Synthesis and characterization of semi-crystalline polyarylene ether nitrile with AIEE feature

Pan Wang, Kui Li, Kun Jia* and Xiaobo Liu*
Centre for Applied Chemistry, High Temperature Resistant Polymer and Composites, Key laboratory of Sichuan Province, University of Electronic Science and Technology of China, Chengdu, China
*Corresponding author e-mail: liuxb@uestc.edu.cn, jiaakun@uestc.edu.cn

Abstract. An AIEgen 1, 2-di (4-hydroxyphenyl)-1, 2-diphenylethene (TPE-2OH) was introduced into the back bone of semi-crystalline poly arylene ether nitriles (PEN). The fluorescence spectra results indicated that the derived polymer displayed a typical aggregation-induced emission enhancement (AIEE) active with an emitting peak at ~470 nm. Then the AIEE active PEN was prepared into films through casting method and realised strong fluorescence emission and excellent mechanics properties. Besides, the crystal AIE active polymer shows sphere micro-morphology along with a strong blue emission. These findings will open a door for further research on the high performance semi-crystalline PEN at flexible display technology and optical sensors.

1. Introduction
During the recent decades, polymeric light-emitting materials have been widely used in optical device, chemical sensor, bioprobe, drug delivery and optical resin due to their good photo stability, high glass-transition temperature, excellent processability and ability of large scale fabrication[1, 2]. Therefore, a tremendous number of new polymeric optical materials have been developed to meet various applications. To date, there is an advanced approach of optical material design protocol which depended on the introduction of aggregation-induced emission fluorogen (AIEgen) [3]. AIEgen is a type of material shows non-fluorescence or negligible fluorescence in single molecule state, but been induced or enhanced emission in aggregation state [4]. Materials can be endowed by AIEgen with aggregation-induced emission (AIE) or aggregation-induced emission enhancement (AIEE) properties to against the tradition abhorrent aggregation-caused quenching (ACQ).

As a type of high performance thermoplastic polymer, Polyarylene ether nitrile (PEN) showing a favorable mechanical strength, high thermostability, radiation resistance, electrical properties and processability [5, 6]. Generally, PEN is applied as an engineering plastic in many files, such as military and defense, aircraft manufacturing and petrochemical. But recently, our laboratory has done several investigations to explore its optical applications. Including colorful rare-earth composite flexible films, Ag nanoparticle synthesized surfactant and heavy metal chemosensor [7-10]. However, these studies all focus on the type of PEN holding phenolphthalin (PPL) fluorogen segment in the structure, which pending with a functional carboxyl group. Other members of polyarylene ether nitrile family with much higher mechanical performance, excellent thermal stability and other functional properties are require for investigation. Since then, we choose a semi-crystalline PEN including
biphenyl segment for fluorescence transformation which has never been studied with optical performance. The synthesized PEN was characterized by fluorescence spectroscopy both in solution and film states, which indicated that the semi-crystalline PEN has been endowed with AIEE feature for the first time, successfully. The chemical structure, molecular weight, UV-visible absorption, mechanical stability, polarized microscope images and micro morphology of crystal were also studied in the present work.

2. Experimental

2.1. Materials
1,2-di(4-hydroxyphenyl)-1,2-diphenylethene (TPE-2OH, CP) was purchased from Beijing HWRK Chem. Co., LTD. Biphenol (BP, AR), resorcinol (RS, AR), 2,6-difluorobenzonitrile (DFBN, AR), potassium carbonate (K2CO3, AR), hydrochloric acid (HCl, 38%), tetrahydrofuran (THF, AR), N-Methyl-2-pyrrolidone (NMP), toluene (AR), dimethylformamide (DMF, AR) and acetone (AR) were obtained from Kelong Chemicals. All the materials were used as received without any further purification.

2.2. Synthesis of AIEE active PEN
The AIEE active PEN was synthesized from bisphenol monomers and DFBN though nucleophilic aromatic substitution polymerization as shown in the synthesized route (Scheme 1). BP (7.37 g, 39.62 mmol), RS (1.10 g, 10.00 mmol), TPE-2OH (0.18 mg, 0.50 mmol), DFBN (6.95 g, 50.00 mmol) and K2CO3 (10.35 g, 75.00 mmol) were added into a three-necked round bottom flask equipped with a knockout. Then, NMP (18 mL) and toluene (6 mL) were added to dissolve the mixture under mechanical stirring. The reaction temperature was heated up to 140 °C and kept for 2 h to promote the formation of phenolate. In this step, the generated water-toluene azeotrope was distilled off though the knockout. After that, the temperature was heated up to 180-190 °C gradually to complete the polymerization. The products were purified with acetone for three times, and boiling with diluted hydrochloric acid and deionized water for three times to remove the excessive K2CO3 and solvents respectively. Finally, the filtration was dried at 80 °C in vacuum oven for 24 h and named as PEN-BP/RS/TPE. FTIR (KBr): $\nu = 1660$ cm$^{-1}$ and $1457$ cm$^{-1}$ (C=C); 1254 cm$^{-1}$ (C-O-C), 1000 cm$^{-1}$ (C-O); 660 cm$^{-1}$ (O-H). The contrast polymer (PEN-BP/RS) is synthesized in our laboratory though the same procedure before. The stoichiometric ratio of BP and RS is 8:2 without TPE-2OH monomer used.

2.3. The fabrications of polymer films and crystals
The films were prepared though classical casting method. 1 g polymer was dissolved in 10 mL NMR solvent and stirring for 30 min to form homogenous solution. Then, the solution was cast on a clean horizontal glass plate in an oven. The temperature was heated at the process of 80, 100, 120, 140, 160, 180, 200 °C for 2h by sequence. After that, the films were cooled to the room temperature naturally and then peeled off from the glass plates. The crystal of polymers were fabricated by dropping the same solution on clean cover glass and then covered with another cover glass. The crystals were generated between two cover glasses after drying in oven with the heating process.

2.4. Characterization
Chemical structure was characterized by Fourier transform infrared (FTIR, 8400S, Shimadzu) spectroscopy. Gel permeation chromatography (GPC) was measured on PL-GPC220 system using polystyrene and THF as the standard and eluent. The absorption results were recorded on an ultraviolet-visible (UV-Vis) photospectrometer (TU-1810, Persee). The fluorescence spectra of polymer solutions and film were measured on a fluorospectrometer (F98, Lengguang), while the fluorescence spectra of polymer crystal were measured on a conventional microscope (BA410e, Motic) equipped with a laser (405 nm) and a portable spectrometer (NOVA, Ideaoptics). Mechanical properties of polymer films were carried out on a SANS CMT6104 series desktop electromechanical universal testing machine after being cut into standard strips (10 mm x 100 mm). The polarized
microscope images of polymer crystal were taken on a polarizing microscope (MP41, MshOt). Otherwise, the micro morphology of crystal was characterized by a scanning electron microscope (SEM, JSM-5900LV, JEOL) operating at 20 kV.

Scheme 1. The synthesis route of PEN-BP/RS/TPE.

3. Results and discussion
The molecular weight and optical properties of synthesized PEN-BP/RS/TPE and PEN-BP/RS were shown in Table 1. The results including number-average molecular weight ($M_n$), weight-average molecular weight ($M_w$) and polydispersity index ($M_w/M_n$) for two polymers were similar with each other to avoid the impact of the molecular weight. The UV-Vis absorption peak at 323 nm and 324 nm is derived from the $\pi$-$\pi^*$ transition of the large number of aromatic units. Otherwise, both polymers show blue emitting at 431 nm and 429 nm, respectively.

| No.          | $M_n$ (kDa) | $M_w$ (kDa) | $M_w/M_n$ | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) |
|--------------|-------------|-------------|-----------|-----------------------|---------------------|
| PEN-BP/RS    | 92.05       | 44.19       | 2.08      | 323                   | 431                 |
| PEN-BP/RS/TPE| 87.84       | 50.84       | 1.73      | 324                   | 429                 |

The fluorescence perperties of aggregated polymers were studied in the mixture of their good solvent and poor solvent (DMF/H$_2$O). As displayed in Figure 1A-B, fluorescence intensity of contrast PEN didn’t show a regular changing with the increase of water content. The new emerge emission peak at 418 nm in fluorescence spectra may be caused by the formation of excimers after the addition of water. In addition, insert in Figure 1B, the slight changes also shown in the corresponding digital photo of polymer in mixture solvent with 0% and 50% water content upon irradiation of UV-light. On the contrary, as shown in Figure 1C-D, the synthesized PEN-BP/RS/TPE gives out a huge difference. The emission intensity gradually increased and red-shift from 429 nm to 466 nm until the water content increased to 50%. More specifically, the highest emitting intensity is about 12-fold than that in pure DMF solvent. The emission comparison also can be observed by naked eye obviously from the digital photo taken under UV-light irradiation (insert in Figure 1D). After that, the fluorescence intensity began to decrease due to the massive aggregates formation. Therefore, the results reveal that PEN-BP/RS/TPE possesses typical AIEE properties after being endowed by AIEgen.
Figure 1. The fluorescence spectra respond to different water fraction and the corresponding fluorescence peak intensity changing trends of PEN-BP/RS (A and B) and PEN-BP/RS/TPE (C and D). The inserts in (C) and (D) are the digital photos of two polymers with 0% and 50% water fraction under the UV light (365 nm) irradiation, respectively. ($\lambda_{ex}=365$ nm)

Depends on the good film-forming property of PEN, the obtained polymer has been fabricated as films through classical casting method. The fluorescence spectra were measured under the film state with emission peak at ~470 nm and ~450 nm for PEN-BP/RS/TPE and PEN-BP/RS, respectively (see in Figure 2A). Combine with the corresponding digital image of films upon UV-light (365 nm) irradiation, the fluorescent of PEN-BP/RS/TPE is much brighter than the contrast polymer. Besides, as shown in Figure 2B, the tensile strength and tensile modulus of PEN-BP/RS/TPE film is ~102 MPa and ~2036 MPa which is not inferior to ~99 MPa and ~2557 MPa of PEN-BP/RS film. The results show that PEN-BP/RS/TPE can be processed into a flexible film with well mechanical property and strong fluorescence emitting.

Figure 2. The fluorescence spectra of films fabricated from two polymers (A) and the corresponding digital photo upon the irradiation of UV light (365 nm). The tensile strength and tensile modulus results of two polymers (B). ($\lambda_{ex}=365$ nm)
Since PEN including BP segments is a type of semi-crystalline polymer, the crystal property of the AIEE active polymer also has been studied. Figure 3A shows the fluorescence intensity of crystal of PEN-BP/RS/TPE is also much high than that of PEN-BP/RS. The polarized microscope images (Figure 3B-C) and the micromorphology images (Figure 3D-E) show that both polymers were fabricated into sphere crystal. In recent years, the AIE/AIEE dye with crystallization-induced emission enhancement (CIEE) effect has become promising materials in gas sensor and organic light emitting diode applications (OLED) [11, 12]. Thus, the relationship between crystallization process and fluorescence properties of semi-crystalline PEN should be further investigated in detail.

![Figure 3. The fluorescence spectra of two polymers under the crystal state (A). The corresponding polarized microscope images and micromorphology of PEN-BP/RS (B and C) and PEN-BP/RS/TPE (D and E). (λ\textsubscript{ex}=405 nm)](image)

4. Conclusion
In summary, a polyarylene ether nitrile contains TPE segment was synthesized through nucleophilic aromatic substitution polymerization. The obtained polymer was confirmed to possess AIEE feature by studying the fluorescence property vary with the water content in mixture of DMF/H\textsubscript{2}O. As a comparison, the similar PEN with no TPE segment didn’t show the AIEE properties. Due to the good film-forming and semi-crystalline property, the obtained AIEE active PEN was prepared as film and crystal forms. The AIEE active PEN exhibits a strong fluorescence emission in both film and crystal state which is far more than the contrast polymer. In addition, the film possesses excellent mechanical properties with tensile strength ~100 MPa and tensile modulus over 2000 MPa. The SEM results and polarize microscope images demonstrate that the synthesized polymer formed as sphere crystal. Above all, these characteristics will provide a basis for future studies on the fluorescence properties of semi-crystalline PEN and potential applications in gas sensor, flexible display technology and OLED fields.

Acknowledgments
This work was financially supported by the National Natural Science foundation of China (No. 51373028, No. 51773028, No. 51403029).

References
[1] A. Bajaj, O. R. Miranda, I. Kim, R. L. Philips, D. J. Jerry, U. H. F. Bunz, V. M. Rotello, Detection and differentiation of normal, cancerous, and metastatic cells using nanoparticle-polymer sensor arrays, Pro. Natl. Acad. Sci. 106 (2009) 10912-10916.
[2] S. R. Tseng, H. F. Meng, K. C. Lee, S. F. Horong, Multilayer polymer light-emitting diodes by blade coating method, Appl. Phys. Lett. 93(2008) 153308.
[3] R. Hu, N. L. Leung, B. Z. Tang, AIE macromolecules: syntheses, structures and functionalities. Chem. Soc. Rev. 43 (2014) 4494-562.
[4] J. Luo, Z. Xie, J. W. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Zhu, B. Z. Tang,
Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. Chem. Comm. 18 (2001) 1740-1741.

[5] Y. Q. Zhan, Y. J. Lei, F. B. Meng, J. C. Zhong, R. Zhao, X. B. Liu, Electrical, thermal, and mechanical properties of polyarylene ether nitriles/graphite nanosheets nanocomposites prepared by masterbatch route. J. Mater. Sci. 46(2010) 824-831.

[6] H. L. Tang, J. Yang, J. C. Zhong, R. Zhao, X. B. Liu, Synthesis and dielectric properties of polyarylene ether nitriles with high thermal stability and high mechanical strength. Mater. Lett. 65 (2011) 2758-2761.

[7] H. L. Tang, Z. J. Pu, X. Huang, J. J. Wei, X. B. Liu, Novel blue-emitting carboxyl-functionalized poly(arylene ether nitrile)s with excellent thermal and mechanical properties. Polym. Chem. 5 (2014) 3673-3679.

[8] P. Wang, L. Y. Zhao, H. G. Shou, J. Y. Wang, P. L. Zheng, K. Jia, X. B. Liu, Dual-emitting fluorescent chemosensor based on resonance energy transfer from poly(arylene ether nitrile) to gold nanoclusters for mercury detection. Sens. Actuators, B 230 (2016) 337-344.

[9] H. L. Tang, Z. J. Pu, J. J. Wei, H. Y. Guo, X. Huang, X. B. Liu, Fluorescence-color-tunable and transparent polyarylene ether nitrile films with high thermal stability and mechanical strength based on polymeric rare-earth complexes for roll-up displays. Mater. Lett. 91 (2013) 235-238.

[10] K. Jia, H. G. Shou, P. Wang, X. F. Zhou, X. B. Liu, Controlled synthesis of silver nanostructures stabilized by fluorescent polyarylene ether nitrile. Appl. Sur. Sci. 377 (2016) 180-183.

[11] Y. Dong, J. W. Lam, A. Qin, Z. Li, J. Sun, H. H. Sung, I. D. Williams, B. Z. Tang, Switching the light emission of (4-biphenyl)phenyldibenzofulvene by morphological modulation: crystallization-induced emission enhancement. Chem. Commun. 1(2007) 40-42.

[12] H. T. Bui, J. H. Kim, H. J. Kim, B. K. Cho, S. Cho, Advantages of Mobile Liquid-Crystal Phase of AIE Luminogens for Effective Solid-State Emission. J. Phys. Chem.: C, 120 (2016) 26695-26702.