Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 180 (2006) 136–142

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Quantum yield enhancement of photoluminescent polycyanate resin by blending with 1-pyrenecarboxylic acid

Cheng-Wei Chiu[a], Jin-Long Hong[a,*], Fu-Kun Su[a], Cheng-Long Chen[b]

[a] *Institute of Materials Science and Engineering, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, ROC*
[b] *Department of Chemistry, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, ROC*

Received 10 July 2005; received in revised form 3 October 2005; accepted 11 October 2005
Available online 29 November 2005

Abstract

Polycyclotrimerization of aromatic dicyanate (i.e. bisphenol A dicyanate (BPADCy)) generates photoluminescent (PL) polycyanate (PCn) crosslinked resin with *s*-triazine ring as the interconnecting point. This inherent *s*-triazine ring in PCn resin is hydrogen-bond (H-bond) acceptor; therefore, an H-bond donor, 1-pyrenecarboxylic acid (PCA), was used in this study to mix and to co-cure with BPADCy to prepare miscible thin films of PCn/PCA blends through the favorable H-bond interactions. The resulting PCn/PCA blends show their emission patterns characteristic of the PCA and PCn components. An energy transfer process from the PCn matrix to the incorporated PCA is the dominant emission process. Addition of ∼0.7 wt% of PCA in PCn results in the great enhancement on the PL quantum yield from a value of 3.9% for the pure PCn to 54.8% for the corresponding blend.

Keywords: Polycyanate; 1-Pyrenecarboxylic acid; Energy transfer; Quantum yield

1. Introduction

Polycyclotrimerization of aromatic dicyanate generates crosslinked polycyanate (PCn) network with *s*-triazine as the interconnecting points (Scheme 1) [1–3]. The resulting PCn resins with the superior dielectric properties, thermal and dimensional stability have facilitated their applications in the area of circuit board fabrications. To improve the toughness toward impact, several thermoplastics [4–7] such as poly(ethyloxazoline), poly(vinylpyrrolidone), poly(ether imide), polysulphone and poly[(ethyl acrylate)-*co*-(acrylic acid)] (PEAc) had been previously used to blend with PCn. Among the above blending systems, PEAc/PCn blend [7] is homogeneous in nature due to the favorable hydrogen-bond (H-bond) interactions between the carboxylic acid (–COOH, as H-bond donor) in PEAc and the *s*-triazine (as H-bond acceptor) ring in PCn resin. Earlier study [3,8,9] by infrared and ^{19}F NMR on model compounds also suggested that the *s*-triazine rings in PCn resin are good H-bond acceptors. It means that through favorable H-bond interaction, miscible blends of PCn and components containing H-bond donating (e.g. –COOH) groups can be prepared.

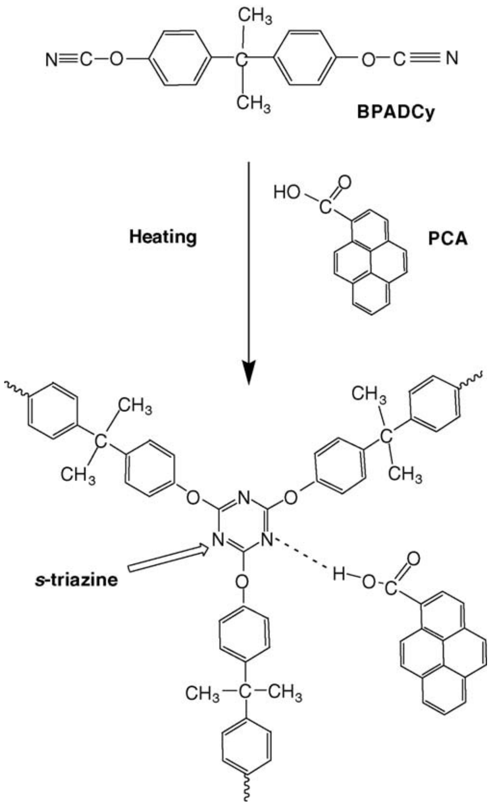
Discovery of fluorescence emission of the cured bisphenol A dicyanate (BPADCy) [10] further extended the applicability of the PCn resin. During cure of BPADCy at 200 °C, the fluorescence emission intensity around 420 nm first increases and then decreases, a trend was claimed to be due to the inner filter effect. Subsequent study on several model compounds [11] concluded that the origin of the observed fluorescence during cure is due to the crosslinker which possesses the aryl *s*-triazine framework (i.e. trimer with central *s*-triazine ring). In addition to the observed fluorescence, phosphorescence at low temperature (77 K) was also reported to vary its intensity with the curing time.

The photoluminescent (PL) property of PCn resin is unexpected in view that the crosslinked structure (cf. Scheme 1) contains no extended resonance structure as usually present in the traditional light-emitting polymers. The absence of extended resonance may be also responsible for the low fluorescence quantum yield (∼3.9%, Φ_F), which greatly restricts its applicability. With regards to the advantageous thermal and electrical stability of the PCn resin, a way to improve its Φ_F was sought in

---

[*] Corresponding author.
E-mail address: jlhong@mail.nsysu.edu.tw (J.-L. Hong).

1010-6030/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2005.10.005



Scheme 1. Polycyclotrimerization of aromatic dicyanate BPADCy and the potential H-bonding of PCA to BPADCy monomer and to the cured PCn.

our laboratory. One simple, reasonable approach is the blending of PCn resin with traditional organic fluorophores with high Φ_F. In considering the H-bond accepting character of the *s*-triazine ring in PCn resin [3,8,9], it is reasonable to use organic fluorophores with inherent H-bond donating group as co-component to homogenously mix with the PCn resin. With this regard, organic fluorophoric 1-pyrenecarboxylic acid (PCA) was chosen in this study in view of its high Φ_F value (=70%) and its capability to H-bond to the *s*-triazine ring through its inherent –COOH group. The resulting PCn/PCA blends of different compositions were characterized in an effort to recognize the H-bond interactions and the dependence of the emission behavior on the degree of association among the aromatic (including *s*-triazine) rings in the PCn resin and in the incorporated PCA.

2. Experimental

2.1. Materials and sample preparations

Tetrahydrofuran (THF) was distilled from a mixture of sodium and benzophenone before use. PCA (from Aldrich) and BPADCy (from Lonza) were used directly without further purification.

BPADCy and PCA were dissolved in THF firstly and then vacuum distilled to yield homogeneous mixture before heated to cure in a stainless apparatus pre-set at 200 °C. The curing was performed at 200 °C for different times under nitrogen flow. Conversion after curing at 200 °C for 160 min was estimated to be 90% according to the exothermic heat evolved during scanning the corresponding samples in differential scanning calorimeter (DSC). The resulting cured products were designated by their molar ratios between PCA and BPADCy applied in the preparation stage (cf. Table 1).

2.2. Instrumentation

Biorad FTS-115 Fourier transform infrared spectrometer was used to probe the H-bond interactions. A cured thin film sample was applied for all samples except the pure PCA powder (KBr pellet). Curing exotherms determined from a Perkin-Elmer DSC 7 model were used to measure the extent of conversion. X-ray diffraction (XRD) was performed with a Siemens Diffraktomerter D 5000 model with Ni-filtered Kα radiation. UV–vis spectra were obtained form a Hitachi U-350 spectroscopy. Emission spectra were obtained from a Lab Guide fluorescence spectrophotometer. Quantum yields were measured in an integrating sphere made by Ocean Optics Inc. The sphere has a diameter of 1.5 in. and sample port aperture (0.375 in.) at the equator. PL excitation (PLE) spectra were obtained from a Hitachi F-4500 fluorescence spectrophotometer.

3. Results and discussion

Calculated amounts of BPADCy and PCA monomer mixtures were cured at 200 °C for 160 min to obtain thin films with the desired PCn/PCA content. All the cured blends have a cyanate conversion of ~90% according to the heat evolved during DSC scans. Selected cured products are shown in Table 1, in which the samples were designated according to their relative molar ratio between BPADCy and PCA applied in the preparation stage. The cured blend with the highest PCA content (i.e. PCn/PCA = 1/0.1) still has the inherent carboxylic acid (–COOH) groups less than the potential H-bond accepting sites (i.e. the nitrogen atoms in the *s*-triazine) in the PCn matrix. All the cured PCn/PCA blends are transparent despite the fact that pure PCA molecules are crystalline. The transparent appearance also indicates that the cured blends are amorphous at least in a macroscopic scale.

Infrared spectra of PCA, BPADCy-derived PCn and the cured PCn/PCA blends in Fig. 1 can be used to evaluate the potential H-bond interactions within the blends. The BPADCy-derived PCn has the characteristic –C=N– stretching of the *s*-triazine ring at 1375 and 1565 cm^{-1}, respectively. For the pure PCA, the carbonyl (–C=O) stretching due to the H-bonded carboxylic acid in the dimeric form locates at 1677 cm^{-1}. The cured PCn/PCA = 1/0.01 and 1/0.5 blends have their –C=O stretching at a higher wavenumber of 1737 cm^{-1}, instead. Previous study on poly(acrylic acid) and poly(4-vinyl pyridine) [12] blends indicated that the –C=O group of the carboxylic acid, once H-bonded to the pyridine ring, has its stretching appeared at 1741 cm^{-1}. Suggestively, the *s*-triazine rings in PCn have similar H-bonding sites (–C=N–) as the pyridine ring; therefore, peak at 1737 cm^{-1} is supposed to be due to the H-bonded carboxylic acid in PCA.

Bonding situation of PCA in the blends can be also evaluated from the XRD pattern given in Fig. 2. Pure PCA powder

Table 1
Compositions used in the preparation of PCn/PCA blends

Sample	Mole ratio between the starting monomers (BPADCy/PCA)	Weight ratio between the starting monomer	Quantum efficiency (%)
PCn/PCA = 0/1[a]	0/1[a]	0/1[a]	70 (in CH_2Cl_2)[b]
PCn/PCA = 1/0.1	1/0.1	1/0.093	27.8
PCn/PCA = 1/0.05	1/0.05	1/0.0465	30
PCn/PCA = 1/0.025	1/0.025	1/0.023	38.3
PCn/PCA = 1/0.01	1/0.01	1/0.0093	50.6
PCn/PCA = 1/0.0075	1/0.0075	1/0.0069	54.8
PCn/PCA = 1/0.005	1/0.005	1/0.046	42
PCn/PCA = 1/0.0025	1/0.0025	1/0.0023	40.7
PCn/PCA = 1/0.001	1/0.001	1/0.00093	14.2
PCn/PCA = 1/0.00002	1/0.00002	1/0.000019	11.9
PCn/PCA = 1/0[c]	1/0[c]	1/0[c]	3.9

[a] Pure PCA.

[b] Reported value from Ref. [13].

[c] Pure polycyanate.

shows various diffraction peaks due to its crystalline structure. In contrast, BPADCy-derived PCn is basically amorphous in view of the broad diffraction pattern in the ranges of $2\theta \sim 10–30°$. Careful inspection reveals that the diffraction actually consists of two in-separate, broad diffraction centering at $2\theta \sim 16°$ (d-spacing = 5.4 Å) and 20° (d-spacing = 4.5 Å, indicated by arrow), respectively. In contrast, the cured PCn/PCA blends exhibit only broad diffraction at similar position with the pure PCn. Here, no distinct crystalline diffraction is detected in the cured blends; therefore, PCA molecules should be no longer crystalline once they were incorporated in the PCn matrix, a result correlated to the fact that PCA molecules in the cured blend are not self-associated as in the dimer form but rather H-bonded to the *s*-triazine ring. The H-bond interaction between PCA and PCn is assumed to destroy the crystalline structure of the virgin PCA. The bonding situation will be further discussed in order to correlate with the emission behavior of the blends.

Emission spectra of the PCn/PCA blends are compared to the pure PCn resin in Fig. 3. Pure PCn has a major emission at 430 nm along with a minor right-shoulder at ~480 nm, a pattern similar to the previous report [10]. With small amounts of PCA component, PCn/PCA = 1/0.00002 exhibits two emission peaks at 430 and 480 nm in addition to a shoulder-like peak at ~450 nm. Here, the relative intensity between 430 and 480 nm bands is not the same with the pure PCn, which indicates the emission mechanisms involved in the pure PCn and in the blends are not the same. Films of PCn/PCA = 1/0.001 and 1/0.02 exhibit no emission at 430 nm and instead, a major emission at 480 nm and a minor emission at 450 nm result. Here, the minor band at 450 nm decreases its intensity with increasing PCA content. The emission pattern shown in Fig. 3 suggests that amounts of the incorporated PCA have a strong influence on the emission of the PCn matrix. Further increase of PCA content to PCn/PCA = 1/0.1 results in one single emission band at ~520 nm. Absence of the characteristic emissions of the pure PCn resin suggests that the main emitter in blends of high PCA content (e.g. PCn/PCA = 1/0.1) is the PCA component rather than the PCn matrix. The cured blends illustrate a rather complicated emission pattern since the referred emissions locate at four different wavelengths of 430, 450, 480 and 520 nm.

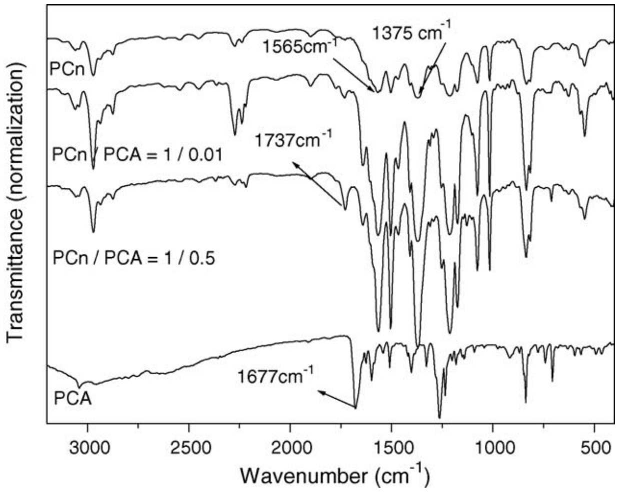


Fig. 1. Infrared spectra of PCA, PCn and selected PCn/PCA blends.

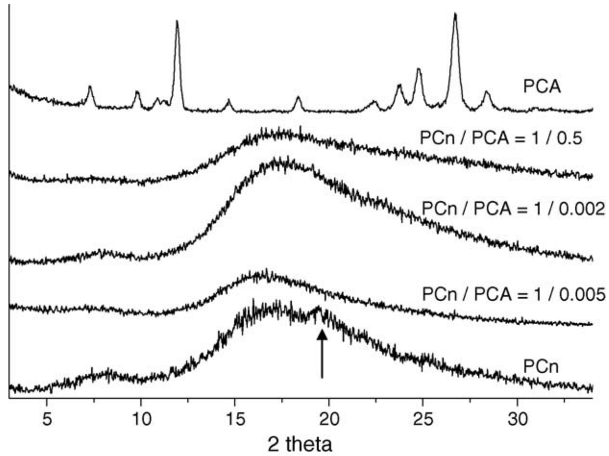


Fig. 2. Wide-angle X-ray diffraction patterns of PCA powder, PCn and PCn/PCA blend.

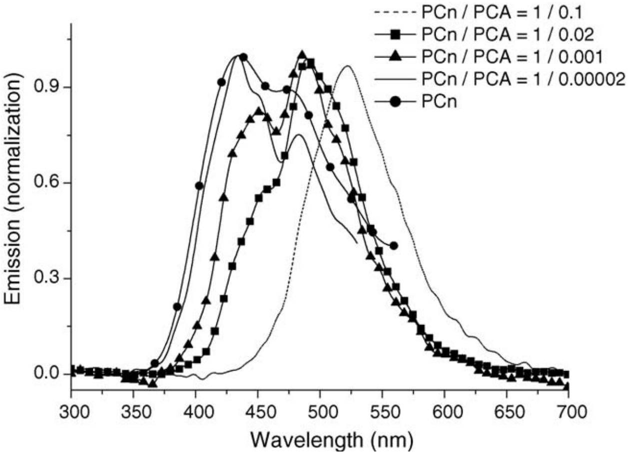


Fig. 3. Emission spectra of PCA powder, PCn and selected PCn/PCA films excited at 256 nm (normalized).

PL excitation spectra were further applied to the selected samples of PCn/PCA = 1/0.00002 and 1/0.001 in order to evaluate the origin of the complicated emissions. The emissions at 430, 450, 480 and 520 nm were collected and illustrated in Fig. 4. PLE spectra for both samples show a similar feature irrespective of the collecting wavelengths, indicating that the four emissions basically come from the same origin. For PCn/PCA = 1/0.00002, the short-wavelength (275–350 nm) excitation contributes to the resulting emissions. For PCn/PCA = 1/0.001, the emissions collected are attributed to both the short-wavelength (275–359 nm) and the long-wavelength (>350 nm) excitations. The long-wavelength (major) excitation contributes most of the emissions collected in comparison to the short-wavelength (minor) excitation, which is different from the situation for PCn/PCA = 1/0.00002 sample. The gradual upward curvature in between the minor and major emissions indicates continuous excitation exists in the intermediate-wavelength ranges.

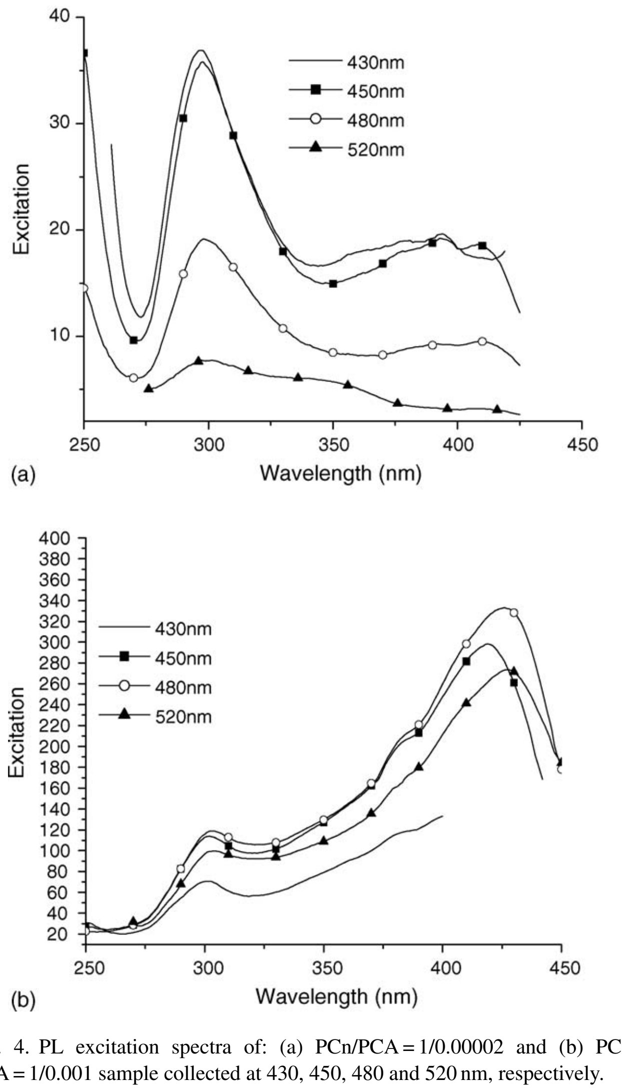


Fig. 4. PL excitation spectra of: (a) PCn/PCA = 1/0.00002 and (b) PCn/PCA = 1/0.001 sample collected at 430, 450, 480 and 520 nm, respectively.

Incorporation of PCA in PCn resin has substantial effect on the fluorescence quantum yield (Φ_F). Pure PCA in CH_2Cl_2 [13] has a high Φ_F value of 70%; in contrast, pure PCn resin has a low Φ_F value of 3.9%. With incorporation of small amounts of PCA, PCn/PCA (1/0.00002) sample has a Φ_F value of 11.9%. Continuous introduction of PCA causes further increase of Φ_F to a highest value of 54.8% for PCn/PCA = 1/0.0075. Here, the content of PCA is less than 1 wt% and the effect on Φ_F is substantial. Further increase of PCA content makes the reverse effect in which the corresponding Φ_F drops from 50.6% for PCn/PCA = 1/0.01 to 27.8% for PCn/PCA = 1/0.1. The results should be related to the association condition of PCA molecules in the PCn matrix since PCA is supposed to be the major fluorescent component in the blend according to the emission study above.

The emission and PLE spectra provided above suggest the operation of energy transfer process from PCn to PCA. This energy transfer process is supposed to occur readily because of the short inter-ring distances between the *s*-triazine and/or the aromatic phenylene rings in the dense crosslinked structure (density = 1.18 g/cm^3) [1] and the favorable H-bond interactions between *s*-triazine ring and PCA. The H-bonding of the *s*-triazine ring to PCA may also keep the lone pair electrons of the nitrogen atoms from entering the intersystem crossing process upon excitation and this will enhance the fluorescence intensity. Nevertheless, this factor should contribute minor since in some blends, the amounts of the incorporated PCAs are only negligible compared to the inherent *s*-triazine rings. The controlling factor should be the key emitter, PCA. Despite its small PCA content (<1 wt%), PCn/PCA = 1/0.0075 has a high Φ_F value of 54.8%. To understand the possible association forms of PCA in the blend, basic properties of pure PCA and PCA in other polymer matrix should be understood.

To probe for the possible arrangement of PCA in the present system, emission of pure PCA at different states was investigated beforehand. As illustrated in Fig. 5, dilute solutions (1×10^{-3} and 1×10^{-4} M) of PCA in THF exhibit only vibronic bands with emission maxima at 386, 406 and 427 nm, which correlate well with the reported [14]. With increasing concentration to 10^{-2} M, extra broad band (centered at ∼505 nm) in corresponding to excimer emission starts to emerge. For solid PCA, only broad emission due to the possible solid-state aggregates is visible at 512 nm. Here, the association (excimer or aggregate) emissions in Fig. 5 center in the ranges of 505–512 nm;

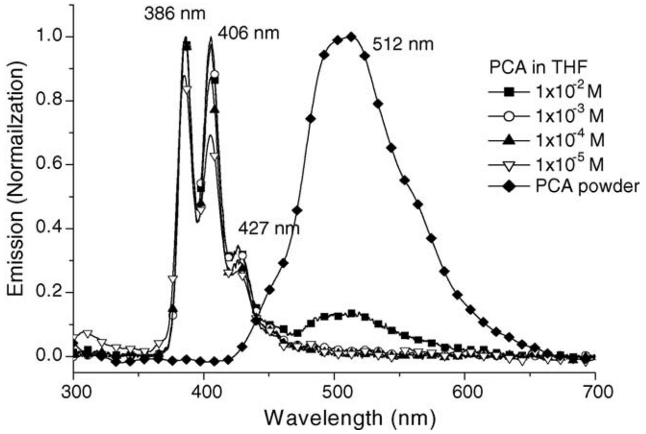


Fig. 5. Emission spectra of PCA solutions of different concentrations in THF and solid PCA (excited at 280 nm).

however, a different association emission is expected for the PCn/PCA blends since in this case, the PCA molecules are confined in the crosslinked structure and the corresponding association forms may be frozen into different patterns (in terms of inter-ring distance and dihedral angle). The influence of matrix on the emission behavior of PCA can be further demonstrated by incorporating PCA molecules with another polymer matrix.

By choosing a non-fluorescent polymer to replace the fluorescent PCn matrix, we may be able to clarify the packing pattern of PCA in PCn. With this purpose, PMMA was used to have a PMMA/PCA blend system, in which an analogous H-bond interaction between carboxylic acid in PCA and ester (–$COOCH_3$) carbonyl group in PMMA exists. PMMA and PCA components were thoroughly mixed by the use of THF solvent and after removal of THF, solid films of different compositions were obtained. Emission spectra of the selected films in Fig. 6 show the vibronic bands at the same positions of 386, 406 and 427 nm and the broad aggregate emission band (∼490 nm) in samples of high PCA content (i.e. weight ratio of PMMA/PCA = 1/0.124 and 1/0.074). It means that sufficient amounts of PMMA (as in sample of PMMA/PCA = 1/0.025 weight ratio) are required to H-bond to all the PCA molecules and to isolate each of them by the polymer chains; therefore, no emission due to the association forms generates. Here, aggregate emission of PMMA/PCA blend locates at wavelength different from that of the pure PCA powder (490 nm versus 512 nm), which also indicates the influence of the polymer matrix on the packing situation of the PCA molecules.

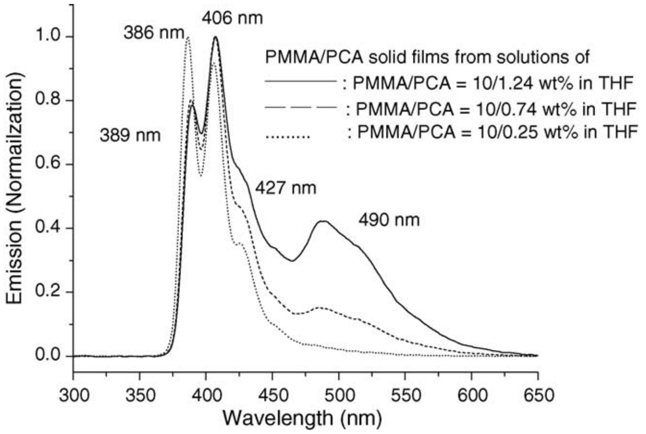
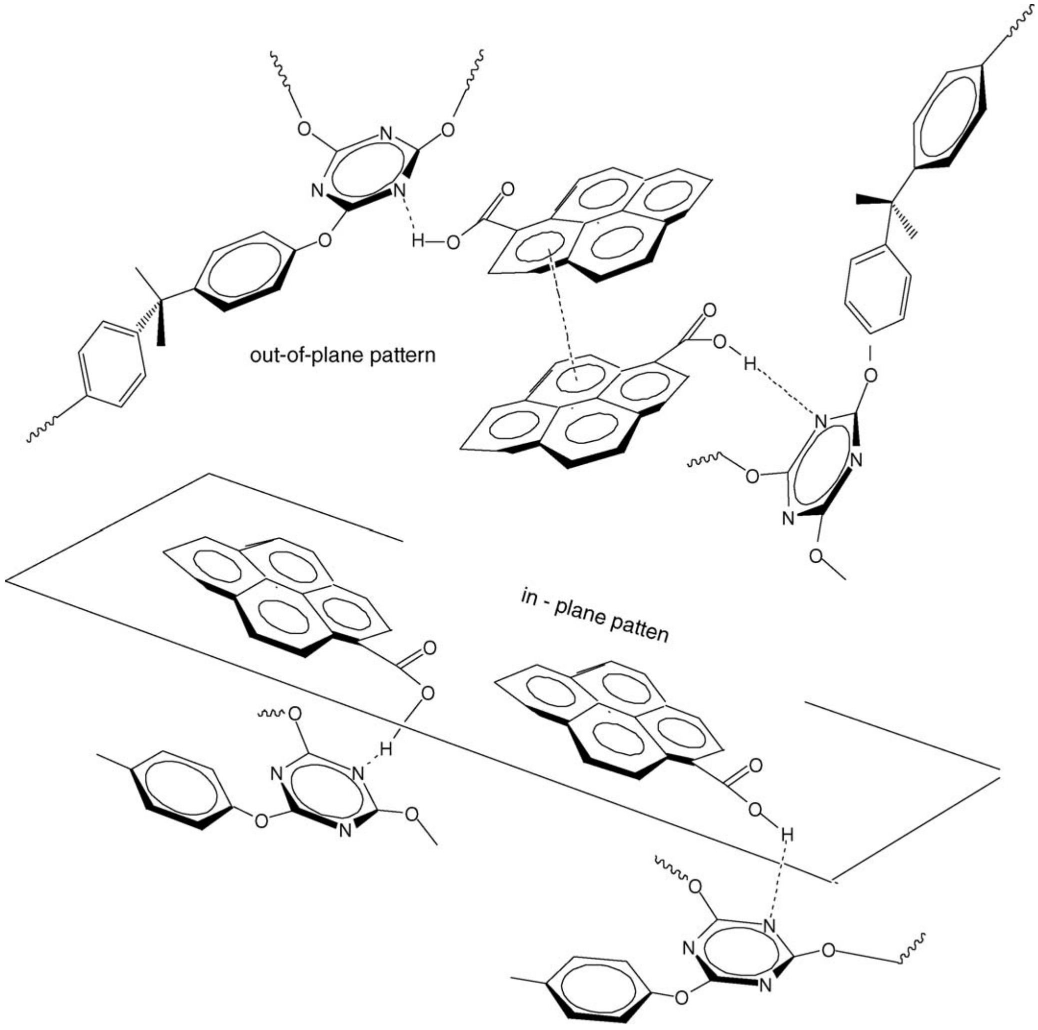


Fig. 6. Emission spectra of PMMA/PCA films prepared from the PMMA/PCA solutions of different concentrations (as indicated in the figure) in THF (excited at 280 nm).

As illustrated in Fig. 2, XRD pattern of the pure PCn resin consists of two broad, in-separate diffractions centered at $2\theta \sim 16^\circ$ (d-spacing = 5.4 Å) and 20° (d-spacing = 4.5 Å). Previous study on polythiophene prepared from electrochemical polymerization revealed a similar XRD pattern with the in-plane and out-of-plane d-spacings at 5.0 and 3.5 Å, respectively [15]. In view of the close d-spacing values in our system with those in polythiophene, near in-plane and out-of-plane packings are supposed to exist in the phenylene and/or the *s*-triazine rings of the PCn resin. The crosslinked structure of PCn tends to confine the inherent phenylene and/or the *s*-triazine rings in favorable distances (e.g. 4–5 Å), which may promote facile $\pi-\pi$ interactions among the neighboring aromatic rings. These $\pi-\pi$ interactions among aromatic rings can be the origin of the emission for the PCn resin. Due to the limited instrumental analysis available on the insoluble, infusible crosslinked system, computer simulation on PCn system is attempted in our laboratory in order to evaluate the relationship between the association pattern of phenylene (or *s*-triazine) rings and the XRD result.

The cured PCn/PCA blends have their emissions at wavelengths longer than the vibronic bands ($\lambda_{\max}$ = 386, 406 and 427 nm) shown for pure PCA, which suggests most of the PCA molecules are situated in the association forms (excimer or aggregate). Emission spectra in Figs. 5 and 6 suggest that the aggregate emissions in pure PCA powder and PMMA/PCA blends locate at different wavelengths, which emphasizes the important roles of the aggregate structure (or the influence of the matrix on the structure). Scheme 2 briefly illustrates the extreme association forms of the H-bonded PCA molecules, i.e. in-plane and out-of-plane patterns, in the PCn matrix. The PCA molecules may be associated in the in-plane and out-of-plane patterns or in any other forms with intermediate conformations dependent on the interchain space available for them (considering the tightly held crosslinked structure). Conceivable, the out-of-plane pattern will be more efficient than the in-plane pattern in accommodating PCA molecules inside the limited space of the crosslinked chains. In addition, PCA molecules associated in a near out-of-plane arrangement will have more intimate $\pi-\pi$ interactions than those with the in-plane pattern, and this will influence the corresponding emission bands. It is then postulated that the H-bonded PCA molecules tend to associate to each other in considering their planar and polyaromatic (extensive $\pi-\pi$ overlapping is expected) structure. Association among PCA molecules still occurs even in sample of low PCA content (e.g. PCn/PCA = 1/0.00002) since some of its emissions (bands at 450 and 480 nm) appear at wavelengths longer than those of the vibronic bands of the pure PCA itself. Association becomes prevalent in blends of high PCA contents and it results in the increasing contribution of the near out-of-plane packing and the intimate $\pi-\pi$ interactions among the PCA molecules, leading to long-wavelength emission at 480 nm. With low PCA con-



Scheme 2. Schematical illustration of the PCA associating forms in the PCn matrix.

tent (e.g. PCn/PCA = 1/0.01), the added PCA molecules emit efficiently without much energy loss. However, conceivable associations occur if PCA content is high (e.g. PCn/PCA = 1/0.1) and in this case, the accompanied non-radiative energy transfer process directly leads to the reduction of Φ_F value (from 54.8% for PCn/PCA = 1/0.0075 to 27.8% for PCn/PCA = 1/0.1). Extensive association can be evidenced for the resolving red-shift to λ_{max} = 520 nm for PCn/PCA = 1/0.1 sample.

Cured product of PCn/PCA = 0.005 sample was selected to prepare thin films of different thickness. As shown in Fig. 7, the three films with thickness ranging from 0.18 to 0.46 nm all exhibit good transparency as evidenced by the clear view of the "NSYSU" mark on the background. With the highest PCA content, PCn/PCA = 1/0.1 is also transparent by the appearance. In general, transparency of the sample films indicates the absence of macroscopic aggregation of PCA molecules in PCn matrix. A transparent sample contributes to an unambiguous characterization on the emission properties by excluding the possible light scattering by any existing PCA crystalline aggregates in the text samples.

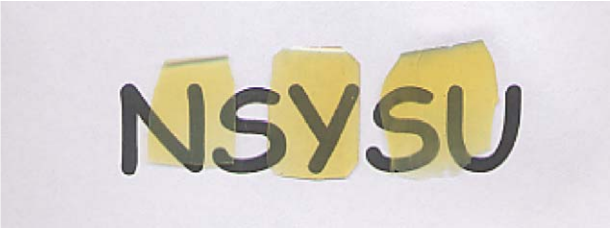


Fig. 7. Transparent PCn/PCA = 0.005 sample films with thickness from 0.18 mm (right), 0.28 mm (middle) to 0.46 mm (left).

4. Conclusion

PCn/PCA blends can be prepared by curing the homogeneous mixtures of PCA and BPADCy. Due to the H-bond interactions between PCA and PCn, the resulting products are macroscopically miscible in all compositions as judged from the transparent appearance of the products. The PCn/PCA blends exhibit emission spectra dependent on their relative compositions. An energy transfer process from the photo-excited PCn to PCA occurs, resulting in a more efficient emission in the PCn/PCA blends as compared to the pure PCn resin. Value of Φ_F increases with the PCA contents from 11.9% for

PCn/PCA = 1/0.00002 to 54.8% for PCn/PCA = 1/0.0075. Further addition of PCA, however, results in the decrease of Φ_F value (27.8% for PCn/PCA = 1/0.1). It is then suggested that associations among the incorporated PCAs in the PCn matrix play important role on the final emission behavior. With small amounts of PCAs in the blends, PCAs packed in an efficient manner and emit with less energy loss. As expected, the fluorescence efficiency of pure PCn can be greatly enhanced with the addition of organic PCAs. With high PCA content, associations of PCAs are serious and result in the prevalence of non-radiative energy transfer pathway and the reduction of the quantum yield.

References

[1] A.W. Snow, in: I. Hamerton (Ed.), Chemistry and Technology of Cyanate Ester Resins, Chapman and Hall, London, 1994 (Chapter 2).

[2] E. Grigat, R. Pütter, Angew Chem., Int. Ed. 6 (1967) 206.

[3] E. Grigat, R. Pütter, Chem. Ber. 97 (1964) 3012.

[4] J.A. Feldman, J. Huang, in: R.A. Dickie, S.S. Labana, R.S. Bauer (Eds.), Crosslinked Polymers, ACS Symposium Series, vol. 367, 1988, p. 245.

[5] E.M. Woo, D.A. Shimp, J.C. Seferis, Polymer 35 (1994) 1658.

[6] E.M. Woo, A.C. Su, J.F. Kuo, J.C. Serfris, Macromolecules 27 (1994) 5291.

[7] J.L. Hong, H.J. Lin, Macromol. Chem. Phys. 200 (1999) 845.

[8] D.W. Brause, R. Radeglia, J. Prakt. Chem. 312 (1970) 797.

[9] A.W. Snow, J.P. Armistead, Am. Chem. Soc., Polym. Mater. Sci. Eng. Prepr. 66 (1991) 508.

[10] Y.E. Xu, C.S.P. Sung, Macromolecules 35 (2002) 9044.

[11] Y.E. Xu, C.S.P. Sung, Macromolecules 36 (2003) 2553.

[12] L. Wang, Y. Fu, Z. Wang, Y. Fan, X. Zhang, Langmuir 15 (1999) 1360.

[13] C. Yao, H.B. Kraatz, R.P. Steer, Photochem. Photobiol. Sci. 4 (2005) 191.

[14] B.H. Milosavljevic, J.K. Thomas, J. Phys. Chem. 92 (1988) 2997.

[15] S. Jin, S. Cong, G. Xue, H. Xiong, B. Mansdorf, S.Z.D. Cheng, Adv. Mater. 14 (2002) 1492.