Synthesis, Photophysics and Morphology of a Conjugated Polymer with Azobenzene Building Block in the Backbone

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A conjugate polymer poly[*p*-(phenyleneethylene)-alt-(phenyleneazophenyleneethylene)] (PPEPAPE) containing azobenzene building block in the polymer backbone was synthesized via Sonogashira cross-coupling of 4,4'-diio-doazobenzene and 1,4-diethynyl-2,5-didodecyloxybenzene. All the monomers and the resulting polymer were well characterized. The polymer had a relatively high molecular weight and showed very good solubility (\geq 10 mg/mL) in common organic solvents. The photophysics of this polymer in solution and in film was investigated. The surface morphology of the films was studied by scanning electron microscope (SEM) and the relationship between the morphology and absorbance was discussed. This polymer has good film-forming property, broad absorbance and no emission, which might make it a good candidate for the photovoltaic material in the solar cell.

Keywords azobenzene, cross-coupling, conjugate polymer, film-forming, photophysics, surface morphology

Introduction

The azobenzene and its derivatives were once widely used as dyes in the industry.¹ The most interesting property of these compounds is the photoisomerization between *trans* and *cis* isomers.²⁻⁴ They were used as additive agents to improve the performance of the polymer matrices, or were incorporated into the polymer molecules through the synthetic effort as a photoactive moiety to modulate the supramolecular structures, photophysics and many other properties.⁴⁻⁶ There were many reports about conjugated polymers with azobenzene moiety as pendant groups,⁷⁻¹⁴ but very few about having azobenzene in conjugated polymer backbone.¹⁵⁻¹⁸ However, the solubility of these polymers is always a challenge in the application where film-forming is required. In addition, the conjugated polymer-based solar cell has aroused renewed interest recently and a variety of conjugated polymers were synthesized for the potential application as the photovoltaic materials.¹⁹ Based on the consideration of meeting the requirements for the photovoltaic materials, such as easiness in the filmforming, the existence of hetero atoms in the backbone as the charge-carrier and broad absorption in the solar spectrum, here we present our work about facile synthesis of a conjugate polymer, poly[p-(phenyleneethylene)alt-(phenyleneazophenyleneethylene)] (PPEPAPE), containing azobenzene building block on the polymer backbone via Sonogashira cross-coupling protocol (Scheme 1). 1,4-Diethynyl-2,5-didodecyloxybenzene was used as the copolymerization monomer to improve the solubility of the conjugated polymer with a rigid-rod backbone. The protocol is easy to be modified for other conjugated polymers with azobenzene building block. The UV-Vis absorbance of this polymer in solution and in film will also be discussed. The surface morphology of these films was studied with scanning electron microscope (SEM), which was consistent with the observed photophysical properties. Experimental results showed that this polymer not only has good film-forming properties, but also has broad absorbance while no emission, which might make it a good candidate for the photovoltaic material in the solar cell.

Scheme 1 Polymerization for poly(aryleneethylene)s under Sonogashira coupling protocol



Experimental

Materials

Tetrakis(triphenylphosphine)palladium [(PPh₃)₄Pd] and cuprous iodide (CuI) were purchased from Alfa



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Aesar Chemical Co. *N*,*N*-Dimethylformamide (DMF), tetrahydrofuran (THF) and ferric chloride (FeCl₃) were from Sinopharm Chemical Reagent Co., Ltd. 4-Iodoaniline was purchased from Fluka. All materials were of analytical grade and used as received unless otherwise noted. Diisopropylamine was distilled from KOH. 1,4-Diethynyl-2,5-didodecyloxybenzene was synthesized according to the literature.²⁰

General methods

¹H NMR spectra were recorded on an Inova 400 MHz NMR spectrometer. FTIR spectrum of the polymer was obtained on a Nicolet 6700 FT-IR spectrophotometer (thermo). The samples were prepared by adding monomers or polymer into KBr, and the mixture was ground to a fine power and pressed to form disks. The elemental analysis was carried out on a Carlo-Erba EA-1110. The molecular weight was determined on a Waters 1515 gel permeation chromatograph with THF as the mobile phase and PS as the standard. The UV-Vis spectra were obtained on a Hitachi U-3900/3900H spectrophotometer. The solution UV-Vis and fluorescence measurement were carried out on CHCl₃ solution of 4,4'-diiodoazobenzene or polymer with a concentration of 1×10^{-5} mol/L (with respect to the repeating unit for polymer systems, the same below). The solid UV-Vis and fluorescence measurement were carried out on the PPEPAPE film on quartz slide prepared by drop-casting or spin-coating with 1×10^{-3} mol/L of PPEPAPE in CHCl₃, or 1×10^{-3} mol/L of PPEPAPE and 10 mg/mL of PMMA codissolved in CHCl₃. The spin coating was carried out on a Spin-coater KW-4A from Chemmat Technology, started with 6 s at the rate of 400 r/min and followed by 10 s at the rate of 2000 r/min. Morphological studies of the films were carried out using a Hitachi S-4700 scanning electron microscope (SEM). Samples for SEM were sputter-coated with a thin layer of Au/Pd prior to the observations to prevent samples-charging problems. The films for SEM were prepared according to the same procedure as in the photophysical study except using the regular glass slides as the substrate.

Synthesis

4,4'-Diiodoazobenzene 4-Iodoaniline (1.000 g, 4.566 mmol), HgO (1.4863 g, 6.849 mmol) and I₂ (1.7397 g, 6.849 mmol) were placed into a round bottom with 50 mL CH₂Cl₂ inside. The mixture was stirred under room temperature for 1 h. The reaction mixture was filtered and the solid was washed by CH₂Cl₂. The combined filtrate was washed by dilute Na₂S₂O₃ and then water in a separatory funnel. The organic layer was collected and dried over anhydrous Na₂SO₄. The solvent was removed by rotary evaporation. The crude product was purified by running chromatography on silica gel with eluent composed by petroleum ether and CH₂Cl₂ (V: V=2:1). The final product was orange solid (0.3) g, yield 30%). ¹H NMR (CDCl₃) δ : 7.86 (d, 4H, Ar-H), 7.64 (d, 4H, Ar-H); IR (KBr) v: 1575, 1470, 1393, 1296,

1278, 1155, 1003, 956, 820, 630, 588, 543, 525 cm⁻¹. Anal. calcd for C₁₂H₈N₂I₂: C 33.18, H 1.84, N 6.45; found C 32.86, H 1.99, N 6.17.

Polymer 4,4'-Diiodoazobenzene (PPEPAPE) (0.1000 g, 0.2304 mmol), 1,4-diethynyl-2,5-didodecyloxybenzene (0.1138 g, 0.2304 mmol), Pd(PPh₃)₄ (0.0133 g, 0.0115 mmol) and CuI (0.0022 g, 0.0115 mmol) were placed into pre-dried 50 mL three-necked round bottom flask. The system was deoxygenated by three cycles of vacuum-argon cycling. 10 mL of anhydrous THF and 2 mL of distilled diisopropylamine were added into the system. The mixture was stirred at 65 °C for 20 h under argon atmosphere. The reaction mixture was added into large amount of methanol. The crude product was redissoved with THF and precipitated out of methanol for several times. The resulting polymer was dried in vacuum to obtain the final product as reddish powders (0.1 g, yield 65%). ¹H NMR (CDCl₃) δ: 7.85-8.1 (4H), 7.6 -7.85 (4H), 6.9-7.2 (2H), 3.4-4.1 (4H), 0.85-1.95 (46H); IR (KBr) v: 2922, 2850, 2200, 1594, 1504, 1455, 1412, 1383, 1273, 1215, 1023, 847, 802, 721, 554 cm⁻¹. $M_{\rm p}: 0.97 \times 10^4, M_{\rm w}: 2.26 \times 10^4, \text{PDI: } 2.34.$

Results and discussion

The polymer PPEPAPE was prepared by a step growth polymerization employing the palladium-catalyzed Sonogashira coupling of 4,4'-diiodoazobenzene and 1,4-diethynyl-2,5-didodecyloxybenzene, as shown in Scheme 2.²¹ The resulting polymer is of reddish powder and very soluble (\geq 10 mg/mL) in common organic solvents such as THF and chloroform. 1,4-Diethynyl-2,5-didodecyloxybenzene was synthesized from 1,4-hydroquinone in four steps as described in the literature.²⁰ 4,4'-Diiodoazobenzene was quickly prepared with a mild reaction condition through a slight modification of a previous literature, by stirring the reaction mixture under room temperature for 1 h (Scheme 3).²²

Scheme 2 Synthetic strategy of PPEPAPE



Scheme 3 Synthetic strategy of 4,4'-diiodoazobenzene



The ¹H NMR spectra of the monomers and the polymer PPEPAPE were shown in Figure 1. There were two sets of doublet with the chemical shift between δ 7.60 and 7.90 in the ¹H NMR spectra. These peaks clearly came from the two types of aromatic protons in 4,4'-diiodoazobenzene, and each proton was coupled to the neighboring proton. Basically, the peaks in the ¹H NMR spectrum for the PPEPAPE could be related to the corresponding peaks in the monomer spectra except being broader, which was consistent with the formation of the polymer. The only questionable proton peak is the small one around δ 3.42, which was very close to the proton peak from terminal alkynes around δ 3.36. However, a strong and sharp absorption at 3286 cm^{-1} for the typical acetylenic C-H stretching vibration in the terminal alkynes, and a weak but sharp absorption at 2106 cm⁻¹ for the C=C stretching vibration in the monomer, were absent in the polymer IR spectra (Figure 2). Instead, a broad and weak absorption around 2193 cm⁻¹ appeared, which was consistent with the formation of internal ethynyl group.²³ Thus, the suspicion of δ 3.42 proton peak coming from the terminal alkynes in the polymer NMR spectra could be ruled out. Another possibility was the split of the proton peak from OCH₂ in the alkoxyl group due to the electron field ununiformity for the protons in the OCH_2 located.²⁴ Such ununiformity, which had also been reported in other examples,²⁴ might come from the regioisomerism, conformation isomerism or configuration isomerism. The characteristic peak for the N=N stretch around 1564 cm^{-1} in 4,4'-diiodoazobenzene moved to 1598 cm^{-1} in the polymer. The molecular weight was relatively high with a PDI value, 2.34, which is very close to the ideal value, 2.00, in a traditional step growth polymerization.

The photophysics of 4,4'-diiodoazobenzene in CHCl₃, PPEPAE in CHCl₃ and PPEPAE in film prepared by drop-casting or spin-coating was studied by UV-Vis absorbance (Figure 3) and fluorescence measurements. The films were prepared from solutions with a relatively low concentration of PPEPAPE, 1×10^{-3} mol/L with respect to the repeat unit, which was based on the consideration of making the film photophysics relatively comparable to the photophysics for polymer in dilute solution. There was no fluorescence observed, as most literature reported.^{2-4,15,17,18} The excitation energy was consumed by the photoisomerization between trans and cis isomers for the azo compound, instead of emitting fluorescence. The monomer was found to have a sharp absorbance peaked around 350 nm, while the PPEPAPE in solution displayed a red-shifted, relatively broad absorbance with a peak around 450 nm and a shoulder around 330 nm. This large red-shift could be explained by the extension of the conjugated length when incorporating the azobenzene moiety into the polymer backbone. In addition, the small molecular system only had one type of chromophore thus displayed relatively sharp absorption peak. However, chromophores with different conjugated length existed in the conjugated polymer system, due to the constructional defects or chain conformation diversity, which accounted for the broadening in the absorption peak. The profiles of absorption spectra for PPEPAPE in the drop-cast film or spin-coated film are



Figure 1 ¹H NMR spectra of 4,4'-diiodoazobenzene (a), 1,4-diethynyl-2,5-didodecyloxybenzene (b) and PPEPAPE (c) in CDCl₃.



Figure 2 FTIR spectra (% transmittance) of 4,4'-diiodoazobenzene (a), 1,4-diethynyl-2,5-didodecyloxybenzene (b) and PPEPAPE (c).



Figure 3 UV-Vis spectra of 4,4'-diiodozaobenzenen in $CHCl_3$, PPEPAE in $CHCl_3$ solution and the PPEPAE in film.

very similar to the spectrum for polymer in solution, with or without the coexistence of the PMMA. except being red-shifted and broader in film. PPEPAPE in the drop-cast film has a broad absorbance between 300 and 540 nm, with a peak around 490 nm and a shoulder around 360 nm. This red-shifting in the spectra, compared to the polymer in solution, could be attributed to the rigidification of polymer chains in solids which resulted in even longer conjugated length. Meanwhile, the restriction of the polymer chain movement in film also increased the constructional defects and chain conformation diversity which might account for the further broadening of the spectra. The absorbance peak for the spin-coated polymer film showed blue-shift to the drop-cast film which suggested that the polymer chains in the spin-coated film took a less ordered and less aligned structure with smaller conjugated length. This phenomenon was within expectation since polymer chain movement was different in various film-forming process. The polymer chain conformations were almost frozen, as in the solution, with the quick evaporation of the solvent in the spin-coating process, while the reorganization of the polymer chains took place together with the slow evaporation of the solvent during the drop cast process. Basically, the addition of the PMMA into the film has negligible influence on the absorbance since

it is transparent within the range of UV-Vis light. However, the coexistence of PMMA with the conjugated polymer in the drop cast system might affect the chain reorganization process and thus led to further red-shifting and broadening in absorbance.

The SEM pictures of the films are shown in Figure 4. All the films were prepared from solutions with 1×10^{-3} mol/L of PPEPAPE. Basically, with the coexistence of PMMA, both drop-cast and spin-coated films had relatively thick and continuous covering on the slides (not shown), but were different in the morphology on the micrometer level (Figures 4a and 4b). The drop-cast film displayed some roughness in the surface but no clear boundary between the conjugated polymer and PMMA matrix, while the spin-coated film had the morphology of many small particles embedded in the matrix. As for the films prepared without PMMA, fibrous structures with diameters around 10 µm were found on the slides (Figures 4c and 4d). This uncontinuity was reasonable since the original solution, 1×10^{-3} mol/L of PPEPAPE, was too dilute to produce continuous film on the 50–100 μ mol•L⁻¹ size level. Getting closer to the "fibers", the drop-cast one displayed continuous structure (Figure 4e) while the spin-coated one had the uncontinuous, "grain-like" morphology (Figure 4f). Comparing morphologies for the films with or without PMMA, conclusion could be made that drop-casting resulted in the continuous PPEPAPE morphology (Figures 4a and 4e), while spin-coating led to the morphology with PPEPAPE existing as small domains embedded in PMMA (Figure 4b), or isolated grains (Figure 4f).

The spectra profiles in different films could be related to the film formation process and their morphology. In the drop-casting process, the solvent evaporated gradually. Therefore the conjugated polymer chains had enough time to relax and aggregate to form continuous morphology with extended conformation in an equilibrium state, which might account for the red-shift in absorbance spectra, compared to the absorbance in the spin-coated film. The existence of PMMA might have some effect on the movement of chains and resulted in more conformations which broadened the spectra. However, in the spin-coating process, the solvent was removed quickly. Thus the polymer chains were in a state more close to the state in solution, with a less extended conformation in an isolated domain, with or without the existence of PMMA. Therefore, the absorbance spectra for films from spin-coating are much closer to the one in solution.

Conclusion

A conjugate polymer PPEPAPE containing azobenzene building block on the polymer backbone was successfully synthesized via Sonogashira coupling. The synthetic strategies for the monomers and polymer were facile and easy to be modified for other related polymers. This polymer showed good film-forming property and



Figure 4 Scanning electron microscopy photographs of films prepared by different methods. (a) PPEPAPE/PMMA drop-cast; (b) PPEPAPE/PMMA spin-coated; (c) PPEPAPE drop-cast; (d) PPEPAPE spin-coated; (e) PPEPAPE drop-cast (enlarged image from some part of c); (f) PPEPAPE spin-coated (enlarged image from some part of d).

broad absorbance in the UV-Vis light range and might be used as photovoltaic material. The surface morphology for each film was consistent with the corresponding absorbance spectrum. Further investigation into the properties of this polymer from other aspects is currently underway in our laboratory.

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