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Enhancement of Fluorescent Intensities of Poly(quinoline)s in Solution and in the Solid State

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ABSTRACT: Poly(2,6-[4-phenylquinoline]), **I**, and poly(2,6-[*p*-phenylene]-4-phenylquinoline), **II**, were synthesized by the self-condensation of 5-acetyl-2-aminobezophenone and 4-amino-4′-acetyl-3-benzoylbiphenyl, respectively. They were soluble in acidic solvents. The UV λ_{max} of **I** in aqueous H_2SO_4 did not change over wide acidity ranges, but the molar extinction coefficient increased with acidity. In low-acidity solutions two broad featureless fluorescent emission peaks at around 450 and 500 nm were observed, whereas in high-acidity solutions (e.g., 96% H_2SO_4), the peak at 500 nm disappeared and the peak at 450 nm greatly increased in intensity. The fluorescent properties of **I** and **II** were investigated as a function of concentration in HCOOH, CCl_2HCOOH, and CH_3SO_3H solutions. At about ~0.5 g/dL, only broad, featureless emission peaks appeared, but in dilute solutions (~0.0005 g/dL) the peaks were blue-shifted and the intensity was greatly increased (>600 times). These results were explained by the formation of an aggregate/excimer in concentrated solutions; upon dilution, the polymer chains were separated, resulting in decreased aggregation quenching. Thin films of **I** and **II** have similarly shaped UV absorption spectra (**I**, λ_{max} 440 nm; **II,** $\lambda_{max} \sim 400$ nm) and broad emission spectra at 550−600 nm. Films of the polymers **I** and **II** blended with poly(vinyl alcohol) (PVA) were prepared. When the quinoline content in the blend is high (quinoline polymer:PVA = 1:1 by weight), the emission peak at 550 nm is broad with low intensity; however, upon increasing PVA concentration, the emission peak shifted to a lower wavelength, ~450 nm, and the intensity was greatly increased. The broad emission peaks at 550 nm correspond to the excimer emission, and the high-intensity emission peaks at around 450 nm were due to the excited state of the isolated chains of the polymers, as a result of dilution. The emission peaks at around 470 nm also appeared when the quinoline moieties of the polymers were protonated or partially methylated and intensities were very high. All these observations suggest that when the amount of positive charge on the nitrogen atom of quinoline reaches a critical value, intermolecular electrostatic repulsion reduces aggregate formation.

Introduction

Electroluminescence devices utilizing π-conjugated polymers as emitting layers have become a subject of great interest since the first report of electroluminescence devices (LEDs) based on poly(phenylenevinylene) in 1990.[1] The application of conjugated polymers as active emitting layers in LEDs offers several advantages such as easy processing by solvent or spin castings from solution and the chemical tailoring of the emitting wavelength.[2,3]

Blue light emitting diodes using poly(pyridine) as the emitting layer have been reported.[4,5] The polymer is soluble in acidic solvents such as formic and dichloroacetic acids, thereby allowing solvent or spin casting. The excitation and emission wavelengths were varied by the quaternization and methylation of the nitrogen atom.[6] Other related basic aromatic π-conjugated polymeric systems are the polyquinolines, which have excellent thermal stability and high mechanical strength.[7,8] Recently, the optoelectronic properties such as photoconductivity, photoluminescence, and nonlinearity of polyquinolines have been extensively investigated by Jenekhe and co-workers.[9−12] However, the effects of the protonation and methylation of polyquinolines on photoluminescent properties have not yet been explored. We have now synthesized two polyquinolines, poly(2,6-[4-phenylquinoline]), **I**, and poly(2,6-[*p*-phenylene]-4-phenylquinoline), **II** (Figure 1), and the photoluminescent properties of these polymers in solution and solid state were investigated in detail.

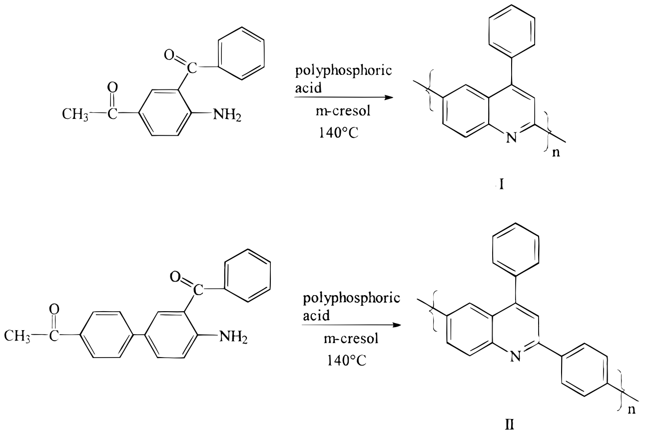

Figure 1. Chemical structures of poly(2,6-[4-phenylquinoline]), **I**, and poly(2,6-[4-phenylene]-4-phenylquinoline), **II**.

Experiment

Materials. All chemicals used in this study were purchased from Aldrich Chemical Co. HCOOH (87%), $Cl_2CHCOOH$ (99%+), CH_3SO_3H (99%+), and H_2SO_4 (96−98%) were used without further purification. Poly(vinyl alcohol) {PVA} (M_w = 50 000) was purchased from Polyscience Co. Poly(2,6-[4-phenylquinoline]), **I**, and poly(2,6-[*p*-phenylene]-4-phenylquinoline), **II**, were synthesized by the self-condensation of 5-acetyl-2-aminobezophenone and 4-amino-4′-acetyl-3-benzoylbiphenyl by the method reported by Stille and co-workers.[7,8]

The self-condensation polymerization was carried out in a mixture of polyphosphoric acid and *m*-cresol. The molecular weights of the polymers obtained were found to be dependent

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Table 1. Viscosities of Polyquinolines

polymer	reaction time (h)	$[\eta]$ (dL/g)[a]	solvent
$\mathbf{I}_a$	2	0.33	H_2SO_4
$\mathbf{I}_b$	72	4.4	H_2SO_4
	70	3.6[b]	H_2SO_4
$\mathbf{II}_a$	2	7.0	H_2SO_4
$\mathbf{II}_b$	24	11.6[b]	H_2SO_4
$\mathbf{II}_a$	2	0.81	$CHCl_2COOH$
$\mathbf{II}_c$	24	1.14	$CHCl_2COOH$
$\mathbf{II}_d$	72	1.38	$CHCl_2COOH$

[a] Intrinsic viscosities measured in concentrated H_2SO_4 or $CHCl_2COOH$ at 25 °C. [b] The intrinsic viscosities of $\mathbf{I}_b$ and $\mathbf{II}_b$ were reported in ref 7.

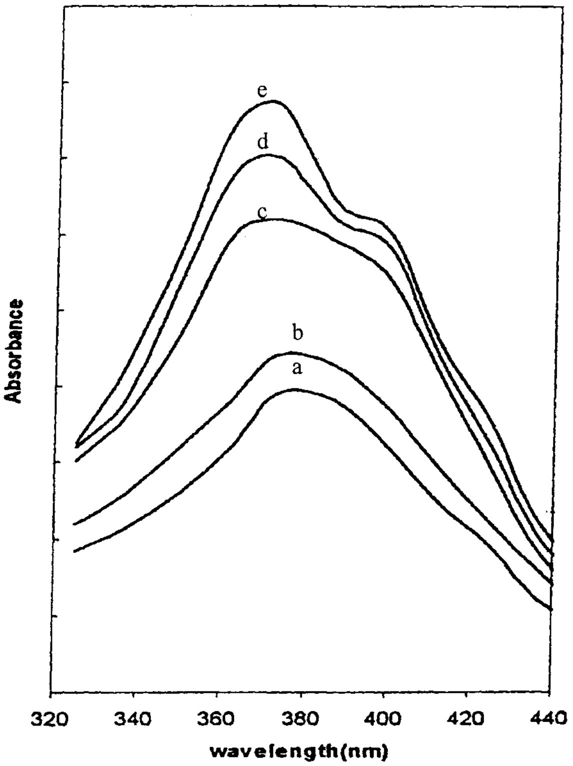

Figure 2. UV absorption spectra of $\mathbf{I}_a$ in aqueous H_2SO_4 solutions: (a) 23%, (b) 43%, (c) 62%, (d) 80%, and (e) 96% H_2SO_4 solutions; concentration of $\mathbf{I}_a$ is 0.0002 g/dL.

on the reaction times, and the typical results are summarized in Table 1.

N-Methylated polyquinolines were prepared by the methylation of polyquinolines with dimethyl sulfate at 100 °C for various times. The reaction mixtures were cooled, and the products were precipitated, washed with ether, and then dried. The degree of the methylation is determined by ^1H NMR spectroscopy. The peak ratios, 4.0 ppm for the methyl group and 7.5−8.5 ppm for the aromatic protons, were determined, and the degrees of methylation were calculated as 84% for 2 h, 87% for 8 h, and 90% for 24 h reaction times for polymer **II**.

Blend Films. Binary blends of polyquinolines and PVA were prepared by first dissolving the mixtures in formic acid. The resulting solutions (0.3−0.5 wt % total polymers in the solvent) were homogeneous. Optical quality thin films of homopolymers or polymer blends were obtained by solvent-casting or spin-coating from formic acid solutions onto quartz substrates. All the films were dried at 60 °C for 24 h in a vacuum, and formic acid was not detected in these films.

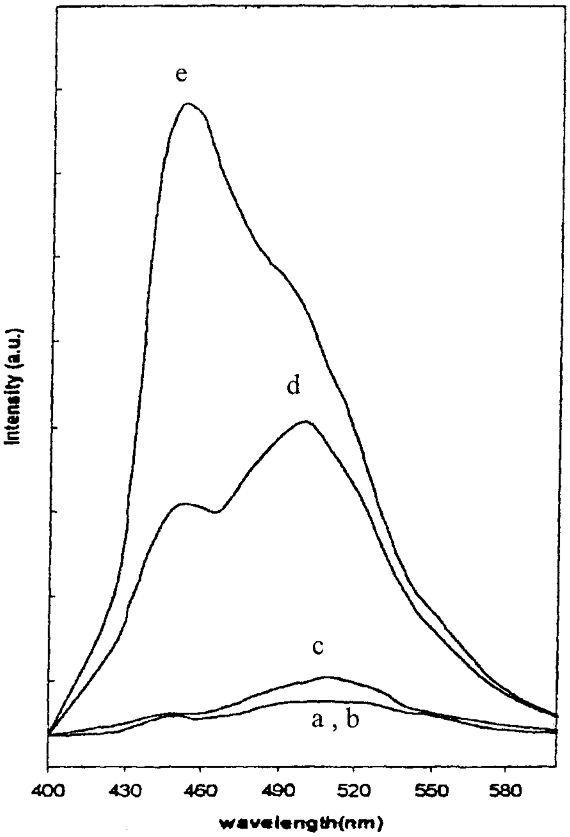

Figure 3. Fluorescence emission spectra of $\mathbf{I}_a$ in aqueous H_2SO_4 solutions: (a) 23%, (b) 43%, (c) 62%, (d) 80%, and (e) 96% H_2SO_4 solutions; concentration of $\mathbf{I}_a$ is 0.0002 g/dL.

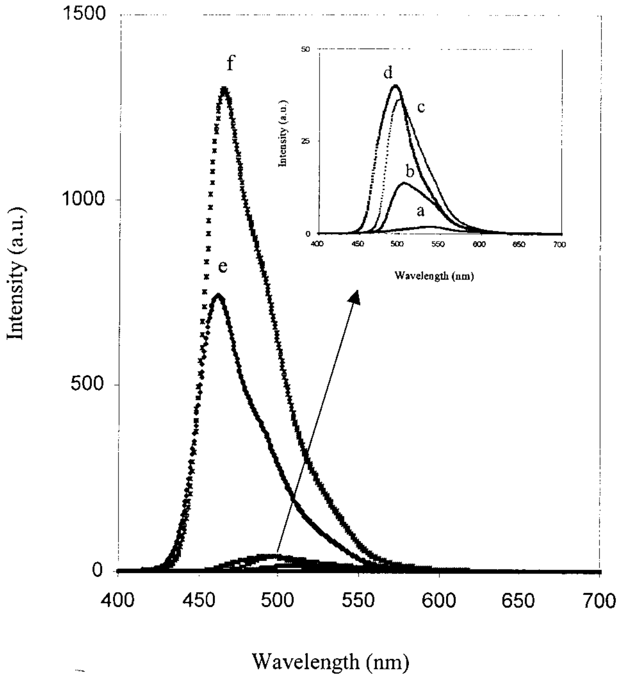

Figure 4. Fluorescence emission spectra of $\mathbf{II}_a$ in dichloroacetic acid solutions at 25 °C: (a) 0.3, (b) 0.18, (c) 0.06, (d) 0.03, (e) 0.002, and (f) 0.0005 g/dL.

Characterization. The inherent viscosity was measured in acidic media at 25 ± 0.05 °C by an Ubbelohde viscometer. FT-IR spectra were obtained with the use of a Perkin-Elmer 1600 FT-IR spectrophotometer. The degree of N-methylation was determined by ^1H NMR (Varian U-plus 300 MHz) measurements as mentioned in above. Thermal gravimetric analysis (TGA) experiments were performed using a Hi-Res TGA 2950 from TA Instruments with a heating rate of 20 °C/min under a nitrogen atmosphere. UV absorption spectra were obtained by using a Varian Cary 2300 spectrophotometer. Steady-state photoluminescence studies were carried out using

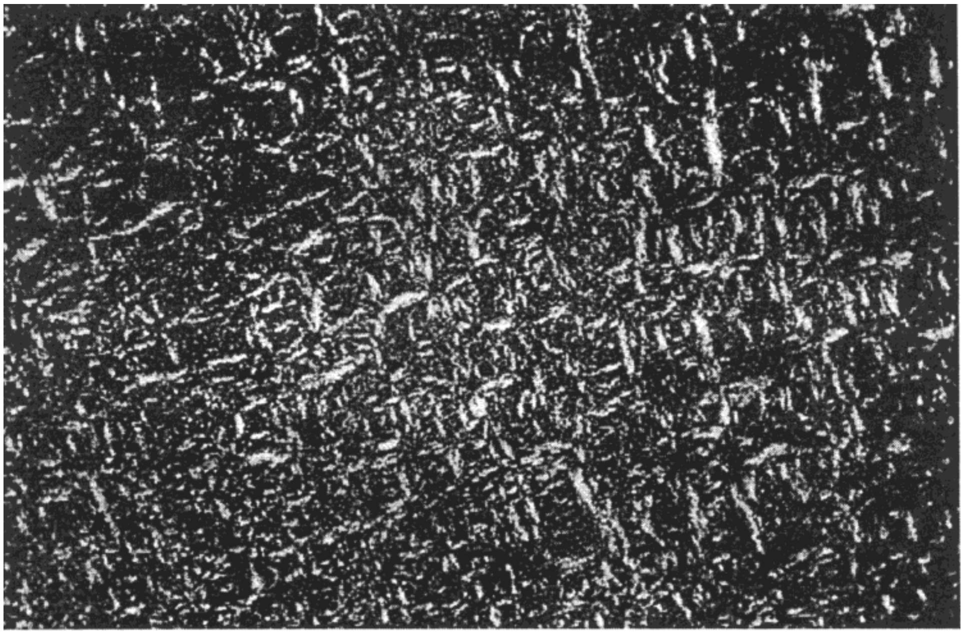

Figure 5. Polarized optical micrograph of the solvent-cast film $\mathbf{I}_b$.

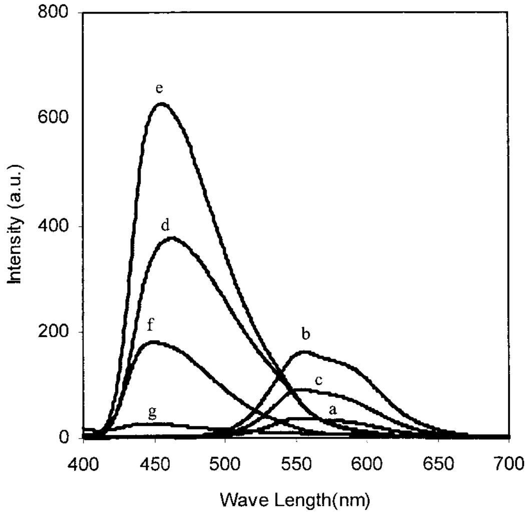

Figure 6. Fluorescence emission spectra of $\mathbf{II}_a$ and PVA blend films: (a) pristine $\mathbf{II}_a$, (b) 80% $\mathbf{II}_a$, (c) 50% $\mathbf{II}_a$, (d) 20% $\mathbf{II}_a$ (e) 5% $\mathbf{II}_a$, (f) 1% $\mathbf{II}_a$, and (g) 0.1% $\mathbf{II}_a$.

Table 2. Fluorescence Intensity of $\mathbf{II}_a$ vs Concentration at 25 °C

concn (M)	solvent	emission λ_{max} (nm)	emission intensity (au)
0.00125	HCOOH	480	7000
0.025	HCOOH	500	90
0.050	HCOOH	510	60
0.10	HCOOH	520	30
0.50	HCOOH	550	7
0.0005	$CHCl_2COOH$	460	1320
0.0020	$CHCl_2COOH$	470	770
0.030	$CHCl_2COOH$	490	40
0.060	$CHCl_2COOH$	500	35
0.20	$CHCl_2COOH$	500	10
0.30	$CHCl_2COOH$	550	2
0.0005	CH_3SO_3H	480	6800
0.0025	CH_3SO_3H	490	6000
0.025	CH_3SO_3H	500	260
0.050	CH_3SO_3H	510	170
0.10	CH_3SO_3H	510	100
0.50	CH_3SO_3H	550	10

a Perkin ELMER LS50B luminescence spectrometer. The fluorescence spectra were recorded using a 1 cm quartz cuvette in the right angle geometry at room temperature.

Results and Discussion

UV Absorption and Fluorescent Properties in Solution. The self-condensations of 5-acetyl-2-aminobenzophenone and 4-amino-4′-acetyl-3-benzoylbiphenyl by the method reported by Stille and co-workers[7,8] produced the quinoline polymers, **I** and **II**. Longer reaction times produced higher molecular weight polymers (Table 1). The UV absorption maxima and fluorescence spectra of these different molecular weight polymers showed little difference The polymers were soluble in acidic solvents such as aqueous formic, dichloroacetic, and sulfuric acids. The UV absorption spectra of $\mathbf{I}_a$ in aqueous H_2SO_4 solutions are shown in Figure 2. The absorption spectra were greatly affected by the acidity of the solutions. The absorption maximum at 373 nm did not change over wide acidity ranges, but the molar extinction coefficient increased with increasing acidity. The acidic solvents assist the dissolution of polyquinolines by protonating (or hydrogen bonding) on the nitrogen atom; hence, the UV absorption of the polymers can be affected not only by the solvent properties (e.g., polarity) but also by the degree of protonation on the nitrogen atom. In strong acidic media, the majority of the quinoline moieties are protonated, and the protonated quinoline chromophores absorb at $\lambda_{max} = 373$ nm. It is well-known that the majority of heterocyclic monoazines such as pyridine and quinoline are either nonfluorescent or weakly fluorescent in nonpolar solvents, but they emitted fluorescence in hydroxyl or acidic solvents (e.g., quinoline,[13] 2-phenylquinoline,[14] and 2-naphthylquinoline[15]). The fluorescence emission spectra of $\mathbf{I}_a$ (0.0002 g/dL) in aqueous H_2SO_4 solutions are shown as a function of the acidity of the solutions (Figure 3). In low-acidity solutions, two broad featureless emission peaks at around 450 and 500 nm were observed. However, when the concentration of the H_2SO_4 solution was increased, the emission spectrum narrowed, the intensity of the emission peak at 450 nm was greatly increased, and the peak at 500 nm almost completely disappeared in 96% H_2SO_4 solution.

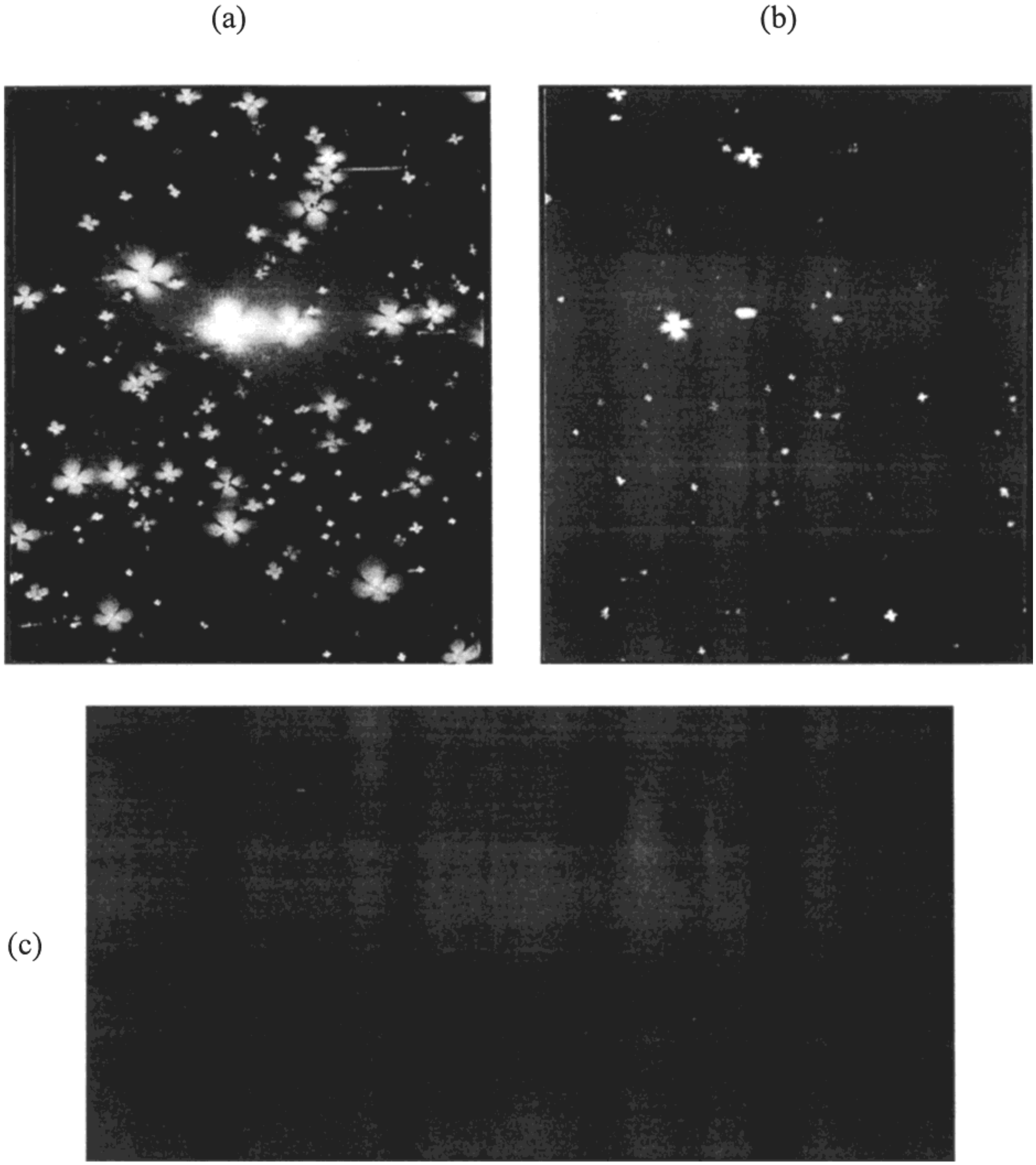

Figure 7. Polarized optical micrograph of **II**$_a$ and PVA films: (a) **II**$_a$/PVA = 80/20, (b) **II**$_a$/PVA = 20/80, and (c) **II**$_a$/PVA = 5/95.

The results indicated that in low-acidity solutions protonated and nonprotonated polyquinolines coexisted, and the formation of aggregates/excimers resulted in decreased emission intensity due to aggregation quenching.[16−18] In the concentrated H_2SO_4 solution (96%), most of quinoline moieties were protonated. The polymer chains were separated due to electrostatic repulsion of their positive charges, and the emission spectra of the isolated polyquinoline chain appeared at 450 nm. The fluorescent properties of polyquinolines were also investigated in formic, dichloroacetic, and methanesulfonic acids. Typical data for the fluorescence intensity vs the concentration are listed in Table 2. The concentrated solutions (∼0.5 g/dL) of **II**$_a$ showed broad featureless emission peaks at 550 nm (excited with ∼380 nm). However, when the solutions were diluted (∼0.0005 g/dL), the peaks shifted to a lower wavelength (∼480 nm). The emission spectra were narrow, and the intensity increased greatly with decreasing concentration. In the case of the dichloroacetic acid solutions of **II**$_a$, the intensity of the emission peaks was increased over 600 times when the solution was diluted from 0.3 to 0.002 g/dL (Figure 4). These results suggested that the polyquinolines formed aggregates/excimers in concentrated solutions, resulting in concentration quenching. Upon dilution, the polymer chains were separated, and the emission spectra at around 550 nm disappeared completely. We interpret the dilute solution emission spectra (∼480 nm) of these polymers as due to the excited state of the isolated chains of the polymers.

Fluorescent Properties in the Solid State. Thin films of polymers of **I** and **II** were prepared on quartz plates by solvent and spin castings. The UV spectra of the films prepared by both methods have identical peaks

($\lambda_{\max}(\mathbf{I}_b) \sim 440$ nm, $\lambda_{\max}(\mathbf{II}_a) \sim 420$ nm). A crossed polarized photomicrograph of the solvent-cast films of $\mathbf{I_b}$, ~100 nm in thickness, is shown in Figure 5. The spin-cast film was much thinner (~1 nm), and we did not observe clear morphological features. In the liquid crystalline states, the polymers were aggregated and formed excimers, resulting in the appearance of a broad emission peak at around 550−600 nm. We then blended the polyquinolines with nonfluorescent polymers such as poly(vinyl alcohol) (PVA). The polymers were not completely miscible over a wide range of the concentration ratio of these two polymers. However, optical clear thin films were obtained, and the typical fluorescence spectra of the $\mathbf{II}_a$−PVA blend systems are shown in Figure 6. It was also shown that, at the high concentration of $\mathbf{II}_a$ in the PVA matrix, the emission peaks at ~570 nm were broad with low intensity; however, upon decreasing the concentration of $\mathbf{II}_a$ in the blends, the emission peak shifted to a low wavelength, ~450 nm, and the intensity greatly increased. This indicated that the polyquinoline chains were separated from each other through the intervention of PVA, resulting in decreased aggregation quenching and high emission intensity. Crossed polarized photographs of these blend systems are shown in Figure 7.The blend film with the molar ratio of polymer $\mathbf{II}_a$/PVA = 8/2 showed a clear liquid crystalline structure (Figure 7a). However, when the ratio was decreased, a smaller number of liquid crystalline domains were present (Figure 7b) which were no longer seen in low-ratio blend films (Figure 7c). The previously discussed fluorescence data are consistent with morphological observations. In a series of additional experiments, thin films of polyquinolines containing various organic solid acids were also prepared by spin-coating of the formic acid solutions. The fluorescence emission spectra of the dried films containing a weak acid such as benzoic acid showed a broad peak at around 580 nm, similar to the peaks without added acid, but on addition of a strong acid such as *p*-methyltoluenesulfuric acid (molar ratio, quinoline:acid 1:>3) the peak was shifted to 470 nm. When the quinoline moiety was partially methylated, a similar tendency was observed. These results suggest that when the positive charge on the nitrogen atom on the quinoline reached a critical value, the intermolecular electrostatic repulsion prevents polymer aggregation, and the emission spectrum of the isolated chain is observed.

Conclusion

Poly(2,6-[4-phenylquinoline]) and poly(2,6-[*p*-phenylene]-4-phenylquinoline formed liquid crystalline structures readily in the solid state. In these liquid crystalline states, the polymers were aggregated, formed excimers, and showed low intensive broad emission peaks at around 550−600 nm. When the polymers were blended with nonfluorescent polymers such as PVA, the emission peaks at 550−600 nm decreased in intensity with increasing PVA concentration. The emission peaks at 550−600 nm completely disappeared in a 95 wt % PVA blend, and an intensive emission peak at 450 nm was observed. The observed emission peak at 450 nm was accounted for by the excited state of the isolated chains of the polymers. When the quinoline moieties of the polyquinoline were protonated or methylated, intensive emission spectra appeared at 450 nm. When the positive charge on the nitrogen atom of the quinolines reaches a critical value, the intermolecular electrostatic repulsion prevents the aggregation, and the emission spectra are those of the isolated chain. These results suggest that an effective blue-light-emitting (~450 nm) diode maybe constructed by the protonation or the methylation of the quinoline moieties or by blending of polyquinolines with a suitable nonfluorescent polymer.

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References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) Jenekhe, S. A., Wynne, K. J., Eds. *Photonic and Optoelectronic Polymers*; ACS Symposium Series 672; American Chemical Society: Washington, DC, 1995.

(3) Miyata, S., Nalaw, H. S., Eds. *Organic Electroluminescent Materials and Devices*; Gordon and Breach: Langhorne, PA, 1997.

(4) Gebler, D. D.; Wang, Y. Z.; Blatchford, J. W.; Jessen, S. W.; Lin, L. B.; Gustafson, T. L.; Wang, H. L.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *J. Appl. Phys.* **1995**, *78*, 4264.

(5) Yamamoto, T.; Lee, B. L.; Saitoh, Y.; Inoue, T. *Chem. Lett.* **1996**, 679.

(6) Yun, H.; Kwei, T. K.; Okamoto, Y. *Macromolecules* **1997**, *30*, 4633.

(7) Sybert, P. D.; Beever, W. H.; Stille, J. K. *Macromolecules* **1981**, *14*, 493.

(8) Pelter, M. W.; Stille, J. K. *Macromolecules* **1990**, *23*, 2418.

(9) Jenekhe, S. A.; Zhang, X.; Chen, L. X. *Chem. Mater.* **1997**, *9*, 409.

(10) Zhang, X.; Shetty, A. S.; Jenekhe, S. A. *Pros. SPIE* **1997**, *3148*, 89.

(11) Agrawal, A. K.; Jenekhe, S. A.; Vanherzeele, H. V.; Meth, J. S. *J. Phys. Chem.* **1992**, *96*, 2837.

(12) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895.

(13) El. Saged, M. A.; Kasha, M. *Spectrochim. Acta* **1960**, *15*, 758.

(14) Mataga, N.; Tsuno, S. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 368.

(15) Thorseh, E. D.; Stermitz, F. R.; O'Donnell, C. M. *Photochem. Photobiol.* **1974**, *19*, 291.

(16) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765.

(17) Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller, T. M. *Phys. Rev. Lett.* **1994**, *73*, 744.

(18) Sun, B. J.; Miao, Y. J.; Bazan, G. C.; Conwell, E. M. *Chem. Phys. Lett.* **1996**, *260*, 186.

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