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Chain conformation dependent fluorescence of blue-emitting poly(arylene ether nitrile)

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ABSTRACT

Poly(arylene ether nitrile) (PEN) containing phenolphthalin moiety is an intrinsically blue-emitting fluorescent polymer with outstanding mechanical and thermal properties. Herein, the fluorescent properties of the fluorescent PEN (FPEN) have been, for the first time, correlated with the conformation manipulation of polymer chain that is enabled by the variation of concentration, molecular weight, polydispersity and aggregation states in solvent-nonsolvent system. The experimental results indicate that the fluorescent emission of FPEN is highly dependent on concentration, with the strongest fluorescence detected at a critical concentration in N,N-dimethylformamide (DMF). In the lower concentration range, where the polymer intermolecular interaction is minimized, the PEN fluorescence is mainly dependent on the molecular weight and local chain organization. On the contrary, the polydispersity index of FPEN plays a dominate role in the fluorescent emission when the concentration is higher than 50 mg mL⁻¹.

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1. Introduction

Fluorescent polymers have gained tremendous attentions due to their tunable fluorescence properties, good optical stability, diverse molecular structure, excellent flexibility and processability [1]. Thus, they have been widely applied in various fields, such as chemical sensors [2,3], optical devices [4,5], biomedicine [6] and optical resin [7]. Poly(arylene ether nitrile) (PEN) is one type of high performance engineering thermo-plastic showing good thermal stability, solubility and film-forming ability [8,9]. It has been reported recently that intrinsically fluorescent PEN (FPEN) can be synthesized via nucleophilic polymerization using phenolphthalin and 2,6-dichlorobenzonitrile [10]. The obtained blue emitting FPEN was highly transparent in solution and film state under visible light. In addition, thanks to the reactivity of carboxyl groups, rare-earth compound and noble metal nanoclusters have been composited or coordinated with FPEN to expand their fluorescent emission [11–13].

However, the underline principle for the fluorescent evolution of FPEN, which is essential for their practical application in various fields, is virtually unexplored in these previously reported works. Generally, the luminescent properties of intrinsically fluorescent polymer are strongly dependent on the chain conformation. For instance, the

fluorescence emission spectra of typical conjugated polymer, such as poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV) [14,15], cyano-containing polyphenylenevinylene (CN-PPV) [16] and poly(phenylene ethynylene) (PPE) [17] can be modulated with the conformation changes (aggregates, agglomerates and collapsed chains) induced by chain length, concentration, solvent-nonsolvent system, etc. Specifically, blue-shift or red-shift of emission spectra was observed due to the relative contribution from intrachain or interchain energy transfer [18].

In this work, a series of FPEN containing phenolphthalin (PPL) with different molecular weight and polydispersity index were synthesized. The chain conformation was controlled in terms of concentration, molecular weight, polydispersity index and solvent-nonsolvent system in order to fully investigate FPEN fluorescent properties.

2. Experimental

2.1. Materials

Phenolphthalin (PPL) was synthesized in our laboratory. 2,6-dichlorobenzonitrile (DCBN, AR), hydrochloric acid, N-methyl-2-pyrrolidone (NMP, AR), N,N-dimethylformamide (DMF, AR), N,N-dimethylacetamide (DMAc, AR), tetrahydrofuran (THF, AR), trichloromethane (CHCl₃, AR), toluene (PhMe, AR) and potassium carbonate (K₂CO₃, AR) were purchased from Tianjin Bodi

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Chemicals. All the materials were used as received without further purification.

2.2. Instrument

Gel permeation chromatography (GPC) analysis was conducted with a PL-GPC220 system using polystyrene as standard (THF eluent). Thermal stability analysis (TGA) was measured by TA Instruments TGA-Q50, at a heating rate of 20 °C min⁻¹ under a nitrogen flowing. The steady state fluorescent spectra were recorded using a fluorescence spectrophotometer (F-4600, Hitachi). The ultraviolet-visible (UV-vis) absorption spectra were measured on a photospectrometer (TU-1810, Persee). The time-correlated photoluminescence decay and fluorescence lifetime were determined by using a Horiba Jobin Yvon TempPro-01 instrument. The Fourier transform infrared (FTIR) spectra were recorded using a Shimadzu 8400S FTIR spectrometer. NMR spectra were obtained with a Bruker AV II-400 spectrometer. The ¹H NMR (400 MHz) chemical shifts were measured relative to DMSO-*d*₆ (*H*: δ=2.50 ppm) as the internal references.

2.3. Synthesis

Five fluorescent poly (arylene ether nitrile)s (FPENs) samples with different molecular weight were synthesized from phenolphthalin (PPL) and 2, 6-dichlorobenzonitrile (DCBN) via nucleophilic aromatic substitution using potassium carboxylate (K₂CO₃) as the catalyst, according to the method previously reported with slight modification [19]. Different molecular weight FPENs were obtained by changing the stoichiometry ratio of PPL and DCBN. In a typical synthesis, PPL (20 g, 0.062 mol) with a certain quantity of DCBN (10.66 g, 0.062 mol) and K₂CO₃ (26 g, 0.190 mol) were mixed in a three-necked flask. Then N-methyl-2-pyrrolidone (30 mL) and toluene (10 mL) were added into flask, followed by heating up to 150 °C with a continuous mechanical agitation for 2 h. After removing the mixture of toluene and water, the temperature was increased to 190 °C and maintained for 3 h. The crude product was poured into cold water, and then boiling in the dilute hydrochloric acid to remove excess K₂CO₃. In order to remove the excess DCBN, the product was washed with hot ethanol and water for three times, respectively. Finally, the collected precipitate was dried at 80 °C for 24 h in a vacuum oven. The obtained FPENs were named according to molecular weight increase as listed in Table 1. ¹H NMR (400 MHz, DMSO-*d*₆, δ): 6.60 (d, *J*=8.4 Hz, 2H; ArH); 6.70 (s, 1H; CH); 7.06 (d, *J*=8 Hz, 1H; ArH); 7.15 (dd, *J*=8.8 Hz, 12 Hz, 8H; ArH); 7.35 (t, *J*=7.6 Hz, 1H; ArH); 7.52 (q, *J*=8.4 Hz, 2H; ArH); 7.82 (d, *J*=7.6 Hz, 1H; ArH), 12.98 (s, 1H; COOH). IR (KBr): ν=2230 cm⁻¹ (C–N); 1718 cm⁻¹ (–COOH); 1245 cm⁻¹, 1022 cm⁻¹ (–C–O–C–).

Table 1
Monomers mass, molecular weight and molecular weight distribution, thermal properties and quantum yield of synthesized FPENs.

| No. | Monomers mass (m _{PPL} / m _{DCBN}) (g/g) | GPC analysis | | | Thermal properties <i>T</i> _{5%} °C | Quantum yield <i>Φ</i> _F |
|--------|--|------------------------|------------------------|---------------------------------|---|--|
| | | \overline{M}_n (kDa) | \overline{M}_w (kDa) | $\overline{M}_w/\overline{M}_n$ | | |
| FPEN-1 | 20.00/32.22 | 3.7 | 5.5 | 1.48 | 328 | 0.08 |
| FPEN-2 | 20.00/18.79 | 4.0 | 5.5 | 1.38 | 394 | 0.04 |
| FPEN-3 | 20.00/13.13 | 8.0 | 12.2 | 1.53 | 384 | 0.07 |
| FPEN-4 | 20.00/10.74 | 12.0 | 21.6 | 1.80 | 324 | 0.20 |
| FPEN-5 | 20.00/10.66 | 14.9 | 23.4 | 1.57 | 361 | 0.14 |

3. Results and discussion

3.1. Molecular weight, thermal stability, quantum yield and optical properties measurement of FPEN

As shown in Fig. 1A, FPEN was synthesized via the nucleophilic aromatic substitution polymerization of DCBN and PPL using K₂CO₃ as catalyst. The monomers of DCBN and PPL were both non-fluorescent, while the products emitted around 420 nm. It was reported that when the PPL introduced into the backbone, the tertiary carbon in the phenolphthalin unit can be excited to be trityl radical, which could be responsible for the blue-emitting fluorescence of FPEN upon ultraviolet light excitation [20]. Gel permeation chromatography (GPC) analysis results are shown in Table 1, including number-average molecular weight (\overline{M}_n), weight-average molecular weight (\overline{M}_w) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) for five synthesized samples. Their molecular weights were increased from FPEN-1 to FPEN-5 with a narrow polydispersity from 1.38 to 1.80. Meanwhile, as shown in Table 1, they all exhibited good thermal stability with 5% loss weight temperature (*T*_{5%}) located in the range of 324–394 °C, which was due to the presence of aromatic structure and nitrile in FPEN backbone. Quantum yield (Φ_F) of FPEN (0.04–0.20) in DMF (1 mg mL⁻¹) were calculated by using Rhodamine B as a reference and the results were listed in the last column in Table 1.

Photophysical properties including UV-vis absorption, fluorescence excitation and emission spectra of FPEN were illustrated in Fig. 1B using FPEN-3 (1 mg mL⁻¹) as an example. The peak wavelength of maximum absorbance at ~318 nm is associated with the π–π* transition of the large number of aromatic units [21]. Excitation and emission spectra displayed the peak at ~328 nm and ~410 nm, respectively. In addition, FPEN can be dissolved in many common organic solvents including N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), tetrahydrofuran (THF), trichloromethane (CHCl₃), N,N-dimethylacetamide (DMAc), etc. In this work, DMF was used as the solvent based on the solvent effect test. FPEN-3 emission spectra in three common organic solvents of NMP, DMAc and DMF have been recorded as shown in Fig. 1C. The results demonstrated that the fluorescence emission of FPEN-3 with same concentration was maximized in DMF. Because FPEN unit contains a polar carboxyl group (–COOH), which will exhibit the strongest solvent effect by forming hydrogen bond with DMF molecules [22,23]. For this reason, DMF has been chosen as the experiment solvent in all tests.

3.2. Concentration dependent fluorescent emission of FPEN

Emission intensity and wavelength of fluorescent polymer are highly dependent on concentration. Generally, fluorescence intensity was proportionally increased with increasing of concentration in a dilute solution. But in the concentrated solution, the emission intensity is often decreased with concentration increasing. The fluorescence quenching at high concentration was mainly attributed to the non-radiation energy transfer by collisional action between excited and ground states, the formation aggregates at high concentrations [24]. In addition, the so-called inner-filter effects, derived from the partial spectral overlap of absorption band and emission band of the fluorophore at high concentration, could also lead to the extinction of fluorescent emission at shorter wavelength [25].

The fluorescence emission of FPEN-3 in DMF solution was recorded in a wide concentration range from 0.05 mg mL⁻¹ to 150 mg mL⁻¹ as shown in Fig. 2A. When the concentration is lower than 50 mg mL⁻¹ the emission intensity was readily increased with concentration increasing. However, fluorescence

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