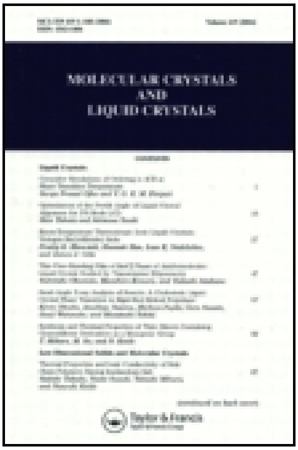

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Synthesis of Electric Conductive Poly(2,5-Pyrrolylene Vinylene) (PPRV)

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SYNTHESIS OF ELECTRIC CONDUCTIVE POLY(2,5-PYRROLYLENE VINYLENE) (PPRV)

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Abstract Poly(2,5-pyrrolylenevinylene)(PPRV) was obtained from the monomer, 2,5-bis(methylenedimethylsulfoniumchloride) pyrrole, which was prepared from 2,5-dimethylpyrrole by the modified sulfonium polyelectrolyte precursor route. The polymerization conditions for the preparation of precursor polymers were examined. The highest yield was obtained when the precursor polymer,poly(α-methoxy-2,5-pyrrolylene)[poly(α-MeO-PRY)], was synthesized at -40℃ with the monomer/base concentration ratios of 0.5/0.2. PPRV obtained by the thermal elimination of the precursor polymer at 220℃ exhibited highest electrical conductivity, being the order of 6.9×10^{-7} Scm^{-1}.

INTRODUCTION

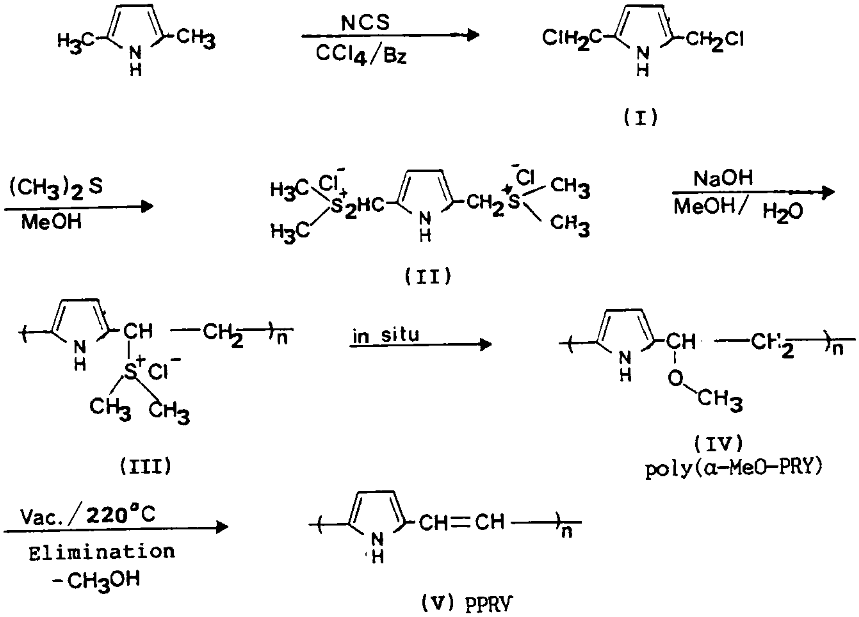
Poly(arylenevinylene)s are attracting much interest as materials for non-linear optics as well as highly conductive polymers, because they can be obtained as dense, tough and flexible films and show superior chemical stability against oxygen and moisture at room temperature[1-3]. Murase et al. and Karasz 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 poly(arylenevinylene)s 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 and coworkers[9,11,12] 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 films of polyarylenevinylenes can thus be obtained through the heat treatment of the precursor polymer films.

The objective of the work is to develop a novel conductive and non linear optical active polymers containing heteroatom, i.e. nitrogen. For the purpose, in this work, poly(2,5-pyrrolylenevinylene)(PPRV) was synthesized by the modified sulfonium polyelectrolyte precursor route. The synthesized monomer, 2,5-bis (methylenedimethylsulfonium chloride)pyrrole and polymers such as poly(α-methoxy-2,5-pyrrolylene)[poly(α-MeO-PRY)] and PPRV were characterized with IR and ^{1}H-NMR spectroscopies and GPC. The electric conductivity of the PPRV was measured by using electrometer.

EXPERIMENTAL

PPRV was synthesized via a modified sulfonium polyelectrolyte precursor route as shown below;



Monomer Synthesis

2,5-bischloromethylpyrrole(I) was obtained from 2,5-dimethylpyrrole according to the work of Lenz et al.[14] with slight modifications. 0.064 mol(6.08g) of 2,5-dimethylpyrrole is reacted with 0.192 mol(25.69g) of N-chlorosuccimide(NCS) in the presence of 0.001 mol(0.4g) of benzoyl peroxide in the mixture of 300ml CCl_4 and 150ml benzene under nitrogen. 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, the 2,5-bischloromethylpyrrole(I) was obtained 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 750 cm^{-1}. The ^1H-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(methylenedimethylsulfoniumchloride) 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 0.0366mol (2,2655g) of dimethylsulfide in a 30ml of methanol. The reaction mixture was kept with stirring at 40℃ for 24hrs. 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.

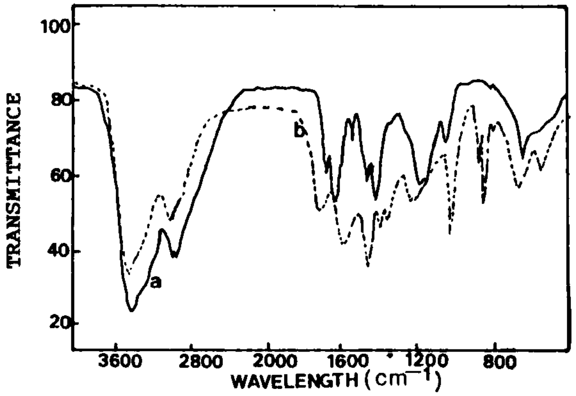


FIGURE 1. IR spectra of a) 2,5-bischlormethylpyrrole and b) 2,5-bis(methylenedimethylsulfoniumchloride)pyrrole (KBr,Pellets).

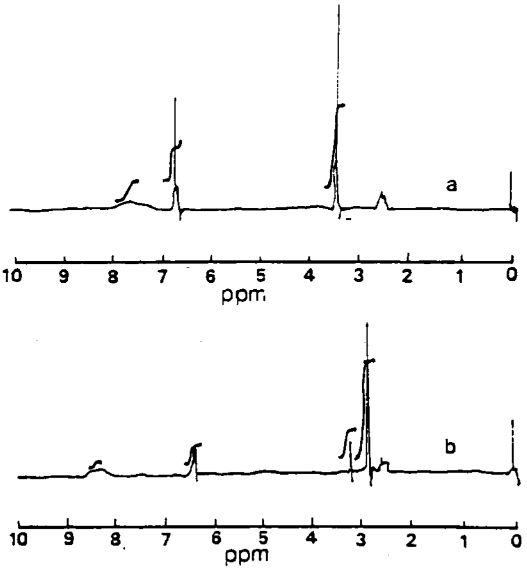


FIGURE 2.NMR spectra of a) 2,5-bischlormethylpyrrole and b) 2,5-bis(methylenedimethylsulfoniumchloride)pyrrole (DMSO-d_6).

Polymerization

The sulfonium salt precursor(Ⅲ) as the intermediates for the methoxy pendant precursors was prepared in water or in a water-methanol mixture by base-induced polymerization. The optimum reaction conditions were investigated to obtain poly(α-MeO-PRY) by varying several experimental conditions such as monomer concentration, reaction temperature and the molar ratio of monomer and base. The sulfonium salt precursor(Ⅲ) was 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, polymerization was quenched by neutralization with 1.0N aqueous HCl. Warming the solution up to room temperature yielded red precipitate. The precipitate, the poly(α-MeO-PRY), was filtered and dried under vacuum at room temperature to a constant weight.

Poly(α-MeO-PRV)(Ⅳ) was subjected to thermal elimination *in vacuo*(10^{-2} Torr) at 220℃ for 8hrs to transform it into the final polyconjugated polymer(PPRV). Thermal elimination was carried out under such experimental conditions as described in Table Ⅱ. The structure of poly(α-MeO-PRY) and PPRV 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 by a UVIKON 860. Melting points were determined with Fisher-Johns melting point apparatus. 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.

Electric Conductivities

For the measurement of conductivity, circular pellets (diameter in 2.3cm and thickness in 0.1-0.3mm) 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 using an electrometer(Takeda Riken TR-8651) in a vacuum of 10^{-3} Torr.

TABLE I. Condition 2,5-bis(methylenedimethylsulfoniumchloride) pyrrol for the polymerization and colors and yields of the obtained polymer.

	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

RESULTS AND DISCUSSION

Preparation of Precursor Polymers[poly(α-MeO-PRY)]

Both the stability and the solubility in organic solvents of the poly(α-MeO-PRY) 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 poly(α-MeO-PRY) was dependent on both the monomer and base 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 typical poly(α-MeO-PRY) was determind as $\overline{Mw}$: 1.8 x 10^5($\overline{Mw}/\overline{Mn}$=2.43). Table Ⅲ shows typical solubility data of the poly(α-MeO-PRY). Poly(α-MeO-PRY) was soluble in THF and DMSO. Figure 3 shows the IR spectra of poly(α-MeO-PRY) prepared under diffrent reaction conditions. The IR specta of the poly(α-MeO-PRY) 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.

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

Thermal elimination temperature (℃)	Conductivity (Scm^{-1})
180	3.7×10^{-9}
200	4.5×10^{-8}
220	6.9×10^{-7}

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

The IR spectra of the poly(α-MeO-PRY) obtained under the C conditions in Table I (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 .

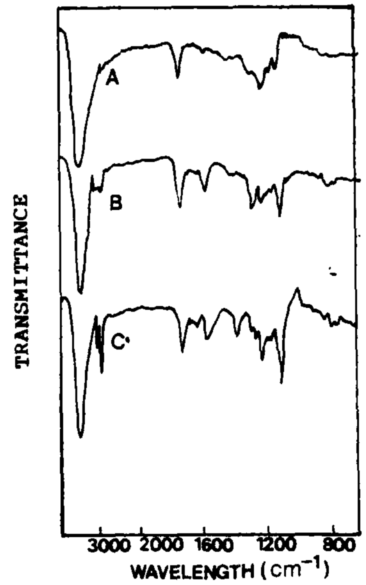


FIGURE 3. IR spectra of the Poly(α-MeO-PRY) obained under various reaction conditions(The details of the conditions A, B and C are described in Table I.) (KBr,Pellets).

TABLE III. Solubility of poly(α-MeO-PRY).

Solvent						
Benzene	Chlorobenzene	THF	CCl$_4$	DMF	MeOH	DMSO
+/-	+/-	+	-	+/-	-	+

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

Thermal elimination

Poly(α-MeO-PRY) was 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[15]. Conversion of the poly(α-MeO-PRY) to the final PPRV was confirmed by IR spectrum(Figure 4). Figure 4 shows the IR spectrum of the PPRV 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

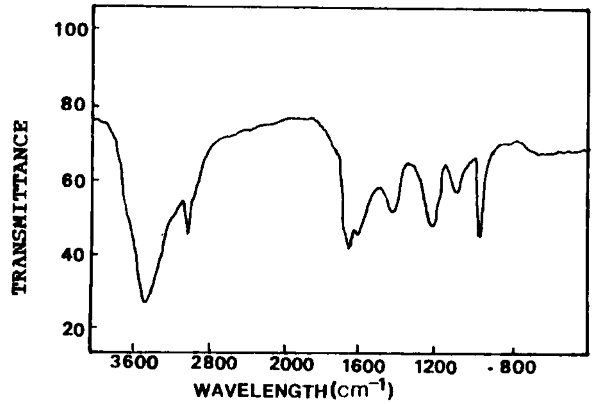


FIGURE 4. IR spectrum of the final conjugated polymer(PPRV) (KBr,Pellet).

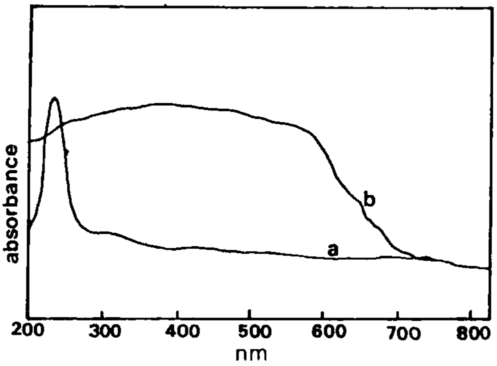


FIGURE 5. UV spectra of a) Poly(α-MeO-PRY) and b) PPRV (in DMSO).

poly(α-MeO-PRY)(a) and a poly(PRV)(b). In this figure, the poly(α-MeO-PRY) was obtained with the optium polymerization conditions mentioned above and the thermal elimination was performed at 220℃. The maximum absorption peak of the poly(α-MeO-PRY) was observed at 235nm but a new peak was observed in the longer wavelength region around 610nm in the PPRV. The new peak around 610nm 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 PPRV.

Electric conductivity

Table Ⅲ shows the conductivities of the final conjugated polymer , poly(2,5-pyrrolylenevinylene) (PPRV) in undoped states, which were obtained under various synthetic conditions and thermal elimination temperatures. It was found that the highest conductivity was given as 6.9 x 10^{-7} Scm^{-1} for the PPRV of which poly(α-MeO-PRY) was obtained with the synthetic condition C in Table I and the elimination temperature of 220℃.

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