Polyarylenevinylene films prepared from precursor polymers soluble in organic solvents

Shizuo Tokito, Tatsuo Momii, Hideyuki Murata, Tetsuo Tsutsui and Shogo Saito*
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816, Japan
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Three polyarylenevinylenes, poly(*p*-phenylenevinylene), poly(2,5-dimethoxy-*p*-phenylenevinylene) and poly(2,5-thienylenevinylene), were prepared through new precursor polymers that were soluble in organic solvents. The new precursor polymers were chemically stable in air below 100°C. Thin precursor polymer films were obtained by spin coating from the organic solutions. Uniform, dense, and tough polyarylenevinylene films were obtained from the precursor polymer films by heat treatment in order to eliminate the pendant group. The optical and electrical properties of those polyarylenevinylenes were investigated. Oriented polyarylenevinylene films were obtained by stretching during thermal treatment.

(Keywords: polyarylenevinylene; soluble precursor; optical properties; conductivity; orientation)

INTRODUCTION

Polyarylenevinylenes 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 sulphonium 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-dimethoxy-*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 sulphonium salt group proceeded quickly even at room temperature, which prevented the fabrication of thin uniform films with good optical quality.

Recently, we[9] and Murase *et al.*[10] 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 sulphonium salt group. The new methoxy precursor was stable up to 100°C even in air. More recently, we 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 paper, the preparations and characterizations of three methoxy precursors of polyarylenevinylenes (PPV, MO-PPV and PTV) that are soluble in organic solvents are described (*Figure 1*). The precursor polymers were converted to polyarylenevinylene films, and their detailed characterizations are given. Then, the electrical conductivities in undoped and doped films are examined. Finally, the preparation of oriented MO-PPV and PTV films through uniaxial stretching is described.

EXPERIMENTAL

Preparation of precursor polymers

Figure 2 shows the general synthetic route of the methoxy pendant precursor polymers. The sulphonium salt precursors 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, such as monomer concentration, reaction temperature and the molar ratio of monomer and base, were delicately dependent on the structures of monomers. The methoxy pendant precursors were derived from the sulphonium salt precursors by the reaction with methanol.

The structures of precursor polymers were characterized by use of i.r. spectra, n.m.r. spectra and elemental analyses.

Conversion to polyarylenevinylene

Methoxy precursors were dissolved in chloroform, and the solutions were cast on flat laboratory dishes that had been treated with dichlorodimethylsilane beforehand. Films with a thickness of 10–20 μm were thus obtained.

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* To whom correspondence should be addressed

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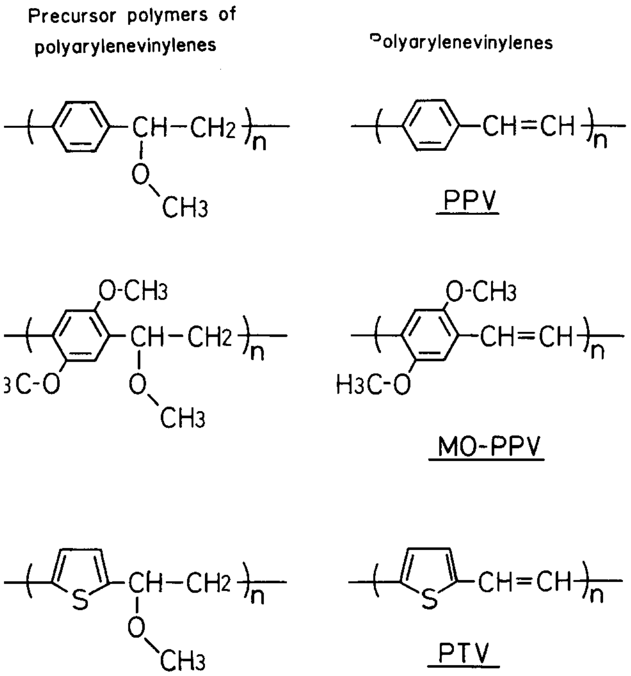
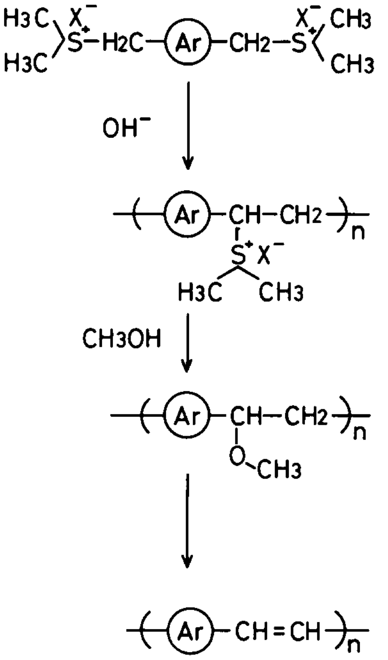


gure 1 Chemical structures of polyarylenevinylene precursors and lyarylenevinylenes



gure 2 Synthetic route of polyarylenevinylenes through methoxy ndant precursors. Ar represents an arylene group

hin films with a thickness less than 0.1 μm for optical ectroscopy were spin coated on glass plates. The sulting transparent precursor films on glass substrates ere converted to polyarylenevinylene (PAV) films by ating treatment at 150–250°C. Heat treatment was rformed under a nitrogen flow to prevent oxidation by r. Both free-standing PAV films with thickness of about μm and ultra-thin PAV films (~0.1 μm thick) on glass bstrates were thus obtained.

I.r. spectra and wide-angle X-ray diffraction experi- ents were conducted on 10 μm PAV films. U.v.-vis. sorption spectra were obtained using thin PAV films glass plates.

Measurements of electrical properties

The conductivities of undoped PAV films were measured by using the sandwich-type electrode arrangement in a vacuum of 10^{-3} Torr; gold electrodes were attached on both surfaces of films by vacuum deposition. Doping of iodine into PAV films was carried out by exposing them to iodine vapour (10^{-2} Torr) at room temperature. The conductivities of doped PAV films were measured by the four-probe method under vacuum.

Preparation of oriented films

Precursor polymer films were stretched under a nitrogen flow at temperatures between 30 and 150°C. The partial formation of the PAV structure by elimination of a methoxy group and orientation of polymer chains were caused simultaneously. To attain full conversion to the PAV structure, the stretched films were treated at 250°C for 4 h. The orientation of molecular chains in the stretched films was examined from the dichroic ratios of i.r. absorption bands and from X-ray diffraction photographs.

RESULTS AND DISCUSSION

Preparation and characterization of methoxy pendant precursors

The central idea of the synthesis of methoxy pendant precursors is the ratio of a sulphonium salt precursor, which is prepared by the conventional method, with methanol. However, one cannot give a universal preparative procedure applicable for any methoxy pendant precursors of PAV, because both the reactivity of sulphonium salt precursors with methanol and the rate of direct conversion to the PAV structure at room temperature are markedly dependent on chemical structure of sulphonium precursors.

The methoxy pendant precursors of PPV and MO-PPV were prepared by the following procedure. The monomer, 1,4-xylylenebis(dimethylsulphonium bromide) or 2,5-dimethoxy-1,4-xylylenebis(dimethylsulphonium bromide), was polymerized in water at 0–10°C using sodium hydroxide as a catalyst. To the solution, an excess amount of *p*-toluenesulphonic acid sodium salt was added, giving a precipitate of the sulphonium salt polymer with a *p*-toluenesulphonate counter-anion. The precipitate was filtered and dissolved in methanol and allowed to react with methanol at 20°C. After 50 h stirring, a powdery precipitate was obtained. The precipitate was filtered and vacuum dried.

In the case of the PTV precursor, the isolation of the sulphonium salt precursor using a *p*-toluenesulphonate counter-anion was unsuccessful. Thus the methoxy pendant precursor of PTV was obtained by the direct reaction with methanol in the as-polymerized sulphonium salt solution. 2,5-Thienylenebis(methylenedimethylsulphonium chloride) (0.1 M) was dissolved in a mixture of water and methanol (1:2), and an equimolar amount of tetramethylammonium hydroxide solution was added at −20°C under a nitrogen flow. After standing at −20°C with stirring for 6 h, a pale yellow solution resulted. The reaction was quenched with the addition of hydrochloric acid. By warming the solution up to 20°C, a yellow precipitate appeared. The precipitate, the methoxy precursor of PTV, was filtered and vacuum dried at room temperature.

The three precursor polymers obtained through the reaction with methanol were no longer soluble in water and completely soluble in chloroform, indicating the disappearance of sulphonium salt groups. The methoxy precursors of PPV and MO-PPV were soluble in chloroform, dichloromethane and tetrahydrofuran. In contrast, the solubility of the methoxy precursor of PTV was inferior to the other two precursors. This originated from the fact that the methoxy pendant group in the PTV precursor was partly replaced by a hydroxy group, as will be evidenced from the spectroscopic data shown later. All precursor polymers were purified by reprecipitation from chloroform solutions into diethyl ether.

The i.r. absorption spectra of the three precursor polymers are shown in *Figure 3*. All precursor polymers possessed strong absorptions at 1100 cm^{-1} assigned to C–O–C stretching. The absorption at 3500 cm^{-1} in the PTV precursor indicates the presence of the hydroxy group. From detailed inspection of the n.m.r. spectra of the three precursors, we ascertained that the prepared PPV and MO-PPV precursors were homopolymers with the repeat unit shown in *Figure 1*. However, the PTV precursor contained about 10% of pendant hydroxy groups:

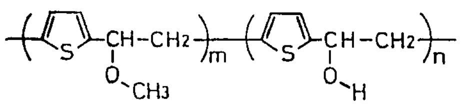


Table 1 shows the results of elemental analyses of the three precursors.

The displacement of hydroxy groups in place of methoxy groups in the preparation of the PTV precursor is due to the particular reaction condition; the reaction of the sulphonium salt precursor with methanol was performed in the presence of water, since the polymerization of PTV monomer was carried out in a water–methanol mixture.

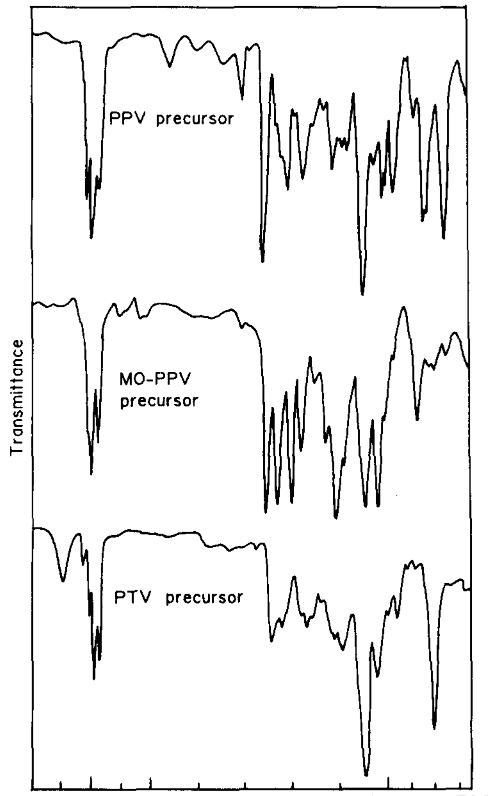


Figure 3 The i.r. spectra of methoxy pendant precursor polymers

Table 1 Elemental analyses of precursor polymers and polyarylenevinylenes

		Precursor		Polyarylenevinylene	
		H	C	H	C
PPV	Found	7.14	77.81	5.88	90.34
	Calcd	7.51	80.56	5.90	94.10
MO-PPV	Found	7.25	67.61	6.16	73.47
	Calcd	7.27	68.02	6.21	74.06
PTV	Found	5.60	59.41	3.71	66.52
	Calcd	5.62^{a}	59.57^{a}	3.73	66.63

^{a} Calculated for the copolymer structure units with 10% pendant hydroxy groups

Conversion to polyarylenevinylene films

The precursor polymer films were heated at 250°C for 5 h under a nitrogen flow. Conversion to the PAV structure was ascertained from the i.r. spectra of the treated films. However, full conversion to the PAV structure could not be attained; the i.r. spectra of the resulting films showed residual methoxy groups, and the visible absorption peaks, which reflect the average conjugation length, were located at wavelengths 20–50 nm shorter than those of PAV films prepared via the conventional sulphonium precursor route. Neither heat treatment at higher temperatures nor prolonged treatment were effective for the improvement of the extent of conversion. Rather, it brought about the formation of a carbonyl group.

We found that the use of acid catalysts brought about a drastic improvement in the elimination reaction. Perfect elimination of the methoxy group was realized when heat treatment was accomplished at 250°C in the presence of a small amount of hydrochloric acid. On the other hand, only a small extent of elimination was observed when thin films on glass plates were heated to 250°C under high vacuum of 10^{-6} Torr for 5 h. Therefore, one should assume that small amounts of impurities in the films, such as a small amount of sulphonium salt residue in the polymers, residual solvents and sorbed water, contributed to the acid-catalysed elimination of the methoxy groups, even in the cases when the elimination apparently proceeded in the films without catalyst.

Figure 4 shows the i.r. spectra of PPV, MO-PPV and PTV films prepared with heat treatment at 250°C in the presence of the acid catalyst. The C–O–C stretch band at 1100 cm^{-1} completely disappeared, and the *trans*-vinylene CH out-of-plane bending band at 940 cm^{-1} (PPV), 960 cm^{-1} (MO-PPV) and 930 cm^{-1} (PTV) and *trans*-vinylene C–H stretch at 3050 cm^{-1} (PPV), 3054 cm^{-1} (MO-PPV) and 3014 cm^{-1} (PTV) appeared. The i.r. spectra evidenced the perfect elimination of the methoxy groups and the production of PAVs. *Table 1* shows the results of elemental analyses of precursor polymers and converted PAVs.

Wide-angle X-ray diffraction measurements indicated that all the PAV films we obtained possessed low

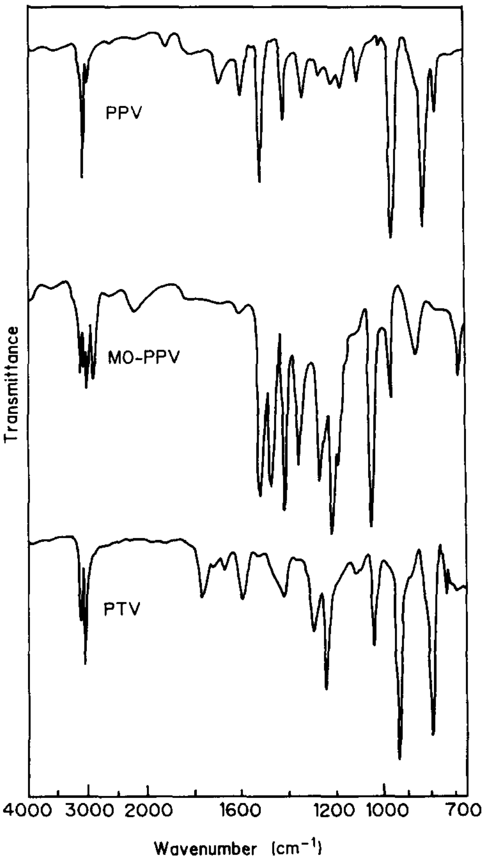


Figure 4 The i.r. spectra of polyarylenevinylenes

crystallinity. The densities of the PAV films measured with the flotation method were found to be 1.28, 1.25 and 1.33 g cm^{-3} for PPV, MO-PPV and PTV, respectively.

Optical properties of polyarylenevinylene films

The colours of the precursor films of PPV, MO-PPV and PTV were light green, light yellow and light yellow, respectively, and showed very weak absorptions in the visible region, indicating that the precursor polymers are very stable at room temperature. The absorption spectra varied drastically with the progress of conversion. The absorption spectra of the fully converted PPV, MO-PPV and PTV thin films are shown in *Figure 5*. The PAV films exhibited a large absorption band, which is associated with π–π^* transition. The shapes of the absorption peaks, which are assumed to reflect the distribution of the π-conjugation length, were delicately dependent on the elimination conditions, but the onsets of the absorptions, which give the optical band gaps, were independent of the condition of heat treatment. An attempt to regulate the distribution of π-conjugation length by means of refinement of the condition for the formation of PAV structures is in progress.

Electrical conductivity of undoped and doped films

As we reported before[12], the conductivities of undoped PAV films measured in air do not give the intrinsic values of PAVs due to the doping effect of oxygen in air. So the intrinsic conductivity of PAV films was obtained from measurements on films annealed at above 150°C under vacuum. The intrinsic conductivity of PPV, MO-PPV and PTV films at room temperature ranged between 10^{-16} and 10^{-14} S cm^{-1}.

The MO-PPV and PTV films could be easily doped by exposing the films to iodine vapour. The conductivities of fully converted MO-PPV and PTV films increased up to 10 and 100 S cm^{-1}, respectively, with iodine doping. The conductivities of iodine-doped films were stable even in air; preferential decreases of the conductivities were not observed after three months.

The conductivities of the doped PAV films were dependent on the extent of conversion to PAV structures. One expects that fully converted PAVs should give the highest conductivities. However, the maximum conductivities were achieved in partly converted films, which possessed a small amount of methoxy pendant residue, prepared under mild heat treatment conditions. The maximum conductivities were 50 and 240 S cm^{-1} in MO-PPV and PTV films, respectively. Both densities and crystallinities estimated from X-ray diffraction patterns increased with the increase of conversion temperature. Possibly, higher density and higher crystallinity of the films prepared at high temperatures prevented the effective diffusion of iodine across the films. Thus, one expects that improvement in doping technique will surely bring about an increase of the conductivity of fully converted PAV films.

Preparation of uniaxially oriented films

The preparation of oriented PTV films has been reported by Murase *et al.*[13]. Elongation of MO-PPV films, however, has not been successful. Our methoxy pendant precursor films are just suitable for the preparation of uniaxially oriented films, because they are dense and tough, and are quite stable at around room temperature. The precursor polymer films could be easily stretched to high stretch ratios during an ascending temperature process. More than five-fold stretch ratios were achieved. The wide-angle X-ray diffraction photographs showed several sharp equatorial reflections and a few first layer line reflections. The polarized i.r. absorption spectra also evidenced the orientation of the MO-PPV and PTV chains. By assuming that the transition moments of the 960 cm^{-1} (MO-PPV) and 930 cm^{-1} (PTV) absorptions are parallel to the chain direction, the dichroic ratios were calculated to be 5.2 in

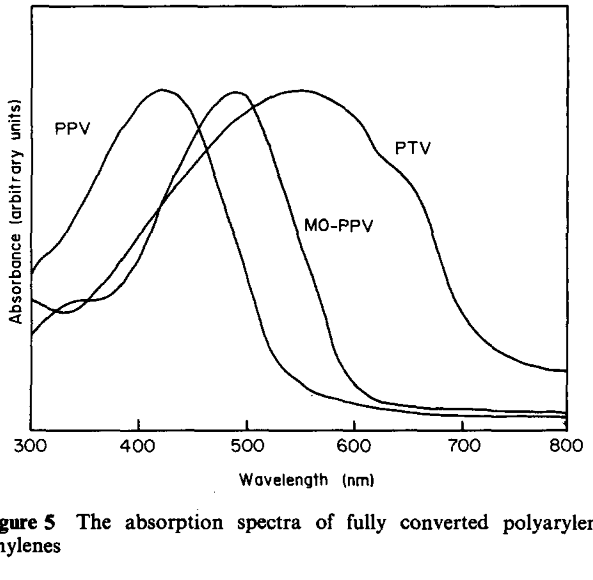


Figure 5 The absorption spectra of fully converted polyarylenevinylenes

the stretched MO-PPV film and 3.0 in the stretched PTV film.

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