Synthesis and Characterization of Photoluminescent Conjugated Polymer Containing *N*-(*α*-Naphthyl)-Carbazole Unit

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ABSTRACT: A novel luminescent conjugated polymer, poly[{9-(*α*-naphthyl)-3,6-divinylenecarbazolylene}-*alt-co*-(1,4-phenylene)] (PNVCP), bearing alternated 9-(*α*-naphthyl)-carbazole and benzene units, was synthesized via a Wittig–Horner reaction. The solubility, thermal, and optical properties were investigated. It was soluble in common organic solvents, such as tetrahydrofuran and 1,2-dichloroethane. Thermogravimetric analysis and differential scanning calorimetry showed that the conjugated polymer exhibited good thermal stability up to 496°C with a glass-transition temperature higher than 110°C. The photoluminescence properties were studied. The polymer emits blue light and the quantum yield is 93% in solution. The emission spectra exhibited an obvious solvent effect. With the increase of the polarity of the solvents, the fluorescence spectra changed obviously and appeared to be redshifted at room temperature. The redshift was more obvious in aromatic solvents than in aliphatic solvents. When *N,N*-dimethylaniline was gradually added into the solution of the conjugated polymer, the emission intensity of the fluorescence decreased. In comparison, the emission intensity of the polymer showed invariability when 1,4-dicyanobenzene was added into the polymer solution. Moreover, the fluorescence of the polymer could be effectively quenched by fullerene. Overall, the synthesized polymer is a potential candidate material for fabrication of polymeric light-emitting devices. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 923–927, 2006

Key words: conjugated polymers; luminescence; monomers; *N*-(*α*-naphthyl)-carbazole; Witting-Hornor reaction

INTRODUCTION

Light-emitting (LE) polymers have attracted much attention in academia and in the optoelectronic industry because of their advantageous properties and potential application in a wide variety of flat-panel displays.[1,2] Since the introduction of the first *π*-conjugated polymer, poly(*p*-phenylenevinylene), in 1990,[3] many research efforts have been made to synthesize and characterize new *π*-conjugated polymers.[4,5] Currently, one of the main research objectives in this field is to develop LE polymers that exhibit both high photoluminescence (PL) efficiency and high stability.[6] The carbazole unit (CZ) is known to be a hole-transporting and LE material. It exhibits intense UV absorption spectra and has been used extensively as a strong electron donor in the study of photoinduced energy transfer. Some conjugated polymers involving carbazole moieties in the main chain have been prepared.[7] However, their PL efficiency and stability, which are directly related to the performance of optoelectronic devices, are not perfect. Therefore, it is necessary to design and synthesize some new conjugated polymers containing CZ. A novel luminescent conjugated polymer, poly[{9-(*α*-naphthyl)-3,6-divinylenecarbazolylene}-*alt-co*-(1,4-phenylene)] (PNVCP), was synthesized by Wittig–Horner polycondensation of 9-(*α*-naphthyl)-3,6-diformyl carbazole (NDFC) with *α,α*-dichloro-*p*-xylene. The photophysical processes, solubilities, and thermal stabilities were examined.

EXPERIMENTAL

Materials and instruments

Reagents and chemicals for the preparation of the monomer and polymer were used as received unless noted otherwise. Cyclohexane, benzene, ether, chloroform, ethanol, toluene, bromobenzene, *N,N*-dimethylaniline (DMA), and 1,4-dicyanobenzene (1,4-DCB) were analytical grade reagents and treated according to standard methods before use; these were all applied in the measurement of the PL properties. The melting points were determined with a Sango Gallenkamp MPD350 melting-point apparatus and uncorrected.
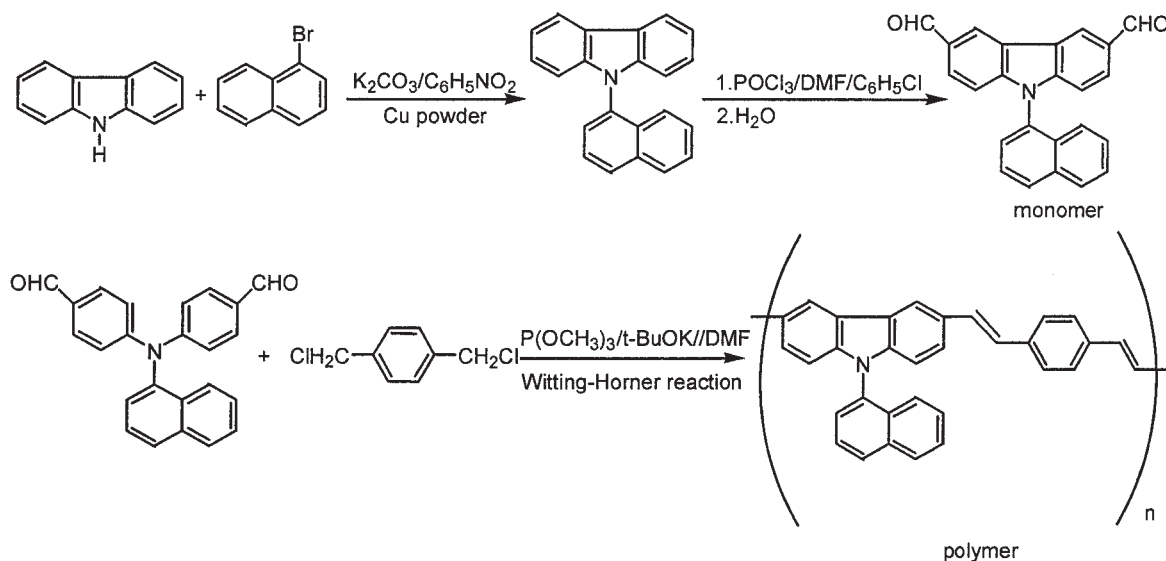
Scheme 1 The chemical structures of PNVCP.

The NMR spectra were measured on a Bruker ARX300 spectrometer in chloroform-d solvent with tetramethylsilane as an internal standard. Fourier transform IR spectra were obtained on a PE-1700 IR spectrophotometer. Elemental analyses were performed on a Vazio Elemental Analyzer. The thermal properties were measured on a PerkinElmer TGA-7 thermogravimetric analyzer and a Mettler–Toledo DSC-822e differential scanning calorimeter under a nitrogen atmosphere at a heating rate of 20.0°C/min. The PL properties were measured on a Shimadzu RF-540 spectrofluorophotometer. Both excitation and emission bands were set at 10 nm in this experimental condition. All experiments were carried out at 25°C. The excitation wavelength was 380 nm for the fluorescence spectra. UV–visible absorption spectra were recorded on a Shimadzu UV-265 spectrophotometer.

Synthesis of monomers

9-(α-naphthyl)-carbazole

We placed 8.4 g (0.05 mol) of carbazole, 11.2 g (0.05 mol) of α-bromonaphthalene, 7.0 g of potassium carbonate, 0.5 g of copper powder, and 100 mL of nitrobenzene in a three-necked flask equipped with a mechanical stirrer and dropping funnel (Scheme 1). The reaction mixture was stirred and heated in an oil bath at 210°C. The water produced by the reaction process was distilled from the reaction system. After refluxing for 10 h, the reaction mixture was cooled and the nitrobenzene was removed by steam distillation. The residues were washed with water until neutral. The crude products were purified by recrystallization in ethyl acetate. Yield 71.4%. mp 123–124°C. ANAL. Calcd

for $C_{22}H_{15}N$: C, 89.66%; H, 5.16%; N, 4.77%. Found: C, 89.56%; H, 5.03%; N, 4.41%. IR (KBr, cm^{-1}): 3032, 1600, 1580, 1470, 775, 765, 750, 752. ^{1}H-NMR (δ): 6.80–8.24 (m).

NDFC

Phosphoryl chloride (37.3 mL, 0.4 mol) was added dropwise into 30.9 mL (0.4 mol) of cooled N,N-dimethylformamide (DMF). The mixture was maintained at room temperature for 1 h, and a solution of 5.8 g (0.019 mol) of N-(α-naphthyl)-carbazole in 15 mL of DMF was added. The reaction mixture was heated at 130°C with stirring for 24 h and then poured into cracked ice. After neutralizing with a base, the mixture was extracted with chloroform. The extract phase was dried with anhydrous magnesium sulfate, and the solvent was removed by distillation in a vacuum. The solid residue was purified by using silica-gel column chromatography (eluent: 1 : 3 ethyl acetate/n-hexane), giving 0.79 g of a white-yellow solid; mp 189–191°C. IR (KBr, cm^{-1}): 3400, 1690, 1590, 1500, 1450, 1240, 800, 770, 750. ^{1}H-NMR (CDCl$_3$, δ): 7.1–8.8 (m, 13H), 10.17(s, 2H). MS (M$^+$): 127.

1,4-Bis(triethoxyphosphonionmethyl)benzene dichloride

This compound was prepared by using α,α-dichloro-p-xylene with trimethyl phosphite according to a literature method.[8]

Synthesis of PNVCP polymer

A mixture of 0.4 g (0.001 mol) of NDFC and 0.33 g (0.001 mol) of 1,4-xylene-bis(diethylphosphate) in 20
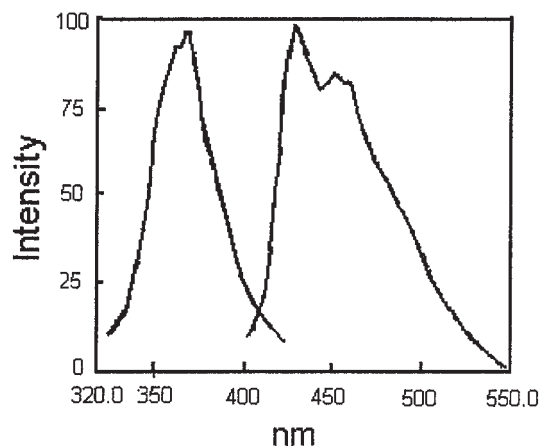
Figure 1 Figure l The emission spectra of 9-(α-naphthyl)-carbazole and the copolymer in cyclohexane.

Figure 2 The emission spectra of 9-(α-naphthyl)-carbazole solution in different solvents.

mL of dried DMF was stirred at room temperature under nitrogen. After 0.448 g (0.004 mol) of solid potassium *tert*-butoxide was added, the reaction solution was heated under reflux for 12 h. The reaction mixture was filtered and the concentrated filter liquor was poured into cold methanol to give a yellow powder. IR (KBr, cm^{-1}): 3200, 1620, 1480, 1395, 1080. ^{1}H-NMR (CDCl$_3$, δ): 7.0–8.0 (m).

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesized monomer (NDFC) and polymer (PN-VCP) were characterized by ^{1}H-NMR and IR spectroscopy. The ^{1}H-NMR spectrum of the monomer shows a chemical shift that is characteristic of the aldehyde group at 10.17 ppm. In comparison, the polymer shows no features at 10.17 ppm.

The IR spectra of the monomer shows a sharp absorption peak at 1690 cm^{-1}, which corresponds to the carbonyl group of formoyl. In the IR spectra of the polymer the peak at 1690 cm^{-1} disappears completely. The results indicate that the conjugated polymer was formed. The polymer exhibited good solubility in some organic solvents, such as tetrahydrofuran (THF), 1,2-dichloroethane, acetone, and so forth. The thermal properties of the polymer were examined with differential scanning calorimetry and thermogravimetric analysis. Its glass-transition temperature was higher than 110°C. Moreover, it exhibited good thermal stability because the weight loss was less 10% on heating to 496°C.

Absorbance and PL properties

The UV–visible absorption spectra of the monomer and polymer in some solvents were measured. The maximum absorptions of the monomer and polymer
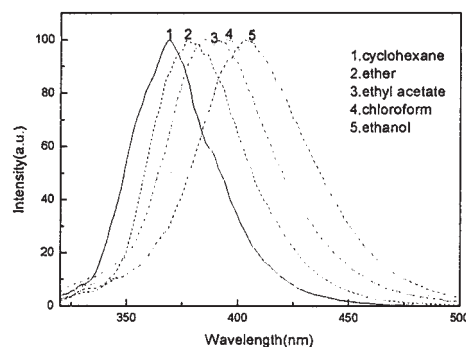
are located at 324 and 345 nm, respectively. Moreover, the polymer shows a broader absorption peak compared to that of its monomer, which can be attributed to the more extended π-conjugation range than the monomer. The PL spectra of the monomer and polymer were measured with excitation wavelengths corresponding to their maximum absorption wavelength. The emission peaks appear to be located in the blue region (Fig. 1). Quite different from the monomer, the emission peak of the polymer is at about 426 nm with a shoulder peak at about 451 nm. It is easy to understand that the emission of the monomer, which contains a local conjugated π system and two carbonyl groups, originated from a π–π* excitonic state. In comparison, the emission of the polymer, which includes an extended conjugated π system, is dominantly originated from some π–π* excitonic states.

Solvent effects on PL

For a deeper understanding of the PL properties of the polymer, the effects of the solvent on the PL were investigated. The fluorescence spectra of the monomer and polymer were measured in different solvents, and all results are shown in Figures 2 and 3. It can be seen from Figure 2 that the fluorescence spectra of the
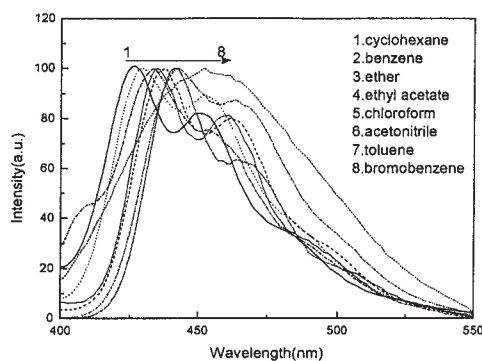

Figure 3 The emission spectra of the polymer solution in different solvents.
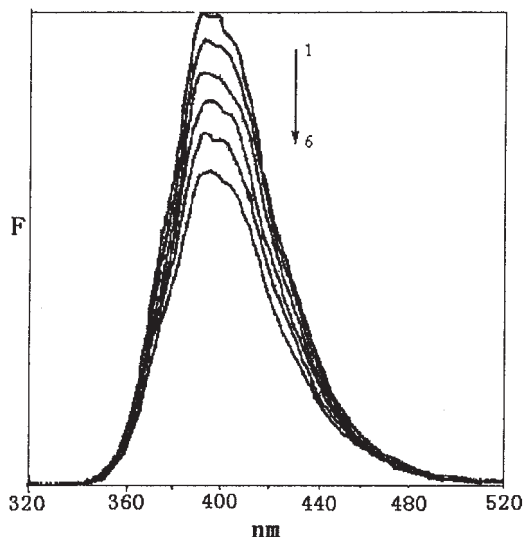
Figure 4 The fluorescence spectra of 9-(α-naphthyl)-carbazole (monomer) at different concentrations of DCB. Concentration of monomer = 4.12×10^{-4} M; concentrations of DCB (mol/L, M) = 0.00 (spectrum 1), 8.67×10^{-5} (spectrum 2), 1.73×10^{-4} (spectrum 3), 3.47×10^{-4} (spectrum 4), 6.94×10^{-4} (spectrum 5), 1.13×10^{-3} (spectrum 6).

monomer obviously change with the increase of the polarity of the solvents.[9] The redshifts of the emission peaks with the increase of the solvent polarities were observed and the half-peak width was simultaneously increased, which was mainly due to dipole–dipole interactions of the excited state of the monomer with different solvents.[10–12] Similarly, redshifts of the emission peaks of the polymer with the increase of the solvent polarity were also observed. However, aromatic solvents, such as benzene, toluene, bromobenzene, and so forth, show stronger solvent effects on the polymer emissions compared to those of aliphatic solvents, such as cyclohexane, ethyl acetate, and so forth. In contrast, the redshifts of the polymer emissions with aromatic solvents are more obvious compared to those with aliphatic solvents. The results could be due to the π-system interactions between the conjugated polymer and aromatic solvents. The conjugated polymer and aromatic solvent both have conjugated π systems, so π–π stacking interactions may exist, except for the general dipole–dipole effect. It has been reported that the chains of polymers may be more rigid in aromatic solvents than in aliphatic solvents. Consequently, the effective extent of the conjugation system of the polymer in aromatic solvents is relatively increased.[13]

Interaction of monomer and polymer with 1,4-DCB and DMA

It is well known that 1,4-DCB is a typical electron acceptor and DMA is a typical electron donor. When

1,4-DCB was gradually added to a solution of the monomer (NDFC) in CHCl$_3$, the emission was quenched and the quenching process followed the Stern–Volmer equation. The apparent quenching coefficient (K_{SV}) is 2.06×10^3 $[M]^{-1}$ (Fig. 4). A similar appearance was observed when DMA was gradually added to a solution of the monomer in CHCl$_3$. The results showed NDFC could act as an electron donor or an electron acceptor in different environments.

In comparison, the emissions of the polymer are not quenched by 1,4-DCB (Fig. 5). The experimental facts might be primarily attributable to the low electron donating ability of the conjugated polymer. The electron motions of the conjugated polymer mainly occurred in the conjugated polymer backbones, so the electron transfer from the polymer molecule to acceptor is not dominant.

Interaction between polymer and fullerene (C$_{60}$)

To study of the interaction between the polymer and C$_{60}$ it is helpful to understand the photoelectronic properties of the polymer materials. It was well known that one of the most remarkable properties of C$_{60}$ related to electron transfer phenomena is that it can efficiently induce a rapid charge separation and a further slow charge recombination.[14]

In this study C$_{60}$ was used as a quencher to investigate the photoinduced electron transfer properties of the polymer. The results are shown in Figure 6. As we can see in the figure, with a progressive increase in the concentration of C$_{60}$, the simple molecule fluorescence of the polymer is quenched efficiently and the quenching process conforms to the Stern–Volmer equation, $F_M^0/F_M = 1 + K_{SV}[Q]$. The K_{SV} is larger (5.54×10^4 $[M^{-1}]$) than that of the other quencher, which demonstrates that strong interactions between the polymer
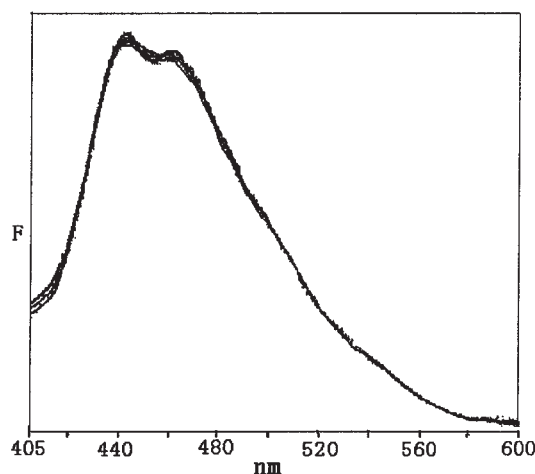

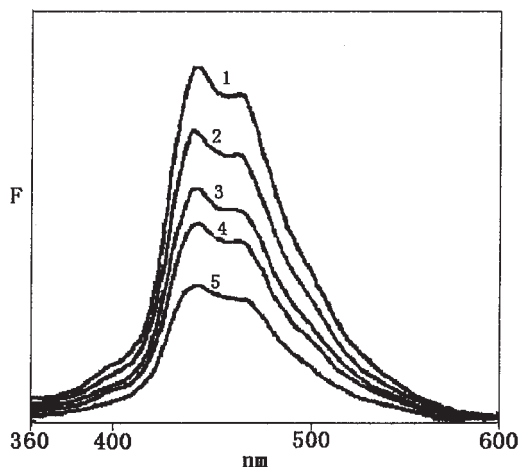**Figure 5** The fluorescence spectra of the polymer at different concentrations of DCB.

Figure 6 The fluorescence spectra of the polymer at different concentrations of C_{60}. Concentration of polymer = 3.33 $\times$ 10^{-4} mg/mL; concentrations of C_{60} (mol/L, M) = 0.00 (spectrum 1), 5.80 $\times$ 10^{-4} (spectrum 2), 1.16 $\times$ 10^{-3} (spectrum 3), 1.74 $\times$ 10^{-3} (spectrum 4), 2.90 $\times$ 10^{-3} (spectrum 5).

and C_{60} are present. The strong interaction might be caused by the photoinduced charge transfer and interactions of their conjugated π system.[15]

CONCLUSIONS

PNVCP, a novel conjugated polymer, was synthesized by Wittig–Horner polycondensation of NDFC with α,α-dichloro-p-xylene.

The polymer was stable beyond 496°C and soluble in THF, acetone, 1,1'-dichloroethane, and so forth. In the solution, the PL and absorption maximum of the polymer were at around 426 and 345 nm, respectively. The quantum yield of PL was 93%. Redshifts of the emission peaks of the polymer were observed with the increase of the solvent polarity. When DMA was added into the solution of the polymer, the emission intensity of the fluorescence was decreased. In comparison, the fluorescence intensity of the polymer was not quenched when 1,4-DCB was added into the polymer solution.

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