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Poly(vinyl diphenylquinoline): A New pH-Tunable Light-Emitting and Charge-Transport Polymer Synthesized by a Simple Modification of Polystyrene

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ABSTRACT: Electroactive and blue light-emitting poly(vinyl diphenylquinoline) (PVQ) was synthesized in nearly quantitative yield by a simple modification of polystyrene. The new polymer and its model compound 2,4-diphenylquinoline were characterized by ^{1}H NMR, FT-IR, photoluminescence spectroscopies, and thermal analysis. PVQ has a glass transition temperature of 185 °C, is soluble in many organic solvents, and is a weak base comparable in basicity to poly(vinylpyridine). It emits blue light in neutral solution and in thin solid films. In acidic solutions, PVQ exhibits a pH-tunable photoluminescence with emission maximum that varies from 486 nm (blue) to 529 nm (green). Intramolecular excimer emission was observed in acidic solutions but not in neutral solutions or thin films of the polymer. The dominant fluorescence lifetimes of the polymer were about 1.2−1.3 ns in thin films or neutral solutions and close to 20 ns in acidic solutions. The coupling of acid−base chemistry to light-emitting and optoelectronic properties in PVQ suggests that it may find applications in electroluminescence, sensors, and catalysis.

Introduction

Most of the polymers currently being developed for electronic, optoelectronic, and photonic applications are based on π-conjugated polymers having main-chain macromolecular architectures.[1,2] Our interest in combining the electronic and photonic properties of π-conjugated polymers with the self-assembly features of conventional flexible-chain block polymers recently led to the creation of electroactive and photoactive rod−coil block copolymers with novel self-assembling features and supramolecular morphology-dependent electronic and photonic properties.[3] Imparting electronic and optoelectronic properties on existing commercial polymers by chemical modification represents another attractive, but yet to be fully explored, option in developing electronic and photonic polymers that could be more readily commercializable.

The commercial vinyl polymer poly(*N*-vinylcarbazole) (PVK) is a well-known electron-donating and hole-transport material which has been used in photocopiers[4a] and more recently in light-emitting diodes.[4b,c] Although PVK is not a conjugated polymer, its electroactive and charge-transport properties arise from radical cation hopping among the discrete electroactive carbazole units on the side chain.[4a] Another important property of PVK in imaging applications is its high glass transition temperature (T_g = 207 °C).[4a] Recent efforts on other side-chain electroactive polymers include a blue light-emitting poly(stilbenenyl-*p*-methoxystyrene) made by Williamson condensation of poly(*p*-acetoxystyrene) and *p*-(chloromethyl)stilbene,[5] a green light-emitting polymethacrylate derivatized by attaching a substituted anthracene,[6] blue light-emitting polynorbornenes containing 9,10-diphenylanthracene or oxadiazole side group,[7] and copolymethacrylates bearing oxadiazoles or oligophenylenevinylenes as side groups.[8] However, there is as yet no side-chain polymer that complements PVK by exhibiting electron-accepting and electron-transport (n-type) properties while having comparable polymer characteristics such as a high T_g which is essential for durable devices. Extensive studies of π-conjugated polyquinolines and related polyquinoxalines and oligomers in our group have demonstrated their excellent electron-transport and electroluminescent properties in device applications.[2,9,10] We thought that incorporation of quinoline or quinoxaline rings or segments as side chains of commercial polymers might impart useful light-emitting and n-type electroactive properties.

In this paper, we report the synthesis of poly(vinyl diphenylquinoline) (PVQ) by chemical modification of polystyrene. The new side-chain polymer was characterized and investigated along with a model compound, 2,4-diphenylquinoline. PVQ has a high glass transition temperature (T_g = 185 °C), emits blue light as a solid film, and exhibits an interesting pH-tunable blue ↔ green luminescence in solution. As a weak base, PVQ undergoes acid−base chemistry that is coupled to and regulates its optoelectronic properties.

Experimental Section

Materials. Polystyrene with molecular weight (M_w) of 31 600 and a polydispersity (M_w/M_n) of 1.09 (Scientific Polymer Products, Inc., Ontario, NY) was used without further purification. 2-Aminobenzophenone, diphenyl phosphate (DPP), aluminum chloride, acetyl chloride, carbon disulfide, *m*-cresol, chloroform, dichloromethane, and formic acid were reagent or spectroscopic grade or better and were used as received from Aldrich.

Synthesis of 2,4-Diphenylquinoline (DPQ). 2-Aminobenzophenone (1.6 g, 8.1 mmol) and acetophenone (1.60 g, 13.3 mmol) were added along with 10 g of diphenyl phosphate and 6.5 g of *m*-cresol in a glass reactor fitted with mechanical stirrer, two glass inlets, and one sidearm. The reaction mixture was purged with argon for 20 min, and then the temperature was raised to 90 °C gradually under argon atmosphere for 1 h

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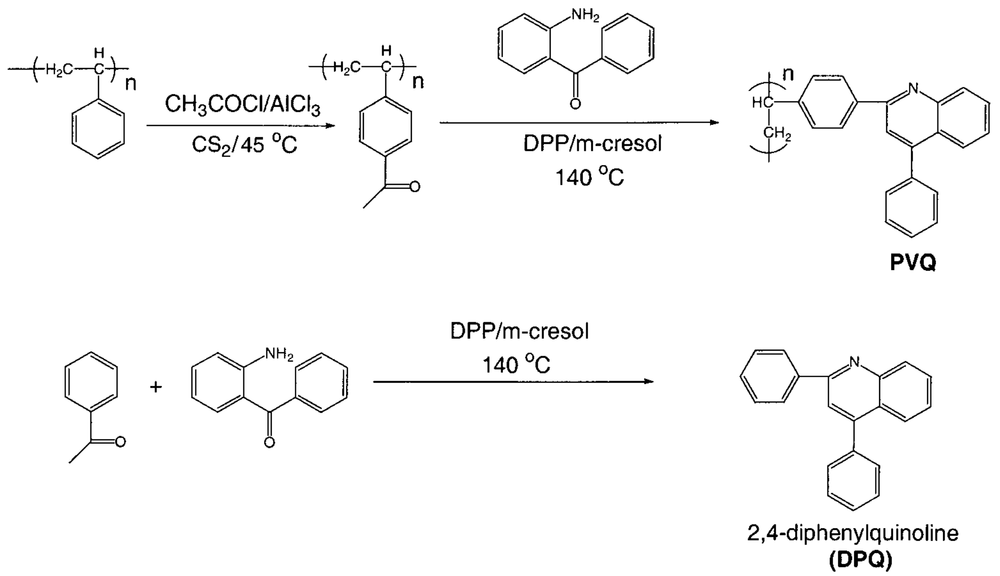
Scheme 1



and then to 140 °C for 4 h. After cooling, methylene chloride (100 mL) and 10% NaOH (100 mL) were added to the reaction mixture. The organic layer was separated and washed with water (50 mL × 5) until it was neutral, then dried over $MgSO_4$, and evaporated under vacuum to yield an off-white solid with some reddish liquid on top. The crude product was filtered and washed with pentane (5 mL × 3) to afford crystalline solid (1.60 g, 70%). Mp: 114 °C. (lit.[11] mp 112 °C). UV/vis, λ_{max} (nm) (formic acid): 346 (log $\epsilon = 4.55$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, $J = 8.8$ Hz, 1H), 8.20 (dd, $J_1 = 1.5$ Hz, $J_2 = 7.0$ Hz, 2H), 7.92 (dd, $J_1 = 1.0$ Hz, $J_2 = 8.4$ Hz, 1H), 7.84 (s, 1H), 7.73 (td, $J_1 = 1.4$ Hz, $J_2 = 7.0$ Hz, 1H), 7.46 (m, 9H).

Synthesis of Poly(4-acetylstyrene).[12] Polystyrene (3.5 g, 33.7 mmol repeat unit), CS_2 (anhydrous, 100 mL), and $AlCl_3$ (10 g, 0.13 mol) were added to a three-neck flask under nitrogen atmosphere. Acetyl chloride (6 mL, 85 mmol) was added dropwise to the reaction mixture which was stirred at 45 °C overnight. Carbon disulfide was removed by heating the reaction mixture in water. The reaction mixture was taken up with 200 mL of CH_2Cl_2 and 100 mL of water. The organic layer was washed with H_2O (2 × 300 mL), dried with $MgSO_4$, and evaporated under vacuum to yield an off-white solid (4.6 g, 94%). ^{1}H NMR (400 MHz/$CDCl_3$) δ: 7.38 (broad, 2H), 6.50 (broad, 2H), 2.52 (s, 3H), 1.43−1.68 (m, broad, 3H). FT-IR (film, cm^{-1}): 2925, 1687, 1609, 1365, 1273, 842.

Synthesis of Poly(vinyl diphenylquinoline) (PVQ). 2-Aminobenzophenone (1.3 g, 6.59 mmol) and poly(4-acetylstyrene) (0.80 g, 5.48 mmol repeat unit) were added along with 10 g of diphenyl phosphate and 6.5 g of *m*-cresol in a glass reactor fitted with mechanical stirrer, two glass inlets, and one sidearm. The reaction mixture was purged with argon for 20 min, and then the temperature was gradually raised to 115 °C under argon atmosphere for 1 h and then to 140 °C for 3 h. The product was precipitated in a solution of 150 mL of 10% triethylamine/ethanol solution after cooling. The crude product was purified by continuous extraction with 10% triethylamine/ethanol solution for 2 days and was dried in a vacuum at 40 °C to afford an off-white solid (1.40 g, 83%). UV/vis, λ_{max} (nm) (CH_2Cl_2): 331 (log $\epsilon = 5.18$); λ_{max} (nm) (formic acid): 355 (log $\epsilon = 4.63$). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.22 (m, 2H), 6.62 (m, 2H), 1.55 (broad, 1H), 1.35 (broad, 2H). FT-IR (film, cm^{-1}): 3067, 3026, 2928, 1598, 1552, 1490, 1423, 1361, 845, 778.

Characterization. Optical absorption spectra were obtained on a Perkin-Elmer Lamda 900 spectrophotometer. Steady-state photoluminescence (PL) studies were done by using a Spex Fluorolog-2 spectrofluorometer with a Spex DM3000f spectroscopy computer. Thin film samples were positioned such that the emission was detected at 22.5° from the incident radiation beam. Fluorescence lifetime measurements were made by doing time-correlated single-photon counting experiments on an instrument consisting of mode-locked Nd:YLF laser (Quantronix) operating at 76 MHz as the primary laser source. The second harmonic (KTP crystal) of the Nd:YLF laser was used to synchronously pump a dye laser (Coherent 700). The pulse width of the dye laser was typically 8 ps and was cavity-dumped at a rate of 1.9 MHz. The dye laser was tuned to the desired excitation wavelength. In general, excitation was at or close to the absorption maximum of a sample, and the fluorescence decay was monitored at or close to the emission maximum. Measurements were made in air at room temperature.

The intrinsic viscosity [η] of the polymers was measured in dilute toluene solutions with concentration in the range 0.2−0.4 g/dL at 30 °C on a Cannon Ubbelohde capillary viscometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and melting points were done on a TA instruments model 3000 thermal analyst based on an IBM PS/253 model 60 computer and equipped with a model 2050 TGA unit and a model 2920 DSC unit. The TGA data and DSC thermograms were obtained in flowing nitrogen at a heating rate of 10 °C/min. The FT-IR spectra were taken on thin films of the polymers deposited on NaCl substrates with a Nicolet model 20SWC Fourier transform infrared spectrometer under nitrogen. ^{1}H NMR spectra were taken at 400 MHz on a Bruker Avance-400 instrument.

Results and Discussion

Synthesis and Characterization. The new vinyl polymer, PVQ, and its model compound, 2,4-diphenylquinoline (DPQ), were synthesized according to Scheme 1. Acetylation of polystyrene by the Friedel−Crafts reaction has previously been reported.[12] A similar acetylation procedure in our hands gave near-quantitative yield (94%) under very mild conditions (e.g., room temperature). Condensation of 2-aminobenzophenone with poly(4-acetylstyrene) via the Friedländer quinoline synthesis[13,14] gave PVQ. The same reaction was also adapted to synthesize 2,4-diphenylquinoline with good yield (70%); this compound was previously synthesized by a complicated three-step method with a low yield.[11]

The complete conversion of poly(4-acetylstyrene) (PAcS) to poly(vinyl diphenylquinoline) was investigated by proton NMR and FTIR spectroscopies and other methods. The ^{1}H NMR spectra of PVQ and its poly(4-acetylstyrene) precursor are shown in Figure 1. The strong resonance at 2.5 ppm due to the methyl protons

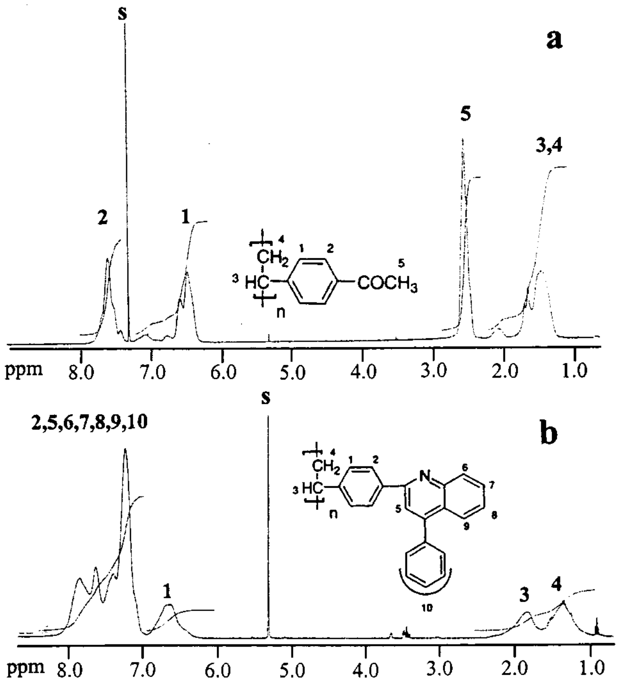


Figure 1. ^{1}H NMR spectra of poly(4-acetylstyrene) in $CDCl_3$ and of PVQ in CD_2Cl_2.

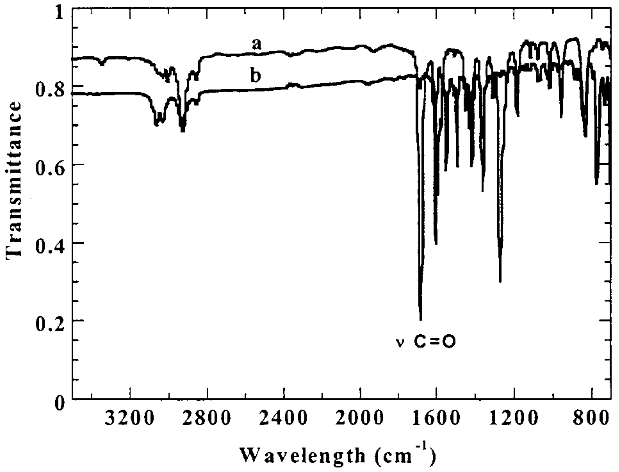


Figure 2. FTIR spectra of poly(4-acetylstyrene) (a) and of PVQ (b).

of the acetyl group (−COCH_3) in PAcS has completely disappeared in the spectrum of PVQ. This means that the acetyl group was completely consumed, i.e., that there is 100% conversion within the limits of NMR detection. The integrated peaks of the NMR spectra of the precursor and PVQ were consistent with the structures of the polymers. For example, new aromatic proton resonances appear at 7−8 ppm in the spectrum of PVQ which are consistent with those of the phenylquinoline ring.[13]

The molecular structures of PVQ and PAcS are also confirmed by the FTIR spectra shown in Figure 2. The strong peak at 1688 cm^{-1} owing to the carbonyl group in PAcS has almost completely disappeared in PVQ. New strong bands between 1600 and 1400 cm^{-1} due to the C=N group have appeared in the spectrum of PVQ. In addition, the aromatic C−H vibrational bands at 3026−3067 wavenumbers are enhanced in the PVQ spectrum. These results confirm the completion of quinoline ring-forming cyclization reaction on the precursor PAcS and the presence of the characteristic phenylquinoline structure in PVQ.[13]

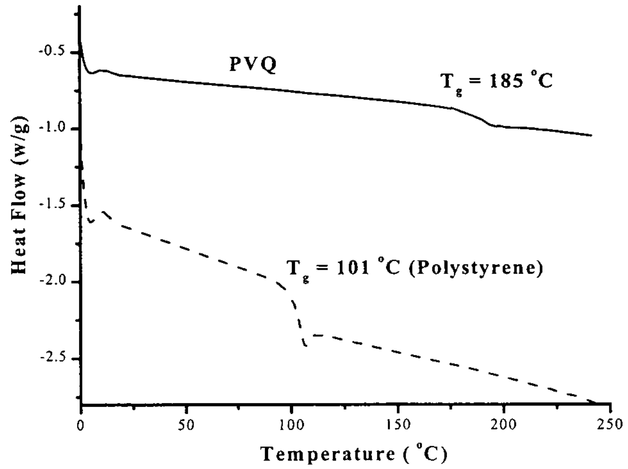


Figure 3. DSC scans of polystyrene and PVQ.

On the basis of the FTIR spectra of poly(4-acetylstyrene) and PVQ, the conversion of the reaction forming PVQ can be estimated. (A list of some of the FTIR spectra peaks is reported in the Experimental Section.) The peak at 846 cm^{-1}, which is characteristic of para-disubstitution of the benzene ring[15] and does not change from poly(4-acetylstyrene) to PVQ, was used as reference to normalize for the possible variation of sample thickness and concentration. The absorbance A (= log (1/T), where T is transmittance) of the carbonyl group peak at 1688 cm^{-1}, which changes with conversion and should be zero if the reaction is complete, was used to calculate the conversion as follows.[15] The percent conversion is given by $100[1 - R^1/R^0]$, where R^1 is the absorbance ratio A^1_{1688}/A^1_{846} in PVQ and R^0 is the absorbance ratio A^0_{1688}/A^0_{846} in the precursor PAcS. The conversion was found to be 97%. This result is in accord with the 100% conversion determined from ^{1}H NMR spectra.

The new side-chain polymer, PVQ, was found to be very soluble in many organic solvents such as toluene, THF, dichloromethane, chloroform, and formic acid. Free-standing as well as spin-coated thin films could be easily cast from the polymer solutions in the above solvents. The intrinsic viscosity of PVQ and the starting polystyrene in toluene at 30 °C were determined to be 0.14 and 0.18 dL/g, respectively. These intrinsic viscosities are consistent with the moderate molecular weight (M_w) of 31 600 and the flexible-coil nature of the starting polystyrene and the new PVQ.

The thermal transitions of PVQ and polystyrene were measured by differential scanning calorimetry (DSC), and the DSC scans are shown in Figure 3. PVQ, with a rigid and bulky phenylquinoline chromophore in the side chain, has a glass transition temperature of 185 °C, which is much higher than that of polystyrene (101 °C). The increase in the T_g of PVQ compared to polystyrene can be understood to be a consequence of the stiffening effect of the bulky side chain on the backbone mobility. Thermogravimetric analysis (TGA) showed that at 450 °C PVQ retained 55% of its mass, whereas polystyrene retained only 15% of its mass. Therefore, PVQ clearly has higher thermal stability than polystyrene.

Photophysical Properties of PVQ and Model Compound. We have studied the photophysical prop-

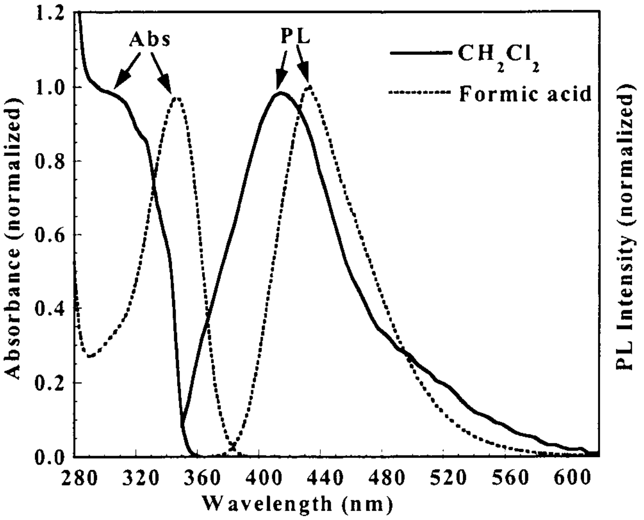


Figure 4. Absorption and emission spectra of 10^{-6} M solutions of DPQ model compound in CH_2Cl_2 and formic acid.

erties of 2,4-diphenylquinoline (DPQ), which is the conjugated chromophore in PVQ, to gain insights into those of the side-chain polymer. The UV−vis absorption and emission spectra of 10^{-6} M DPQ in dichloromethane and formic acid are shown in Figure 4. The model compound does not have an absorption maximum in dichloromethane above 280 nm; instead, a shoulder at about 330 nm is seen. However, in formic acid DPQ exhibits an intense absorption with a maximum at 346 nm (log $\epsilon = 4.55$). This red shift of the absorption spectrum of DPQ is due to protonation of the imine nitrogen of the quinoline ring to form the quinolinium ion. Such an effect of protonation on optical absorption has previously been observed in conjugated oligoquinolines[10a] and polyquinolines.[13] The corresponding emission spectra of DPQ in both solvents are shown in Figure 4. The emission band in dichloromethane is centered at 413 nm, and that in formic acid has a peak at 433 nm. The small red shift of the emission band in formic acid is in line with a similar red shift in the absorption band. Since these emission spectra were taken in dilute solutions where intermolecular interactions between the chromophores can be excluded, we assign them to monomer emission of DPQ and its protonated form.

The UV−vis absorption and emission spectra of PVQ (ca. 10^{-6} M) in dichloromethane and formic acid and in solid film are presented in Figure 5. The absorption spectra of PVQ in dichloromethane and as a solid film are identical to that of the model compound in dichloromethane. In formic acid, the absorption spectrum of PVQ is also very similar to that of the model compound. There is very small red shift of the absorption maximum from 346 nm in DPQ to 355 nm (log $\epsilon = 4.63$) in PVQ. The emission spectra of PVQ as a thin film and in dilute CH_2Cl_2 solution (Figure 5) are identical in line shape, but they have maxima at 435 and 425 nm, respectively. These emission spectra are also similar to those of the model compound. However, the emission band of PVQ in formic acid has a maximum at 509 nm, and it is much broader. This represents a 74−84 nm emission band red shift compared to PVQ in CH_2Cl_2 or as a thin film or compared to the model compound in formic acid. This tunable blue (435 nm) ↔ green (509 nm) photoluminescence of PVQ is clearly due to the acid−base interaction of the side chain diphenylquinoline chromophore (Scheme 2). Since the emission of PVQ in formic acid is dramatically different from the model compound in the same solvent, *intrachain* or *intramolecular* chromophore interactions are clearly involved.

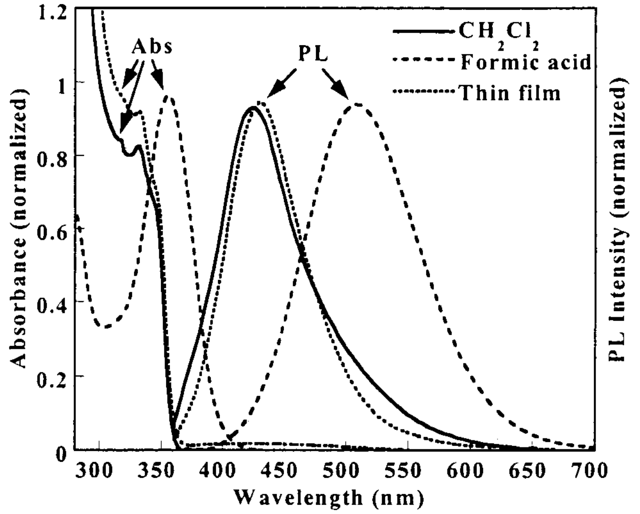
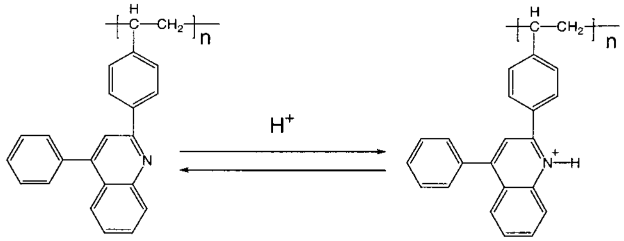


Figure 5. Absorption and emission spectra of PVQ thin film and solutions (10^{-6} M) in CH_2Cl_2 and formic acid.

Scheme 2



Aromatic vinyl polymers, including polystyrene, are well-known to form intramolecular excimers, even in dilute solution, due to the proximity of chromophores within a polymer chain.[16] Conjugated oligoquinolines, polyquinolines, and heterocyclic polymers are also known to form emissive intermolecular excimers very efficiently.[2a,10,17] However, we can exclude excimer emission as the origin of the observed blue photoluminescence of both PVQ and the model compound in dichloromethane and also thin film in the case of PVQ. While intramolecular excimer formation is the likely origin of the emission of PVQ in formic acid, it is unclear how protonation in solution mediates the close chromophore/chromophore interactions essential to excimer formation. To clarify the possible mechanism of excimer formation in dilute acid solutions of PVQ, we have examined the UV−vis absorption and emission spectra of PVQ and model compound DPQ in four organic acids with varying acid strength (pK_a) as shown in Figure 6: trifluoroacetic acid (pK_a = 0.23), formic acid (pK_a = 3.77), acetic acid (pK_a = 4.74), methanesulfonic acid (pK_a = −1.2).[18] For comparison, quinoline (pK_a = 4.8) is a weak base of comparable basicity as pyridine (pK_a = 5.2).[18] The UV−vis absorption spectra of both model compound and PVQ were unchanged when the acid strength was varied. Similarly, the emission band of the model compound did not change with acid strength. However, the emission band of PVQ was found to vary significantly with the pK_a (Figure 6b). The emission maximum changed from 486 nm (blue light) in trifluoroacetic acid to 529 nm (green light) in acetic acid. Thus, in acidic media, the emission band maximum increases

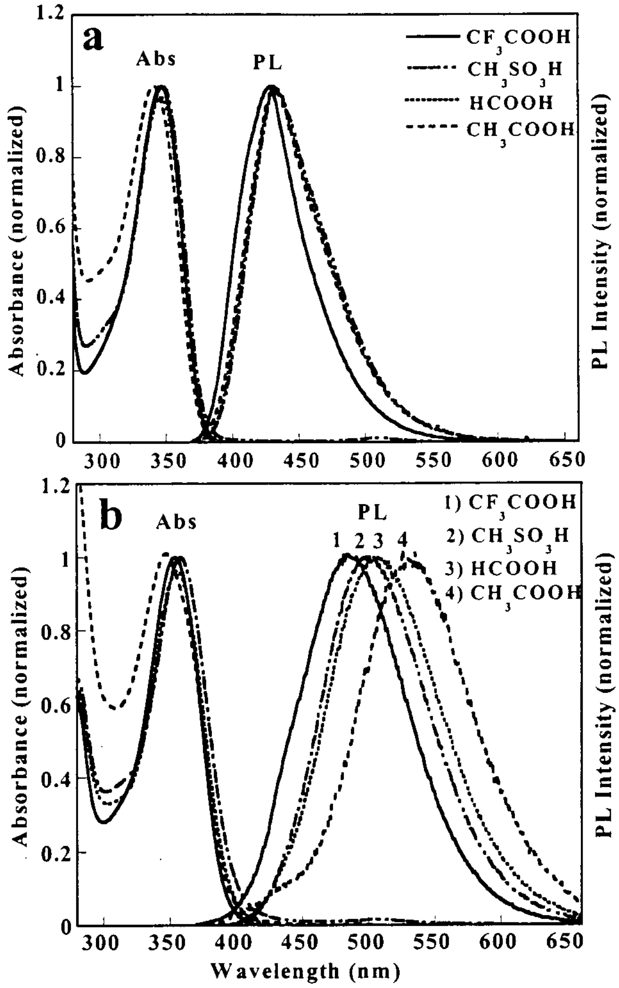


Figure 6. Absorption and emission spectra of DPQ model compound (a) and PVQ (b) in organic acid solvents of varying pK_a.

with increasing pK_a. These results suggest that the degree of protonation varies with the pK_a and hence that both protonated and neutral forms of PVQ exist in equilibrium (Scheme 2). In such a mixture, protonated and neutral DPQ chromophores within the PVQ chain could pair up with or without hydrogen bonding to facilitate intramolecular excimer formation.

The time-resolved photoluminescence (PL) decay dynamics of PVQ and model compound DPQ are exemplified by the representative PL decay curves and data shown in Figure 7 and Table 1. The PL decay dynamics of DPQ in formic acid (FA) was well described by a single exponential and a lifetime of 6.5 ns (Table 1). In aprotic solvent (dichloromethane), the PL decay of DPQ was not monoexponential; the two dominant lifetimes were in the 1.54−3.95 ns range. The PL decay of PVQ in dichloromethane solution and in solid film were best described by three exponentials, and the dominant one had an amplitude of about 60% and a lifetime in the range 1.2−1.3 ns (Table 1). The PL decay dynamics of PVQ in dichloromethane is very similar to that of the model compound. This suggests that the emission of PVQ in dichloromethane and thin solid film is mainly from monomer emission. However, the lifetime of the dominant excited-state component of PVQ in formic acid is much longer, nearly 20 ns. We conclude from these results that intramolecular excimer emission dominates the luminescence of PVQ in formic acid.

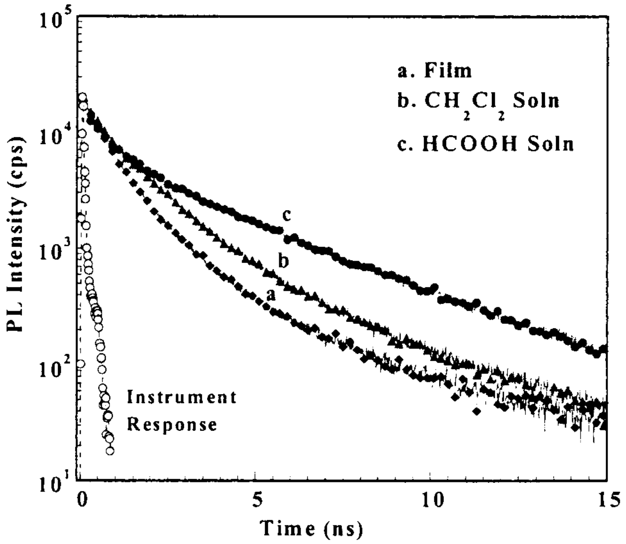


Figure 7. PL decay curves of PVQ thin film (a) and 10^{-6} M solutions in CH_2Cl_2 (b) and formic acid (c).

Table 1. PL Decay Dynamics of PVQ and Model Compound DPQ

	τ_1, ns	τ_2, ns	τ_3, ns	amplitude % $\tau_1/\tau_2/\tau_3$	χ^2
DPQ (FA)	6.53	0.018		99.4/0.6	1.64
DPQ (CH_2Cl_2)	3.95	1.54	0.023	22.6/71.1/6.3	1.91
PVQ (FA)	19.7	5.88	1.03	67.2/27.3/5.6	1.64
PVQ (CH_2Cl_2)	4.23	1.29	0.23	21.9/67.8/10.3	1.42
PVQ (film)	5.01	1.17	0.40	14.3/56.9/28.8	1.18

Fluorescence quantum yields of the model compound DPQ and polymer PVQ in both dichloromethane and formic acid solutions (~10^{-6} M) were determined by comparison with a quinine sulfate standard (10^{-6} M in 0.1 N H_2SO_4, $\Phi_f = 0.55$).[19] The fluorescence quantum yield of the model compound was 2 and 21% in dichloromethane and formic acid, respectively. In the same solvents the quantum yield of PVQ was 7 and 10.3%, respectively. The higher fluorescence efficiency in formic acid, especially for the model compound, is consistent with the observed lifetimes in the two solvents.

Conclusions

Poly(vinyl diphenylquinoline), PVQ, has been synthesized in nearly quantitative yield by condensation of poly(4-acetylstyrene) with 2-aminobenzophenone. The polymer is a blue light-emitting material in the solid state while its luminescence in solution is tunable from blue to green by acid−base chemistry. We found from steady-state and time-resolved photoluminescence studies of PVQ and its model compound that intramolecular excimer emission dominated the luminescence of the polymer in acidic solutions whereas monomer emission was observed in solid films and in neutral solutions. PVQ is a new polymeric base capable of acid−base and hydrogen-bonding interactions that are similar to poly(vinylpyridine) while also exhibiting tunable optoelectronic properties not found in poly(vinylpyridine).

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References and Notes

(1) For some recent reviews, see: (a) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (c) Reddiger, J. L.; Reynolds, J. R. *Adv. Polym. Sci.* **1999**, *145*, 57. (d) Jenekhe, S. A., Wynne, K. J., Eds. *Photonic and Optoelectronic Polymers;* ACS Symp. Ser. No. 672; American Chemical Society: Washington, DC, 1997.

(2) (a) Zhang, X.; Shetty, A. S.; Jenekhe, S. A. *Macromolecules* **1999**, *32*, 7422. (b) Zhang, X.; Jenekhe, S. A. *Macromolecules* **2000**, *33*, 2069. (c) Jenekhe, S. A.; Yi, S. *Appl. Phys. Lett.* **2000**, *77*, 2635. (d) Jenekhe, S. A.; Yi, S. *Adv. Mater.* **2000**, *12*, 1274.

(3) (a) Jenekhe, S. A.; Chen, X. L. *Science* **1998**, *279*, 1903. (b) Jenekhe, S. A.; Chen, X. L. *Science* **1999**, *283*, 372. (c) Jenekhe, S. A.; Chen, X. L. *J. Phys. Chem. B* **2000**, *104*, 6332.

(4) (a) Borsenberger, P. M.; Weiss, D. S. *Organic Photoreceptors for Imaging Systems*; Marcel Dekker: New York, 1993. (b) Hu, B.; Yang, Z.; Karasz, F. E. *J. Appl. Phys.* **1994**, *76*, 2419. (c) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281.

(5) Aguiar, M.; Karasz, F. E.; Akcelrud, L. *Macromolecules* **1995**, *28*, 4598.

(6) Bouche, C.-M.; Berdague, P.; Facoetti, H.; Robin, P.; Le Barny, P.; Schott, M. *Synth. Met.* **1996**, *81*, 191.

(7) Boyd, T. J.; Geerts, Y.; Lee, J.-K.; Fogg, D. E.; Lavoie, G. G.; Schrock, R. R.; Rubner, M. F. *Macromolecules* **1997**, *30*, 3553.

(8) Li, X.-C.; Grimsdale, A. C.; Cervin, R.; Holmes, A. B.; Moratti, S. C.; Yong, T. M.; Gruner, J.; Friend, R. H. In ref 1d, pp 322−344.

(9) (a) Jenekhe, S. A.; Zhang, X.; Chen, X. L.; Choong, V.-E.; Gao, Y.; Hsieh, B. R. *Chem. Mater.* **1997**, *9*, 409. (b) Zhang, X.; Shetty, A. S.; Jenekhe, S. A. *Acta Polym.* **1998**, *49*, 52. (c) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1996**, *8*, 579.

(10) (a) Shetty, A. S.; Liu, E. B.; Lachicotte, R. J.; Jenekhe, S. A. *Chem. Mater.* **1999**, *11*, 2295. (b) Alam, M. M.; Jenekhe, S. A. *J. Phys. Chem. B* **2001**, *105*, 2479.

(11) Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 804.

(12) Kenyon, W. O.; Waugh, G. P. *J. Polym. Sci.* **1958**, *32*, 83.

(13) (a) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895. (b) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1993**, *5*, 633. (c) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1992**, *4*, 95.

(14) Stille, J. K. *Macromolecules* **1981**, *14*, 870.

(15) (a) Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Organic Structural Spectroscopy*; Prentice Hall: Upper Saddle River, NJ, 1998. (b) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry,* 4th ed.; McGraw-Hill: London, UK, 1987.

(16) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, UK, 1985; Chapter 7.

(17) (a) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765. (b) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules* **1994**, *27*, 739.

(18) Streitwieser, Jr., A.; Heathcock, C. *Introduction to Organic Chemistry*, 3rd ed.; Macmillan: New York, 1985; pp 1154−1156.

(19) (a) Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107. (b) Osaheni, J. A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 7389.

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