Restraining the Associations of Anthracene Fluorophore by Chemically Linking to Poly(methyl methacrylate)

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ABSTRACT: Associations (dimer or aggregate) of anthracene (An) fluorophores tend to interrupt the monomer emission and reduce the quantum yield (Φ_{PL}); therefore, poly(methyl methacrylate) (PMMA) chain was used in this study to chemically link to anthracene and to block the mutual associations among the anthracene fluorophores. With this aim, the target polymers were prepared by anionic polymerizations with 9,10-dibromoanthracene/s-butyllithium as initiating system to proceed polymerizations of methyl methacrylate (MMA) directly or in the presence of 1,1-diphenylethylene (DPE). Use of DPE before addition of MMA produces stable initiating anionic species and avoids potential side reactions during polymerization; however, it also introduces four β-phenylene rings around the central anthracene ring, which interfere with the corresponding emission pattern and reduce the Φ_{PL} (32%) value due to potential interactions between phenylene rings and anthracene. On the contrast, polymerization without participation of DPE results in polymer with central anthracene ring directly connected to two PMMA chains, which gives clean vibronic emission pattern with limited association emissions and enhanced Φ_{PL} (52%) value. Physical blending of anthracene by PMMA is less efficient to restrain the associations and results in a film of lower Φ_{PL} (20%). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 124–131, 2008

**Key words:** fluoropolymers; anionic polymerization; photochemistry

INTRODUCTION

Many aromatic organic fluorophores have desirable UV absorption and visible emission,[1] and dependent on the extent of inter-reaction, different types of associations among the fluorophores exist. For example, mutual association involving a pair of molecules in the excited and in the ground states form excimer, an association form quite common for organic fluorophores in the concentrated solution or in the solid state and causes the decrease of emission intensity.[2] In addition to excimer, there is evidence for the formation of multi-molecular aggregates, a ground-state complex involving more than two molecules or two chains, such as micelles[3,4] in biological studies. Aggregate also results in an excimer-like emission and the undesired internal quenching process to result in the decrease of emission intensity, too.

Previous efforts to reduce the emission from the aforementioned associations (excimer or aggregate) include the dispersion of the organic fluorophores in an inert, inactive polymer to afford a molecular doped polymer (MDP)[5–7] system. By selecting appropriate polymer, the dispersed organic fluorophores can be isolated from each other by the polymer separator and the associations among them can be effectively reduced. In regards to the potential stability problem in the physical blending system, chemical methods was alternatively considered in which the organic fluorophores were chemically linked to polymer chains to exert the same isolation effect. Previously, there are several reports[8–15] relating to these fluorophore-centered polymers. For example, dihydropyrrolpyrrolidone fluorophore was build as the center of a dendrimer and investigated by confocal microscope to distinguish the emission of single molecule from the aggregated cluster.[8] Pyrene was also incorporated as the pendant group to prepare a system of "hydrophobically modified alkali swellable emulsion polymer (HASE)." By selecting tetrahydrofuran or water as the dispersive medium, emission from the isolated or the aggregated pyrene can be both detected.[9] In distinct to above dendrimeric or side-chain system, fluorophores were also incorporated as center of linear polymers such
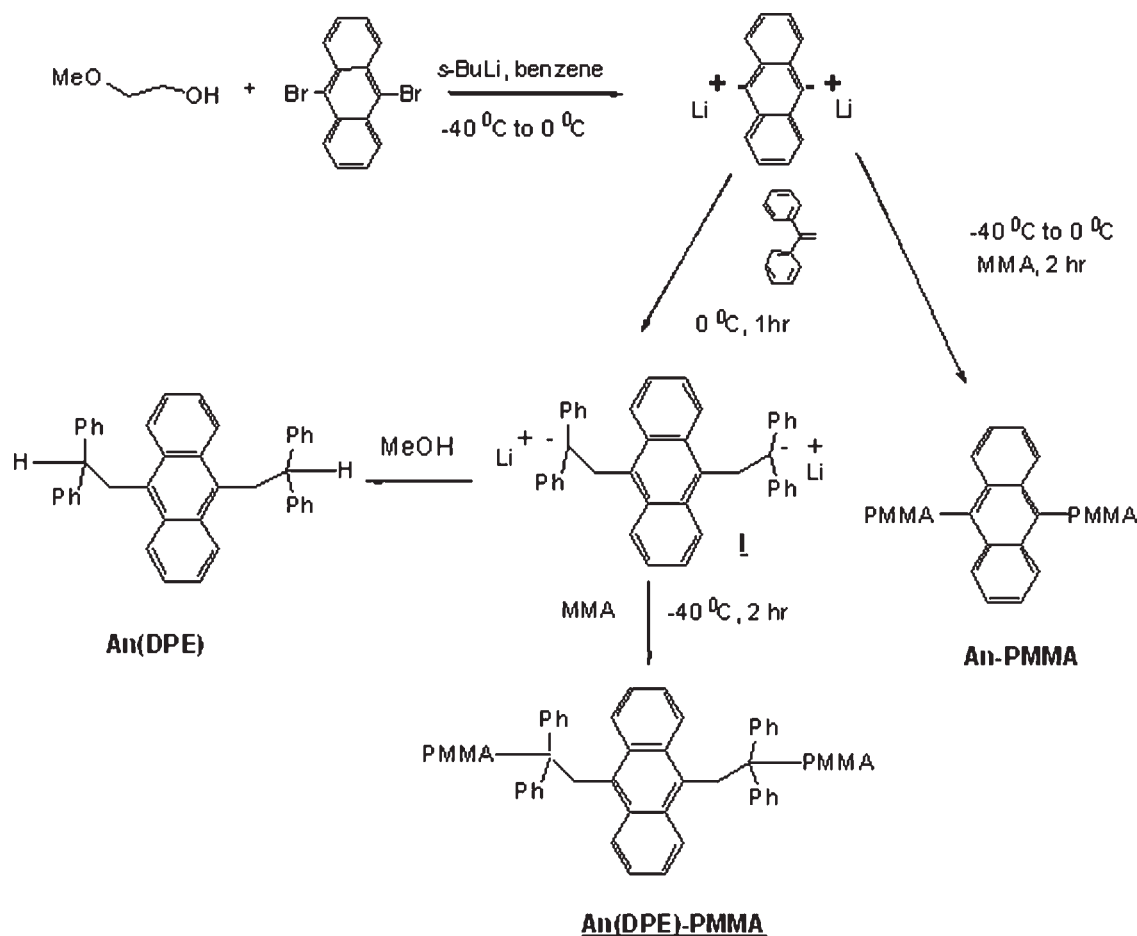
Scheme 1 Syntheses of anthracene-centered PMMAs, An-PMMA, and An(DPE)-PMMA and model compound, An(DPE).

as polystyrene-[10,11] and polyisoprene–poly(methyl methacrylate)[12] diblock copolymers; and the ratios of the microdomain size to thickness of boundary-domain interphase can be formulated from their corresponding emission spectra. In addition, elastomeric polystyrene–polyisoprene–polystyrene triblock copolymer with central mono- or di-carbazole fluorophore[13] had been successfully prepared by anionic polymerization. This study did mention that the corresponding copolymers emit without the excimer emission at ∼ 420 nm; however, this study was devoted to characterize the emission response during the mechanical stretching of this elastomeric copolymers. Basically, detailed study on the blocking effect of polymer on the surrounding fluorophores is scarce at the present time.

To evaluate the possible blocking effect of polymer chain in isolating the attached fluorophore, we prepared two polymers with central anthracene ring attached to two poly(methyl methacrylate) (PMMA) chains in this study. Polymers with the same architecture had been prepared previously[14,15] by atom-transfer radical polymerization (ATRP) of methyl methacrylate (MMA) from a bromine-containing anthracene derivative. In this contribution, anionic polymerizations were performed to prepare An-PMMA and An(DPE)-PMMA with two different central fluorophores shown in Scheme 1. Use of anthracene ring as central fluorophore is due to the easy identification of the monomer from the excimer emissions, since the distinct vibronic emissions in the ranges of 380–421 nm make the characterization a simple task. An(DPE)-PMMA, with four additional phenyl rings on the β-position of the central anthracene ring, turned out to have different emission behavior from An-PMMA. To clarify the role of the four β-phenyl rings, a model compound An(DPE) (cf. Scheme 1) was also synthesized to serve as a model for the emission behavior of An(DPE)-PMMA. Solution and solid states emissions of the corresponding polymers were conducted to evaluate the effect of surrounding polymer chains as steric blocker to isolate the attached, central anthracene fluorophore. In addition, blend of anthracene/PMMA was prepared in this study and the corresponding emission spectrum was evaluated to clarify the roles of PMMA as physical blocker in the blend and as chemical blocker in An-PMMA.

EXPERIMENTAL

Materials and instrumentation

Tetrahydrofuran (THF) and benzene was vacuum distilled after dehydration by sodium/benzophenone. 2-Hydroxylethanol and methanol was distilled from magnesium (Mg). Methyl methacrylate (MMA) monomer was purified by dehydration and distillation from CaH_2 before storage over molecular sieve. Sec-Butyllithium, diphenylethylene, 9,10-dibromoanthracene, and anthracene were purchased from Aldrich Chemical and used directly without purification. PMMA ($M_n = 14,000$, PDI = 1.41) was prepared as described previously[16] and was used directly to prepare blend with anthracene.

Proton ^1H and ^{13}C spectra were recorded from a Varian VXR 300 MHz model and tetramethylsilane was used as internal standard. Mass spectra (MS) were obtained from a VG Quattromass spectrometer at an ionizing voltage of 70 eV. Elemental analysis was measured from a Heraeus CNH-OS rapid elemental analyzer. Molecular weight of polymers was determined from a Waters 510 GPC model equipped with UV–vis detector. THF was used as eluent (flow rate = 1.0 mL/min) and mono-dispersed polystyrene molecular weight standards were used for calibration. UV–vis spectra were recorded from a Hitachi U-3501 spectrometer. Emission spectra were obtained using a Lab Guide fluorescence spectrophotometer. Quantum yield was measured in an integrating sphere made by Ocean Optics. The sphere has a diameter of 3.81 cm and sample port aperture (0.95 cm.) at the equator. Photoluminescent excitation spectra were obtained from Hitachi F-4500 spectroscopy.

Syntheses

Synthesis of An(DPE)

A mixture of 0.17 g (0.5 mmol) of 9,10-dibromoanthracene, 0.76 mL (4.5 mmol) of 2-hydroxylethanol, and 20 mL of benzene were freeze-dried for three times before cooling down to $-40°C$ to add sec-BuLi (3.80 mL, 5.0 mmol) under nitrogen atmosphere. The whole apparatus was then allowed to rise to 5°C, stirred for few minutes, and then cooled to $-40°C$ again to add 0.24 g (1.2 mmol) of diphenylethylene. The temperature was gradually raised to room temperature and let the reaction continue for another 2 h. Excess degassed methanol was added to quench the reaction and the whole mixtures were subjected to vacuum distillation. The resulting crude product was then separated by column chromatography (eluent: hexane) to obtain the final product with 30% yield. Anal. Calcd for $C_{42}H_{34}$: C, 93.64, H, 6.36. Found: C, 92.86, H, 5.91. ^1H NMR (300 MHz, $CDCl_3$): δ 6.90–7.80 (m, 28 H, aromatic Hs), δ 2.40 (t, 2H, $—(C_6H_5)_2CH$), δ 2.12 (d, 4H, $—CH_2—CH(C_6H_5)_2)$). mp = 169°C. ^{13}C NMR (300 MHz, $CDCl_3$): δ 137.7, 135.3, 132.2, 131.9, 127.9, 126.5, 123.6, 50.1, 41.7. MS: m/z 538.

Synthesis of An-PMMA

Mixture of 34 mg (0.1 mmol) of 9,10-dibromoanthracene, 0.07 mL (0.9 mmol) of 2-hydroxylethanol in 12.2 mL of benzene was freeze-dried for three times and cooled to $-40°C$ before adding sec-butyllithium (0.8 mL, 1.0 mmol). The whole mixture was stirred for 1 h and MMA (20.0 mmol) was then added drop by drop at $-40°C$. The temperature was gradually raised to room temperature and the reaction continued for another 2 h before precipitated from degassed methanol. The precipitates were filtered and dried to obtain the final polymers of An-PMMA. ^1H NMR (300 MHz, $CDCl_3$): δ 3.57 (s, 3H, $COOCH_3$), δ 1.82 (s, 2H, $—C(CH_3)—CH_2—$), δ 0.82 (s, 3H, $—C(CH_3)—CH_2—$). $M_n = 14,300$, PDI = 1.53 (GPC).

Synthesis of An(DPE)-PMMA

Mixture of 34 mg (0.1 mmol) of 9,10-dibromoanthracene, 0.07 mL (0.9 mmol) of 2-hydroxylethanol in 12.2 mL of benzene was freeze-dried for three times and cooled to $-40°C$ before the addition of sec-butyllithium (0.77 mL, 1.0 mmol). The whole mixture was stirred for another 1 h and the temperature was raised to 5°C to add excess diphenylethylene within a period of 1 h. The whole mixture was then cooled to $-40°C$ to add MMA (20.0 mmol) slowly. The temperature was allowed to gradually rise to room temperature and let the polymerization run for 2 h. Degassed methanol was used to precipitate the polymer. The precipitates were then filtered and dried to obtain the final polymers of An(DPE)-PMMA. ^1H NMR (300 MHz, $CDCl_3$): δ 3.57 (s, 3H, $COOCH_3$), δ 1.82 (s, 2H, $—C(CH_3)—CH_2—$), δ 0.82 (s, 3H, $—C(CH_3)—CH_2—$). $M_n = 7900$, PDI = 1.4 (GPC).

RESULTS AND DISCUSSION

Anthracene was incorporated with PMMA by the use of anionic polymerization. As shown in Scheme 1, sec-BuLi reacts with 9,10-dibromoanthrancene to generate lithiated carbanion, which can be used to initiate the anionic polymerizations of MMA monomer to prepare An-centered PMMAs such as An(DPE)-PMMA and An-PMMA. Two primary considerations were for the polymerization. First, lithiated carbanion was generated at low temperature and in the presence of chelating 2-hydroxylethanol to pull out the lithium cation and to generate anion with better activity.[16] Second, in addition to the direct process, polymerization of
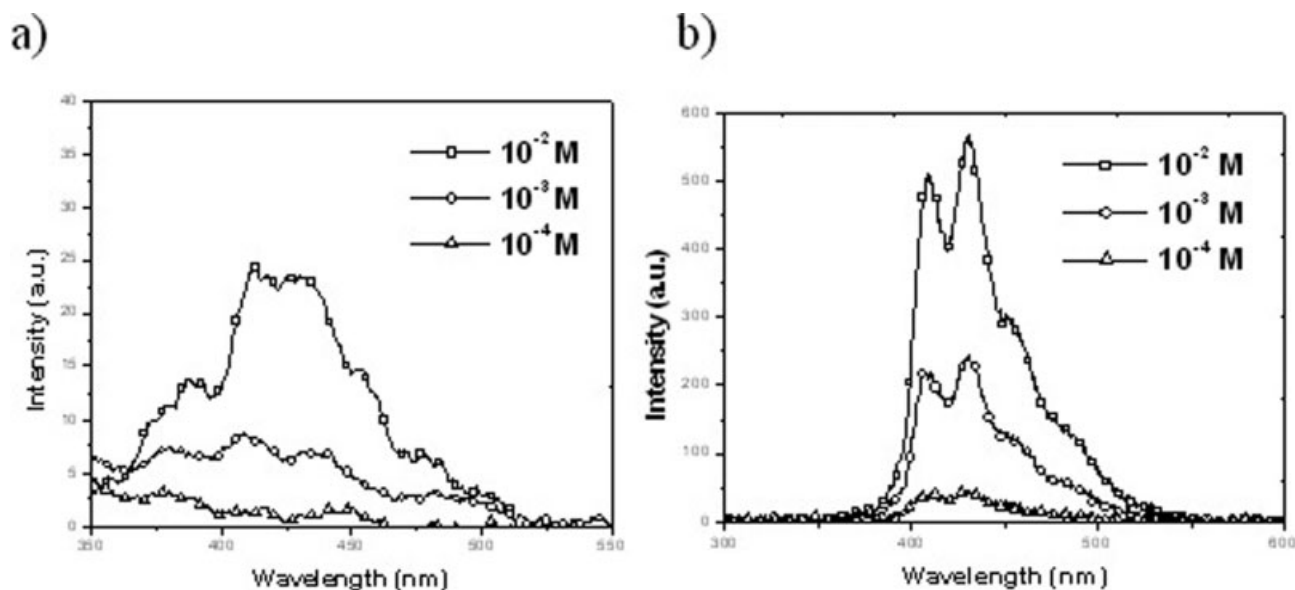
Figure 1 Solution emission spectra of (a) An(DPE)-PMMA and (b) An-PMMA in THF (excited at 250 nm).

MMA was also performed with the participation of 1,1-diphenylethene (DPE), which is supposed to reduce the possible side reaction originating from the nucleophilic addition of the carbanion on the ester carbonyl group of MMA monomer. By adding DPE before polymerization, the resulting anionic species I (cf. Scheme 1) has less nucleophilicity (due to the stabilization effect of the two phenyl rings α- to the anionic center) and proceeds to produce polymer An(DPE)-PMMA upon addition of MMA monomer. Analogous polymerization without DPE resulted in An-PMMA with the polydispersity higher than An(DPE)-PMMA (1.53 versus 1.40). On the aspect of polydispersity, An(DPE)-PMMA has advantage; however, the four phenyl rings β- to the central anthracene ring add complication to the emission pattern, an issue we will discuss later. In addition to An-PMMA and An(DPE)-PMMA, we also prepared model compound An(DPE) by hydrolyzing the anionic specie I (cf. Scheme 1) with methanol according to the procedures described in the Experimental section. This organic compound An(DPE) serves as model for the emission behavior of An(DPE)-PMMA.

Emission spectra of An(DPE)-PMMA and An-PMMA solutions of different concentrations in THF are illustrated in Figure 1(a,b), respectively. The concentration (10^{-4}–$10^{-2}M$) used here only counts the mole of the central fluorophore relative to all diluents, including the connected polymer and the solvent. The trend of the progressive increase of intensity with the fluorophore concentration is visible for both polymers. Notably, the concentration increase does not increase the relative contribution from emission region ≥ 500 nm, at which are the emission ranges for the association forms (e.g., excimer and aggregate)

of the central anthracene ring as we will discuss later. Both spectra exhibit the vibronic band emissions; however, for An(DPE)-PMMA, several minute bands in the ranges of 350–500 nm are visible and the overall band are basically broader than those in An-PMMA, whose emissions contain only three distinct vibronic bands in the wavelength ranges of 400–500 nm.

Model compound An(DPE) was used to clarify the complicated emission pattern of An(DPE)-PMMA. By hydrolyzing the anionic species I with methanol, An(DPE) was prepared and its emission behavior can be served as model for An(DPE)-PMMA. To clarify the role of the four β-phenylene rings, absorption and emission spectra of An(DPE) were given in Figure 2(a). The broad absorption pattern of An(DPE) is possibly due to the complicated π–π interactions between the central anthracene and the neighboring phenylene rings. This complicated absorption pattern also results in a broad emission band with its location similar to those for An(DPE)-PMMA [cf. Fig. 1(a)]. The emission behavior of An(DPE) and An(DPE)-PMMA are basically different from the pure anthracene in the solution and in the condensed solid states as shown in Figure 2(b), in which the discrete emission bands are clearly viewed in all cases. With increasing concentration from 10^{-4} to $10^{-2}M$, anthracene in THF all exhibits the same vibronic emission bands located at 380, 400, and 421 nm (below 500 nm); however, for the pure anthracene solid, a total of six new emission bands with their maxima three below and three above 500 nm are visible. It is difficult to tell the origin for the three bands located below 500 nm but for the three bands at $\sim$ 500, 540 and 580 nm, they may be due to the excimer emission as
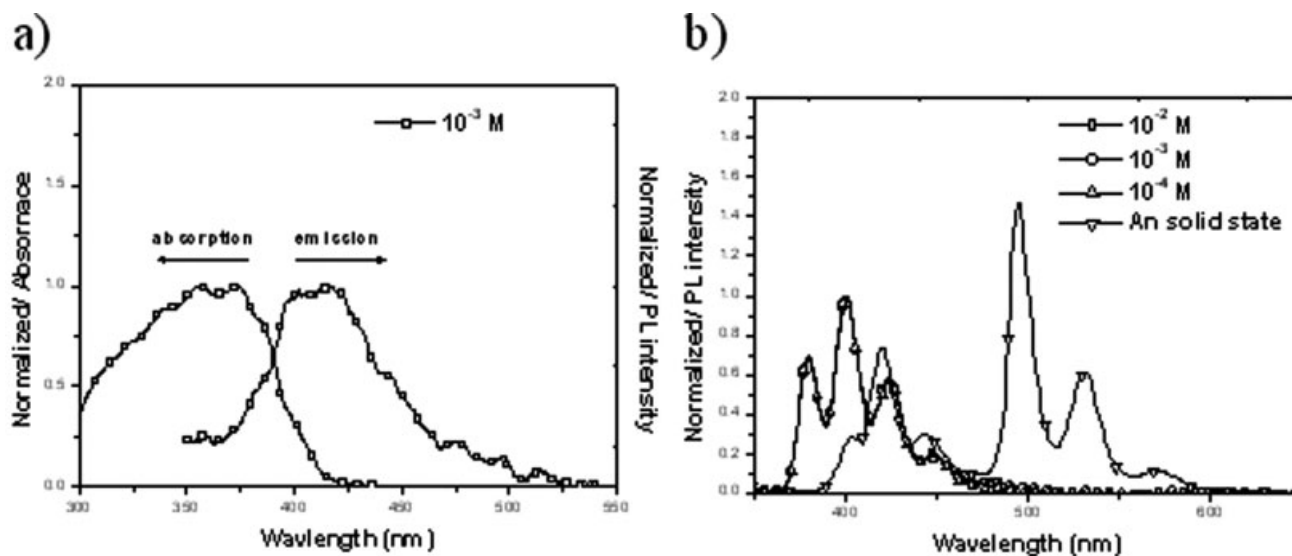
Figure 2 Normalized (a) solution absorption and emission spectra of An-DPE in THF and (b) solution and powder emission spectra of anthracene (excited at 250 nm).

generally occurs in the densely-packed solid state. The different possible orientations between an anthracene pair may contribute to the distinct three-band pattern above 500 nm. Previously, a dimeric compound with two anthracene rings connected to one central $-CH_2CH_2-$ chain had been studied[17,18] to observe the similar emission bands during heating this compound from low temperatures. These bands are attributed to three excimer formations that result from three conformational isomers origination from the varied overlaps and orientations between the two anthracene rings in the same dimer. Reasonably, we suggest that the emission bands above 500 nm are due to the excimer forms in the condensed solid state of anthracene. The distinct emission pattern above 500 nm makes it convenient for the excimer identification. In view of the minor emission intensity at wavelength ≥500 nm in Figure 1(b), a limited excimer emission for An-PMMA is therefore confirmed.

An-PMMA polymer was then examined by PL excitation (PLE) spectrum to find out any other possibility of association forms. Since association among the inherent fluorophores is a function of concentration, An-PMMA solutions of 10^{-2}, 10^{-3} and $10^{-4}M$ in relative to the anthracene units were prepared and examined by PLE. The emissions at 420, 450, 500, and 520 nm were collected and any detectable difference from them was analyzed. As shown in Figure 3, PLE spectra of An-PMMA solutions of different concentrations show similar pattern with the resulting emission maxima excited by light of the same wavelengths (i.e., $\sim$ 350, 365, 380, and 410 nm, respectively). More notably, excitation spectra are basically the same irrespective of whether the

collection wavelength is at 420, 450, 500, or 520 nm, indicating that emissions collected from all four wavelengths are originated from the same excitation mechanism, most possibly from the vibronic band emission. Here, the emissions collected at 500 and 520 nm are primarily concerned, since they are the regions where the association emission mainly occurs. Supposed aggregates exist in the solution state, we may expect higher extents of aggregation in more concentrated solutions (e.g., 10^{-2} versus $10^{-4}M$ solutions). Varied aggregation extents in solutions of different concentrations should result in different spectra collected at ≥ 500 nm, since upon photo-irradiation, aggregations with their varied ground state energy should emit with different patterns. The PLE spectra in Figure 3(c,d) basically follow a similar pattern with those collected at 420 and 450 nm, if disregarding the intensity difference, thereby, no detectable emission from aggregate is evidenced in this case.

Thin film of An-PMMA prepared from the THF solution was then tested by PLE spectrum. Figure 4 shows the result that describes a similar emission pattern with those obtained from the solution state (cf. Fig. 3). If An-PMMA in dilute solution (i.e., $10^{-4}M$) is immune from any association forms, we would expect limited associations existing in the condensed thin film state, since both spectra are similar in appearance. Except the intensity difference, the spectra in Figure 4 follow the same emission pattern disregarding the difference in collecting wavelength, which indicates the involved emission maxima come from the same excitation mechanism (mostly likely, vibronic band emission). This result is virtually the same with the solution cases, suggest-
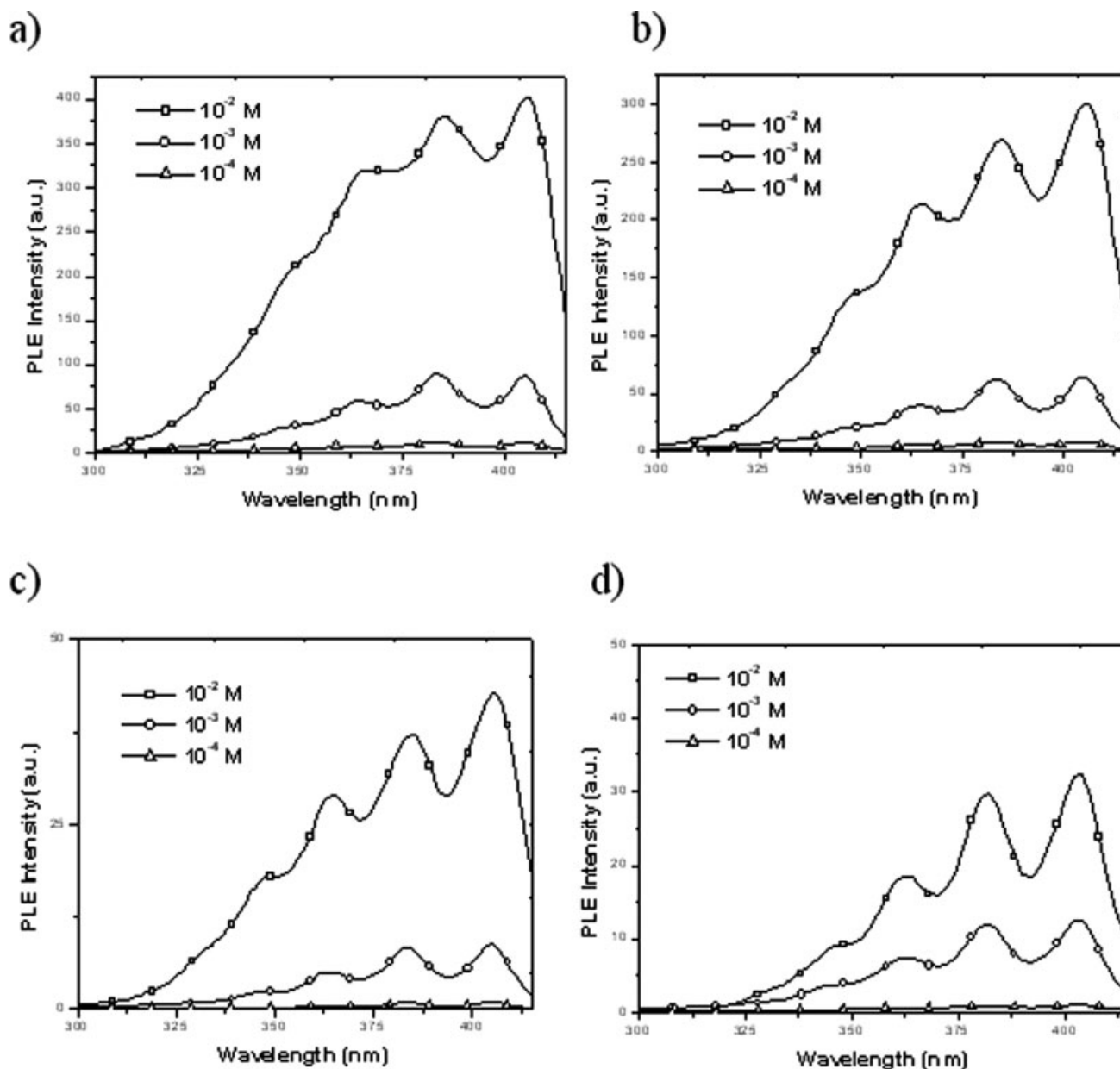
Figure 3 PL excitation spectra of An-PMMA solutions collected at (a) 420, (b) 450, (c) 500, and (d) 520 nm.

ing that aggregation emissions are also limited in the concentrated solid film state.

Thin film of An-PMMA thus prepared was heated to different temperatures before cooled down to test its thermal stability by the corresponding emission spectra. Previous study[19–21] had shown that formation of excimer can be enhanced by thermal annealing, e.g., thermal treatment of the polyfluorenes (PFs) at 200°C induced the corresponding excimer emission band at ∼ 520 nm. The emission spectra shown in Figure 5 are basically similar to each other irrespective of the thermal history of the film samples. Notably, certain treatments performed at temperatures higher than T_g (∼ 120°C) of PMMA segment still resulted in samples without excimer

emission. This observation indicates that even in the isotropic liquid state, the PMMA chains function well as steric blocker for the central anthracene fluorophore.

To compare, blend of anthracene/PMMA (=1.27 wt %) was then prepared from the corresponding solution in THF. Solution of anthracene/PMMA in THF (concentrations = $10^{-3}M$) show an emission pattern (Fig. 6) similar to those for An-PMMA [cf. Fig. 1(b)]. Absence of association emission in this case refers to the fact that anthracene fluorophores can be effectively isolated to each other by the surrounding PMMA polymer chain and the solvent media. However, solid film prepared from this blend solution exhibits an emission spectrum completely
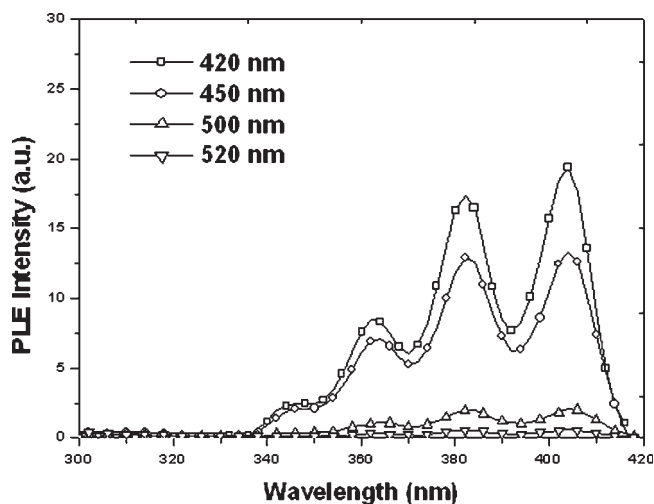
Figure 4 PLE spectra of An-PMMA film collected at different wavelengths.

Figure 6 Normalized emission spectra of anthracene/ PMMA in THF solution ($10^{-3}M$) and in the film state (excited at 250 nm).

different from An-PMMA film. Here, the distinct emissions above 500 nm are identical to those for solid anthracene [cf. Fig. 2(b)] and are attributed to the excimer emissions from solid anthracene crystal. This result indicates that use of PMMA as physical blender is ineffective in suppressing the association tendency of anthracene. With PMMA link to anthracene by chemical bond, An-PMMA is more effective in preventing the association as compared to the blend.

Associations of the fluorophores should affect the quantum yield (Φ_{PL}); therefore Φ_{PL} values of the involved polymers and model compounds were measured and summarized in Table I. For either anthracene or An(DPE), samples in dilute solutions ($10^{-5}M$) have a higher Φ_{PL} value than in its pure solid state, a result related to the possible aggregated
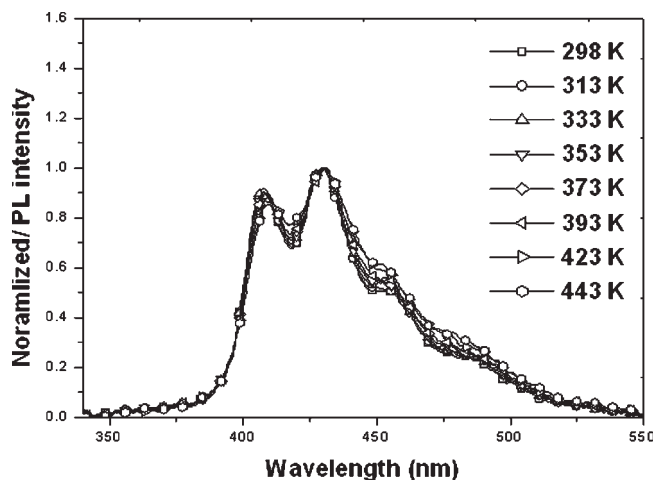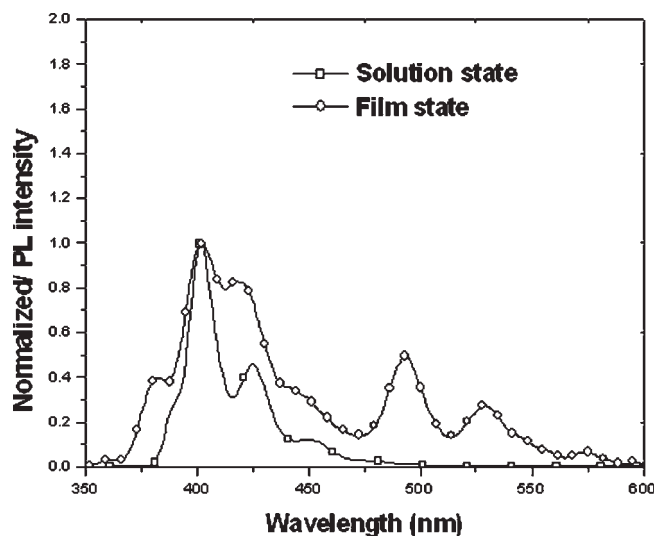
forms in the solid samples. For dilute solution of anthracene in THF, the resulting Φ_{PL} value (33.5%) is comparable to those reported values of anthracene in ethanol (=27%) and in cyclohexane (=30%).[1] In either the solution or solid states, anthracene has a higher Φ_{PL} value than An(DPE), a trend also observed in the solid films of the polymer analogues if we compared Φ_{PL} of An-PMMA (=52%) with An(DPE)-PMMA (=32%). It is then confirmed the interference effect of the four phenyl rings β to the central anthracene ring. In coordinating to the spectra result, anthracene/PMMA film shows a Φ_{PL} value (=20%) lower than that for An-PMMA, indicating the ineffectiveness of PMMA as physical blender to isolate the anthracene fluorophores.

Figure 5 Absorption and emission spectra of An-PMMA after heated at elevated temperatures (excited at 250 nm).

TABLE I
Quantum Yield of Model Compound, Anthracene, An(DPE), Anthracene/PMMA Blend and Polymer An-PMMA, An(DPE)-PMMA

Sample	Quantum yield Φ_{PL} (%)
Anthracene	33.5[a], 16.7[b]
An(DPE)	17.7[a], 7.2[b]
An-PMMA[c]	52[b]
An(DPE)-PMMA[c]	32[b]
Anthracene/PMMA[c]	20[b]

[a] Quantum yield was determined from dilute solution ($10^{-5}M$) in THF.
[b] Evaluated from thin film of An-PMMA, An(DPE)-PMMA, and anthracene/PMMA blend (=1.27 wt %) or from solid state of anthracene and An(DPE).
[c] Thin film prepared from the corresponding solution (concentration = $10^{-3}M$) in THF.

CONCLUSIONS

An-centered PMMAs, An(DPE)-PMMA and An-PMMA, can be successfully prepared via the anionic polymerization in the presence of chelating agent, 2-methoxyethanol. Use of DPE before the addition of MMA monomer will produce An(DPE)-PMMA with smaller polydispersity than An-PMMA from direct polymerization; however, the β-diphenyl rings thus generated can be potential light absorber and result in the reduction of the corresponding emission. In any case, the build-in PMMA chains are more effective steric blockers compared to PMMA in anthracene/PMMA blend. The chemical-linked PMMA in An-PMMA effectively inhibits the associations of the central anthracene rings, which result in higher Φ_{PL} values than the monomer analogues, anthracene, and An(DPE).

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