emitting diodes (LEDs). Interest in luminescent organic dye molecules is also high as an alternative approach to molecular LEDs.[11–16] Although fluorescent organic dyes exhibit very high luminescence quantum efficiencies compared to π-conjugated polymers,[16] the latter materials are more desirable because of their robust mechanical properties, thermooxidative stability, and ease of fabrication into large area or flexible devices.[1–4] There is thus a growing need for more efficient luminescent polymeric materials and a fundamental understanding of the structural factors that govern efficient light emission in polymers. Here, we report on the luminescence of novel polymer nanocomposites consisting of random rod–coil copolymers, poly(benzobisthiazole-1,4-phenylene)-*co*-poly(benzobisthiazoledecamethylene), in which 2–10 nm long electroactive and photoactive rodlike segments of benzobisthiazole-1,4-phenylene chromophores are dispersed in the matrix of the flexible coil segments. The photoluminescence quantum efficiency of the polymer nanocomposites was as high as 37% which represents over 6-fold increase compared to the corresponding "bulk" conjugated polymer. These results suggest that control of supramolecular structure and morphology is the key to efficient luminescence and photophysical properties of polymers.

The photophysics,[1–16] especially luminescence, of organic dye molecules and π-conjugated polymers is currently being investigated in connection with their application as emitters in electroluminescent devices. Many dye molecules in the form of evaporated thin films[11–14] or as solid solutions in polymers (i.e., "molecularly doped" polymers)[15] exhibit high photoluminescence (PL) quantum efficiency (Φ_f), good charge transport of injected or photogenerated carriers, but poor mechanical strength and thermal oxidative stability.[11–16] Conjugated polymers, on the other hand, have excellent mechanical properties, thermal stability, and good processing characteristics.[1–10] However, the *solid-state* Φ_f values of current π-conjugated polymers are rather low, of order 10^{-3}–10%, which is from 1 to several orders of magnitude smaller than those of highly fluorescent dyes.[6,7,16] We have previously reported that several π-conjugated rigid-rod polymers exhibit PL quantum efficiency of 100% in solution but only 5–10% in solid films.[7] Others have similarly found that soluble derivatives of poly(p-phenylenevinylene) have Φ_f values of order 50–60% in solution but much lower values (5–10%) in thin films.[6] There is clearly a need to bridge this gap between the *solid state* and *solution* photoluminescence quantum efficiencies and elucidate the structural factors that govern efficient photophysical properties in polymers.

The origin of the low PL quantum yield in π-conjugated polymers has been the subject of recent studies and controversy.[5–7,9,10,16] Among the prior explanations of photoluminescence quenching in π-conjugated polymers are (i) intrachain defects, (ii) impurities, (iii) photochemical oxidation (in the specific case of vinylene polymers), and (iv) polaron pair formation. We recently proposed *excimer formation* as the dominant intermolecular mechanism for PL quenching in π-conjugated rigid-rod polymers.[17] A key prediction from the excimer mechanism is that enhancement of PL quantum yield can be achieved through control of the interchain packing distances.[17] Here we focus on the rod–coil copolymers and polymer nanocomposites which provide molecularly well-defined ways to explore the role of *supramolecular structure and morphology* on the luminescence of polymers.

Figure 1A shows the chemical structure of the random rod–coil copolymer system which contains block repeat units of the conjugated rigid-rod homopolymer poly(p-phenylene benzobisthiazole) (PBZT) and the flexible-coil homopolymer poly(benzobisthiazoledecamethylene) (PBTC10). The segmented rod–coil copolymers of varying composition were prepared by condensation copolymerization of varying ratios of terephthalic acid and decamethylenedicarboxylic acid with 2,5-diamino-1,4-benzenedithiol, similar to the preparation of the corresponding homopolymers.[18] The composition, molecular structure, and chain microstructure of the rod–coil copolymers were established by several techniques including ^{1}H NMR, ^{13}C NMR, infrared, and optical spectroscopies as will be reported in detail in a forth-

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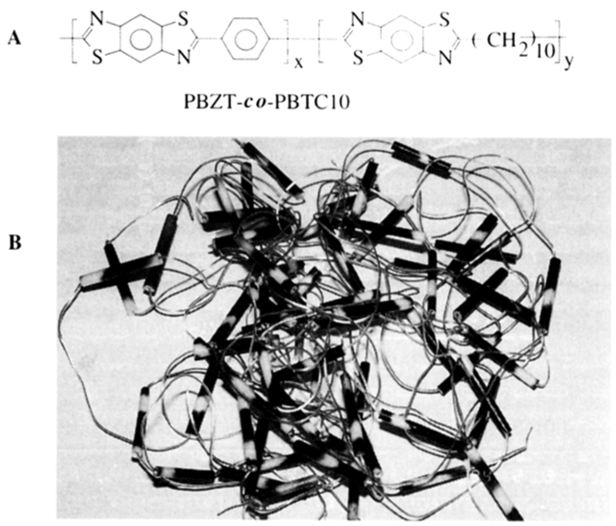

Figure 1. (A) Chemical structure of rod–coil copolymers that form polymer nanocomposites when $x/(x + y)$ is less than 0.5. (B) Model of the supramolecular structure and morphology of the polymer nanocomposites, showing the assembly of rod–coil copolymer chains at one rod/coil ratio. The morphology is controlled through the rod/coil ratio and the sizes of the rods and coils.

coming paper.[19] The morphology of the polymer nanocomposites was found to be amorphous by X-ray diffraction and polarized optical microscopy.[19] Figure 1B shows a model of the supramolecular structure and morphology of the polymer nanocomposites.

Films of the copolymers and homopolymers were spin casted from their solutions in nitromethane/$AlCl_3$ similar to techniques described elsewhere.[18,20] The spin-coated films were washed in water and vacuum dried at 60 °C. Optical absorption and steady-state PL spectra were obtained with instrumentation previously described.[7,8] The polymer films (~25–80 nm thick) on glass slides were positioned such that the emission was detected 22.5° from the incident radiation beam. The PL quantum yield Φ_f was measured by comparing the integration of the emission spectrum of a sample to a standard of known Φ_f under identical optical conditions.[21–23] A thin film of 10^{-3} M 9,10-diphenylanthracene in poly(methyl methacrylate) ($\Phi_f = 83\%$)[23] was used as the fluorophore standard. The measured quantum yields were reproducible from different films of comparable optical densities. Picosecond time-resolved PL decay measurements were made by using the time-correlated single-photon-counting technique and laser system described previously.[7,8] All the photophysical measurements were made at room temperature.

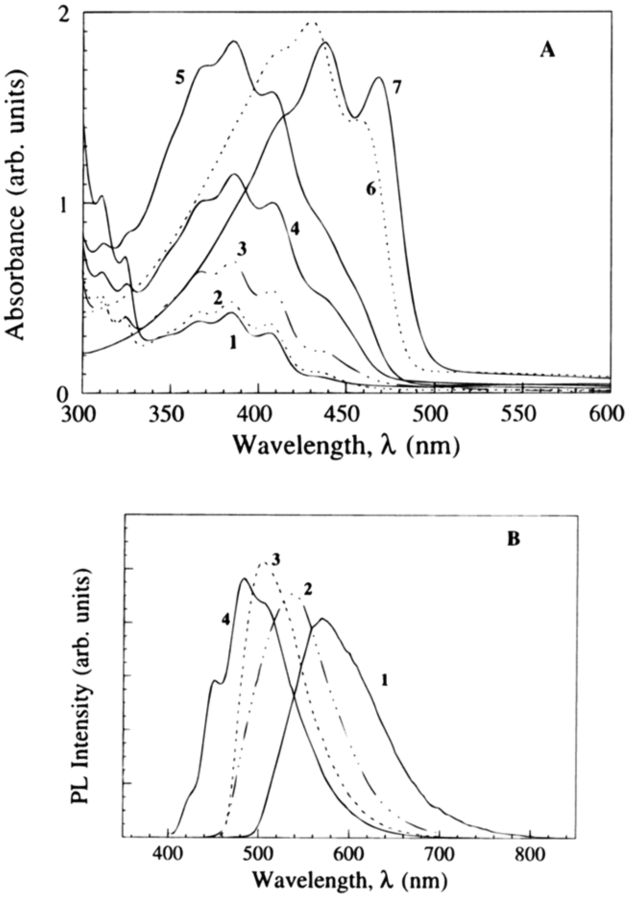

Figure 2. (A) Optical absorption spectra of films of several copolymers (curves 1–6) and the conjugated homopolymer (7): 1, 5%; 2, 10%; 3, 20%; 4, 30%; 5, 40%; 6, 80%; 7, 100% PBZT. (B) PL spectra of PBZT and copolymers: 1, 100% PBZT; 2, 40%; 3, 20%; 4, 5%. The excitation wavelengths for the PL spectra were 384 nm for the 5–40% copolymers and 440 nm for PBZT.

The optical absorption spectra of films of several copolymers are shown in Figure 2A along with the spectrum of the conjugated homopolymer PBZT. The coillike nonconjugated polymer (PBTC10) does not absorb light at 340 nm or longer wavelength. What is most remarkable about the optical spectra of the copolymers at less than 50 mol % composition is their highly structured features which are due to the distribution of chromophores of different excitation energies which in turn reflect the distribution of block lengths of the rodlike π-conjugated PBZT repeat units incorporated into the copolymer chains. Much less structured absorption spectra were observed in the copolymers of 50 mol % rods or higher, but the increasing red shift of the absorption maximum was evident, reflecting the increasing block lengths of the π-conjugated chromophores as the copolymer system approaches the PBZT homopolymer. These results also suggest that the optical absorption in the copolymers and PBZT is of molecular (excitonic) origin.

The PL emission of the rod–coil copolymers varied with composition (Figure 2B), indicating that the emission color can be tuned between the extremes of yellow (100%) and UV (<5%). The 5% copolymer emits blue, whereas the 20% emits green. The nonlinear dependence of emission peak with copolymer composition reflects the similar dependence of the optical absorption on composition, and both are due to the unique nanostructure and morphology of the materials. All the copolymer PL spectra in Figure 2B are broad and structureless except in the 5% composition where hints of structure are seen. This is in sharp contrast to the highly structured optical spectra of the same materials. The likely explanation of the broad and structureless emission spectra is either: excitation migration among

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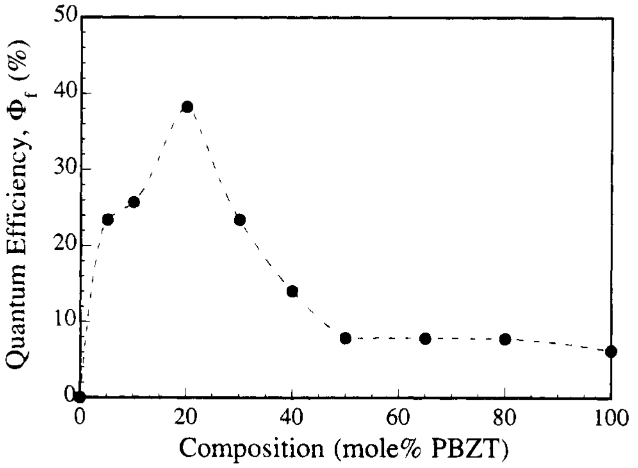

Figure 3. Composition dependence of PL quantum efficiency of rod–coil copolymers. Note the sharp increase of Φ_f in the nanocomposite region of composition (<50 mol % PBZT). The excitation wavelengths for the emission spectra were the absorption maxima: 384 nm for 5–40% copolymers and 440 nm for the 80% copolymer and pure PBZT.

the distribution of conjugated segments and emission from the lowest energy chromophore;[9] or some remaining aggregation of chromophores and consequent excimer type emission. However, the large variation of emission peak with copolymer composition in the 5–40% range where there is no variation of absorption maxima rules out the former explanation.

The composition dependence of the PL quantum efficiency of the copolymers is shown in Figure 3. At 50 mol % or higher when the coillike polymer segments are dispersed in the matrix of the rodlike segments the quantum yield of the copolymers is identical to the "bulk" PBZT (~6%). The PL quantum efficiency is significantly enhanced relative to the pure PBZT at copolymer compositions in the range 5–40%, where the nanocomposite morphology is achieved, reaching a peak of 37% for films of 20 mol % copolymer. This corresponds to over a 6-fold enhancement of PL quantum efficiency. This high solid-state PL quantum efficiency is already approaching values typical of chromophores in solution or even organic dye molecules. However, the solid-state PL quantum yield of the polymer nanocomposites could still be increased by a factor of 2.7 to reach the 100% achieved in dilute solutions of PBZT. The observed slight decrease of the quantum yield in the 5–10% compositions compared to the 20% copolymer is a result of phase separation and aggregation of the rodlike segments as evidenced by differential scanning calorimetry.[19]

The observed large enhancement of the luminescence quantum yield in the polymer nanocomposites (<50 mol %), compared to the conjugated polymer PBZT, can be explained in terms of interchromophore packing distances, excimer formation, and self-quenching which are regulated by the supramolecular structure and morphology of the materials.[17] In the "bulk" conjugated polymer and copolymers of high composition (≥50 mol %), the small interchromophore distances of order 3–4 Å allow a high degree of chromophore aggregation, excimer formation, and self-quenching.[17] At lower copolymer compositions (<50%), where the nanocomposite morphology is attained, the rodlike π-conjugated chromophores are dispersed in the matrix of the flexible coil segments, resulting in greater interchromophore distances and consequent reduction of the degree of luminescence self-quenching.

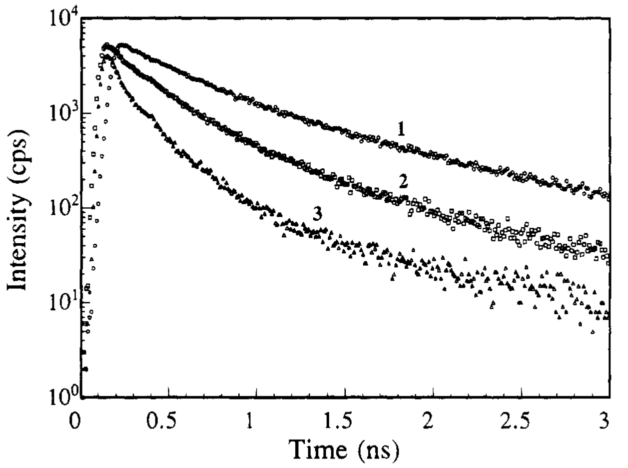

Figure 4. Time-resolved PL decay dynamics of rod–coil copolymers: 1, 20%; 2, 40%; 3, 80% PBZT. The emission wavelengths for the decay curves were 502, 536, and 550 nm for the 20%, 40%, and 80% copolymers, respectively. The PL decay of the 20% copolymer followed a single exponential with a lifetime of 0.9 ns. The PL decay of the 80% copolymer is nonexponentional as was the pure PBZT and copolymers with greater than 50% composition.

The picosecond time-resolved PL decay dynamics of the copolymers photoexcited at 380 nm showed a remarkable composition dependence similar to the quantum yield results. The PL decay dynamics of the 502 nm peak emission of the 20% copolymer, which had the largest quantum yield, was well described by a single exponential with a lifetime of 0.9 ns (Figure 4) and an amplitude of >80%. The other copolymers in the nanocomposite region (5–40 mol %) deviated from the single-exponential decay to varying degrees. The copolymers of higher compositions (≥50%) had decay dynamics that were dramatically nonexponential and similar to PBZT.

Observation of large enhancement of luminescence in polymer nanocomposites has implications for fundamental understanding of efficient light emission in polymers[17] and for practical application of polymers in optoelectronics. The present results support the view that the generally low photoluminescence quantum yield of π-conjugated polymers is due to intermolecular excimer formation and self-quenching facilitated by the relatively ordered aggregation of chains.[17] Molecular regulation of luminescence yield thus reduces to control of interchromophore packing distances and hence the overall supramolecular structure and morphology: for example, through copolymerization, as demonstrated here or alternatively via bulky side groups. The polymer nanocomposites are new electroactive and photoactive materials whose supramolecular structure and morphology is designed to enhance solid-state photophysical properties. The entire rod–coil copolymers represent new materials that unify the two prior approaches to molecular materials for devices—dye molecules[11–16] and π-conjugated polymers[1-10]—and hence should help to bridge the gap in theoretical understanding and practical applications of both classes of materials.

In summary, the effect of supramolecular structure and morphology on the solid-state luminescence of polymers is explored through a rod–coil copolymer system, poly(benzobisthiazole-1,4-phenylene-*co*-poly(benzobisthiazoledecamethylene), which forms nanocomposites at compositions below 50 mol % rods. The composition dependence of the photoluminescence quantum efficiency exhibited a sharp change corresponding to a change in supramolecular structure of the copolymers. The photoluminescence quantum efficiency of the polymer nanocomposites was as high as 37% which represents over 6-fold enhancement compared to the corresponding "bulk" conjugated polymer. These results have implications for the fundamental understanding of the origin of luminescence quenching in conjugated polymers, and they also suggest that control of supramolecular structure and morphology is key to efficient solid-state luminescence in polymers.

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