Influence from Thermal Elimination Temperature of Precursor Polymer and Film-forming Methods on the Photophysics of the Poly(2,5-didodecyloxy-*p*-phenylenevinylene)

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A series of poly(*p*-phenylenevinylene)s (PPVs) with good solubility were synthesized from thermal elimination of precursor poly(2,5-didodecyloxy-*p*-phenylenevinylene) at different temperature via Wessling method. The polymer photophysics were influenced by the thermal elimination condition, which was consistent with NMR and IR characterizations. The additional absorption peak at longer wavelength and the red-shifted emission maximum both in solution and in film, for PPVs obtained at high elimination temperature, indicated the existence of longer conjugated blocks in these systems. The emission maximum for drop-cast film (436 nm) for PPV obtained under 200 ℃ (PPV200) was 16 nm blue shifted to the spin-coated films (452 nm) or 29 nm to the solution (465 nm). The SEM study showed drop-cast film had the morphology of isolated conjugated particles in the matrix while blurry linear structure was found for spin-coated film, which was consistent with the photophysics. The discussion about this difference was carried out based on the consideration of the flexibility of the polymer chains and different conjugated length of PPV in different states.

Keywords poly(*p*-phenylenevinylene), synthetic methods, photophysics, polymer precursor, morphology

Introduction

Poly(*p*-phenylenevinylene) (PPV) is one of the most extensively studied conjugated polymers and has been widely used in the light emitting device.[1-7] There are several routines, such as Wessling,[8] Glich,[9,10] Wittig,[11] and Heck Coupling[12] to prepare PPV. Wessling method was demonstrated irreplaceable advantages in some respects due to the easiness in handling and characterization of the polymer precursor. The photophysical properties of PPV had been tuned by varying the polymer structure, such as, assembling electron-withdrawing or electron-donating side groups onto the backbone,[13,14] controlling the different conjugated length by selective elimination.[15,16] However, all these methods required additional synthetic effort, while the properties of PPV could be simply controlled by changing thermal elimination condition of the precursor polymer.[17,18] Thus, here we present our preparation of a poly-(2,5-didodecyloxy-*p*-phenylenevinylene) sulfonium bromide precursor polymer with a modified method compared to the literature, and the systematical investigation into the relationship between the properties of the organic-solvent-soluble PPV and the thermal elimination temperature. The thermal elimination condition had been tracked in several other PPV systems[17-20] by some *in-situ* techniques, such as FTIR, UV-vis, TGA, *etc*., directly in film or in solution where the reaction took place. These *in-situ* techniques gave clear pictures of the gradual elimination of sulfonium groups and the formation of PPV. In this contribution the property studies were carried out after the thermal elimination in solid in glass containers and then the products were taken out for future investigation in solution or in solid, which was very different from those reported dynamic *in-situ* studies and would provide more information for real application for these PPVs.

Experimental

Materials

Bromododecane ($C_{12}H_{25}Br$) and tetrahydrothiophene (THT) were purchased from Alfa Aesar Chemical Co. *N*,*N*-Dimethylformamide (DMF), tetrahydrofuran (THF) were from Sinopharm Chemical Reagent Co., Ltd. All materials were of analytical grade and used as received

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unless otherwise noted. Methanol and acetone were dried over molecular sieve. 1,4-bis(dodecyloxy)benzene was synthesized by an adapted literature procedure.[15]

General methods

^{1}H NMR spectra were recorded using an Inova 400 MHz NMR spectrometer with $CDCl_3$ as the solvent and TMS as the internal reference. FTIR spectra of the monomers, the precursor polymer and the PPV polymers were obtained on a Nicolet 6700 FT-IR spectrophotometer (thermo). The samples were prepared by adding monomers, precursor polymer or PPVs 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 using a Hitachi U-3900/3900H spectrophotometer. The solution UV-vis and fluorescence measurements were carried out in THF with a concentration of 1×10^{-5} mol/L with respect to the repeating unit of precursor polymer. The solid UV-vis and fluorescence measurements were carried out with the PPV film on quartz slides, prepared through drop-casting or spin-coating technique, with a concentration of 1×10^{-2} mol/L with respect to the repeating unit of prepcusor polymer in $CHCl_3$, and 20 mg/mL of PMMA codissolved in $CHCl_3$. 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 1000 r/min. The drop-casting was carried out at room temperature (around 20 ℃) for 8 min. Morphological studies of the films were carried out using a Hitachi S-4700 scanning electron microscope (SEM).

Synthesis

1,4-Bis(bromomethyl)-2,5-bis-(dodecyloxy)benzene Formaldehyde (0.145 g, 48.30 mmol), 1,4-bis(dodecyloxy)benzene (5.100 g, 11.20 mmol), HBr (17.5 mL, 50 wt% in acetic acid) and 30.0 mL of acetic acid were placed into a round bottom flask. The mixture was stirred under room temperature for 30 min and 80 ℃ for 3.0 h. Then the solvents were completely removed under reduced pressure. The crude product was purified by redissolving it in chloroform and reprecipitated out of ethanol to give a white power (5.450 g, yield 77%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.85 (s, 2H), 4.53 (s, 4H), 3.93—4.02 (m, 4H), 1.76—1.87 (m, 4H), 1.20—1.52 (m, 36H), 0.84—0.92 (m, 6H); IR (KBr) v: 2918, 1627, 1510, 1473, 1413, 1313, 1226, 1033, 863, 719, 690 cm^{-1}. Anal. calcd for $C_{32}H_{56}O_2Br_2$: C 60.76, H 8.86; found C 60.62, H 9.08.

1,l'-[((2,5-Didodecyloxy)-*p*-phenylene)bis(methylene)]bis[tetrahydrothiophenium]dibromide 1,4-Bis-(bromomethyl)-2,5-bis(dodecyloxy)benzene (1.950 g, 3.10 mmol), and anhydrous methanol (20.3 mL) were placed into pre-dried 50.0 mL two-necked round bottom flask. The system was deoxygenated with three cycles of vacuum-argon cycling. Tetrahydrothiophene (2.000 g, 23.00 mmol) was added into the system. The mixture was stirred at 55 ℃ for 22 h under argon atmosphere. The solvent was completely removed with rotary evaporation and the residue was purified with dry acetone. The mixture was then filtered and the resulting solid was dried in vacuum to give a white solid (1.302 g, yield 52%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.85 (s, 2H), 4.53 (s, 4H), 3.94—4.01 (m, 4H), 2.78—2.86 (m, 8H), 1.88—1.97 (m, 8H), 1.75—1.85 (m, 4H), 1.06—1.52 (m, 36H), 0.82—0.90 (m, 6H); IR (KBr) v: 2917, 1627, 1510, 1475, 1415, 1398, 1322, 1233, 1110, 1029, 865, 794, 713, 653 cm^{-1}. Anal. calcd for $C_{40}H_{72}S_2O_2Br_2$: C 59.40, H 8.91; found C 59.48, H 8.83.

The precursor polymer of poly(2,5- didodecyloxy-*p*-phenylenevinylene) (pre-PPV) 1,l'-[((2,5-Didodecyloxy)-*p*-phenylene)bis(methylene)]bis[tetrahydrothiophenium]dibromide (1.009 g, 1.23 mmol), and 26.0 mL of THF were placed into pre-dried 50.0 mL two-necked round bottom flask. The system was deoxygenated by three cycles of vacuum-argon cycling and maintained the temperature at 0 ℃. 2.0 mL of ice-cold, Ar-purged methanolic NaOH solution (1.25 mol/L) was added in a slow stream to the system. The mixture was stirred at 0 ℃ for 1 h followed adding of 2.0 mL of HCl (1.00 mol/L) into the system. The mixture was then dialyzed with cellulose membrane dialysis tubing with a molecular mass cutoff of 3500 Da in water for 12 h, during which the water was changed for every 2 h. The mixture inside the membrane was filtered. The precursor polymer was collected as a pale yellow powder and dried in vacuum overnight. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.82—6.93 (m, 2H), 4.36—4.47 (m, 1H), 3.91—4.00 (m, 4H), 3.47 (s, 2H), 2.80—2.87 (m, 4H), 1.91—1.97 (m, 4H), 1.71—1.83 (m, 4H), 1.18—1.51 (m, 36H), 0.84—0.92 (m, 6H); IR (KBr) v: 2921, 1618, 1513, 1467, 1417, 1384, 1307, 1218, 1108, 1041, 952, 896, 865, 825, 721 cm^{-1}. Anal. calcd for $(C_{36}H_{63}SO_2Br_2)_n$: C 67.60, H 9.86; found C 68.45, H 10.52.

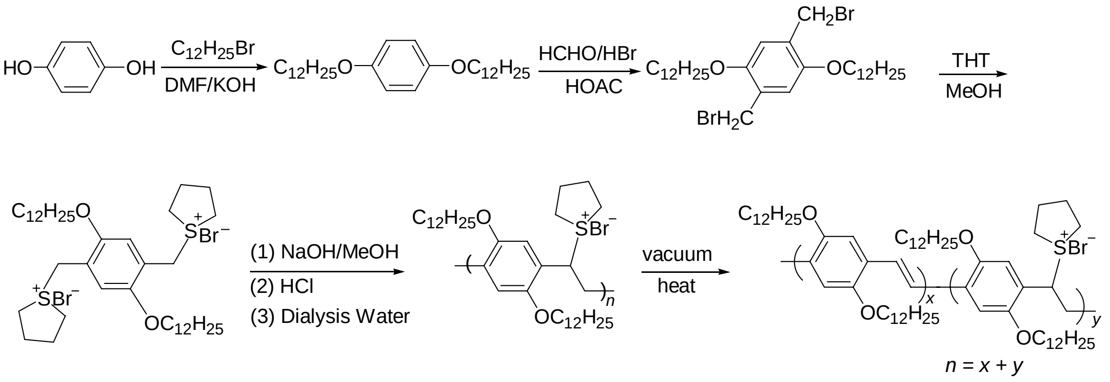
Thermal elimination

The precursor polymers were heated at 60, 100, 120, 140, 160 and 200 ℃ for 2 h in vacuum to a series of poly(2,5-didodecyloxy-*p*-phenylenevinylene)s (PPVs) with various elimination extent. The PPVs were named as PPV60, PPV100, PPV120, PPV140, PPV160, and PPV200 respectively according to the thermal elimination temperature. All the PPVs were powder in different shades of yellow.

Results and discussion

The PPVs were synthesized based on the Wessling method as shown in Scheme 1. The precursor polymer was prepared by a modification of previous literature reports.[15] The ^{1}H NMR spectra of the monomers,

Scheme 1



1,4-bis(bromomethyl)-2,5-bis(dodecyloxy)benzene, and 1,l'-{[(2,5-didodecyloxy)-*p*-phenylene]bis(methylene)}bis[tetrahydrothiophenium] dibromide, were shown in Figure 1. The peaks around *δ* 2.00—2.80 demonstrated the successful replacement of the Br on the benzyl bromide by the tetrahydrothiophenium group. The reaction condition for the synthesis of the precursor polymer was optimized. Initially methanol was used as the solvent for the polymerization. However, it was proven not the best option since some of the tetrahdrothiophenium could be substituted by the methoxy group.[16] Thus THF was used as the alternative to reduce the side reactions. After the polymerization, the whole reaction mixture was placed into a cellulose membrane dialysis tubing with a molecular mass cutoff of 3500 Da in water for 12 h, during which the water was changed for every 2 h. The mixture inside the membrane was filtered and the solid was dried in vacuum. Then the thermal elimination was carried out by placing the precursor polymers in vacuum under various temperatures in different batches. The resultant polymers, namely PPV60, PPV100, PPV120, PPV140, PPV160 and PPV200, according to the thermal elimination temperature, were very soluble in common organic solvents such as THF and chloroform. The ^{1}H NMR spectra of the pre-PPV and the PPVs prepared under different elimination temperatures were shown in Figure 2. Basically, there was negligible change for the peaks belong to the protons on the alkoxyl side group (around *δ* 4.00 and between *δ* 0.80—1.80) and the protons on the bezenze ring (between *δ* 6.75—7.00). The disappearing of the peaks for the protons on the tetrahydrothiophenium (*δ* 2.80 and 2.00) in the PPVs was reasonable, as well as the decrease in the peak for the proton next to

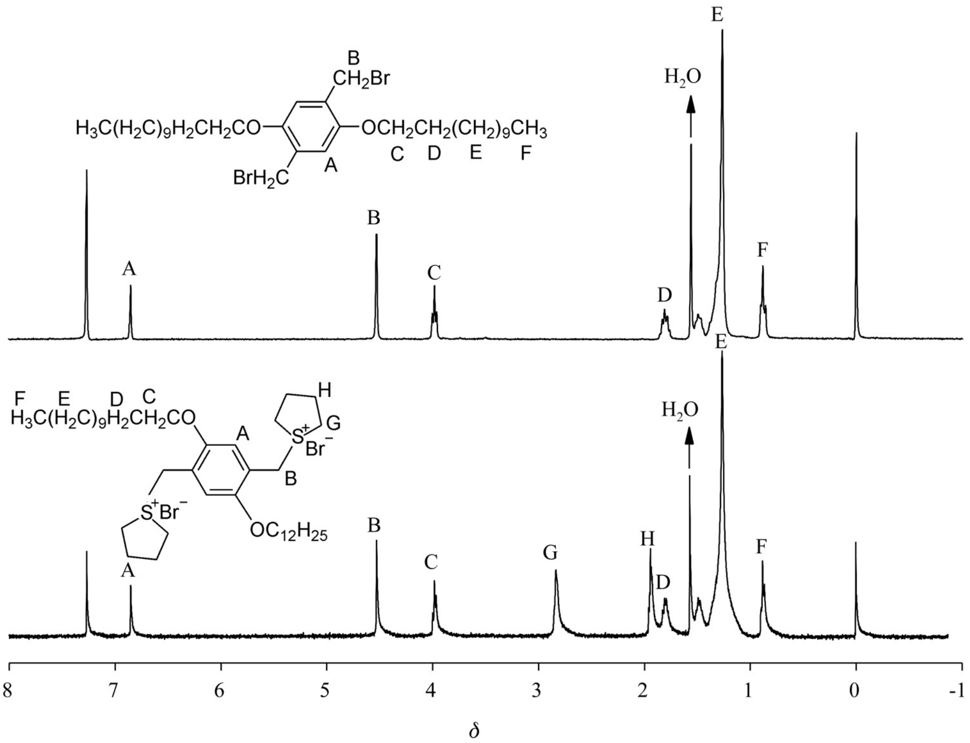


Figure 1 ^{1}H NMR spectra of monomers of PPV.

the saturated carbon on the polymer backbone (δ 4.50 and 3.50) and the emerging of the peak for the vinyl protons (between δ 6.60 and 6.75) with increasing the elimination temperature. Interestingly, as least seen from the NMR spectra, the formation of the double bond did not come together with the lose of the tetrahydrothiophenium group, in the case of using low elimination temperature. Significant NMR signal for double bonding formation could only be seen in PPVs obtained under 160 and 200 ℃. Even in the case of PPV200, the peaks for the saturated proton still existed, indicating the backbone was not fully conjugated. However, the peaks for the PPV200 appeared much broaden than other PPV, very likely due to the rigidity caused by the higher conjugation extent. Figure 3 shows the IR spectra of this series of polymers. A sharp and weak absorption around 1680 cm^{-1}, which could be attributed to the C=C stretching vibration, appeared in the case of PPV160 and PPV200, which was consistent with NMR spectra, indicating the formation of double bonds in main chain. The molecular weights of the pre-PPV and PPVs were determined by the GPC. All the polymers had a similar M_n, between 4.30×10^5 and 4.70×10^5, and a PDI around 1.70. That means there was no significant degradation of the main chain.

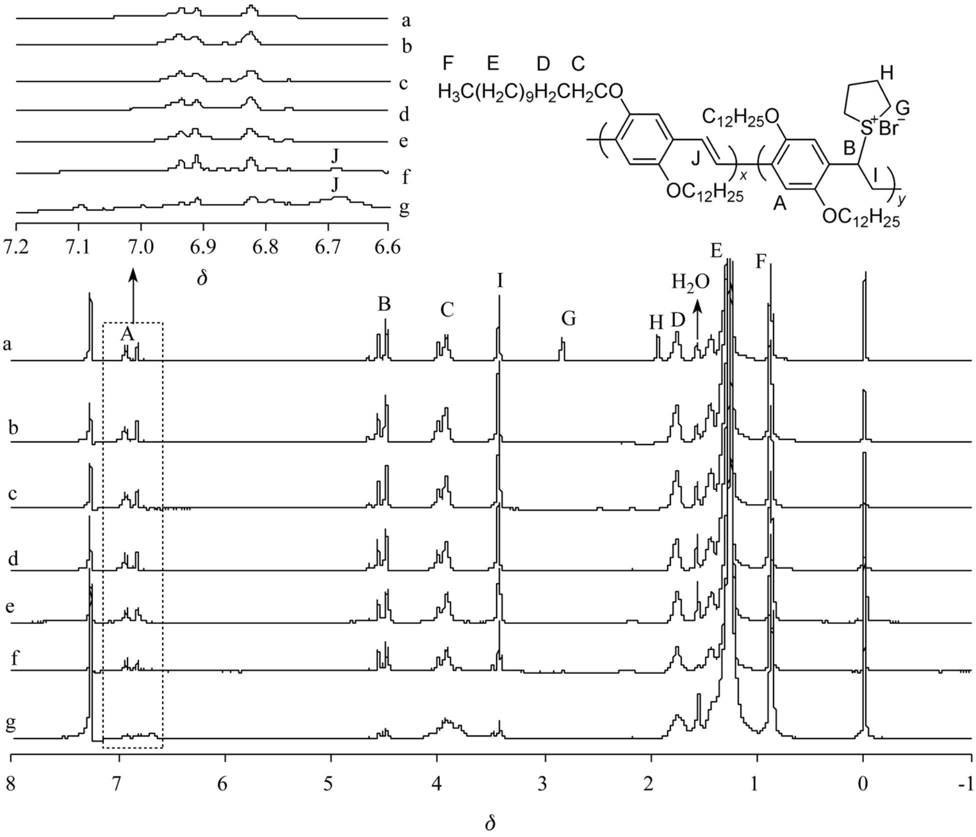


Figure 2 ^{1}H NMR spectra of (a) pre-PPV; (b) PPV60; (c) PPV100; (d) PPV120; (e) PPV140; (f) PPV160; (g) PPV200.

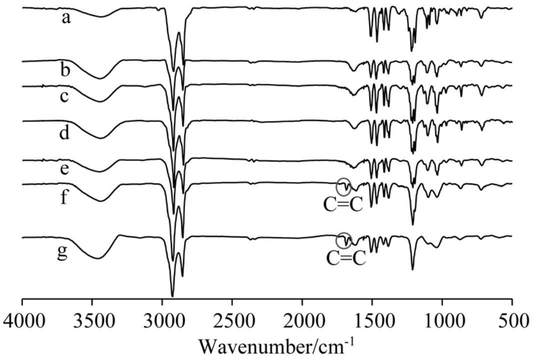


Figure 3 FTIR spectra (% transmittance) of (a) pre-PPV; (b) PPV60; (c) PPV100; (d) PPV120; (e) PPV140; (f) PPV160; (g) PPV200.

The photophysics of PPVs, both in THF solution and film, was studied. Both the spin-coated and drop-cast films were prepared from solutions with a relatively low concentration of PPVs, which was based on the consideration of making the photophysics of film relatively comparable to the photophysics in dilute solution.

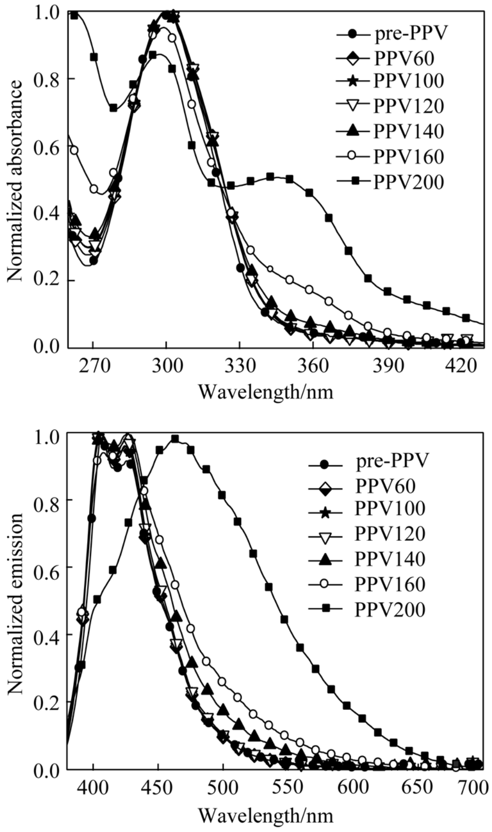


Figure 4 Normalized UV-vis absorbance (top) and fluorescence emission (λ_{ex}=357 nm) (bottom) spectra of pre-PPV and PPVs in THF.

The normalized absorbance and emission spectra of pre-PPV and PPVs were shown in Figure 4. Basically, the spectra for PPVs obtained below 140 ℃ were very similar. Those polymers had one absorption maximum around 300 nm and double emission peaks around 405 and 427 nm. The absorbance shoulder around 354 nm gradually appeared in the PPV140, PPV160 and PPV200. In the emission spectra, PPV200 displayed a broad emission with a peak around 465 nm and a small shoulder around 405 nm. However, the PPV140 and PPV160 still have very similar emission to other PPVs with very slight emission increase in the longer-wavelength area. Thus, it is very likely that vinyl formation on the backbone took place only in the case of using relatively high elimination temperature. In addition, high conjugation degree was obtained only in PPV200 which displayed significant red-shift in the emission maximum. The broad emission of PPV200 also indicated the existence of many conjugated blocks with various conjugated length.

The PPV films were prepared by spin-coating and drop-casting, using PMMA as the inert matrix due to its transparency within the UV-vis range. Basically, the profiles of absorbance and fluorescent emission spectra for these polymers in films (Figure 5 and Figure 6) were similar to those in solution. In the UV-vis spectra of spin-coated films (Figure 5 top), PPVs obtained below 140 ℃ had exactly same profile as the pre-PPV. The absorbance at higher wavelength gradually appeared and increased when the elimination temperature was 140 ℃ and higher. In the emission spectra of spin-coated film (Figure 5 bottom), pre-PPV, PPV60, PPV100, PPV120 and PPV140 had very similar profile while PPV160 showed small red-shifting and broadeing and PPV200 displayed even greater red-shifting and broadening. This phenomenon is consistent with soltion spectra, except the small difference in the case of PPV160 due to the restricted movement effect in the solids. In the drop-cast film, the absorbance spectra were similar to those in solutions or in spin-coated films. However, the emission of PPV160 and PPV200 showed less red-shifting and less broadening, which was not common since the polymer chains in drop-cast film usually has well-organized structure and more π-stacking resulted in red-shifting, since the slow evaporation process allows the reorganization of the molecules.[21] Thus, detailed discussion related to this abnormality will be carried out in the following paragraphs.

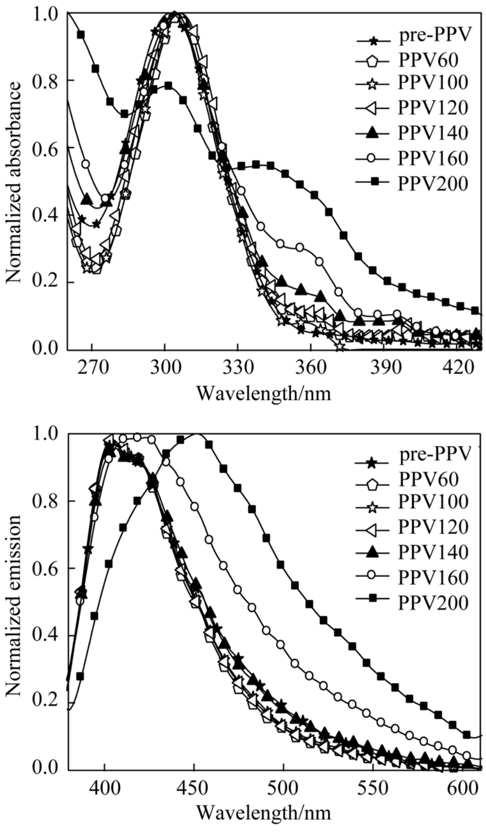


Figure 5 Normalized UV-vis absorbance (top) and fluorescence emission (λ_{ex}=357 nm) (bottom) spectra of pre-PPV and PPVs in spin-coated film.

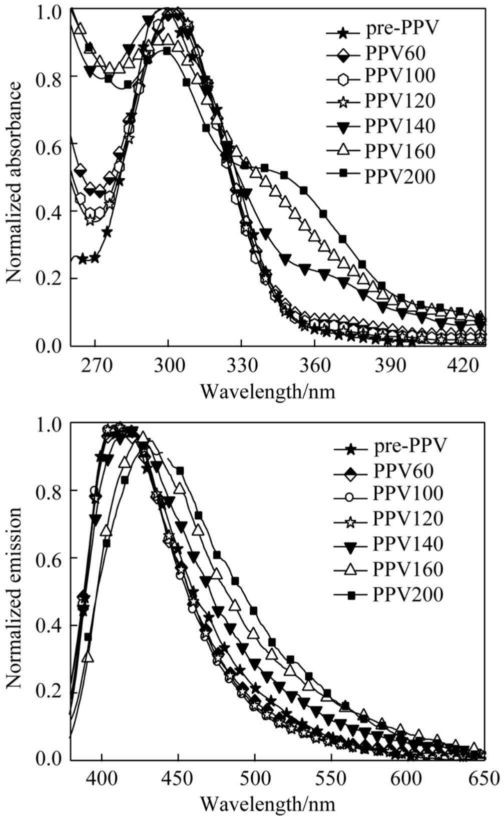


Figure 6 Normalized UV-vis absorbance (top) and fluorescence emission (λ_{ex}=357 nm) (bottom) spectra of pre-PPV and PPVs in drop-cast film.

Figure 7 shows the comparison of the absorbance and emission spectra of PPV 200 in various states. All the absorbance spectra had the similar profile, with peaks around 300 and 354 nm. However, there was significant difference in the emission, with peak around 465 nm in solution, 452 nm in spin-coated film and 436 nm in drop-cast film. In most conjugated polymer systems the emission peaks had the reversed sequence compared to our system. That is, the drop-cast film would be the most red-shifted one and the solution would be the most blue-shifted one, which was explained by the enhanced intermolecular π-stacking, rigidification and enhanced conjugation or well-organized structure in solid, especially in drop-cast film.[22-25] Thus, the PPVs here were different from other conjugated polymer systems.

To further clarify this issue, the morphology study was carried out on the PPV200 drop-cast film and spin-coated film (Figure 8). Interestingly, the drop-cast film showed some isolated domain embedded in the matrix while the spin-coated film had relatively smooth feature with some blurry linear structure on the surface. It was well-known the state of the polymer in spin-coated film is much closer to its state in solution due to the quick evaporation of solvent and limited reorganization of polymer chains. Correlating the photophysics with the morphology, one conclusion could be made that the PPV200 in solution was in an extended state and had long conjugation length, while the PPV200 in drop-cast film was in a curved state and therefore had short conjugation length and blue-shifted emission. Additional information from these studies was that the PPV200 was more flexible than other common conjugated polymer, which resulted in the easiness of chain folding instead of π stacking induced aggregation. The NMR spectrum of PPV200 in Figure 2 also showed that there existed quite a few relatively flexible saturated bonding on the polymer backbone together with the rigid conjugated blocks.

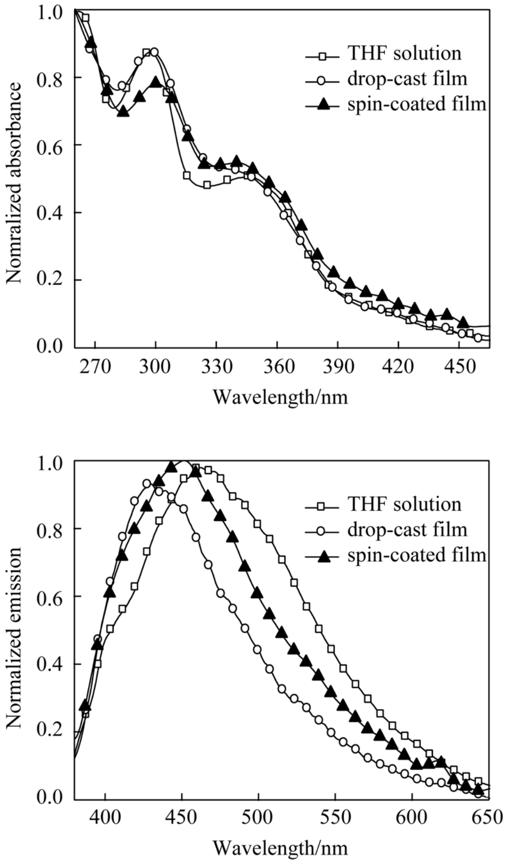


Figure 7 Normalized UV-vis absorbance (top) and fluorescence emission (λ_{ex}=357 nm) (bottom) spectra of PPV200 in different states.

Conclusions

A series of PPVs were synthesized via Wessling route from the same polymer precursor but under different thermal elimination temperature in vials, using common vacuum oven. These polymers were demonstrated to be very soluble in common solvent and ready for all characterization and future study. NMR and IR characterization indicated that only PPVs obtained under high thermal elimination temperature, such as 160 and 200 ℃, had significant formation of vinyl bonding on the polymer backbone. Photophysical study of these polymers, both in solution or in films, basically was consistent with the NMR and IR study. The emergence of new absorption peak at longer wavelength in UV-vis

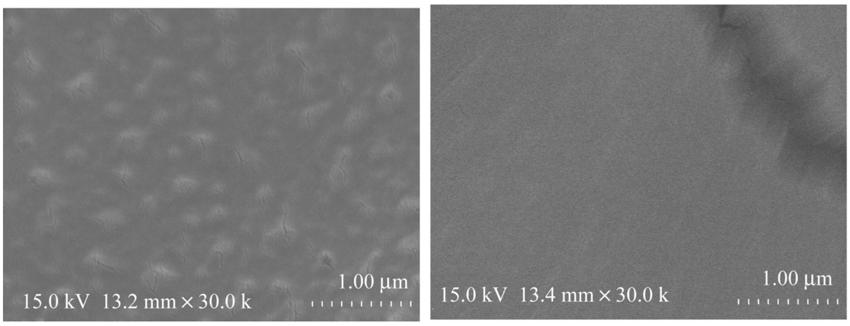


Figure 8 SEM of PPV200 films prepared by drop-casting (left) and spin-coating (right)

spectra and the red-shifting of the emission maximum were reasonable since longer conjugated blocks existed for the PPVs obtained under higher elimination temperature. The SEM images of PPV200 films suggested the existence of saturating part on the backbone resulted in the relative flexibility of the polymer. The difference in morphology of drop-cast film and spin-coated film matched their difference in photophysics, which might be useful in adjusting the photophysics of these polymers simply by controlling the film-forming process instead of synthesizing polymers with different chemical structures.

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