Notes

Photoluminescence Characteristics of a Highly Soluble Fullerene-Containing Polymer

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Abstract : We investigated the photoluminescence (PL) characteristics of a highly soluble, fullerene-containing copolymer in both solution and film states. In solution state, the copolymer showed different PL characteristics depending on the aromaticity of the solvent. The PL from polystyrene segments of the copolymer was strongly quenched in an aromatic solvent, while the PL from fullerene remained unchanged. However, the films cast from an aromatic and a nonaromatic solvent demonstrated very similar PL characteristics, implying that the chain alignment or orientation and packing in the films occur in a similar way irrespective of the solvent.

Keywords : fullerene, fullerene-containing polymer, photoluminescence.

Introduction

Since buckminsterfullerene (C_{60}) consisting of all carbons was discovered in 1985, it has received a great attention because of its potential applications in variety of fields.[1] In addition, the development of the mass production method of C_{60} in 1990 triggered a great deal of researches concerning the C_{60}-related materials.[2] Especially, C_{60} possesses several interesting optoelectronic and electro-optic properties: For instance, when the C_{60} is excited by a frequency-doubled Nd-YAG laser with 8 ns pulses it shows an optical limiting response.[3] It has been reported that the light-emitting diodes (LEDs) prepared from the blend film of C_{60} adduct, T_h-hexapyrrolidine, poly(N-vinylcarbazole), and 2,5-bis-(4-naphthyl)-1,3,4-oxadiazole exhibited white electroluminescence (EL).[4] However, C_{60} is so poorly soluble in organic solvents except for a few aromatic ones[5] that many attempts have been made to overcome this defect.[6,7]

In this work, we present the photoluminescent (PL) prop-erties of a highly soluble C_{60}-containing polymer. The PL spectra were investigated in both solution and solid states. Especially, the effect of two different solvents (aromatic vs non-aromatic) on PL characteristics was investigated. The copolymer solutions showed very different PL characteristics according to the aromaticity of the solvent.

Experimental

Sec-BuLi-initiated polymerization of styrene was carried out in cyclohexane at 30 °C under high vacuum using a break-seal technique. All the reactions were carried out by the procedure which was modified based on the literature reported by Ederle *et al.*[8] Poly(styryl)lithium was reacted with purified C_{60} in the cyclohexane/THF cosolvent. Purified THF was then delivered into the reactor after complete removal of the solvents from the living polymer solution, followed by distillation of methyl methacrylate (MMA) to synthesize heteroarm star copolymer, $(PS)_xC_{60}(PMMA)_y$. Polymerization was carried out at −78 °C for 6 h in THF, followed by termination with degassed methanol. All the products were precipitated in excess methanol and dried in a
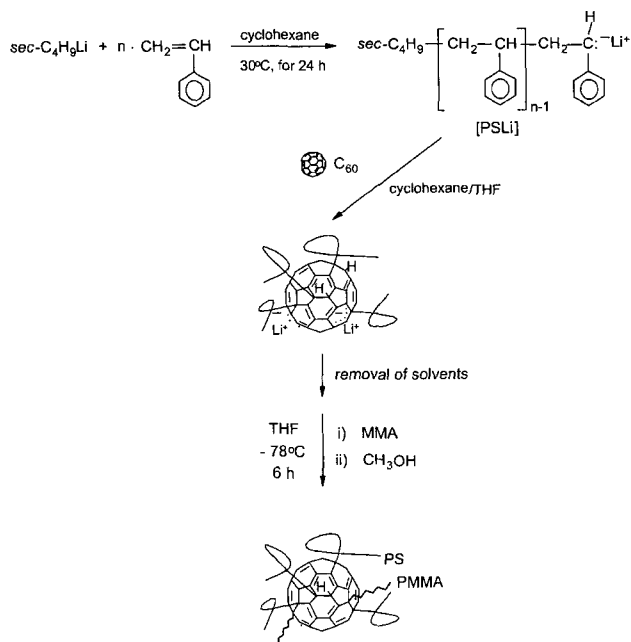
Figure 1. Synthetic scheme of the C_{60}-containing copolymer, $(PS)_xC_{60}(PMMA)_y$.

vacuum oven at 25 °C for at least 48 h prior to characterization. Figure 1 illustrates the copolymerization scheme. Details of the synthesis procedure and the results of characterization are described elsewhere.[9]

$(PS)_xC_{60}(PMMA)_y$ dissolved in dichloroethane or chlorobenzene was spin-cast on quartz substrates to obtain neat films. PL spectra of the dilute solutions and films were measured by using an ISS PC1 photon counting spectrofluorometer.

Results and Discussion

Figure 2 shows the PL spectra of the C_{60} copolymer in both chlorobenzene and dichloroethane solutions. We measured the PL spectra of the chlorobenzene solution at different excitation wavelengths as shown in Figure 2(a). As the excitation wavelength gets longer, the emission peak wavelength also shifts to longer wavelengths. This kind of excitation wavelength dependent emission typically indicates an inhomogeneous distribution of emitting sites.[10] According to the PL spectra of pure polystyrene (PS) shown in Figure 2(a), the peak maximum was located at 312 nm in chlorobenzene solution and the PL intensity was very weak. On the other hand, the copolymer gave a higher PL intensity when the solution was excited at a higher wavelength, where the PL originated from C_{60} in the copolymer because the PL of C_{60} is usually observed around 410 nm as shown in Figure 2(a). It is very interesting to observe that the PL intensity of the PS segments is so weak in the aromatic solvent but the emission from C_{60} in the copolymer is much higher in the
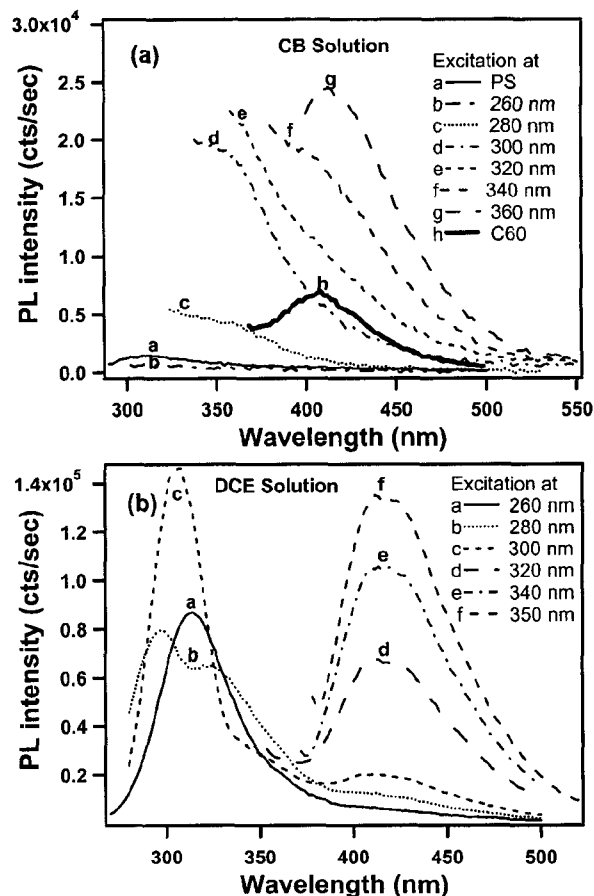

Figure 2. Photoluminescence (PL) spectra of the $(PS)_xC_{60}(PMMA)_y$ solutions in (a) chlorobenzene and (b) dichloroethane.

solvent. On the other hand, the copolymer in the non-aromatic solvent of dichloroethane showed a strong emission from the PS segments. The absolute intensity is much higher than that in chlorobenzene solution. Therefore, emission from the PS segments is quenched in chlorobenzene but not in dichloroethane. The fluorescent aromatic rings in PS are so compatible with the aromatic solvent that the emission would be quenched because of the interaction at excited states. But the chromophores of PS are isolated with each other in the non-aromatic solvent so that PS shows stronger PL. On the other hand, it is worthwhile to note that the PL emission of the copolymer in the dichloroethane solution demonstrated each contribution from PS and C_{60}. In other words, the PL behavior of the solution looks like that of the blends of PS and C_{60}. Although C_{60} is well known as a strong quencher, it is not a predominant factor for the observed PL quenching of the PS segments because the PL of pure PS is also strongly quenched in chlorobenzene.

Figure 3 clearly shows that the origin of the copolymer emission in chlorobenzene is different from that in dichloroethane. In the figure, PL excitation (PLE) spectra were measured by recording the PL intensities at different emission
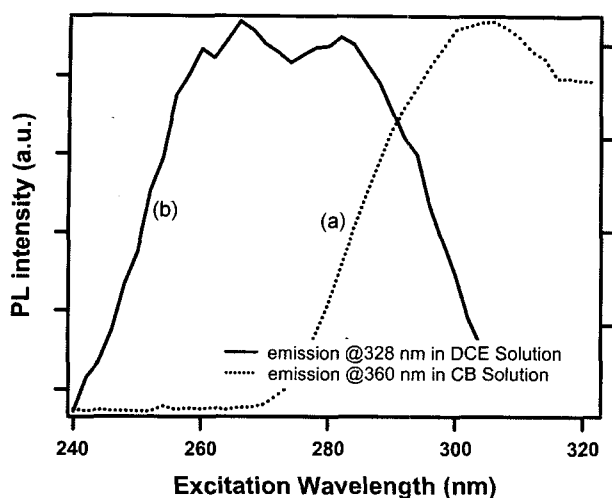
Figure 3. PL excitation (PLE) spectra of the $(PS)_xC_{60}(PMMA)_y$ solutions in (a) chlorobenzene and (b) dichloroethane.
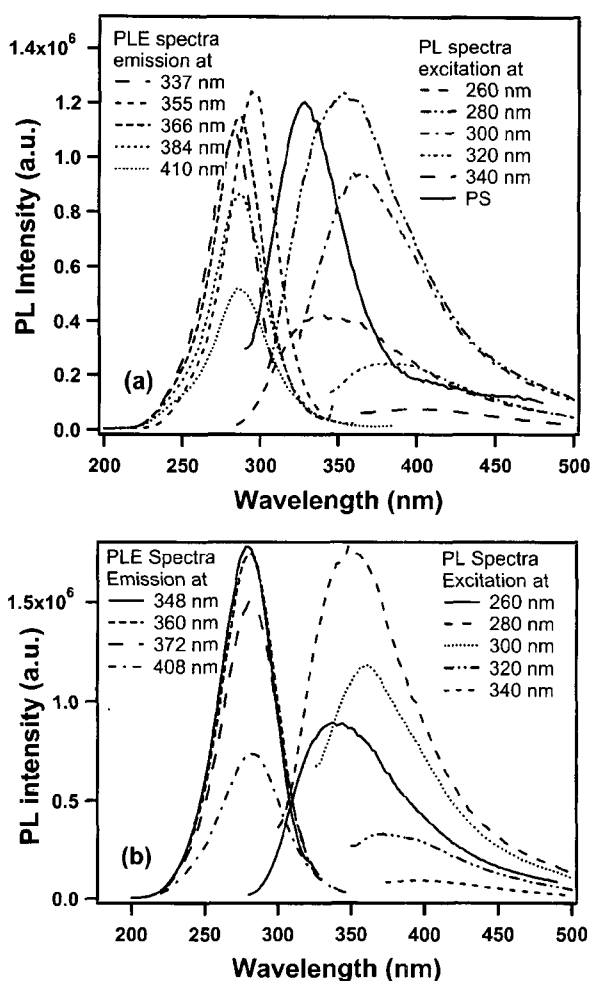

Figure 4. PL and PLE spectra of the $(PS)_xC_{60}(PMMA)_y$ films spin-cast from (a) dichloroethane and (b) chlorobenzene solutions.

wavelengths while varying the excitation wavelengths. The PL in dichloroethane is strong in the excitation wavelength range of 260-285 nm, while that in chlorobenzene was strong in the range of 300-310 nm. This also supports that the PL from the PS segments is quenched in an aromatic solution.

On the other hand, the films cast from the two different solutions showed very similar PL characteristics. Figure 4(a) and (b) are the PL spectra of the films spin-cast from chlorobenzene and dichloroethane solutions, respectively. Although the film absorbs the excitation source light at 260 nm most strongly, the emission is the strongest when excited at 280 nm. The fluorescence spectrum obtained at the excitation wavelength of 260 nm is similar to that of pure PS although the spectrum of the copolymer film is spectrally broadened. While the fluorescence spectral features are similar, the fluorescent yield of the copolymer is smaller than that of pure PS, which can be attributed to the quenching through intramolecular excited-state energy transfer[11,12]: The C_{60}-containing sites may act as energy traps. To find out the origin of the fluorescence, we measured the PLE spectra. However, they are all the same irrespective of the emission wavelengths. But this does not necessarily imply that all the emission originated from the excitation at 280 nm. Since the absolute PL intensity over the whole emission wavelength range examined was the strongest when the film was excited at 280 nm, the PLE spectra measured at various emission wavelengths reflect only the emission triggered by the excitation at 280 nm. It is very interesting to note that the fluorescence from the PS segments does not be quenched in solid state although it is strongly quenched in the chlorobenzene solution (see Figure 2), which may imply that the fluorescence from PS segments may be quenched when mediated (or surrounded) by aromatic rings. When we compared the PL of the solid film with that of the solution, a red-shift of 30-50 nm was found, which suggests that the interchain interactions in the film generates a red-shifted excimer emission.[13] The very similar PL spectra of the two films cast from the two different solvents (Figure 4) indicate that the chain alignment or orientation along the substrate and the chain packing density in the films are very similar irrespective of the casting solvent.

Conclusions

The fullerene-containing copolymer showed different PL characteristics depending on the aromaticity of the solvent. The PL from the PS segments of the copolymer in an aromatic solvent is strongly quenched while that from C_{60} in the copolymer is not affected. However, the films cast from the two different solvents show similar PL characteristics. $(PS)_xC_{60}(PMMA)_y$ was highly soluble in common organic solvents so that it has a potential to be employed for several different electro-optic devices such as electroluminescent

devices,[14] photovoltaic devices, photorefractive devices, field-effect transistors,[15] and etc.

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