

Restraining the Aggregation of Poly(9,9-dihexylfluorene) by Crosslinked Poly(methyl methacrylate) Networks

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ABSTRACT: A crosslinked network was used to restrain undesired interchain aggregation of fluorescent polymers in this study. Primarily, solutions of poly(9,9-dihexylfluorene) (PF) in toluene and in curable liquid monomer mixtures of methyl methacrylate (MMA) and ditrimethylolpropane tetracrylate (DTTPT) were compared to study the effect of concentration on absorption and emission behaviors. Results from ultraviolet–visible absorption, photoluminescence (PL) emission, and PL excitation reveal that the degree of aggregation depended strongly on the concentration and was correlated to the size of the polymer coil as determined from light scattering. Solutions of known PF content in MMA/DTTPT were then photoirradiated to yield PF/crosslinked poly(methyl methacrylate) (X-PMMA) composite films. Comparison among the pure PF, PF/MMA/DTTPT mother liquid, and PF/X-PMMA solid composites were then con-

ducted to evaluate the effect of crosslinking on the degree of aggregation. With small amounts of imbedded PF (0.0015 wt %), the PF/X-PMMA composite had a PL quantum yield (0.70) higher than the pure PF (0.65) itself. Most notably, the PF/X-PMMA composites after annealing at 120 and 200°C for 5 h still retained a reasonable emission efficiency (with related PL quantum yields of 0.61 and 0.43), in contrast to the large PL quantum yield reductions to 0.32 and 0.19 for the annealed PFs after the same treatment. Suggestively, interchain aggregation during a high-temperature annealing process can be largely inhibited by the surrounding cross-linked network matrix. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3308–3314, 2007

Key words: association; fluorescence; crosslinking; photopolymerization

INTRODUCTION

Since the first report on electroluminescent poly(*p*-phenylenevinyl)¹ in 1990, a large amount of interest in polymeric light-emitting diodes has been triggered.^{2–4} Among versatile polymeric light-emitting diodes, blue-light emitting polyfluorenes⁵ have become one intensely researched class because of their advantageous properties^{6–8} and ease of further chemical formulation.⁹ Despite these promising properties, the association (excimer formation and/or aggregation) of polyfluorenes at low or high temperatures has become one major issue of concern because it is detrimental to the emission efficiency. It is well recognized that conjugated polymer chains can associate to form electronic species with excited and/or ground state properties distinct from that of the isolated polymer chain. For polyfluorenes in dilute solution, the polymer chains are presumably

isolated; the corresponding photoluminescence (PL) and ultraviolet–visible (UV–vis) absorption are characterized by a single relaxation time,¹⁰ and the vibronic bands are virtually originated from the non-interacting single chains.^{11,12} In concentrated solution and films of polyfluorenes, however, PL emission at longer wavelengths is rather featureless and related to the emission from excimer or aggregate.¹³ An excimer¹⁴ is a pair of associating species with one in the excited and one in the ground states, whereas an aggregate is characterized by the delocalization of the electronic states among two or more chains in both the ground and excited states. Both of them have emission patterns different from the noninteracting chains and, most importantly, cause the great reduction on the PL quantum yield.^{14,15}

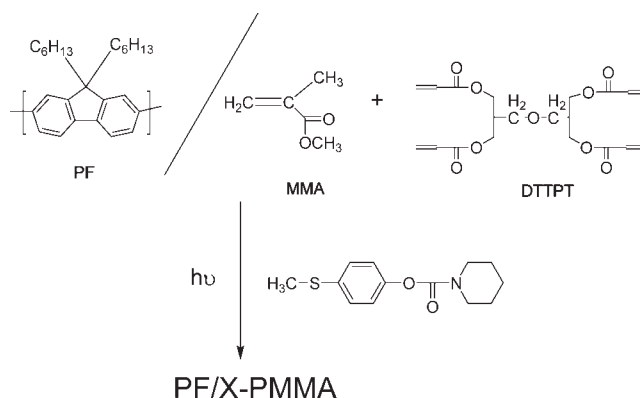
Previously, several attempts have been made to suppress detrimental excimer and aggregate formation in polyfluorenes. Through the introduction of small amounts of low-band-gap chromophores (e.g., perylene or α -cyanostilbene) into the backbone, the excimer emission of polyfluorenes can be successfully reduced.^{16,17} The suppression of excimer emission is explained by the efficient energy trapping of the originally excited fluorene units by these low-band-gap chromophores.¹⁸ An alternative approach

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by the same group was the copolymerization of fluorene with some spirofluorene units,¹⁹ by which the rigid, hindered spiral centers imposed difficulties for intermolecular contact and interchain interactions. The solid films were reported to have long-time stability at high temperatures without excimer and aggregate formation. Copolymers of polyfluorene containing bulky, dendrimer-like pendant groups were also prepared²⁰ to successfully demonstrate the function of the bulky pendant group in sterically shielding polymer main chains from intermolecular contacts and preventing aggregation.

Aggregate formation is actually related to interchain interaction between the conjugated polymers according to a study on poly(phenylene vinylene)s (PPVs).^{21,22} Practically, one can control the degree of interchain interactions and morphology in conjugated polymer films by altering the chain conformation in the solution from in which the film is cast. The degree of interchain interaction and the aggregation of PPVs are directly related to both the concentration of polymer in the solution and the choice of solvent. The memory of chain conformation and the extent of aggregation of PPVs in solution are possibly retained through the solvent-evaporation (e.g., spin-casting) process, which results in the final chain conformation and, therefore, controls chain conformation in solution, is the key to manipulating photo-physics in final polymer films. A previous study^{21,22} indicated that it is possible to have fluorescent solid films with little interchain interaction if the chain morphology in the dilute solution can be preserved. With routine evaporation, the preservation of chain conformation is difficult because possibility of interchain contacts gradually increases with the reduction of solvent media during the course of evaporation. Nevertheless, it is possible to achieve this goal if curable liquid monomers are used as a solvent for fluorescent polymers; then, the subsequent crosslinking reaction on the curable monomers will generate a system with chain conformations of the fluorescent polymers locked in the so-formed crosslinked matrix.

In this study, a dilute solution of poly(9,9-dihexylfluorene) (PF) in a mixed liquid monomers of methyl methacrylate (MMA) and ditrimethylolpropane tetraacrylate (DTTPT) was photoirradiated to generate the desired PF/crosslinked poly(methyl methacrylate) (X-PMMA) composite (Scheme 1). Solution light scattering and PL spectra of the polymers in two solvents (MMA/DTTPT and toluene) were preliminarily surveyed to disclose the relationship between interchain interaction and solution concentration. We then studied the solution samples and compared our results with the results from the cured PF/X-PMMA to evaluate the effectiveness of this crosslinking strategy. Finally, the thermal stability of the cured PF/X-PMMA was determined by the comparison of



Scheme 1 Photoirradiation of PF in MMA/DTTPT to form PF/X-PMMA composites.

the PL quantum yields of the samples before and after thermal annealing at elevated temperatures (i.e., 120 and 200°C). This result was compared with that of pure PF to demonstrate the effectiveness of the crosslinked matrix in promoting emission stability at high temperatures.

EXPERIMENTAL

Materials and instrumentation

MMA (Aldrich, St. Louis, MO), 4-(methylthio)phenyl piperidine carboxylate (MPPC; Sartomer, Exton, PA) initiator, and DTTPT (Sartomer) crosslinker were used directly without purification. PF was prepared according to reported procedures²³ and had a number-average molecular weight of 9800 g/mol, a weight-average molecular weight of 17,700, and a polydispersity index of 1.81 as determined from gel permeation chromatography measurements.

UV-vis spectra were obtained with a Hitachi (Minato-Ku, Tokyo, Japan) U-3501 spectroscope. PL spectra were recorded with a LabGuide (Taipei, Taiwan) fluorescence spectrophotometer. Quantum yields were measured in an integrating sphere made by Ocean Optics, Inc. (Dunedin, FL). The sphere had a diameter of 1.5 in. and a sample port aperture (0.375 in.) at the equator. Photoluminescence excitation (PLE) spectra were obtained from a Hitachi F-4500 spectroscope. The chain dimension of the dilute polymer solution was measured from light scattering with a Marlvern (Malvern, Worcs, WR, UK) PCS 4700 with a He-Ne laser light source (wavelength = 632.8 nm) at a fixed angle of 90°.

Sample preparation

The calculated amount of PF was dissolved in toluene or the mixed MMA/DTTPT (4 : 1, v/v) and then stirred at 60°C for 4 h to remove any preliminary aggregates before further measurements. To the solutions of PF in MMA/DTTPT, the initiator MPPC

(1 wt % initiator) was added, and the whole mixtures were then deposited on an aluminum disc and irradiated with UV light for 10 min to prepare the cured composites. A UV lamp (Synrex Instrument, model SSP-01A, Taipei, Taiwan) with a 259-nm light source and 120 W of power was used for photoirradiation. Solution samples of PF in MMA/DTTPT were situated 10 cm away from the UV lamp and irradiated for 10 min to complete the curing process.

RESULTS AND DISCUSSION

Dilute solutions of PF in MMA/DTTPT and toluene

To carry out the crosslinking reaction, a preliminary study on a dilute solution of PF in the curable liquid monomers (MMA/DTTPT) was necessary and was conducted first. To fully understand the effect of media, we chose an alternative solvent of aromatic toluene for study, too, by considering its distinct properties from MMA/DTTPT and good solubility toward the aromatic PF.

The absorption and PL emission spectra of dilute PF (1×10^{-6} M, 0.001% w/v) solutions in toluene were more redshifted than those of MMA/DTTPT, as shown in Figure 1. The redshift of the absorption spectrum deserves certain comments. If this shift were due to the different extents of solvation on the ground and excited states, the nonpolar ground state of PF would have been stabilized more by the nonpolar, aromatic toluene as compared to the polar MMA/DTTPT solvent. Therefore, we would have expected the redshift of PF in MMA/DTTPT rather than PF in toluene, a rationale that did not fit this result and the fact that MMA/DTTPT is a poor solvent for PF. Alternatively, the shift could be explained by a change of the conjugation length of

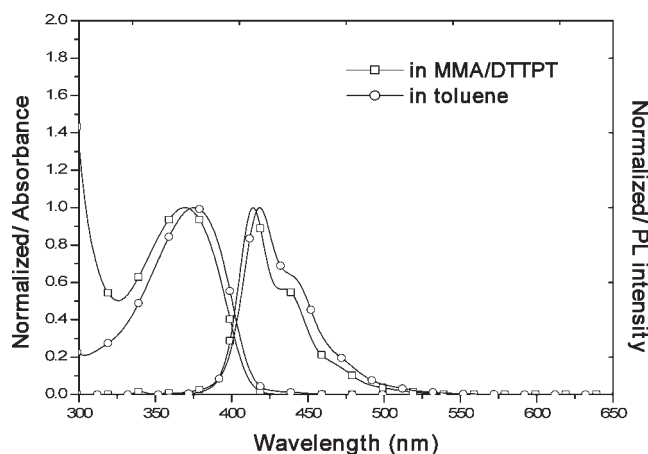


Figure 1 Normalized absorption and PL spectra of PF in dilute solutions of the solvents MMA/DTTPT (1×10^{-6} M) and solvent (1×10^{-6} M; excitation at 360 nm).

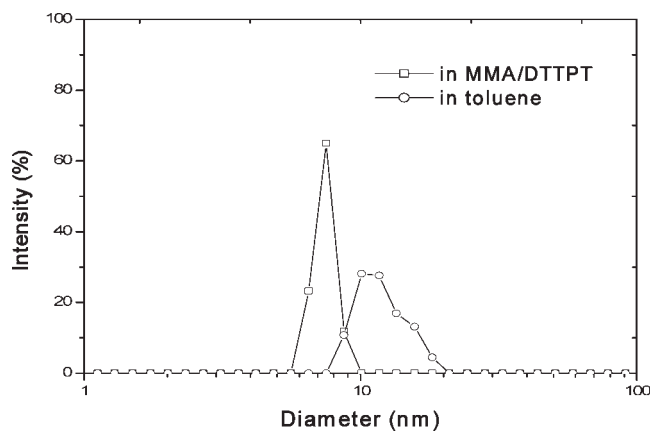


Figure 2 Size distributions from the light scattering of solutions of PF (1×10^{-6} M) in the solvents MMA/DTTPT and toluene.

PF in different solvents, an idea that was presented on the basis of a study on oligomeric²⁴ and polymeric²⁵ poly(5-methyl-2-(2'-ethylhexyloxy)-*p*-phenylenevinylene) (MEHPPV). The excitation energy tended to migrate through the inhomogeneous density of states. The blueshifted absorption and emission spectra of PF in MMA/DTTPT were, therefore, attributed to a shorter average conjugation length of PF in the nonaromatic MMA/DTTPT than PF in the aromatic toluene.

Light-scattering experiments on PF were then performed to evaluate the relative dimensions between PF in toluene and PF in MMA/DTTPT. As expected, the experiments showed that the conformation of PF chains in solution was altered by the solvent-polymer interaction. Figure 2 shows typical light-scattering size distributions for the dilute solutions (1×10^{-6} M) of PF in MMA/DTTPT and PF in toluene. The average diameter of PF in toluene (12 ± 4.5 nm) was obviously larger than PF in MMA/DTTPT (7.4 ± 2.2 nm). In the favorable solvent toluene, PF tended to extend its dimension to maximize favorable π - π interactions between the polymer and the solvent. On the contrary, the polymer was expected to coil more tightly to minimize the number of aromatic repeat units interacting with the nonaromatic solvent of MMA/DTTPT.

The tighter polymer coil in MMA/DTTPT may imply a greater number of torsional defects along the backbone and hence, a lower PL quantum yield, a result previously reported for MEHPPV in tetrahydrofuran and in chlorobenzene.²⁵ Despite this potential drawback, we focused our further characterizations on the MMA/DTTPT system by considering its curability to attain the desired network structure. As we examined Figure 2 carefully, except the broad size distribution for PF in toluene, we noted that there was also a right shoulder in the regions of

higher sizes, which suggested the possible existence of aggregation in toluene. These portions of aggregated chains constituted a single entity distinct from the unassociated chains, a coil size distribution typical for fully dissolved conjugated polymers²⁶ in a good solvent. The more extended chain conformation in the good solvent toluene increased the possibility of interchain contacts, which should have been conceivably avoided by the use of the poor solvent MMA/DTTPT. To obtain a PF/crosslinked network system of less aggregated forms, system of PF in MMA/DTTPT was thereby chosen for further study.

Increasing the polymer concentration in solution offered greater opportunity for the overlaps and interactions among the π electrons of the aromatic rings on different polymer chains; as a result, the possibility for interchain aggregates increased. This effect was readily demonstrated by solutions of PF polymer with varied concentrations in MMA/DTTPT. To clearly view the wavelength shift and intensity difference, unnormalized and normalized solution PL emission spectra of PF are given in Figure 3(a,b), respectively. Careful inspection suggests that there were only minor differences in the results from low-concentration (1×10^{-6} and 1×10^{-5} M) solutions, but for solutions of higher concentrations (3×10^{-5} and 7×10^{-5} M), redshifts of the band maxima were accompanied by a reduction in the emission intensity. As the concentration increased, an emission tail was present as the red edge above 500 nm [cf. the inset in Fig. 3(a)] and increased its contribution to the red of the polymer emission spectrum. Careful inspection also revealed that this low emission feature increased in magnitude and redshifted relative to the main emission band. The increase of the red tail was correlated to the decrease of the main emission, which all suggest that a large fraction of the emission above 500 nm was caused by a new species, most likely aggregate, originated from the increasing interchain interactions during the concentration process.

To clarify the origin of the emission tail above 500 nm, PLE spectroscopy was further applied. The solution PLE spectra of PF in MMA/DTTPT in Figure 4 show that the maximum absorption positions contributing to the emission at 520 nm shifted from 368 to 380 nm with increasing concentration, indicating the increasing content of fluorophore associates, which absorbed light at long wavelengths than the isolated fluorophore units in dilute solution. Excitation energy by direct absorption was thereby redshifted to longer wavelength by aggregates of fluorophores. As the PF concentration was raised, aggregation provided more delocalized chain segments, which led to a red ground-state absorption and an increase in the total number of species that produce emission in the red edge over 500 nm.

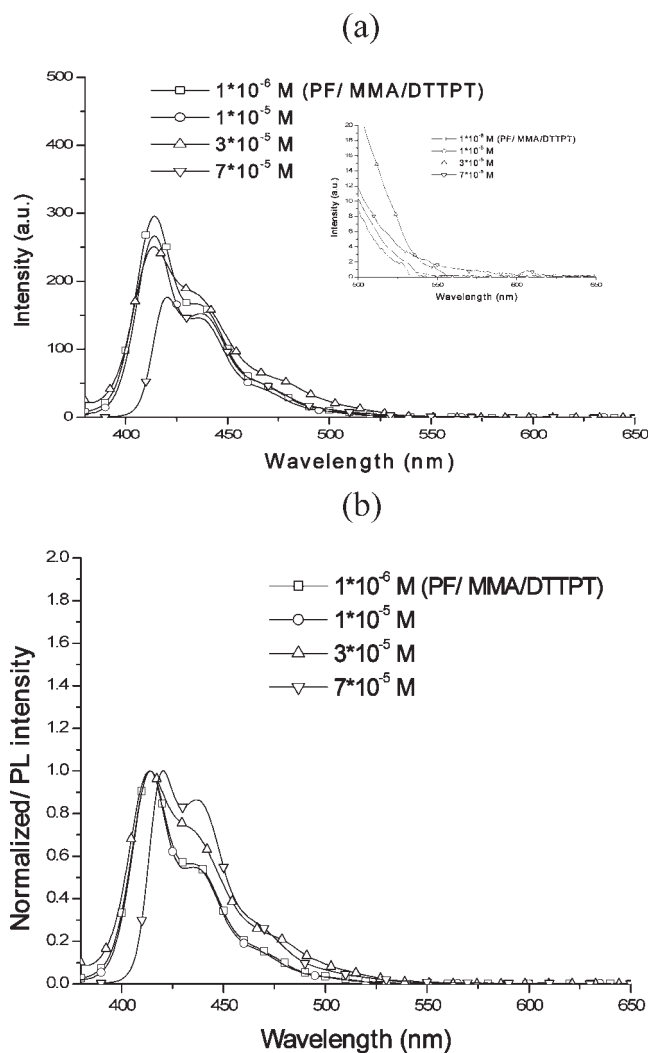


Figure 3 Solution PL emission spectra of PF in MMA/DTTPT with (a) the unnormalized intensities (the magnified red edge is shown in the inset) and (b) the normalized intensities (excitation at 360 nm).

Solid composites of PF in the X-PMMA matrix

PF/X-PMMA composites with known PF contents were prepared from room-temperature photoirradiation of the mother PF/MMA/DTTPT solutions. When concentration of the starting PF/MMA/DTTPT were controlled from 1×10^{-6} to 7×10^{-5} M, the resulting PF/X-PMMA composites had the desired arrangement with the fluorescent PF immersed in the crosslinked matrix.

The normalized PL spectra of the cured PF/X-PMMA are compared with the pure PF film in Figure 5, in which the included inset illustrates the magnified red edges at wavelengths greater than 500 nm. The PL spectra of PF/X-PMMA with higher PF (7×10^{-5} M) were relatively redshifted and had higher contributions of the red-edge portions compared to those with lower PF content (1×10^{-6} and 1×10^{-5} M), whose spectra were basically the same.

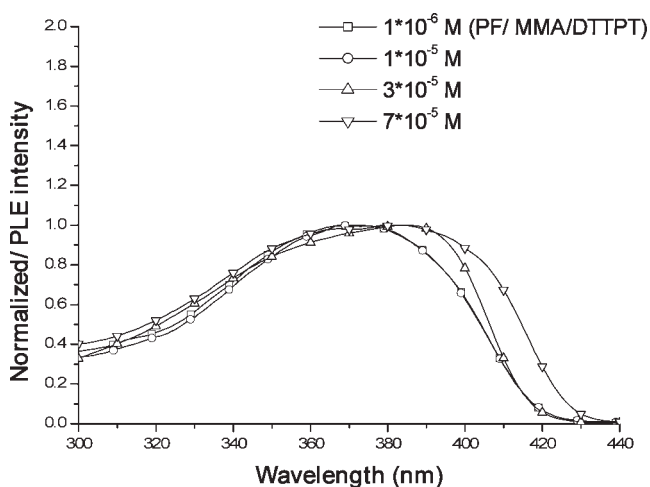


Figure 4 Normalized PLE spectra of solutions of PF in MMA/DTTPT monitored at 520 nm.

Comparatively, the PL spectrum of the pure PF film was roughly similar to that of PF/X-PMMA ($7 \times 10^{-5} M$), but careful inspection revealed that pure PF actually possessed a higher content of the red-edge emission (cf. the inset), which may have indicated the operation of crosslinking strategy in restraining aggregation of the imbedded fluorescent polymer.

Thermal stability of the resulting PF/X-PMMA were then evaluated. The absorption and emission spectra of PF and PF/X-PMMA ($1 \times 10^{-6} M$) films before and after thermal annealing at 120 and 200°C for 5 h were then compared and are shown in Figure 6(a,b). For samples annealed at 120°C for 5 h [Fig. 6(a)], PF had its absorption and emission spectra redshifted more than those for PF/X-PMMA, but the difference was relatively small when compared to results from

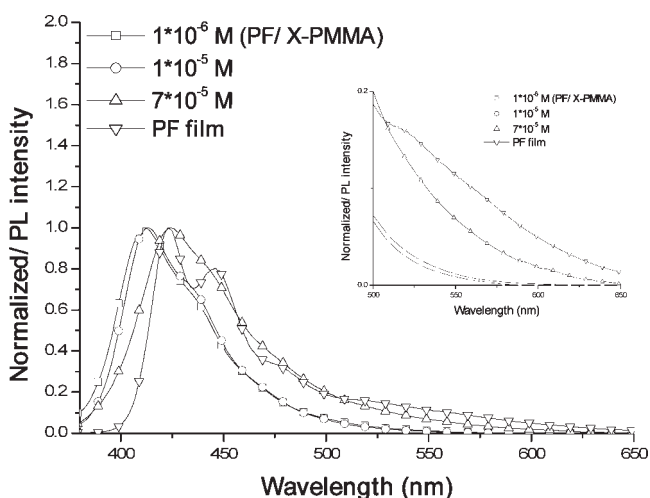


Figure 5 Normalized PL emission spectra of solid PF/X-PMMA and pure PF films (the magnified red edges are shown in the inset; excitation at 360 nm).

200°C annealing [Fig. 6(b)], where a new association band centered at 520 nm emerged and became one of the major emission bands for the annealed PF, a feature in distinct from the intact emission observed for the annealed PF/X-PMMA (cf. Fig. 5 for the unannealed sample). The large association emission band for the annealed PF was ascribed to both excimer and aggregate formation, as indicated previously.²⁷ In any cases, the extents of shifting and tailing on thermal annealing were greatly reduced for PF/X-PMMA; that is, when the PF was frozen in the network system, the chain mobility of PF was greatly reduced and so was the inter-chain association process at elevated temperatures.

The effect of thermal annealing was further evaluated by measurement of the PL quantum yields of different solid films before and after annealing. The results are summarized in Table I. The comparison

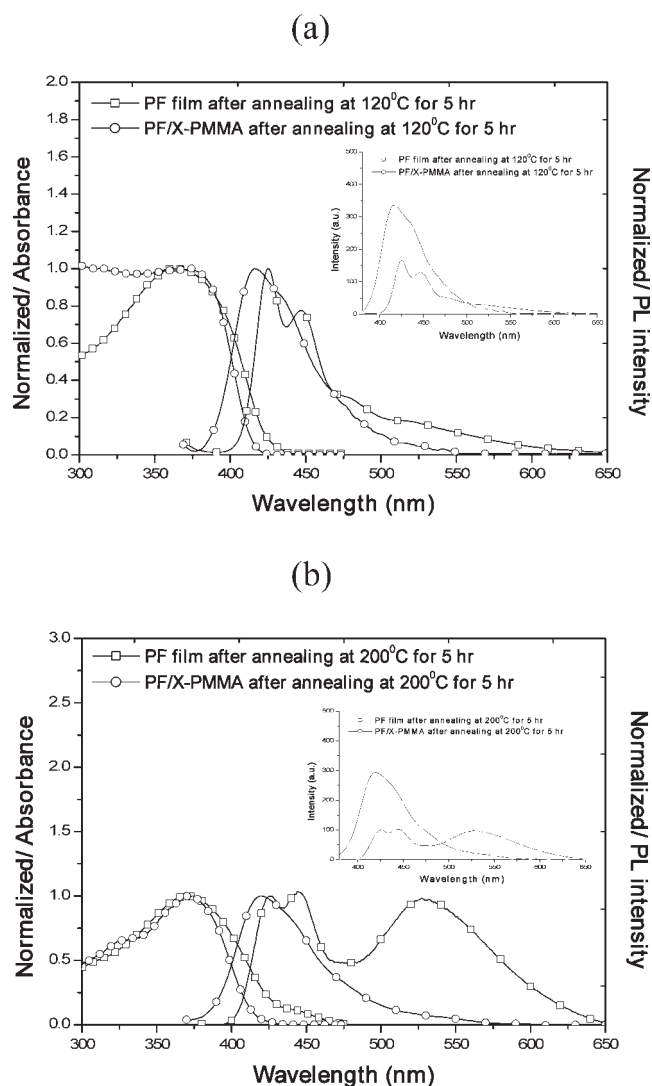


Figure 6 Absorption and emission spectra of PF and PF/X-PMMA after annealing at (a) 120 and (b) 200°C for 5 h (unnormalized emission spectra are included in the insets; excitation at 360 nm).

TABLE I
PL Quantum Efficiencies of PF and PF/X-PMMA Films
Before and After Thermal Annealing

Sample	Before annealing	After annealing at 120°C for 5 h	After annealing at 200°C for 5 h
PF	0.65	0.32	0.19
PF/X-PMMA ^a	0.70	0.61	0.43

^a PF/X-PMMA was prepared from a 1×10^{-6} M solution of PF in MMA/DTTPT.

of the unannealed samples was primarily made here. As discussed previously, chains of the conjugated polymers could be isolated from each other in dilute solution and in the derived crosslinked matrix formed by the subsequent curing. The isolated chain morphology in PF/X-PMMA, therefore, contributed to a higher PL quantum yield than did PF (0.70 vs 0.65). Here, the difference was significant when we considered the low content (0.0015 wt %) of the fluorescent PF in PF/X-PMMA composite. This result suggests that the exclusion of aggregation and/or any form of nonradiative pathways was very important in obtaining an efficient emission pattern. For PF, thermal treatments at 120 and 200°C caused drastic reductions in the PL quantum yield from 0.65 to 0.32 and then to 0.19, but comparatively, fewer reductions (from 0.70 to 0.61 and 0.43, respectively) were observed for the cured PF/X-PMMA film. In this case, the interchain aggregation of PF at elevated temperature was successfully inhibited by the freezing of the chain mobility with the surrounding network matrix.

The low solubility of the PF polymer toward MMA/DTTPT imposed limitations on the crosslinked strategy used in this study; therefore, new curable liquid monomers remain to be developed. In addition, limitations originating from the inherent nature of a semirigid polymer such as PF should be considered; that is, semirigid polymers in solution generally have lower overlap concentrations for the polymer chains to start to contact to each other when compared to coil structures formed by flexible polymers in solution.²⁸ Conceptually, the overlap concentration may be the onset concentration for interchain interaction and aggregation process for fluorescent polymers. The low overlap concentration for most of the semirigid fluorescent polymers may impose difficulties in preparing solutions with high polymer content but still with limited interchain aggregation.

CONCLUSIONS

We have shown that the conformation of PF varied greatly in solvents of toluene and MMA/DTTPT. PF

chains in toluene solution were much more extended and open than those in MMA/DTTPT solutions, as evidenced by (1) the size distributions measured directly by light scattering and (2) the redshift of the UV-vis absorption and PL emission in toluene solution. Moreover, the photophysics of PF polymer in solution was also seen to vary with concentration. PLE spectra showed a redshift of band and a long-wavelength red edge with its magnitude increasing with polymer concentrations in solution. Suggestively, this red edge was due to aggregate formation. Suggestively, the degree of aggregation was solvent-dependent; that is, with a more open chain than the conjugated polymer in toluene, a more efficient interchain interaction will promote aggregation, in distinct from the tighter coil formed when polymers were in the nonaromatic MMA/DTTPT.

Photoirradiation of the fluorescent PF in MMA/DTTPT yielded crosslinked composites with enhanced photochemical stability at high temperatures. The emission band of PF/X-PMMA composites was also redshifted with increasing PF content; however, the magnitude of the shift was smaller than the pure PF itself. Cured PF/X-PMMA composites also maintained their emission pattern even after long-time annealing at high temperatures such as 120 and 200°C, in contrast to the emergence of association emission for pure PF after annealing. These results are in accordance with the trend observed for PL quantum yields; that is, the significant PL quantum yield reduction for the annealed PF was largely prohibited by the trapping of PF in the crosslinked X-PMMA matrix. Suggestively, the frozen chain segments in the crosslinked network successfully prevented easy aggregation of the imbedded PF.

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