Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis of Electric Conductive Poly(Arylene Vinylene) Containing Vinyl Pyrrole (PVP)

Dae Young Kim [a], Chang Six Ha [a] & Won Jei Cho [a]

[a] Department of Polymer Science and Engineering, Pusan National University, Pusan, 609-735, Korea

Version of record first published: 04 Oct 2006.

To cite this article: Dae Young Kim , Chang Six Ha & Won Jei Cho (1994): Synthesis of Electric Conductive Poly(Arylene Vinylene) Containing Vinyl Pyrrole (PVP), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 247:1, 1-10

To link to this article: http://dx.doi.org/10.1080/10587259408039185

Mol. Cryst. Liq. Cryst. 1994, Vol. 247, pp. 1–10
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SYNTHESIS OF ELECTRIC CONDUCTIVE POLY(ARYLENE VINYLENE) CONTAINING VINYL PYRROLE (PVP)

DAE YOUNG KIM, CHANG SIK HA, and WON JEI CHO
Department of Polymer Science and Engineering,
Pusan National University, Pusan 609-735, Korea

Abstract A new polyarylenevinylene containing vinyl pyrrole (PVP) was obtained from the monomer, 2,5-bis(methylenedimethylsulfonium) chloride pyrrole, which was prepared from 2,5-dimethylpyrrole by the modified sulfonium polyelectrolyte precursor route. The polymerization conditions for the preparation of precursor polymers are described. The highest yield was obtained when the PVP was synthesized at -40°C with the monomer/base concentration ratios of 0.5/0.2 and thermally eliminated at 220°C. The electrical conductivity of the PVP synthesized with aforementioned conditions was given as 6.8×10^{-7} Scm^{-1}.

INTRODUCTION

Poly(arylene vinylene)s are attracting much interest as materials for non-linear optics as well as highly conductive polymers, because they can be obtained as dense, tough and flexible films and show superior chemical stability against oxygen and moisture at room temperature[1-3]. Murase et al. and Karasz et al. have established the procedure to obtain high-molecular-weight polymer films of poly(p-phenylenevinylene)(PPV) through a water-soluble precursor route[4-6]. The precursor route involves the synthesis of a water-soluble sulfonium salt polyelectrolyte and subsequent conversion to linear π-conjugated structures by thermal elimination. The synthesis of polyarylenevinylenes through the

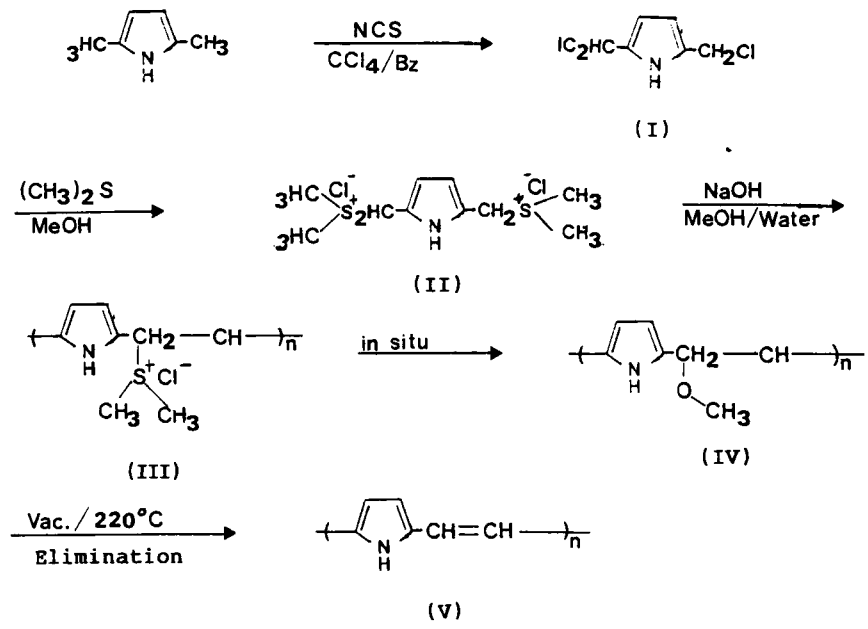
precursor route is one of the most promising methods to obtain polymer films with extended π-conjugated structures that are not soluble in any solvents. The precursor route has been applied to the preparations of other polyarylenevinylenes such as poly(2,5-dimethyoxy-p-phenylenevinylene)(MO-PPV)[7] and Poly(2,5-naphthalenevinylene)[8]. However, in many cases, the precursor polymers were not stable enough to give uniform solid precursor films; the partial elimination of a sulfonium salt group proceeded quickly even at room temperature, which prevented the fabrication of thin uniform films with good optical quality.

Recently, Saito et al[9,12] and Murase et al[10,13] have found that poly(2,5-thienylenevinylene)(PTV) could be prepared through a new precursor polymer soluble in organic solvents. The new precursor polymer possessed a methoxy leaving group in place of a sulfonium salt group. The new methoxy precursor was stable up to 100℃ even in air. More recently, they have succeeded in the preparation of MO-PPV through a similar new precursor soluble in organic solvents[11]. Solvent casting or spin coating of the new precursor polymers yields uniform thin films of the precursor polymers, because the new precursor polymers are soluble in organic solvents such as chloroform, dichloromethane and tetrahydrofuran. Uniform thin cells of polyarylenevinylenes can thus be obtained through the heat treatment of the precursor polymer films.

In this work, a new poly(arylene vinylene) containing vinyl pyrrole (PVP) was synthesized by the modified sulfonium polyelectrolyte precursor route. The synthesized monomer and polymer were characterized with IR and ^{1}H-NMR spectroscopies.The electric conductivity of the poly(arylene vinylene) containing vinyl pyrrole was measured by four-point probe method.

EXPERIMENTAL

The samples of PVP were synthesized via a modified sulfonium polyelectrolyte precursor route as shown below;



Monomer Synthesis

2,5-bischloromethylpyrrole(I) was prepared by reacting 0.064 mol(6.08g) of 2,5-dimethylpyrrole and 0.192 mol(25.69g) of N-chlorosuccimide(NCS) with 0.001 mol (0.4g) of benzoyl peroxide in the mixture of 300ml CCl_4 and 150ml benzene under nitrogen[14,15]. After the reaction mixture was refluxed at 70℃ for 10hrs, the mixture was cooled and filtered to remove unreacted succimide by extracting with hot CCl_4. Solvents were removed on a rotary evaporator from the combined filtrate and extracts. Then, 2,5-bischloromethylpyrrole(I) was obtanied by recrystallizing twice the remained viscous liquid with ethanol to remove traces of monochlorinated and unchlorinated by-products.

The yield was 34% (m.p. 82-83℃ ; For $C_6H_7NCl_2$ calculated; C: 43.9%, H:4.29%, N: 8.53%, Cl:43.22% found; C: 43.67%, H:4.18%, N: 8.21%.). The compound (I) was identified by IR and ^{1}H-NMR spectroscopies as well as elemental analysis. The IR spectrum, shown in Figure 1-a exhibits a characteristic peaks due to NH at 3400 cm^{-1}, CH at 2980 cm^{-1}, CH_2 at 1470 cm^{-1},and C-Cl at 850 cm^{-1}. The ^{1}H-NMR spectrum showed characteristic peaks due to methylene(4H) at 3.47ppm, pyrrole(2H) at 6.87ppm, and NH pyrrole(1H) at 7.97ppm, as shown in Figure 2-a.

The monomer, 2,5-bis(methylenedimethylsulfonium)chloride pyrrole (Ⅱ) was prepared from compound(Ⅰ) by the following precedure; Into a round-bottom flask equipped with a magnetic stirrer was placed 0.0061 mol(1g) of compound(I) and 0.0366 mol(2,2655g) of dimethylsulfide in a 30ml of methanol. The reaction mixture was kept with stirring at 40℃ for 24 hrs. Solvent was evaporated on a rotary evaporator, and the product was precipitated in cold diethylether.

The yield was 42 % (m.p. 103-104℃; For $C_{10}H_{19}NS_2Cl_2$, calculated ; C:41.66% H:6.64% N:4.85% S:22.24% Cl:24.59% found; C:41.07% H:6.43% N:4.64% S:22.07%). The IR spectrum, shown in Figure 1-b, exhibits characteristic peaks due to NH at 3400 cm^{-1}, CH at 2980 cm^{-1}, CH_2 at 1470 cm^{-1}, CH_3 at 1440 cm^{-1}. The ^1H-NMR spectrum showed characteristic peaks due to methyl(12H) at 2.97ppm, methylene(4H) at 3.32ppm, pyrrole(2H) at 6.42ppm, and NH pyrrole (1H) at 8.32ppm, as shown in Figure 2-b.

Polymerization

The sulfonium salt precursors(Ⅲ) as the intermediates for the methoxy pendant precursors were prepared in water or in a water-methanol mixture by base-induced polymerization. The optimum reaction conditions were investigated to obtain the precursors by

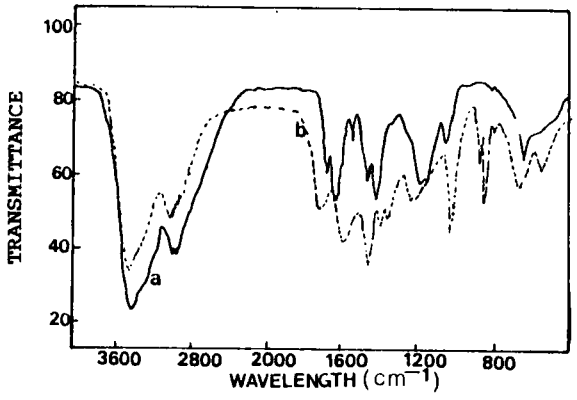


FIGURE 1. IR spectra of a) 2,5-bischlormethylpyrrole and 2,5-bis(methylenedimethylsulfonium)chloride pyrrole (KBr, Pellets).

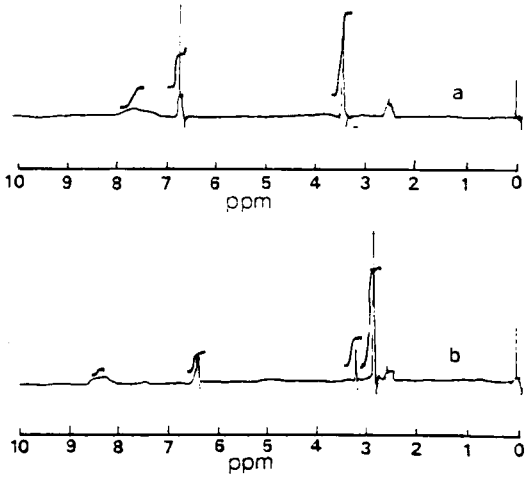


FIGURE 2.NMR spectra of a) 2,5-bischlormethylpyrrole and 2,5-bis(methylenedimethylsulfonium)chloride pyrrole (DMSO-d_6).

varying several experimental conditions such as monomer concentration, reaction temperature and the mole ratio of monomer and base. The sulfonium salt precursors were polymerized by mixing equal volumes of 0.2M of the monmoner(Ⅱ) and 0.2M of NaOH at a given temperature with stirring under nitrogen. Polymerizations were carried out under the various experimental conditions as shown in Table Ⅰ. After a homogeneous viscous solution was obtained, the reaction was quenched by neutralization with 1.0 N aqueous HCl. Warming the solution up to room temperature yielded red precipitate. The precipitate, the methoxy precursor polymer, was filtered and dried under vacuum at room temperature.

The precursor polymers(Ⅳ) were subjected to thermal elimination *in vacuo*(10^{-2} Torr) at 220℃ for 8hrs to transform them into the final polyconjugated polymers. Thermal elimination was carried out under such experimental conditions as described in Table Ⅱ. The structure of precursor polymers and final polymers were charaterized by IR and UV-vis spectra.

Characterization

Elemental analysis was performed on Perkin-Elmer 240C elemental analyzer. ^{1}H-NMR spectra were obtained on a Varian 60 spectrometer and IR spectra were obtained on a Perkin-Elmer 1330. UV-vis spectra were obtained a UVIKON 860. Melting points were determined with Fisher-Johns melting point apparatus.

Electric Conductivities

For the measurement of conductivity, circular pellets (diameter in 2.3cm and thickness in 0.1-0.3 mm) from the powdery samples were prepared by a pressure of 90kg/cm^2. Gold electrodes were attached on both surface of the pellets together with a guard electrode by vaccum evaporation. The conductivity measurement were carried out by four-point probe DC method in a vacuum of 10^{-3} Torr.

RESULTS AND DISCUSSION

Preparation of Precursor Polymers

Both the stability and the solubility in organic solvents of the precursor polymers markedly depended on the polymerization conditions. In particular, the selection of the reaction temperature and the base-to-monomer ratio were found to be most important. Table I summarizes the reaction conditions and the yields of the precursor polymers. The yields of the precursor polymers were dependent on both the monomer and base

	Concentration(M) monomer	base	Molar ratio base/monomer	Temperature (℃)	Solvent MeOH/H_2O	Color	Yield (%)
A	0.1	0.2	1.5	-10	1/1	yellow	16.1
B	0.5	0.2	1.0	-20	1/1	orange	30.2
C	0.5	0.2	1.0	-40	1/1	red	44.3

TABLE Ⅱ. Effect of thermal elimination temperature on the conductivity of the final conjugated polymer.*

Thermal Elimination temperature (℃)	Conductivity (Scm^{-1})
180	3.67×10^{-9}
200	4.47×10^{-8}
220	6.86×10^{-7}

* The reaction contion of the precursor polymer is C in Table I.

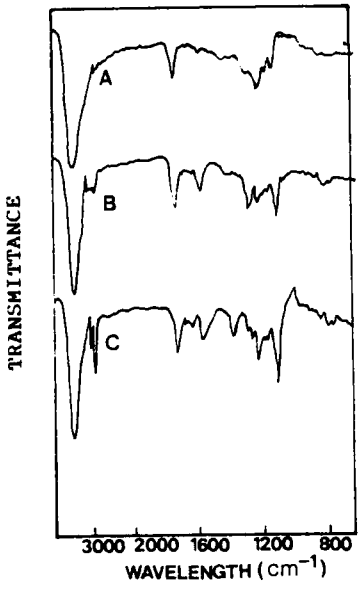


FIGURE 3. IR spectra of the precursor polymers obtained under various reaction conditions(The details of the conditions A, B and C are described in Table I.) (KBr,Pellets).

concentrations, and reaction temperatures. The highest yield was obtained as 44.3% when the reaction was carried out under the following conditions; monomer concentration: 0.5M, base concentration: 0.2M, molar ratio of base to monomer: 1.0, reaction temperature : -40℃ ,and reaction time : 6hrs. The molecular weight of the precursor polymer was determined by gel permeation

chromatography(GPC) (waters 244). The measurements were conducted in THF and the appratus was calibrated with PS standards. The molecular weight of the typical precursor polymer was determind as Mw: 1.8 x 10^5(Mw/Mn=2.43). Table Ⅲ shows typical solubility data of the precursor polymer. The precursor polymer was soluble in THF and DMSO. Figure 3 shows the IR spectra of precursor polymers prepared under diffrent reaction conditions. The IR specta of the precursor polymers show characteristic absorption peaks due to NH at 3400 cm^{-1}, CH at 2980 cm^{-1}, CH_2 at 1470 cm^{-1}, CH_3 at 1440 cm^{-1}, and C-O-C at 1100 cm^{-1},respectively.

The IR spectra of the precursor polymers obtained under the optimum conditions (a typical spectrum is shown in Figure 3-c) gave a strong absorption band at 1090cm^{-1}, which was attributed to C-O-C stretching vibration .

Thermal elimination

Precursor polymer samples were loaded into a glass tube oven. The hydrochloric acid was supplied in vapor phase with N_2 gas flow to proceed the thermal elimination under the acid atomosphere. Conversion of the precursor polymer to the final conjugated polymer was confirmed by IR spectrum(Figure 4). Figure 4 shows the IR spectrum of the final conjugated polymer prepared with the thermal elimination temperature of 220℃ in the presence of the acid catalyst. The C-O-C stretching vibration band at 1100 cm^{-1} completely disapperared and the trans-vinylene CH out-of-plane band at 940 cm^{-1} and trans-vinylene C-H stretching vibration at 3050 cm^{-1} appeared. Figure 5 shows the UV spectra of a precusor polymer(a) and a final polymer(b). In this figure, the precursor polymer was obtained with the optium polymerization conditions mentioned above and the thermal elimination was performed at 220℃. The characteristic peak of the precursor polymer was observed at 235nm but a new peak was observed in the longer wavelength region around 650nm in the final conjugated polymer. The new peak around 650nm is associated with the phi-phi* transition of conjugated double bonds. The IR and UV spectra prove the perfect elimination of the methoxy groups and the production of the final conjugated polymer.

TABLE Ⅲ. Solubility of precursor polymer

Solvent						
Benzene	Chlorobenzene	THF	CCl_4	DMF	MeOH	DMSO
+/-	+/-	+	-	+/-	-	+

+ : Soluble ; +/- : Partially soluble ; - : Insoluble

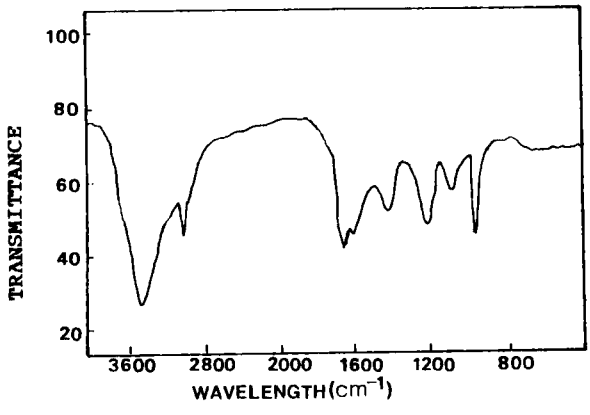


FIGURE 4. IR spectrum of the final conjugated polymer (KBr,Pellet).

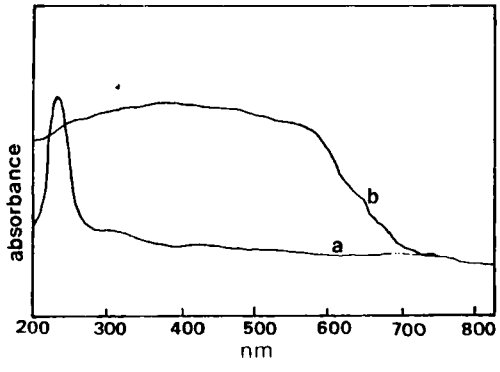


FIGURE 5. UV spectra of a) a precursor polymer and b) a final conjugated polymer (in DMSO).

Electric conductivity

Table Ⅲ shows the conductivity of the final conjugated polymer, poly(arylenevinylene) containing vinyl pyrrole(PPV) in undoped states, which were obtained under various synthetic conditions and thermal elimination temperatures. It was found that the highest conductivity was given as 6.8×10^{-7} Scm^{-1} for the PVP of which precursor polymer was obtained with the synthetic condition C and the elimination temperature of 220℃.

REFERENCES

1. T.Kaino,K.Kubodera,S. Tomaru, T. Kurihara, S. Saito, T.Tsutsui, and S.Tokito, Electron. Lett. 23,1095,(1987)
2. D.McBranch, M. Sinclair, A.J. Heeger, A.O. Patil, S. Shi, S.Askari, and F.Wudl, 'Proc. ICSM',(1988)
3. T.Kaino, K. Kubodera, H. Kobayashi, T. Kurihara, S. Saito, T.Tsutsui, S. Tokito, and H. Murata, Appl. Phys. Lett. 53,2002,(1988)
4. D.D.C.Bradley, J. Phys. (D) 20,1389,(1987)
5. I.Murase, T. Ohnishi, T. Noguchi, and M.Hirooka, Polym.Commun. 25,327,(1984)
6. D.R.Gagnon, J.D. Capistran, F.F. Karasz, R.W. Lenz, and S. Antonn, Polymer 28,567,(1987)
7. I.Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, Polym. Commun. 26,362,(1985)
8. S.Antonn, D.R. Gagnon, F.F. Karasz, and R.W.Lenz, J. Polym. Sci. (C) 24,503,(1986)
9. S.Yamada, S. Tokito, T. Tsutsui, and S. Saito, J. Chem. Sci., Chem. Commun. 1448,(1987)
10. I.Murase, T.Ohnishi, T. Noguchi, and M.Hirooka, Polym. Commun. 28,229,(1987)
11. T.Momii, S. Tokito, T. Tsutsui, and S. Saito, Chem. Lett. 1201,(1988)
12. S.Tokito, T. Tsutsui, S. Saito, and R.Tanaka, Polym. Commun. 27,333,(1986)
13. I.Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, Polym. Communm. 28,229,(1987)
14. J.I.Jin, J.C.Kim, and H.K.Shim, Macromolecules.,25,5519,(1992).
15. S.Antoun, D.R.Gagnon,F.E.Karase. and R.W.Lenz, J.Polym.Sci., Polym. Lett.,24,503,(1986)