

SYNTHESIS OF SOLUBLE POLY(3-HEXYL-2,5-THIENYLENE VINYLENE) FROM THIOPHENE*

Gui-jiang Zhou and Cheng Ye**

Center for Molecular Science, Organic Solids Lab., Chinese Academy of Sciences, Beijing 100080, China

Abstract Soluble poly(3-hexyl-2,5-thienylene vinylene) (PHTV) was readily synthesized from thiophene in a yield better than that of the precursor method to prepare poly(thienylene vinylene) (PTV). The bandgap of the polymer is about 1.8 eV, which is comparable with that of PTV. Owing to the introduction of alkyl side groups onto the backbone of the polymer, it can be dissolved in common organic solvents such as chloroform, THF and toluene. The synthesis of soluble PHTV is a very important approach to preventing oxidation and to improving the properties and the processibility of the PTV. The existence of alkyl side groups in PHTV does not affect its bandgap and thermal properties as compared with PTV. After doping with FeCl_3 , the conductivity of PHTV is as high as $1.1 \times 10^{-2} \text{ S/cm}$. The soluble PHTV can be easily transformed into thin film with much better quality than that of the PTV film prepared by the traditional precursor method, which is very important for fabricating devices with good properties.

Keywords Poly(3-hexyl-2,5-thienylene vinylene), Solubility, Conjugated polymer

INTRODUCTION

Conjugated polymers have attracted more and more attention since the discovery of highly conductive polyacetylene^[1–3]. Their possible applications in sensors, and electroluminescence devices^[4–5] *etc.* have also stimulated the synthesis of new conjugated polymers. Because of the presence of π -conjugated bonds in the backbone, they have band structures (such as the energy level of HOMO and LUMO, bandgap *etc.*) similar to those of inorganic semiconductors such as silicon; conjugated polymers can also find various applications in semiconductor devices. Among them, field-effect transistors^[6–8] are one of the most commercially promising applications for deposited semiconducting films. Among all the conjugated polymers, PTV has attracted some attention because it has the ability to replace the phenyl ring in poly(phenylene vinylene) (PPV) by the electron-rich thiophene ring which has a positive effect on both conductivity and stability of the doped polymers^[9]. But PTV's poor processibility caused by its insolubility and nonfusibility has greatly restricted its practical utilization. The most common way employed to solve this difficulty is to prepare a soluble precursor polymer. Afterwards, the precursor polymer is converted into PTV by a thermal elimination reaction. Although it is an effect approach, there are some drawbacks^[10]. The high temperature required for the thermal elimination reaction will easily lead to the oxidation of PTV. The small molecules released during the thermal elimination reaction will affect the properties of thin film electronic devices. To avoid the difficulties mentioned above, soluble PTV will have to be synthesized.

EXPERIMENTAL

Materials

Unpurified commercial thiophene was used directly as starting material. Bromine, N,N,N',N' -

* This work was supported by the Chinese Academy of Sciences (No. KJCX2-H1).

** Corresponding authors: Cheng Ye (叶成), E-mail: yec@iccas.ac.cn

Received August 20, 2003; Revised October 8, 2003; Accepted November 19, 2003

tetramethylethylenediamine (TMEDA) and *n*-hexylbromide were used as received. [1,3-Bis(diphenylphosphino)propane]nickel(II) chloride (NiDPPPCl₂) was purchased from Acros. *n*-Butyl lithium was prepared in our lab following the literature method. All the solvents used were purified by conventional methods.

Characterization

The UV-vis spectra of PHTVs were taken on a Shimadzu UV-1601PC spectrophotometer. FT-IR spectra were recorded with a Perkin-Elmer Model 7 spectrophotometer. ¹H-NMR spectra were recorded on a Varian T-200 spectrometer. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 thermogravimetric analyzer. Cyclic voltammetry was studied on a PE EG&G 283 electrochemical analytical system with a saturated calomel electrode as the reference electrode and Pt sheet as the working electrode and a Pt wire as the counter electrode. The molecular weight of PHTV was determined by a GPC system (Waters Assoc.). A two-probe method was used to carry out conductivity measurement. The SEM microphotographs of the polymer film were obtained on a JOEL 6700 system.

Synthesis

2,3,5-Tribromothiophene^[11]

Thiophene (15.77 g, 0.19 mol) and chloroform (6 mL) were charged into a 100 mL three-necked flask immersed in a cold-water bath. Bromine (90.81 g, 0.57 mol) was added dropwise to the stirring mixture over a period of about 5 h. After the addition, the reaction mixture was stirred overnight. Then, it was heated at 50°C for 5 h, and washed with 2 mol/L NaOH solution. The washed reaction mixture was refluxed with a mixture of 10 g KOH and 20 mL 95% ethanol for 2 h, and then poured into water. The organic layer was separated, washed with water, dried over anhydrous CaCl₂ and distilled to give 2,3,5-tribromothiophene (48.68 g, yield 81%) with a m.p. of 26–28°C. The ¹H-NMR of the product (acetone-*d*₆) shows δ 7.26 (1H, s), and MS *m/z*: 319 and 321 (M⁺).

3-Bromothiophene^[11]

Zinc powder (17.00 g, 0.26 mol) and acetic acid (15.2 mL) were added to water (40.3 mL) with stirring. The mixture was heated to reflux, and then the heating bath was removed. 2,3,5-Tribromothiophene (27.92 g, 0.087 mol) was added at such a rate as to keep the reaction mixture still refluxing. After the addition, the reaction mixture was refluxed for other 3 h. Then the reaction mixture was distilled until no more organic substance was distilled out with water. The heavier organic layer was separated, washed with 20 mL 10% Na₂CO₃ solution and 20 mL water, dried over anhydrous CaCl₂, and distilled to collect the fraction boiled at 157–159°C to give 3-bromothiophene (12.62 g, yield 89%). ¹H-NMR of the product (DMSO-*d*₆) shows δ 7.12 (dd, 1H, *J* = 2 Hz, *J* = 2.4 Hz), 7.62 (m, 2H), and MS *m/z*: 162, 164 (M⁺).

3-Hexylthiophene^[12]

To a suspension of magnesium (1.40 g, 0.058 mol) in 20 mL dry ethyl ether, *n*-hexyl bromide (9.41 g, 0.057 mol) in 6 mL anhydrous ether was added dropwise under N₂ atmosphere. After addition, the mixture was refluxed for 30 min. Then the Grignard reagent prepared above was added dropwise to a mixture of 3-bromothiophene (6.96 g, 0.043 mol) and NiDPPPCl₂ (0.03 g) in 20 mL dry ether at 0°C under N₂ atmosphere. After addition, the reaction mixture was allowed to return to room temperature under stirring. After stirring for 2 h at room temperature, the reaction mixture was refluxed for 20 h and then it was cooled in an ice bath and hydrolyzed with 50 mL 2 mol/L HCl solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer and extracts were washed successively with water, saturated Na₂CO₃ solution, and again with water, then dried over anhydrous CaCl₂. The solvent was removed under reduced pressure to give a brown oil, which was chromatographed on a silica gel column with petroleum ether as the eluent. 3-Hexylthiophene was obtained as pale yellow oil (5.02 g, yield 70%). ¹H-NMR of the product (acetone-*d*₆) shows δ 7.3 (dd, 1H, *J* = 3 Hz, *J* = 2 Hz), 7.03 (m, 1H), 6.96 (dd, 1H, *J* = 1 Hz, *J* = 3.8 Hz), 2.26 (t, 2H, *J* = 7.6 Hz), 1.62 (m, 2H), 1.28 (m 6H), 0.88 (t, 3H, *J* = 4.7 Hz), and MS *m/z*: 168 (M⁺).

3-Hexyl-2,5-thiophenedicarboxaldehyde

Under N₂ atmosphere, 1.6 mol/L *n*-butyllithium (13.3 mL) was added to a mixture of 3-hexylthiophene (1.5 g,

0.0089 mol), dry TMEDA (2.47 g, 0.0214 mol), and dry hexane (2.5 mL). The mixture was refluxed for 30 min, then was cooled to -40°C , and dry THF (10 mL) was added, followed by addition of an excess of DMF (1.71 g, 0.0235 mol) over a period of 10 min. The temperature was gradually raised to room temperature and stirring was continued for further 30 min. Subsequently, the reaction mixture was poured into 1 mol/L HCl solution (90 mL) at $0 - 5^{\circ}\text{C}$ under vigorous stirring. A saturated NaHCO_3 solution was added to adjust the pH of the aqueous layer to 6–7. The organic layer was separated and the aqueous layer extracted with chloroform. The combined organic solution was dried over anhydrous MgSO_4 , and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with dichloromethane:petroleum ether (3:2) as eluent to give 3-hexyl-2,5-thiophenedicarboxaldehyde (1.52 g, yield 70%), $^1\text{H-NMR}$ of the product (CDCl_3) shows δ 10.02 (s, 1H), 9.98 (s, 1H), 7.62 (s, 1H), 3.02 (t, 2H, $J = 5$ Hz), 1.6 (m, 2H), 1.38 (m, 6H), 0.88 (t, 3H, $J = 4.7$ Hz); HRMS Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2\text{S}$ shows m/z 224.0853. Found: 224.0895.

Poly(3-hexyl-2,5-thienylene vinylene) (PHTV) ^[13]

To a stirred mixture of zinc powder (5.28 g, 0.086 mol) and dry THF (110 mL), TiCl_4 (4.38 mL, 0.0386 mol) was injected at -10°C under N_2 atmosphere. The suspension was refluxed for 1 h. A solution of 3-hexyl-2,5-thiophenedicarboxaldehyde (1.50 g, 0.0067 mol) in dry THF (10 mL) was syringed into the mixture. Then the reaction mixture was refluxed for 16 h. After cooling to room temperature, a 10% K_2CO_3 solution (120 mL) was added under stirring, and the stirring was continued for 30 min. The precipitation formed was filtered off and dried under vacuum, then it was extracted in a Soxhlet extractor first with 100 mL THF for 15 h, then with 100 mL chloroform for 20 h. After concentration of the combined extracts, they were poured into methanol. The polymer was precipitated as red-black powder (0.58 g, yield 45%). Elem. Anal.: Calcd. for $(\text{C}_{12}\text{H}_{16}\text{S})_n$: C 74.94%; H 8.39%. Found: C 75.28%; H 8.55%.

PTV

PTV was synthesized by the method described in ref. [10].

Doping

FeCl_3 doping was achieved in a 0.1 mol/L solution of nitromethane; its conductivity was measured by using a two-probe method after washing with fresh nitromethane and drying under vacuum.

RESULTS AND DISCUSSION

Synthesis

Synthesis of PHTV

From Scheme 1, it can be seen that all the intermediates were obtained in good yield. This indicates that the synthetic route is a proper way to synthesis PHTV. It is worthy of note that synthesis of 3-hexyl-2,5-thiophenedicarboxaldehyde is the crucial step. In general, Vilsmeier reaction, which is the classic and common method of introducing aldehyde group into an aromatic ring, was employed to introduce aldehyde group into the thiophene ring. However, the $^1\text{H-NMR}$ spectrum of the product shows that 3-hexyl-2,5-thiophenedicarboxaldehyde was not obtained and only the mono-substituted product was formed. A split of the two peaks at $\delta = 7\text{--}8$ (Fig. 1), which is assigned to the spin coupling between the hydrogen atoms at 4 and 5-position, confirms that the product is 3-hexyl-2-thiophenecarboxaldehyde.

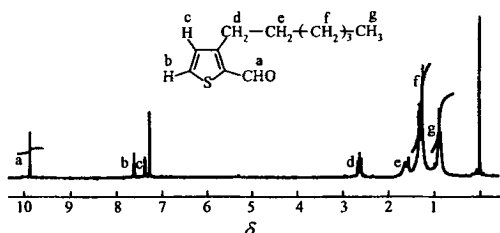
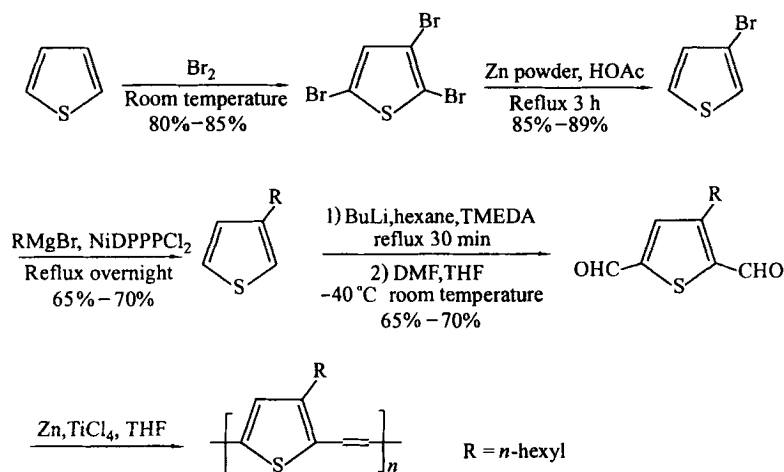


Fig. 1 $^1\text{H-NMR}$ spectrum of 3-hexyl-2-thiophenecarboxaldehyde



Scheme 1 Synthesis of PHTV

In order to obtain dicarboxaldehyde product, longer reaction time, higher reaction temperature and larger ratio of DMF/3-hexylthiophene *etc.* have been tried, but without success. This may be due to the fact that the Vilsmeier reaction is an electrophilic substitution reaction. From the charge density distribution graph of 3-hexylthiophene obtained by theoretical calculation, which is based on the AM1 Hamiltonian in the MOPAC package to optimize the molecular geometric structure and the Hyper Chem Version 5.0 to obtain the charge properties^[14] (Fig. 2a), we concluded that the first aldehyde group should substitute the hydrogen atom at 2-position to form 3-hexyl-2-thiophenecarboxaldehyde due to its greater negative charge density, which has been confirmed by our experiment. Although the electron-rich thiophene ring will facilitate the electrophilic substitution reaction, introduction of the first aldehyde group leads to the reduction of negative charge density on the carbon atom at 5-position (Fig. 2b) of 3-hexyl-2-thiophenecarboxaldehyde, which makes the electrophilic substitution reaction of introducing a second aldehyde group difficult to conduct due to the strong electron-drawing property of the aldehyde group. According to Refs. [13, 15], thienyllithium derivatives are active nucleophilic addition reagents; they can easily undergo nucleophilic addition reaction with DMF to form active intermediates, which can conveniently be hydrolyzed to their corresponding carboxaldehyde derivatives. In order to override this obstacle, an attempt was made to replace the electrophilic substitution reaction with the nucleophilic addition reaction. We try to employ the reaction between 3-hexylthiophene and *n*-butyl lithium to form 3-hexyl-2,5-thienyllithium, and then conduct the nucleophilic addition reaction between thienyllithium derivative and DMF in dry THF. Then the reaction mixture was hydrolyzed to obtain the target product. The result shows that this method is very effective and 3-hexyl-2,5-thiophenedicarboxaldehyde can be obtained in good yield (70%). Its ¹H-NMR spectrum is shown in Fig. 3.

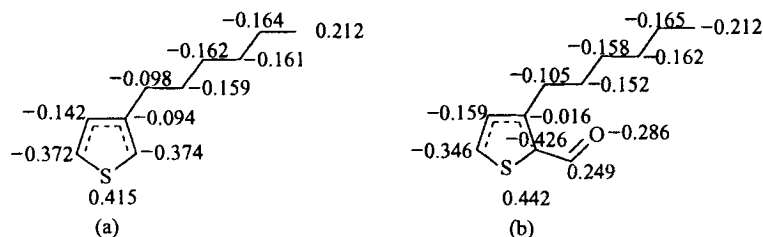


Fig. 2 Charge density distribution graph of 3-hexylthiophene a) and 3-hexyl-2-thiophenecarboxaldehyde b)

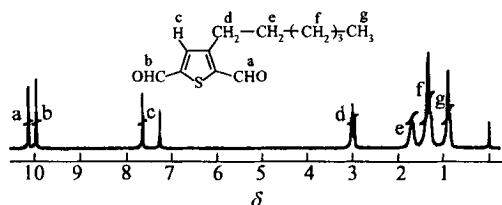


Fig. 3 ^1H -NMR spectrum of 3-hexyl-2,5-thiophenedicarboxaldehyde

PHTV can be synthesized from 3-hexyl-2,5-thiophenedicarboxaldehyde in about 45% yield. It should be mentioned here that all the intermediate compounds are obtained in a yield of 70%–80%. On the contrary, the yield of intermediate required to synthesize PTV from thiophene is about 45% and the yield of the precursor polymer is only 20%–30%. If commercially available 3-alkylthiophene is used as starting material, PHTV can be obtained in only two reaction steps.

Synthesis of PTV

As to the thermal elimination reaction for converting precursor polymer to PTV, after it was treated at 200°C for 30 min the absorption peak at $\sim 1095\text{ cm}^{-1}$ which is assigned to $\nu_{\text{C-O-C}}$ of the precursor polymer weakens while the peak at $\sim 928\text{ cm}^{-1}$ which is assigned to the $\delta_{\text{trans-CH=CH-}}$ appears. This indicates that the elimination reaction has actually occurred. After the polymer was heat treated at 200°C for 3 h, the absorption peak at $\sim 1095\text{ cm}^{-1}$ almost vanishes and the peak at $\sim 928\text{ cm}^{-1}$ is further enhanced. But the absorption peak at $\sim 1760\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$) appears. With the increase of thermal treatment time, the 1760 cm^{-1} band strengthens further (Fig. 4b, 4c and 4d). This shows that PTV is oxidized during the thermal treatment. Evers *et al.*^[9] have treated the precursor polymer at a lower temperature (90 – 165°C), but its IR spectra also showed an absorption peak at $\sim 1760\text{ cm}^{-1}$. These results indicate that the oxidization of PTV during the thermal treatment occurs easily. The presence of the C=O group will break the conjugation structure of PTV, and thus affect the properties of electronic devices prepared by PTV^[10]. From the FT-IR spectrum of PHTV (Fig. 4a), it can be seen that the absorption peak at $\sim 928\text{ cm}^{-1}$ and at $\sim 1650\text{ cm}^{-1}$ ($\nu_{\text{C-C}}$) of the thiophene ring and the strong absorption peaks at ~ 2855 , 2926 , 2954 cm^{-1}

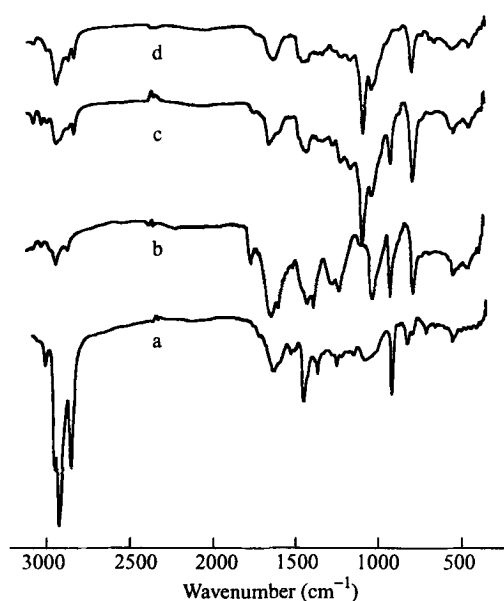


Fig. 4 FT-IR spectra of precursor polymer of PTV, the thermal treatment products of the precursor polymer and PHTV

a) PHTV; b) Thermally treated at 200°C for 30 min;
c) Thermal treatment at 200°C for 3 h; d) Precursor polymer

($\nu(\text{CH}_2)$) and ($\nu(-\text{CH}_3)$) are evident. But a $\sim 1760\text{ cm}^{-1}$ peak is absent. So the synthesis of soluble PHTV is a very important approach to override the oxidation of PTV, to improve the properties and to confer good processibility upon PTV.

Physical and Chemical Properties

Owing to the introduction of longer alkyl side group on the backbone of the PTV, PHTV can be easily dissolved in common organic solvent, such as chloroform, THF and toluene. 0.5 g PHTV can be dissolved instantaneously in 10 mL chloroform to form a homogeneous solution. Its good solubility imparts fine processibility to PHTV, which will widen its application in electronic devices.

The molecular weight of PHTV determined by GPC are 15,300 (M_n) and 31,900 (M_w) respectively, and the polydispersity $D = 2.08$.

The thermal behavior of PHTV represented by the TGA curve is shown in Fig. 5. There is only one major weight loss at over 400°C due to the decomposition of PHTV. As a comparison, PTV has two major weight loss ranges at $100\text{--}195^\circ\text{C}$ and around 400°C ^[10], of which the first weight loss is attributed to the elimination of water and methanol from the precursor polymer, whereas the second one characterizes the thermal properties of PTV. So it can be concluded that PHTV and PTV possess quite similar thermal properties, and the introduction of alkyl side groups on the polymer backbone does not affect its thermal property. The difference between the TGA curves of the two polymers also indicates that the synthesis of soluble PHTV does not need thermal treatment, which is required in the synthesis of PTV and leads to its oxidation.

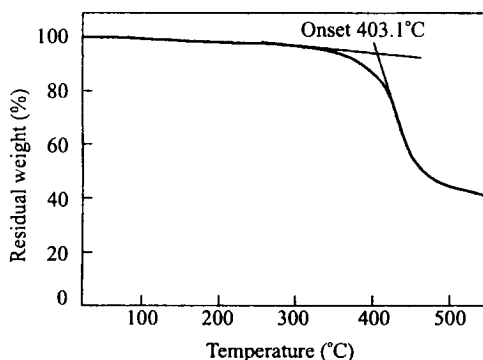


Fig. 5 TGA curve of PHTV

Electrochemical Properties and Electrical Conductivity

The electrochemical properties of PHTV are characterized by cyclic voltammetric study in 0.1 mol/L tetrabutylammonium hexfluorophosphate acetonitrile solution with a sweep rate of 20 mV/s. The result is shown in Fig. 6, the oxidation potential (E_{ox}) of PHTV can be observed at 0.4 V versus SCE, and the oxidation process is reversible. From the UV-Vis absorption spectrum of PHTV in dilute chloroform solution (Fig. 7a), it can be seen that the absorption onset is at about 680 nm, which corresponds to the LUMO-HOMO bandgap (E_g) of 1.8 eV. This value is comparable with that of PTV synthesized by the soluble precursor route (1.7–1.8 eV)^[16]. This indicates that the alkyl side chain on the backbone of the PTV has little effect on the E_g of PHTV. According to the following equation^[17].

$$E_g/e = E_{\text{ox}} - E_{\text{re}}$$

where e is the elementary charge, E_{ox} and E_{re} refer to the onset potentials of oxidation and reduction of PHTV respectively, we can estimate the reduction onset of PHTV to be -1.4 V versus SCE.

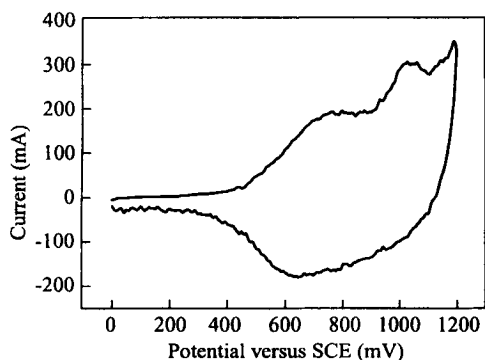


Fig. 6 Cyclic voltammogram of PHTV

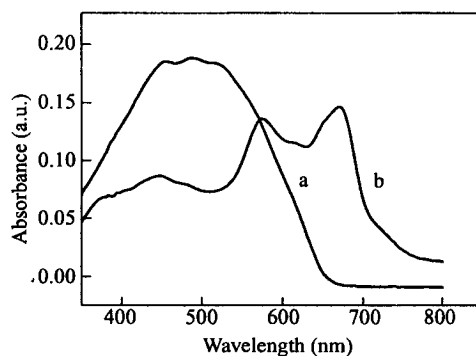


Fig. 7 UV-Vis spectra of the undoped and doped PHTV
a) undoped; b) after doping for 45 min

The onset oxidation potential of 0.4 V versus SCE for PHTV indicates that it will be easily doped with FeCl_3 and I_2 . After doping with 0.1 mol/L FeCl_3 in nitromethane solution, the λ_{max} of PHTV is shifted bathochromically from 490 nm to 670 nm (Fig. 7). In the FT-IR spectrum (Fig. 8) of the doped polymer, the essential structure of PHTV still remains after doping, which is characterized by the presence of absorption peaks at about 920, 1650, 2855, 2926 and 2954 cm^{-1} . Some new absorption peaks appear at 1063, 1132, 1180 and 1540 cm^{-1} in comparison with those of the undoped PHTV. This indicates the formation of charge transfer complex between PHTV and FeCl_3 . The complex is stable because its FT-IR spectra (Fig. 8c) remain almost the same as that of the fresh sample (Fig. 8b) after 4 days.

The dependence of conductivity of PHTV film on doping time is shown in Fig. 9. With increasing doping time, the conductivity increases rapidly during the first 15 min, and then slower to reach a saturated conductivity as high as $1.1 \times 10^{-2} \text{ S/cm}$.

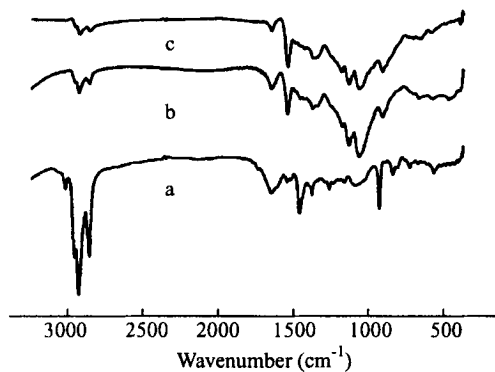


Fig. 8 FT-IR spectra of undoped and doped PHTV
a) Undoped; b) Freshly doped sample;
c) 4 days after doping.

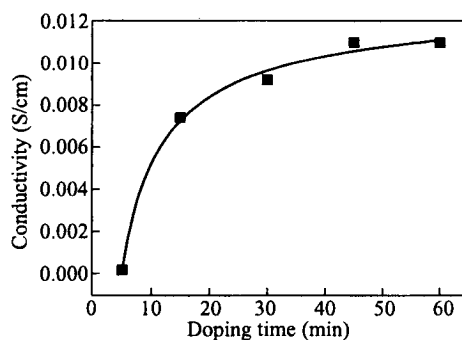


Fig. 9 Dependence of conductivity of PHTV on doping time

Surface Morphology of the Polymer Films

One of the most important applications of the conjugated polymer is to fabricate electronic devices, the properties of which are determined by the quality of the conjugated polymer film. Therefore, the spin-coating film quality of PTV and PHTV is studied by using SEM and the result is illustrated in Fig. 10. PTV film (Fig. 10a) exhibits poor quality and there are many protuberances and pin-hole structures on its surface. The pin-hole structures are magnified and can be seen more clearly from Fig. 10(b). The poor film quality can be attributed to the inherent drawback of the traditional precursor method, because the original precursor polymer film must be thermally treated to convert it into the experimental PTV film. The release of small molecular compounds (such as H_2O , CH_3OH) during the thermal treatment will easily cause the protuberance and even the

pin-hole structure on the surface of PTV film. However, the film of soluble PHTV has good quality and its surface is very smooth (Fig. 10c)). So it can be concluded that the precursor method might not be a good method to prepare PTV film with high quality and synthesis of soluble PTV can provide another choice.

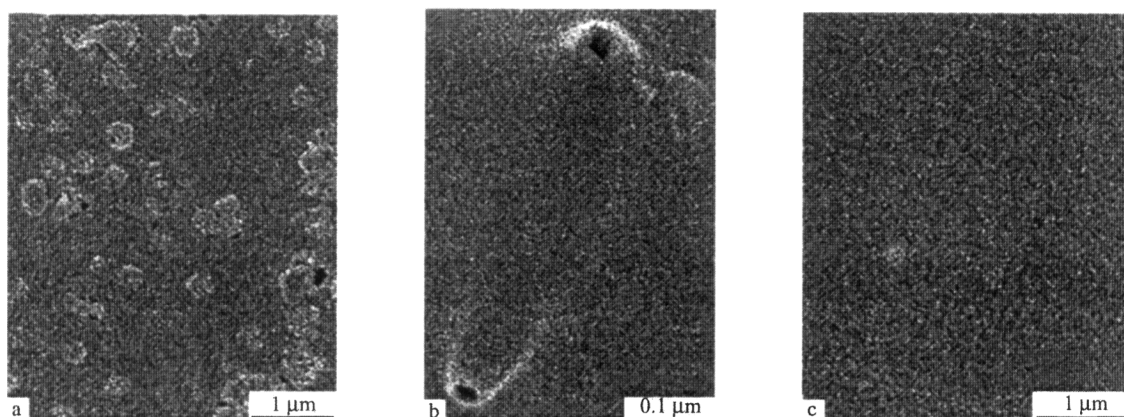


Fig. 10 SEM microphotograph of the polymer film

- a) PTV film
- b) Pin-hole structure on the PTV film
- c) PHTV film

CONCLUSION

Soluble poly(3-hexyl-2,5-thienylene vinylene) is synthesized readily from thiophene with good yield. The crucial intermediate compound 3-hexyl-2,5-thiophenedicarboxaldehyde was prepared with *n*-butyl lithium and DMF through the nucleophilic addition reaction instead of the traditional electrophilic substitution reaction (Vilsmeier reaction) by virtue of the strong electron-drawing property of the aldehyde group. The starting material is commercially available, so the method is very convenient for synthesizing soluble PHTV with higher yield compared with that of the synthesis of PTV. Owing to the introduction of alkyl side group on the backbone of the polymer PHTV, it can be dissolved in common organic solvents such as chloroform, THF and toluene. The synthesis of soluble PHTV is a very important approach to override the oxidation of PTV, to improve the properties of PTV and to afford its good processibility at the same time. The introduction of alkyl side group does not affect the bandgap and thermal properties of PHTV compared with those of PTV. After doping with FeCl_3 , the conductivity of PHTV reaches values as high as $1.1 \times 10^{-2} \text{ S/cm}$. The results of the SEM study of the polymer film surface show that the spin-coating film of PHTV possesses better quality, which is very important for fabricating devices with good properties, than the PTV film prepared by the traditional precursor method. These properties will open important applications in electronic devices to PHTV.

REFERENCES

- 1 Su, W.P., Schrieffer, J.R. and Heeger, A.J., *Phys. Rev. Lett.*, 1979, 42: 1968
- 2 Bredas, J.L., Themans, B. and Andre, J.M., *Phys. Rev. B*, 1983, 27: 7827
- 3 Goldberger, J.B., Crowe, H.R., Newman, P.R., Heeger, A.J. and MacDiarmid, A.G., *J. Chem. Phys.*, 1979, 70: 1132
- 4 Tran, V.H., Massardier, V., Nguyen, T.P. and Davenas, T., *Polymer*, 1996, 37: 2061
- 5 Schafer, O., Greiner, A. and Guss, W., *Synth. Met.*, 1996, 82: 1
- 6 Fuchigami, H., Tsumura, A. and Koezuka, H., *Appl. Phys. Lett.*, 1993, 63: 1372
- 7 Brown, A.R., Jarrett, C.P., Leeuw, D.M.de and Matters, M., *Synth. Met.*, 1997, 88: 37

- 8 Sirringhaus, H., Tessler, N. and Friend, R.H., *Science*, 1998, 280: 1741
- 9 Evers, W., Schrijver, D., De, Dierick, T., Peten, C., Van Der Looy, J. and Geise, H.J., *Synth. Met.* 1992, 51: 329
- 10 Xie, H.Q., Liu, C.M. and Guo, J.S., *Eur. Polym. J.*, 1996, 32: 1131
- 11 Gronowitz, S. and Raznikiewicz, T., *Org. Synth. Coll.*, John Wiley and Sons, Inc., New York, 1973, V, p.149
- 12 Van Pham, C., Mark, H.B. and Zimmer, H., *Synth. Commun.*, 1986, 16: 689
- 13 Elandalousi, E.H., Frere, P., Richomme, P., Orduna, J., Garin, J. and Roncali, J., *J. Am. Chem. Soc.*, 1997, 119: 10774
- 14 Wang, P., Zhu, P.W., Wu, W., Kang, H. and Ye, C., *Phys. Chem. Chem. Phys.*, 1999, 1: 3519
- 15 Feringa, B.L., Hulst, R., Riker, R. and Brandsma, L., *Synth. Commun.*, 1988, 316
- 16 Yamada, S., Tokito, S., Tsuisui, T. and Saito, S., *J. Chem. Soc., Chem. Commun.*, 1987, 1448
- 17 Li, Y.F., Cao, Y., Gao, J., Wang, D.L., Yu, G. and Hegger, A.L., *Synth. Met.*, 1999, 99: 243