

Synthesis of Luminescent Polystyrene with π -Conjugated Pendant†

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AJC-13309

One novel polystyrene-based copolymer (PS-PF) with π -conjugated unit (fluorenyl and phenyl rings) as pendant was designed and synthesized using radical polymerization method and initiated by AIBN (2,2'-azobisisobutyronitrile) from the new functional monomer, which contained the conjugated unit and reactive double bond. Nuclear magnetic resonance, FT-IR and UV-visible spectra were used to characterize the structure of intermediate and copolymer. The PS-PF is easily dissolved in organic solvent such as THF and CH_2Cl_2 and to be formed thin film by spin coating. The ink-jet printing method was applied to form blue pattern. The strongest emission of the as prepared copolymer was at 416 nm with shoulder peak of 441 nm in the solution and 440 nm with shoulder peak in the film state.

Key Words: Polystyrene, Conjugated unit, Pendant, Photoluminescent.

INTRODUCTION

π -Conjugated polymers or oligomers have been subject of growing interest in the past decades because they have been found wide applications in polymeric light-emitting diodes, solar cells, transistors chem.-sensors, *etc.*¹⁻⁴. Remarkable progresses have been achieved in the development of these kinds of conjugated polymers and oligomers, particularly those π -conjugated polymer with special molecules structure, such as block copolymer containing the rod-coil segment in the main-chain, dendrimer and hyper-branched conjugated polymer⁵⁻⁷. There is little report to synthesize polymer containing π -conjugated unit as pendant.

Polystyrene (PS) is often regarded as general polymeric materials. Many efforts have been done to introduce special functional to polystyrene by co-polymerization route⁷⁻⁹. Reactive Fe-phthalocyanine was used to react with styrene monomer to produce magnetic micro spheres⁷. Chochos *et al.*⁸ synthesized the dumbbell-like C70 polystyrene derivatives. Copolymer of polystyrene containing liquid crystalline unit was obtained by Tzolakis *et al.*⁹. Thermo-sensitive functional polymer based on polystyrene was prepared by using macromonomer poly (*N*-vinylformamide)¹⁰.

In this paper, it is designed and prepared one reactive monomer with double bond and classic radical polymerization method can be used to conjugated polymer, which can provide a new method to introduce photo-luminescent property to general polymers like polystyrene. This route to synthesize

copolymer of polystyrene and conjugated polymers can free from rigid conditions needed in ATRP or RAFT routes.

EXPERIMENTAL

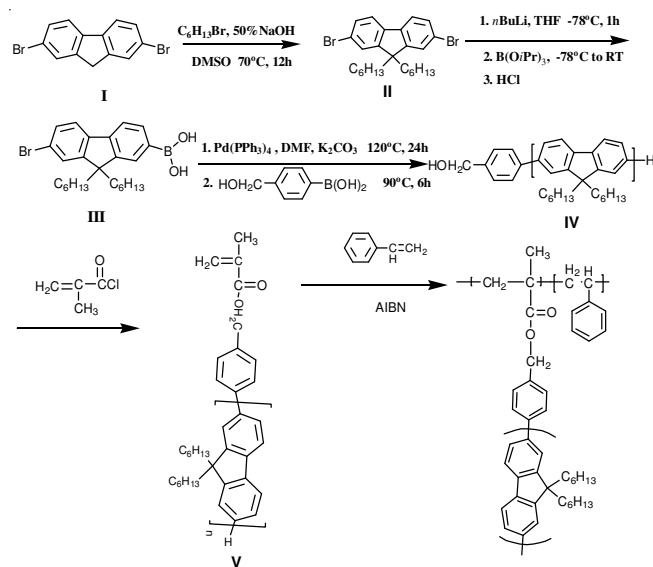
The reactive monomer V (**Scheme-I**) containing double bond was first synthesized. The monomer V was synthesized from 2,7-dibromo-fluorene (I). The middle-product of 2,7-dibromo-9,9-di-*n*-dodecylfluorene (II) and the 3,7-bromo-9,9-di-*n*-dodecylfluorene-2-ylboronic acid (III) in **Scheme-I** were prepared by the previous literature⁸.

The title copolymer of PS-PF was synthesized according to the reaction sequence outlined in the **Scheme-I**. Styrene (St) was purified by treating with 5 wt % aqueous NaOH to remove the inhibitor. AIBN is re-crystallized from THF before usage. Monomer V and styrene (1:1 molar ratio) were dissolved in 20 mL anhydrous DMF and flowed with pure nitrogen to remove O_2 for 30 min. The reaction system were heated to 800 °C for 36 h. The viscosity of the reaction system increased obviously. The fresh copolymer was dissolved in THF and deposited by adding methanol, then filtered and vacuum dried. The product PS-PF was powder-like.

Nuclear magnetic resonance (^1H NMR) spectra were collected on Bruker Avance 300, with chloroformd as a solvent and tetramethylsilane (TMS) as an internal standard. Fourier transform infrared (FT-IR) spectrum was recorded on Shimadzu IR prestige-21 spectrometer. Ultraviolet-visible (UV-VIS) absorption and fluorescence property were measured

†Presented to the 6th China-Korea International Conference on Multi-functional Materials and Application, 22-24 November 2012, Daejeon, Korea

by using a Shimadzu UV-3150 UV-VIS-NIR spectrophotometer and RF-5300PC luminescence spectrometer with a xenon lamp as light source, respectively. The gel permeation chromatography analysis was conducted on Shimadzu 10A in the eluent tetrahydrofuran with polystyrene as the standard.



Scheme-I: Synthetic route to polystyrene copolymer with conjugated unit as pendant

RESULTS AND DISCUSSION

In this paper, monomer V is prepared by monomer IV (containing OH group) and methacryloyl chloride, rather than methacrylic acid, is because of its stronger reactive activity. Fig. 1 is the ^1H NMR spectrum of the monomer V and the copolymer of PS-PF. The values of δ (ppm) at 7.29-7.91 are indexed to H atoms in phenyl and fluorenyl ring. The $\delta = 6.23$ and 5.66 in the NMR spectra of the monomer V indexing to H atoms of reactive double bond is disappeared at the spectra of the copolymer PS-PF, which implied that the monomer V and styrene had been polymerization initiated by AIBN.

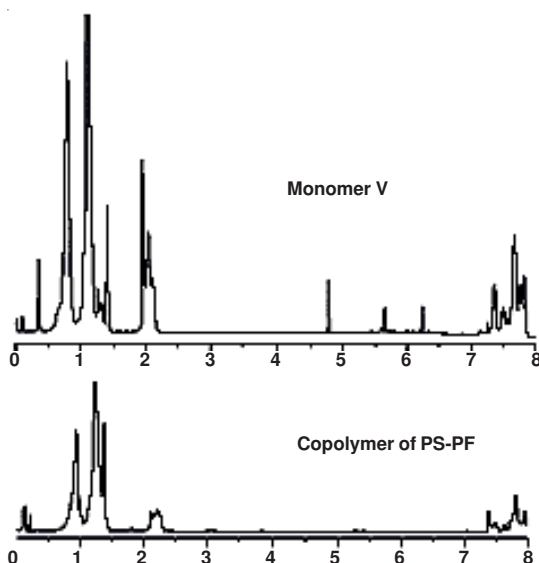


Fig. 1. ^1H NMR spectra of monomer V and PS-PF

FT-IR spectrum is applied to confirm the structure of the copolymer described in **Scheme-I** and is shown in Fig. 2. The absorption of double bond ($\text{C}=\text{C}$) in $1640\text{--}1630\text{ cm}^{-1}$ could not be seen in the spectrum. The molecular weight measurement is performed by gel permeation chromatography in the eluent THF using the calibration curve of polystyrene standards. From the gel permeation chromatography curve, it could be seen that the number average-molecular weight (M_n) and the weight-average molecular weight (M_w) of the resulted PS-PF are 15,600 and 23,700 Daltons, respectively. Single peak appeared in the gel permeation chromatography curve (Fig. 3), suggesting that product is copolymer, rather than the physical mixed system.

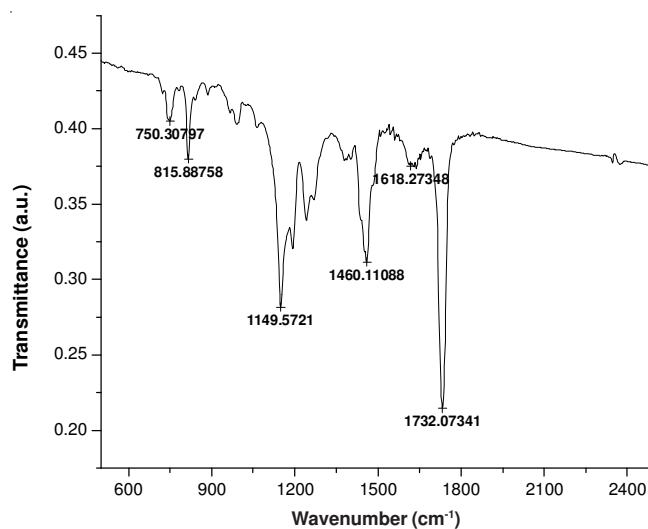


Fig. 2. FT-IR spectra of PS-PF

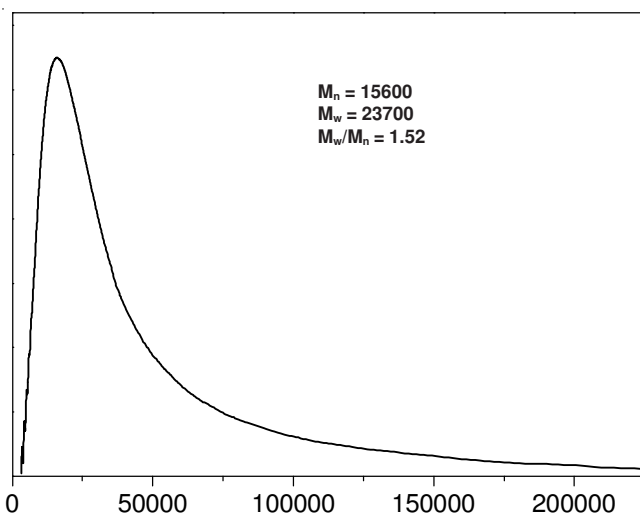


Fig. 3. Gel permeation chromatography analysis of the PS-PF

Fig. 4 is the UV-visible absorption spectra of PS-PF in the THF dilute solution. Its strongest absorption is at 377 nm (4.29 eV) is related to π - π transition of π -conjugated fluorenyl and phenyl pendant and observed in many other reported π -conjugated polymers and oligomers. The film of PS-PF on glass is produced using the spin coating from THF solution of PS-PF. The photoluminescent properties of the thin film are determined on the RF-5300PC (Shimadzu), which is shown

in Fig. 5. It could be seen that two emission peaks of as-obtained PS-PF are at 443 nm and 418 nm. The two emission peaks of PS-PF in THF dilute solution are close to its thin film state. The difference of photo-luminescent properties between two states is that 443 nm is strongest in the state of thin film, while 418 nm in the THF solution. The longer emission in of π -conjugated polymer is related to "excimers" formation resulted of the interaction between conjugated units. This kind interaction is stronger in the film state than in THF solution. In general, the property of photo-luminescent is introduced to polystyrene, one kind of general polymer. If co-polymerization monomer is methyl methacrylate or methyl acrylate, rather than styrene, the property of photo-luminescent could introduce their polymers.

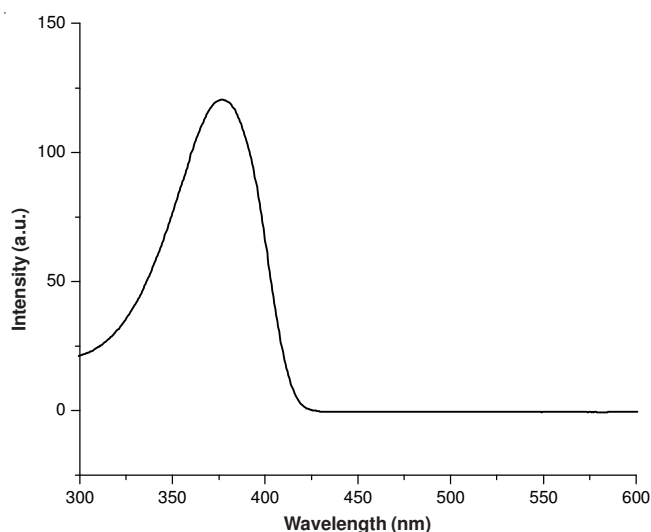


Fig. 4. UV-VIS spectrum of the THF solution of PS-PF

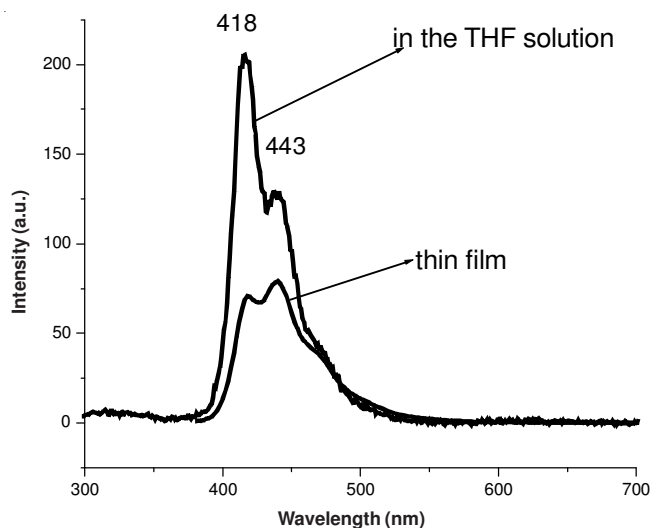


Fig. 5. Photoluminescent spectra of the PS-PF

The ink-jet printing is used to produce the pattern in white paper shown in Fig. 6. The pattern displayed strong blue colour when is irradiated by the laser of 330 nm wavelengths.



Fig. 6. Pattern on white paper by ink-jet printing

Conclusion

In conclusion, it has been succeeded in synthesizing luminescent polystyrene with π -conjugated pendant. It provided one new and simple method to combine general polymers (PS, PMMA *etc.*) such as elasticity and mechanical property, with optical activity fluorescence. This polystyrene can be used as smart polymeric material and when it is stimulated by light (short wavelength), it emission quickly within nano-seconds.

ACKNOWLEDGEMENTS

The project is supported by Science and Technological Fund of Anhui Province for Outstanding Youth (06044097) and Nature Research Program of Anhui Education Department (KJ2009A148 and KJ2012Z052).

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