Preparation and Photophysical Properties of Organic Fluorescent Polymers and Their Nanoparticles

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ABSTRACT: New classes of stable organic florescent polymer nanoparticles were prepared from the corresponding tetrahydrofuran (THF) solutions, upon slow evaporation of solvent under a mild vacuum. Uniform spherical nanospheres having mean diameter of ~ 500–700 nm, showed enhanced fluorescence emission in solution, but it diminished when it is destroyed using an organic base. These end-capped fluorescent polymers are highly stabilized in the excited states at higher concentration in solution, leads no more intra- and intermolecular interactions among the excited molecules, because of the absence of free functional groups. The significant enhancement in fluorescence emission was attributed to the high level of molecular stacking in the fluorescent nanoparticles, when compared with micron-sized isolated powder sample. In addition, these fluorescent polymers exhibited significant thermal properties, along with better solubility in most of common organic solvents for their future application. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5344–5350, 2006

Key words: fluorescent polymers; light emitting diode; nanoparticles; bathochromic shift; fluorescence

INTRODUCTION

Fluorescent inorganic semiconductor or metal nanoparticles have been extensively investigated for various potential applications including the fluorescent biological labels,[1] photovoltaic cells,[2] light-emitting diodes (LEDs),[3] and optical sensors.[4] However, organic polymer-based materials are finding broad applicability in light-emitting diodes (LEDs),[5] light-emitting electrochemical cells (LECs),[6] plastic lasers,[7] solar cells,[8] batteries,[9] field-effect transistors,[10] and sensors.[11]

In advance to this, the fluorescent organic nanoparticles have received considerable attractive research interactions, because of the high flexibility in material synthesis and ease for nanoparticles generation. However, investigations are in initial stage research, very few research groups were working in this area.[12–15] As far as the application is concerned, Nakanishi et al.,[16–19] who have demonstrated that perylene and phthalocyanine nanoparticles showed size-dependent fluorescent properties from those of bulk samples. Recently, Yao et al. reported similar results with pyrazoline nanoparticles.[20] However, deeper studies on the fluorescent organic nanoparticles (FONs) are expected for significant progress toward the future electronic applications. Because of their very high flexibility and variability in materials synthesis, nanoparticle preparations are advantageous. In recent years, a few cases of enhanced emission in the solid state of specific organic molecules have been reported and interpreted in terms of the intra- and intermolecular effects exerted by fluorophore aggregation.[21–24]

We focused mainly to synthesize various types of light-emitting polymers for potential applications, as LUCO materials to be combined with blue LEDs. Hence, we reported in our earlier work about the syntheses and characterization of various fluorescent polymers.[13] In continuation to this, we herein attempted to describe the preparation and photophysical properties of organic fluorescent polymer nanoparticles with respect to polymer concentration and pH dependence on nanoparticles morphology.

EXPERIMENTAL

Materials and measurements

Fluorescein, terephthaloyl chloride, benzoyl chloride, and bisphenol A were purchased from Aldrich Chemical (Yongin-city, Korea), and used without purification. All other reagents and solvents of laboratory

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grades were used as received. The UV-visible spectra were obtained from a Shimadzu UV-2501, spectrophotometer. The fluorescence spectra were obtained from Aminco–Bowman series-2, luminescence spectrometer. Photoluminescence spectra (PL) were taken in He-Ne laser at room temperature with 325 nm as an excitation wavelength. The scanning electron microscopy (SEM) was performed, using a JSM-6400 scanning electron microscope (JEOL, Japan), with an acceleration voltage of 20 kV. To prepare samples for SEM experiment, the polymer solution in THF was dropped on a clean glass substrate, and then evaporated by purging nitrogen gas at room temperature.

Synthesis

Poly(fluoresceinyl terephthalyl benzoate) [Polymer 1]

The synthetic procedures for the fluorescent polymers were fully described and reported elsewhere.[13] Briefly, fluorescein (3.32 g, 9.99 mmol) was dissolved in DMF (7.5 mL) in the presence of pyridine (4 mL) at room temperature for 15 min to obtain a dark brown solution, followed by the slow addition of terephthaloyl chloride (2.28 g, 11.23 mmol) solution of DMF (5 mL) and nitrobenzene (7.5 mL) for 20 min at room temperature, under nitrogen atmosphere. The reaction was carried out for 20 h at room temperature, followed by addition of excess benzoyl chloride, and is continued for another 20 h at room temperature. The resulting viscous solution was poured into methanol to obtain the polymer **1** as precipitate. The product was purified by repeating this precipitation procedure. The light yellow solid was collected using filtration, after washing it with hot methanol and an isolation yield of 80%.

Poly(fluoresceinyl terephthalyl benzoate-co-bisphenol A terephthalate) [Polymer **2**]

Fluorescein (1.16 g, 3.49 mmol) and bisphenol A (1.14 g, 4.99 mmol) were dissolved in DMF (7.5 mL) in the presence of pyridine (4 mL) at room temperature for 15 min to obtain a dark brown solution, followed by the slow addition of a solution of terephthaloyl chloride (2.03 g, 9.99 mmol) in DMF (5 mL) and nitrobenzene (7.5 mL) for 20 min at room temperature, under nitrogen atmosphere. The reaction was carried out for 20 h at room temperature, followed by addition of excess benzoyl chloride, and the reaction is continued for another 20 h at room temperature. The resulting viscous polymer solution was poured into methanol to obtain the polymer as precipitate. The light yellow solid was collected by filtration. The dissolution and precipitation procedure were repeated to obtain the product (isolation yield 83%). The structural confirmation was done using FTIR and proton NMR. The structures of end-capped fluorescent polymer **1** and **2** were shown in Figure 1.

Preparation of polymer nanoparticles

The synthesized fluorescent polymer was completely dissolved in appropriate quantity of THF at room temperature. The clear solution was filtered to remove any unknown particles, followed by the slow evaporation of solvent under mild vacuum to obtain the corresponding fluorescent nanoparticles. The mean diameters of isolated stable nanoparticles were found to be around ~500–700 nm.

To prepare a stable and uniform fluorescent polymer nanoparticles, three different solvents such as chloroform, DMF, and THF were used. Uniform

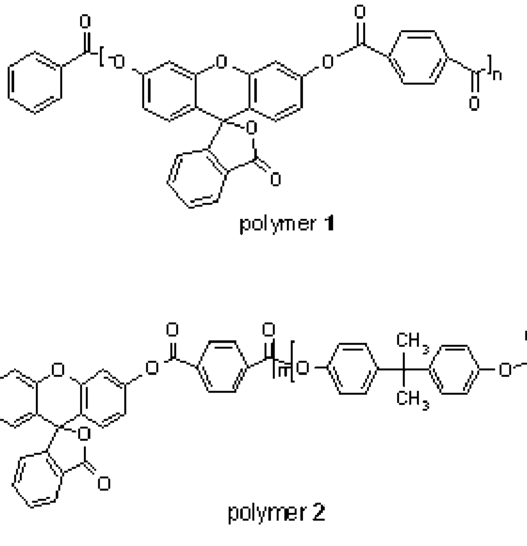

Figure 1 Structures of fluorescent polymers.

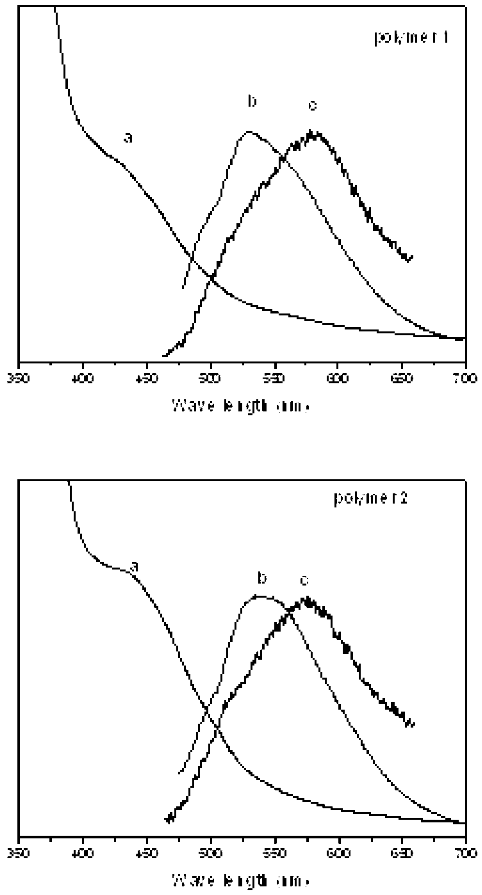

Figure 2 (a) Absorption, (b) fluorescence spectra in DMF, and (c) PL spectra of powders.

spherical nanoparticles were obtained only in THF solvent, though we obtained nano- to micron-size particles in DMF, which are totally irregular in shape and sizes of particles, but no such particle has been generated in chloroform solvent.

RESULTS AND DISCUSSION

Absorption and emission spectra

Figure 2 illustrates the absorption and fluorescence spectra of polymer **1** and **2** in DMF, as well as the PL spectra of their corresponding solids. A broad absorption band occurred in the range of 400–525 nm in both, which corresponds to the characteristic absorption of fluorescein moieties. But these end-capped fluorescent polymers exhibited less intense and broader absorption than that of fluorescein. This result was not surprising because the reduction in absorption intensity resulted from the reduced concentrations of fluorescein moieties in the polymer samples because of the presence of benzoyl and bisphenol A moieties in the polymer backbone. However, unprotected fluorescent polymers showed strong absorption edges than that of end-capped polymers.[13]

TABLE I
Photophysical Properties of Fluorescent Polymers

Polymer	λ_{max}^{Abs} (nm)[a]	λ_{max}^{FL} (nm)[b]	λ_{max}^{PL} (nm)[c]
Polymer **1**	426	530	576
Polymer **2**	436	550	582

[a] Broad absorption maximum in DMF.
[b] Maximum fluorescence in DMF.
[c] Maximum photoluminescence in solid.

Photophysical properties of fluorescent polymer **1** and **2** were calculated from the absorption, fluorescence, and photoluminescence spectral curve and summarized in Table I. The λ_{max} of fluorescence emissions of both polymers were appeared in the region of greenish yellow at 530 and 550 nm, respectively, in DMF solution. However, pure yellow emission (576 and 582 nm) was observed in PL spectra from the powder. The red-shifted PL spectrum of the polymers when compared with the fluorescence spectrum of the same compound in DMF, is probably due to the stronger interactions between the fluorescein units of the polymers in the solid state.[25,26]

Effect of polymer concentration on fluorescence spectra

The emission spectra of polymer **1** and **2** were obtained in chloroform with different concentrations, as shown in Figure 3(a). With increasing the concentration of polymers, the intensity of fluorescence emission also ultimately increased, with ~ 5 nm red shifting from 0.5 to 10 wt % polymer solutions.

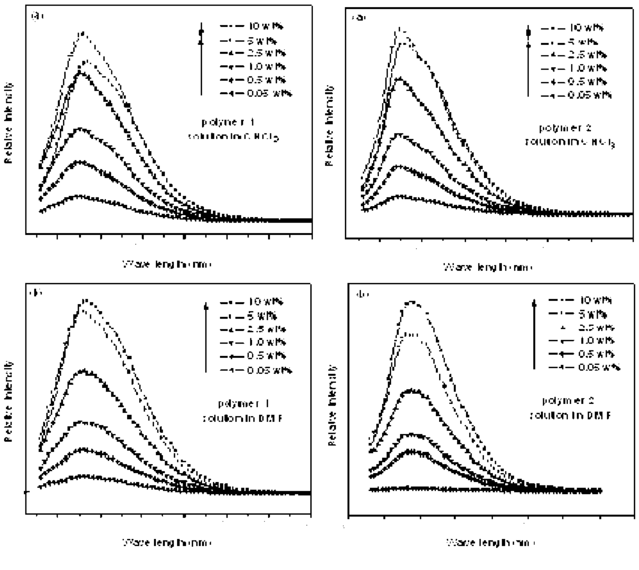

Figure 3 Concentration dependence of fluorescence spectra of polymer solutions in (a) chloroform and (b) DMF.

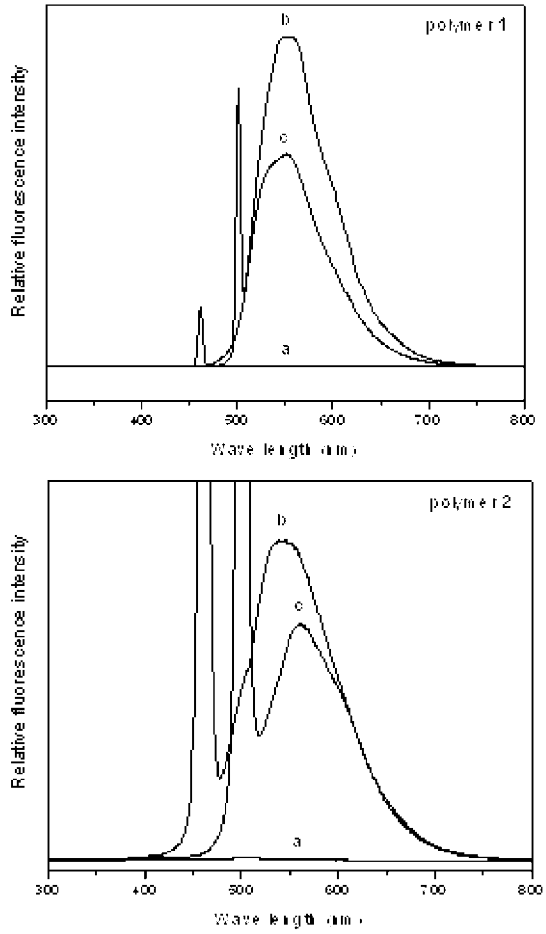

Figure 4 Fluorescence spectra with different excitation wave length of (a) 325, (b) 460, and (c) 500 nm [5 wt % solution in DMF].

Similar tendency of red shifting is observed in both polymers. However, unprotected polymers of **1** and **2** showed almost 20 nm bathochromic shift[13] with the same concentration difference. It is noteworthy to state that, these end-capped polymers are highly stabilized in the excited states at higher concentration in solution, which means no more interactions among the excited molecules because of the absence of free functional groups.[12] Ultimately, the intermolecular interactions among the polymer molecules were also in control, when compared with unprotected polymers.[13] In addition, the stabilization of the excited molecules were further improved with increasing the polarity of the solvent. For example, the fluorescent intensity of both polymer solutions in highly polar DMF solvent shows increasing trend up to 10 wt % in DMF [Fig. 3(b)]. But in chloroform, the intensity increases up to certain concentration of 5 wt % [Fig. 3(a)] polymer solution and then decreased. This result indicated that the excited molecules of both polymers were highly stabilized in polar DMF solvent than in chloroform.

Effect of excitation wavelength on fluorescence spectra

The effect of excitation wavelength on fluorescence intensity of the polymers were studied and compared among the polymers.[12] Fluorescence spectra of 5 wt % solution in DMF of polymer **1** and **2** were recorded with different excitation wavelengths, as shown in Figure 4. The intensity of fluorescence emission increased with increasing the excitation wavelength from 325 to 460 nm, but it decreased at 500 nm. This observation indicated that the maximum emission corresponds to the absorption maximum of the polymers, for example, a broad absorption peak appeared in the range of 400–525 nm, and hence, no emission peak observed at 325 nm excitation source. In fact, the maximum emission noticed at 460 nm excitation wavelength, which supports our aim of this work as LUCO materials, using 460 nm blue light as a primary pumping source to obtain white light.

Effect of pH on fluorescence spectra

The changes in fluorescence spectra were recorded with different pH of polymer solution, using triethylamine (TEA) base, as illustrated in Figure 5. The initial pH of the 3 wt % polymer **2** in THF was 6.13, with a fluorescence maximum at 530 nm. However, by increasing the pH of the medium, while maintaining particular concentration of solution, the emission maximum was shifted to the higher wavelength region.[20] Noticeably, the fluorescence emission intensity increases up to certain pH of 7.76, and then reduces with increasing the TEA contents, along

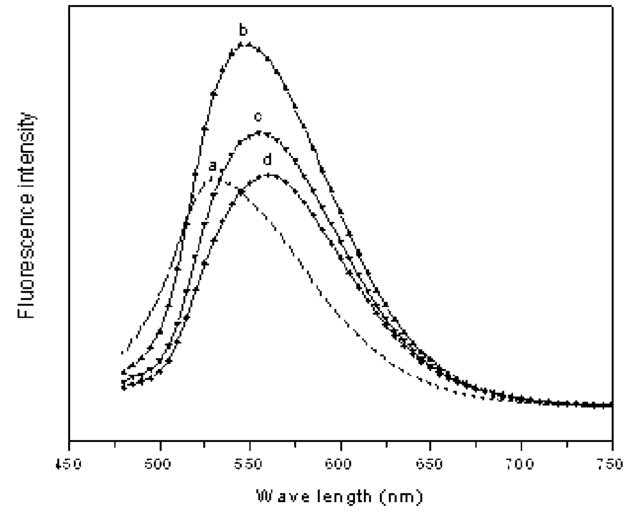

Figure 5 pH dependence of fluorescence spectra of 3 wt % polymer **2** in THF: (a) 6.13, (b) 7.76, (c) 8.37, and (d) 9.07 pH.

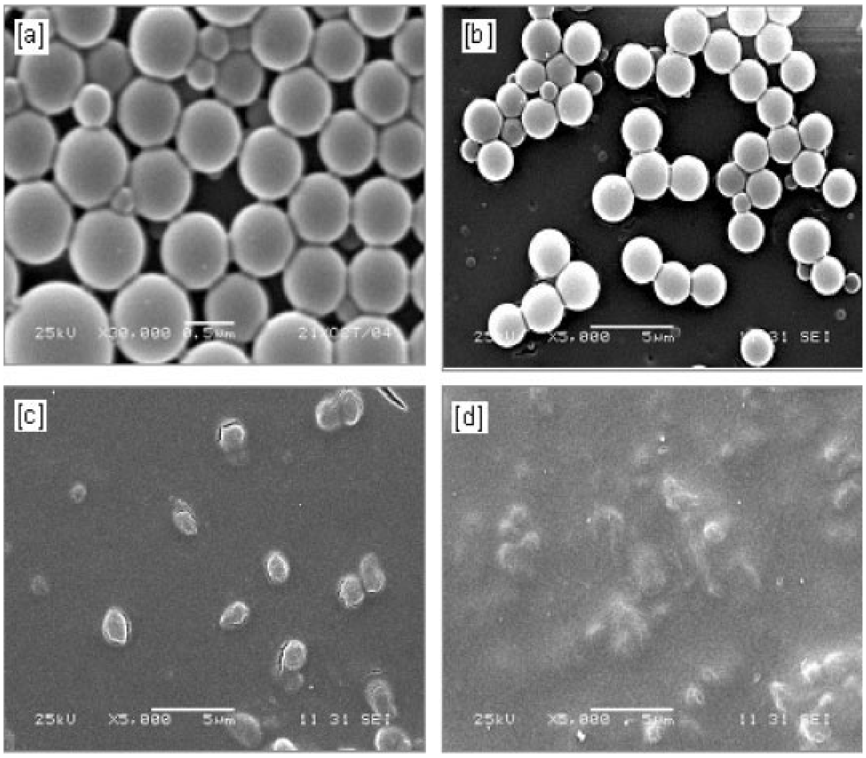

Figure 6 SEM images of 3 wt % polymer **2** in THF: (a) 6.13, (b) 7.76, (c) 8.37, and (d) 9.07 pH.

with shifting of emission peak. To clarify this effect, scanning electron microscopy (SEM) was used to check their morphological features of the polymers with respect to the TEA, as shown in Figure 6. The morphology of the polymers seems to be extremely uniform spherical sphere, with a mean particles size of ~ 500–700 nm, in both polymers at pH 6.13. Interestingly, by increasing the pH of polymer solution using TEA, the distinct and uniform spherical spheres were observed with slightly higher particle sizes. For example, the particle sizes before and after pH adjustment were ~ 500–700 nm and ~ 1–2 μm, respectively. Comparably, the distinct uniform spherical spheres were observed at 7.76, which exhibit very high fluorescence emission than in pH 6.13. However, after certain pH of above 7.76, the spherical sphere-shaped nanoparticles get disturbed and finally destroyed fully with increasing the TEA content at pH 9.07. These results indicated that, as long as the uniform spherical shape of polymer nanoparticles retains their morphology, the fluorescence intensity increases considerably. It has been observed that, an optimum pH is required to retain the uniform shape of the nanoparticles in solution, to get very high fluorescence efficiency.

Effect of nanoparticles on fluorescence spectra

The fluorescent polymer nanoparticles were successfully prepared from the corresponding THF solutions, upon slow evaporation of solvent under a mild vacuum. Figure 7 illustrates the SEM images of powder (as synthesized) and their nanoparticles prepared from the polymer **2** in THF solution. The morphology of nanoparticles were quite regular and smooth spherical spheres, while the powder polymer **2** material did not show any definite size and shapes in the SEM micrograph. However, the regular and smooth nanospheres were obtained from the micron size domains by simple evaporation method, with the average diameter of fluorescent polymer nanoparticles lies between 500 and 700 nm.

The fluorescence emission spectra of powder and their nanoparticles of 1 wt % polymer **2** solutions in THF were depicted in Figure 8. The fluorescence intensity of polymer **2** nanoparticles showed drastic improvements in fluorescence emission at the same concentration than that of micron-sized powder material. On the other hand, maximum peak emission in the fluorescence spectra of polymer **2** nanoparticles was blue shifted from 545 to 526 nm, when compared with isolated materials. The emission enhancement and the peak shifting in fluorescent nanoparticles were mainly attributed to the effect of particle sizes in the polymer **2**.[20] As the particle sizes of fluorescent material decreases from micron to nanoscale range, the peak emission also shifted to higher energy region (blue shift). Here, an extended charge-transfer state stemming from fluorescent molecules were closely stacking in nanoparticles, and

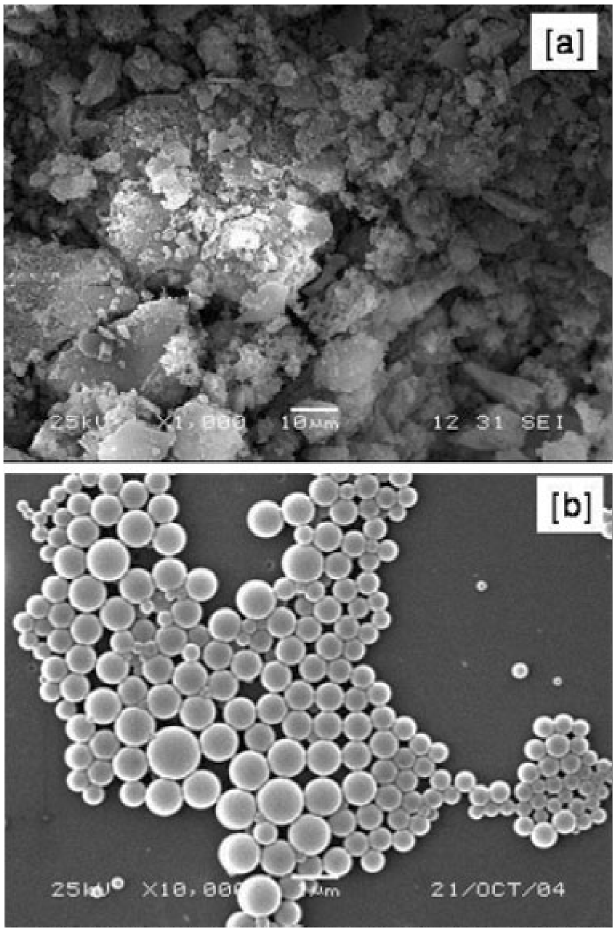

Figure 7 SEM images of polymer **2**: (a) powder and (b) nanoparticles (obtained from THF solution).

observed its shift to the high-energy side with decreasing nanoparticles size because of the exciton confinement. These arguments are in good agreement with other organic materials reported in the literature.[18,20,27,28]

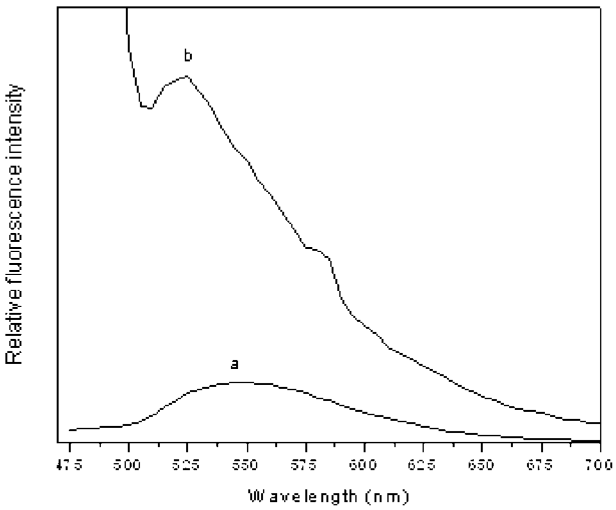

Figure 8 Fluorescence spectra of 1 wt % polymer **2** solution in THF: (a) powder and (b) nanoparticles, with an excitation wavelength 460 nm.

CONCLUSIONS

We successfully prepared the organic florescent polymer nanoparticles from their THF solution, with a mean diameter of $\sim$ 400–500 nm. As long as the morphology of (uniform sphere) polymer nanoparticles remains as such, the fluorescence emission will retain their efficiency in solution. It was found that the fluorescent polymer molecules were closely stacked when the particle sizes were reduced to nanoscale from micron-size domains, which enhance the fluorescence emission drastically along with peak shifting to the higher energy side. In addition, they exhibit a significant thermal property and better solubility in most common organic solvents. Finally, these yellow emitting fluorescent polymers are promising candidate for generating the white light, using blue LED as a primary pumping source. The performance of fabricated white light emitting diodes using these fluorescent polymers are quiet encouraging, further investigations are under progress.

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