Synthesis and electrical conductivity of poly(1,4-phenylenevinylene-*co*-2-n-butoxy-5-methoxy-1,4-phenylenevinylene)s and poly(1,4-phenylenevinylene-*co*-2-n-dodecyloxy-5-methoxy-1,4-phenylenevinylene)s

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A series of copolymers containing 1,4-phenylenevinylene (PV) and either 2-n-butoxy-5-methoxy-1,4-phenylenevinylene (BMPV) or 2-n-dodecyloxy-5-methoxy-1,4-phenylenevinylene (DDMPV) units were prepared in the form of thin films from their water-soluble sulfonium-salt precursor polymers. The electrical conductivity of the I_2- and $FeCl_3$-doped copolymers exhibits a steep initial increase with an increase in the content of the BMPV or DDMPV units, followed by a slower increase to finally reach the values of that of the corresponding homopolymers, PBMPV and PDDMPV, respectively. The conductivities of the I_2- and $FeCl_3$-doped, drawn BMPV copolymer films ranged from 35 to 266 S cm^{-1}, and from 10^{-1} to 256 S cm^{-1}, respectively, depending on the composition. PDDMPV films could be uniaxially drawn at 150–160°C to a draw ratio of 5, and gave an electrical conductivity value of 27 S cm^{-1} when doped with I_2, whereas I_2-doped PDDMPV films, obtained from the precursor polymer that itself had been pre-drawn to the draw ratio of 5, exhibited a conductivity of 46 S cm^{-1}. PDDMPV was found to be soluble in *p*-xylene, but PBMPV was insoluble in this solvent. The presence of the long dodecyloxy group enables the precursor polymer of PDDMPV to form an ordered structure. The u.v.–vis. spectra of the dialkoxy substituted homopolymers and their corresponding copolymers were red-shifted relative to the parent PPV, suggesting a decreased bandgap, which was consistent with the electron-donating nature of the alkoxy substituents. In general, the electrical conductivities of the DDMPV copolymers were lower than those of the BMPV copolymers, which can be ascribed to the presence of longer insulating alkoxy groups in the former.

(Keywords: phenylenevinylene copolymers; electrical conductivity; ordered structure)

INTRODUCTION

High-molecular-weight poly(1,4-phenylenevinylene) (PPV), and its derivatives can be prepared in the form of films from their water-soluble polyelectrolyte precursors[1–7]. The PPV derivatives are proving to be not only very important as electrically conducting materials, after treatment with various dopants such as I_2, $FeCl_3$, AsF_5, etc.[8–11], but are also attracting a great deal of interest as potential non-linear optical materials[12,13]. Recent reports on the photo (Ph) and electroluminescence (EL) properties of PPV and its derivatives give a strong indication of the potential development of these materials for diode device applications[14–16]. Substitution with different types of electron-donating or electron-withdrawing groups on the phenylene ring of PPV has significant electronic, steric and morphological influences on the resulting polymer. For example, poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMPV), can be doped with iodine to give a material with an electrical conductivity of 10–10^2 S cm^{-1}, while PPV, in contrast, is hardly doped at all by treatment with the same dopant[3,17].

In the preparation of these polymer films, water-soluble sulfonium-salt precursor polymers are first produced, which are then usually cast into films. They are then subjected to thermal elimination to give the final polyconjugated polymers. Alternatively, one can transform the water-soluble precursor material into an organic solvent soluble species prior to the final elimination step[18,19]. The precursor film can be uniaxially drawn, either before or during the thermal elimination reaction, as required. Such oriented films show a significantly greater conductivity along the draw direction on doping and reveal an anisotropy in the conductivity[3]. The drawability of the precursor polymer films, however, appears to depend on the structure of the

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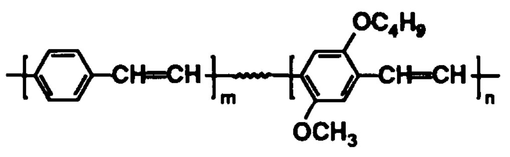
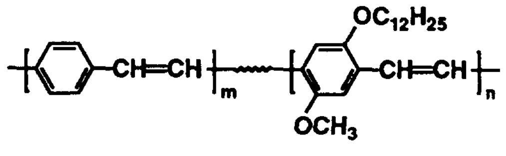
polymers themselves. In contrast to PPV, the precursor polymer of PDMPV can be drawn hardly at all, either during or prior to the elimination process[8,9,17]. We[10] have found, however, that the precursor polymer of poly(2-n-butoxy-5-methoxy-1,4-phenylenevinylene) (PBMPV) can be uniaxially drawn at approximately 110–130°C up to a draw ratio of 4.

Recently, we reported the synthesis and electrical conductivities of a number of series of PPV copolymers containing comonomer units having electron-donating as well as electron-attracting groups. In our work, we have studied the effects of methoxy[20], methylthio[6], methyl[11], nitro[21], methoxy[22], and bromo[22] substituent groups. Lahti and co-workers[23] recently reported the synthesis and characterization of halogenated PPVs. One of the common features of these copolymers is the surprising fact that copolymerization enhances the doping ability of oxidants such as I_2 and $FeCl_3$, and thus leads to an increase in electrical conductivity, regardless of whether the substituent is electron-donating or electron-withdrawing[24]. In particular, the inclusion of relatively small amounts (1–10 mol%) of comonomer units in PPV increases the electrical conductivity to a remarkable extent.

In this investigation, we have prepared two series of new PPV copolymers which contain either 2-n-butoxy-5-methoxy-1,4-phenylenevinylene (BMPV) or 2-n-dodecyloxy-5-methoxy-1,4-phenylenevinylene (DDMPV) units, and have studied their electrical properties. These copolymers have the following structures:



Poly(PV-co-BMPV)



Poly(PV-co-DDMPV)

EXPERIMENTAL

Synthesis of 2-n-butoxy-5-methoxy-1,4-phenylenedimethylene bis(tetramethylenesulfonium chloride) (3)

1-n-Butoxy-4-methoxybenzene (**1**) was prepared by reacting *p*-methoxyphenol with n-butyl bromide at 60°C in methanol which contained potassium hydroxide[25]. 1-n-Butoxy-4-methoxybenzene (18.0 g, 0.10 mol), as prepared, was dissolved in 50 ml of dioxane, and this solution was then mixed with 70 ml of conc. HCl and 50 ml of formalin (37 wt%). The mixture was stirred for 4 h at 70°C while a stream of HCl gas was passed through it. The precipitate that was formed was thoroughly washed with water[26]. Pure 1,4-bis(chloromethyl)-2-n-butoxy-5-methoxybenzene (**2**) was obtained by recrystallizing the crude product from a mixture of ethanol/acetone (=2/1 (v/v)); m.p. = 82°C, yield = 14.4 g (52%). The ^1H n.m.r. (300 MHz, $CDCl_3$, TMS) spectrum showed peaks at $\delta = 6.9$ (d, –CH=, 2H), 4.6 (d, –CH_2Cl, 4H), 4.0 (t, OCH_2, 2H), 3.8 (s, OCH_3, 3H), 1.7–1.8 (m, CH_2, 2H), 1.5–1.6 (m, CH_2, 2H) and 1.0 (t, OCH_3, 3H) ppm. The i.r. (KBr) spectrum showed peaks at 1512 (arom. C=C str.), 1033 (Ar–O–C str.), and 688 (C–Cl str.) cm^{-1}. Elemental analysis: calculated for $C_{13}H_{18}Cl_2O_2$ (277.2): C 56.32, H 6.50, Cl 25.77%; found: C 55.94, H 6.43, Cl 25.63%.

Compound **2** (16.6 g, 0.060 mol) and excess tetrahydrothiophene were reacted for 21 h at 50°C in methanol. The solution was concentrated by distilling off four-fifths of the methanol, and the remaining tetrahydrothiophene, by using a rotary evaporator. The residue was then poured into acetone and the resulting precipitate was thoroughly washed with acetone and dried. The yield of 2-n-butoxy-5-methoxy-1,4-phenylenedimethylene bis (tetramethylenesulfonium chloride) (**3**) was 21.5 g (79%). The ^1H n.m.r. (300 MHz, D_2O, TMS) spectrum showed peaks at $\delta = 7.3$ (s, –CH=, 2H), 4.6 (d, CH_2Cl, 4H), 4.2 (t, OCH_2, 2H), 4.0 (s, OCH_3, 3H), 3.6–3.5 (m, $-^+SCH_2$, 8H), 2.4–2.3 (m, CH_2, 8H), 1.9–1.8 (m, CH_2, 2H), 1.6–1.5 (m, CH_2, 2H) and 1.0 (t, CH_3, 3H) ppm. The i.r. (KBr) spectrum showed peaks at 3600–3100 (OH str.), 1511 (arom. C=C str.), 1041 (Ar–O–C str.), and 704 (C–Cl str.) cm^{-1}.

Synthesis of 1,4-phenylenedimethylene bis(tetramethylenesulfonium chloride) (4)

An identical procedure was used to obtain compound **4** from 1,4-bis(chloromethyl)benzene and tetrahydrothiophene. Synthesis of this compound has been reported earlier by others[27].

Synthesis of 2-n-dodecyloxy-5-methoxy-1,4-phenylenedimethylene bis(tetramethylenesulfonium chloride) (7)

1-n-Dodecyloxy-4-methoxybenzene (**5**) was prepared from 4-methoxyphenol and n-dodecyl bromide via the same procedure used for the synthesis of compound **1**; m.p. = 57°C, yield = 88%. The ^1H n.m.r. (80 MHz, $CDCl_3$, TMS) spectrum showed peaks at $\delta = 6.8$ (s, –CH=, 4H), 3.8–4.0 (t, OCH_2, 2H), 3.8 (s, OCH_3, 3H), 1.4–1.7 (m, CH_2, 4H), 1.3 (s, CH_2, 16H) and 0.8–0.9 (t, CH_3, 3H) ppm. The i.r. (KBr) spectrum showed peaks at 1513 (arom. C=C str.), 1031 (Ar–O–C str.), and 721 (CH_2 wagging) cm^{-1}. Elemental analysis: calculated for $C_{19}H_{32}O_2$ (292.5): C 78.08, H 10.96%; found: C 77.69, H 11.07%.

Compound **5** (20 g, 0.07 mol), as prepared, was dissolved in 100 ml of dioxane. This solution was mixed with 8 ml of formalin (37 wt%), and the mixture was stirred for 10 h at 80°C while HCl gas was bubbled through it. At the end of the reaction, 150 ml of water were added to the reaction mixture to precipitate the product, **6**. The crude product was recrystallized from chloroform; m.p. = 77°C, yield = 8.2 g (31%). The ^1H n.m.r. (300 MHz, $CDCl_3$, TMS) spectrum showed peaks at $\delta = 6.9$ (d, –CH=, 2H), 4.6 (d, CH_2Cl, 4H), 4.0 (t, OCH_2, 2H), 3.8 (s, OCH_3, 3H), 1.8 (m, CH_2, 2H), 1.4–1.5 (m, CH_2, 2H), 1.3 (s, CH_2, 16H) and 0.8–0.9 (t, CH_3, 3H) ppm. The i.r. (KBr) spectrum showed peaks at 1513 (arom. C=C str.), 1031 (Ar–O–C str.), and 688 (C–Cl str.) cm^{-1}. Elemental analysis: calculated for $C_{21}H_{34}Cl_2O_2$ (389.4): C 64.78, H 8.74, Cl 18.25%; found: C 64.31, H 8.90, Cl 18.24%.

The sulfonium salt monomer **7** was obtained by the same procedure as described for the synthesis of compound **3**; yield = 80%. The ^1H n.m.r. (300 MHz, D_2O, TMS) spectrum showed peaks at $\delta = 7.3$ (s, –CH=, 1H), 7.2 (s, -CH=, 1H), 4.5 (d, CH_2Cl, 4H), 4.0 (t, OCH_2, 2H), 3.8 (s, OCH_3, 3H), 3.6–3.4 (m, $^{+}SCH_2$, 8H), 2.3–2.2 (m, CH_2, 8H), 1.7 (m, CH_2, 2H), 1.3 (m, CH_2, 18H), and 0.9 (t, CH_3, 3H) ppm. The i.r. (KBr) spectrum showed peaks at 3600–3200 (OH), 1515 (arom. C=C str.), 1033 (Ar–O–C str.), and 691 (C–Cl str.) cm^{-1}.

Polymerization

The synthetic methods that were used in this work for the production of both the homopolymers and the copolymers were the same as reported previously, both by us[5,6,11,20–22], and by other groups[3,4,8,9]. A solution of the sulfonium salt monomer (0.4 M) in NaOH solution (0.8 M) was polymerized under a nitrogen atmosphere at 0°C. A homogeneous viscous precursor polymer solution was obtained. In the case of the copolymers, the total number of moles of the respective monomers was kept constant, but the mole ratio was varied. The polyelectrolyte precursor polymers were dialysed against deionized water for 3 d using a dialysis tube (Sigma) with a molecular-weight cut-off at 12000. The precursor polymer films, cast from aqueous solution, were subjected to thermal elimination *in vacuo* (1.33 Pa). The PBMPV precursor film was held *in vacuo* at 50°C for 9 h, at 150°C for 3 h, at 180°C for 7 h, and finally at 200°C for 1 h, to effect transformation into the final polyconjugated polymer film. Poly(PV-*co*-BMPV)s were obtained by a thermal elimination process involving the respective precursors under the same conditions. In addition, however, they were subjected to an additional treatment *in vacuo* (1.33 Pa), i.e. at 230°C for 10 min. The precursors of PDDMPV and poly(PV-*co*-DDMPV)s were kept *in vacuo* at 35°C for 8 h, at 150°C for 3 h, at 180°C for 7 h, and finally at 200°C for 1 h. However, the poly(PV-*co*-DDMPV)s had an additional treatment, i.e. at 230°C for 10 min. If required, the precursor polymer films were uniaxially drawn at 80–120°C by using a zone-heating apparatus.

Analytical methods

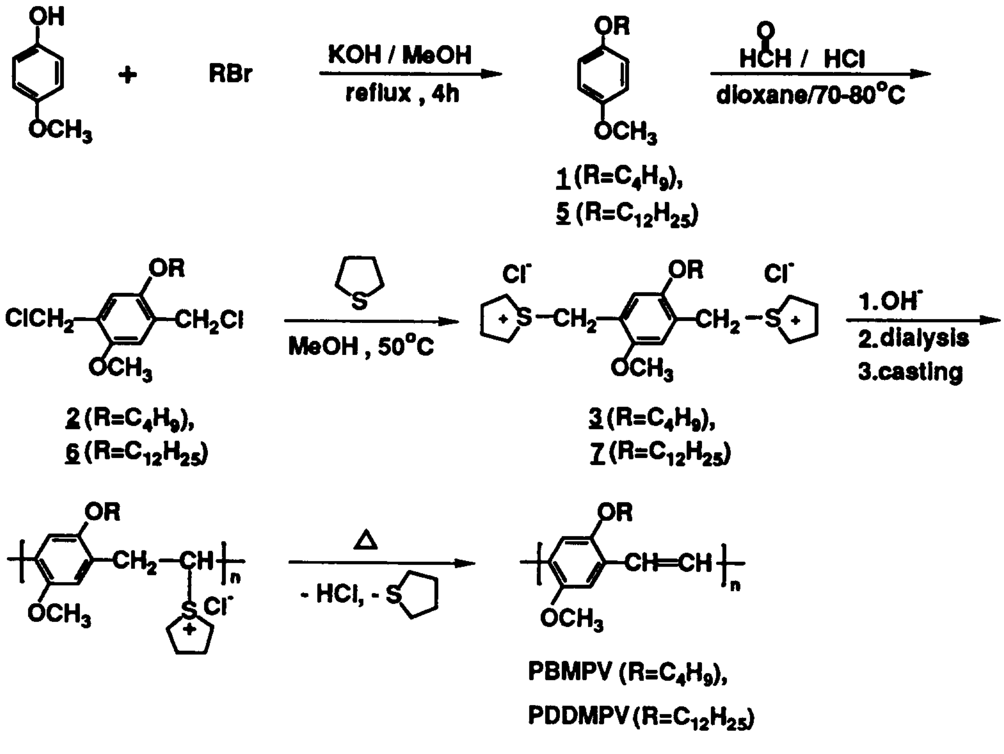
^1H n.m.r. spectra were recorded on Brucker AM300 and Bruker SW80SY spectrometers. I.r. spectra were obtained on a Mattson Alpha Centauri *FT*i.r. instrument, while u.v.–vis. spectra were obtained on a Hewlett–Packard 8452A spectrometer. Thermogravimetric analyses (t.g.a.) were performed with a Mettler 3000 thermogravimetric analyser, while differential scanning calorimetry (d.s.c.) thermograms were recorded on a Du Pont DSC-910 instrument. Small-angle X-ray scattering diffractograms were obtained by Professor H. Chen and Dr H. Hong, at the University of Illinois, on a Rigaku RU300 instrument. The CuKα radiation was selected by a graphite monochromator and narrowed by a slit, with each data point being taken for 60 s.

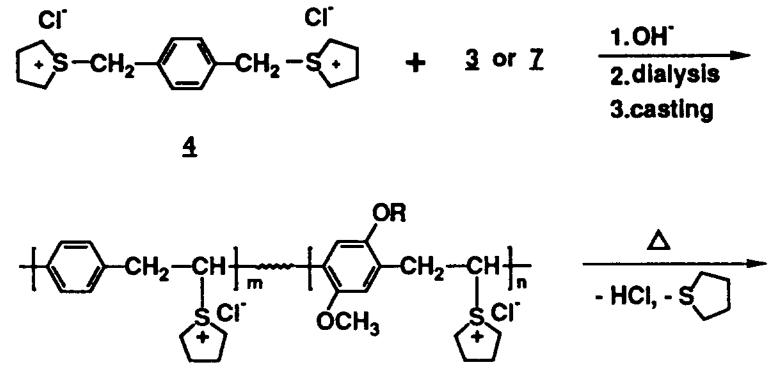
The solution viscosities of the dialysed precursor polymers were determined at 25°C, for 0.2 g dl^{-1} solutions in water which contained Na_2SO_4 (0.05 M). The addition of Na_2SO_4 was necessary in order to avoid possible complications arising from the extended-chain conformations that occur in dilute solutions of polyelectrolyte polymers[3]. Elemental analyses were performed by the Analytical Department of the Korea Research Institute of Chemical Technology. Conductivity measurements were carried out by using a four-in-line-probe method with graphite (Electrodag) as the contact material. For uniaxially drawn films, electrical conductivity was measured along the stretching direction.

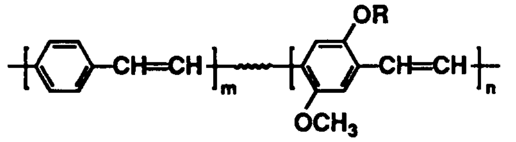
RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic schemes for the preparation of PBMPV, poly(PV-*co*-BMPV), PDDMPV and poly(PV-*co*-DDMPV) are shown below:







Poly(PV-co-BMPV) (R=C_4H_9),
Poly(PV-co-DDMPV) (R=$C_{12}H_{25}$)

All of the polyelectrolyte, sulfonium precursor polymers were water soluble, and dialysed in a dialysis tube with a molecular-weight cut-off at 12000. *Tables 1* and *2* summarize the data obtained for the conversion of the monomers to the precursor polymers, plus polymer yields, viscosities and polymer compositions as calculated from the results of elemental analyses. The degree of monomer conversion to precursor polymer from 50 to approximately 75% was determined by titration of the unreacted hydroxide ions in the final polymerization mixture with standard 1.0 M HCl solution[3]. Polymer yields were estimated gravimetrically from the final weights of the thermally treated films. Values for the degree of monomer conversion and polymer yields are comparable to, or slightly lower than those reported previously[3,6,11].

Solution viscosities of the precursor copolymers having higher contents of BMPV units could not be determined because the addition of a salt such as Na_2SO_4 caused precipitation of the polymer. However, high solution viscosities (3.0–3.8 dl g^{-1}) were obtained in the case of the copolymers having the lower contents of BMPV units (see *Table 1*). This suggests that the molecular weights of the present polymers are high. All of the precursor polymer films which had been cast from aqueous solution after dialysis appeared homogeneous and transparent, and could be oriented uniaxially by drawing before the final elimination process. Poly(2-n-dodecyloxy-5-methoxy-1,4-phenylenevinylene) (PDDMPV), however, was unique in that it could be stretched uniaxially at 150–160°C, even after it had been formed through thermal elimination of the precursor polymer. In addition, it could be hot-pressed into a thin film at 150–200°C, under a pressure of 2.0×10^6 Pa. Interestingly enough, PDDMPV was found to be soluble in *p*-xylene, and a uniform film can be cast from this solution. Certainly the presence of the long dodecyloxy group results in an improvement in solubility.

As shown in *Tables 1* and *2*, the content of the BMPV and DDMPV units incorporated into the copolymers is significantly higher than that in the monomer salt mixtures, suggesting that BMPV monomer **3** and DDMPV monomer **7** are more reactive than PV monomer **4**.

Characterization of precursor and final polyconjugated polymers

The elimination reactions of the precursor polymers were studied by t.g.a. and d.s.c. using a heating rate of 10°C min^{-1} in both cases. Representative t.g.a. and d.s.c. thermograms for both series are given in *Figures 1* and *2*. A major weight loss occurred from approximately 80°C onwards according to the t.g.a. thermograms. The d.s.c. thermograms, however, exhibit two major endothermic processes over the temperature ranges 80–130 and 150–210°C. The low-temperature endotherm corresponds to loss of water, which is absorbed in the precursor polymer film, and the higher-temperature one to the elimination of tetrahydrothiophene and HCl. The weight losses above 400°C are attributable to decomposition of the polymers[28].

The d.s.c. thermogram of the precursor polymer of PDDMPV (see *Figure 2b*) is peculiar in that it shows a distinct exothermic process at ~100–140°C that is not observed in the copolymers. Moreover, this exothermic peak appears only in the first heating cycle, and not in further heating cycles; the middle curve in *Figure 2b* is the thermogram that was obtained (on a 2nd heating cycle) for a sample that had been previously heated to 142°C and then cooled to room temperature. Therefore, we believe that the exotherm centred at 126°C corresponds to an ordering process of the long dodecyloxy groups.

Figure 3 compares the small-angle X-ray scattering (SAXS) diffractograms of PDDMPV precursor polymers having different thermal and mechanical histories. All of the diffractograms exhibit a small-angle diffraction peak at $2\theta \sim 4°$, which corresponds to a spacing of about 22 Å. This spacing coincides with the molecular 'breadth' (22 Å) of the 2-n-dodecyloxy-5-methoxybenzene structure in the precursor polymer of PDDMPV, when all of the CH_2 groups in the alkoxy substituents are assumed to have a *trans* conformation. This suggests that molecular ordering into a layered structure is induced thermally as well as by mechanical means, i.e. stretching. The peak intensity at this diffraction angle decreases in the following order: sample heated to 142°C and cooled > sample drawn at 80°C > sample obtained at room temperature. However, a significant destruction of this layered structure appears to take place during the thermal elimination reactions of the precursor polymers at 200°C, as shown by the SAXS diffractograms of the final polymer films (see *Figure 4*). According to the diffractograms shown in this figure, even the uniaxially

Table 1 Synthetic results obtained for the BMPV series of copolymers

Copolymer[a]	Feed mole ratio of 4:3	Actual mole ratio of PV:BMPV	Monomer conversion (mol%)	Polymer yield[b] (wt%)	η_{inh} (dl g^{-1})
11-Poly(PV-*co*-BMPV)	98.0:2.0	89.1:10.9	50	20	3.01
21-Poly(PV-*co*-BMPV)	95.0:5.0	79.1:20.9	50	19	2.96
49-Poly(PV-*co*-BMPV)	90.0:10.0	51.4:48.6	51	23	3.83
76-Poly(PV-*co*-BMPV)	80.0:20.0	24.2:75.8	65	27	–
92-Poly(PV-*co*-BMPV)	50.0:50.0	8.1:91.9	69	30	–

[a] The numbers 11, 21, etc. indicate the content of BMPV units in the final copolymer as determined by elemental analysis

[b] Figures represent the values obtained after dialysis of the precursor polymer followed by thermal elimination

Table 2 Synthetic results obtained for the DDMPV series of copolymers

Copolymer[a]	Feed mole ratio of 4:7	Actual mole ratio of PV:DDMPV	Monomer conversion (mol%)	Polymer yield[b] (wt%)	η_{inh} (dl g^{-1})
7-Poly(PV-*co*-DDMPV)	98.0:2.0	93.2:6.8	51	16	2.29
17-Poly(PV-*co*-DDMPV)	95.0:5.0	83.0:17.0	51	20	2.73
37-Poly(PV-*co*-DDMPV)	90.0:10.0	63.1:36.9	53	19	2.37
66-Poly(PV-*co*-DDMPV)	80.0:20.0	33.8:66.2	59	24	3.01
PDDMPV	0:100	0:100	75	33	–

[a] The numbers 7, 17, etc. indicate the content of DDMPV units in the final copolymer as determined by elemental analysis

[b] Figures represent the values obtained after dialysis of the precursor polymer followed by thermal elimination

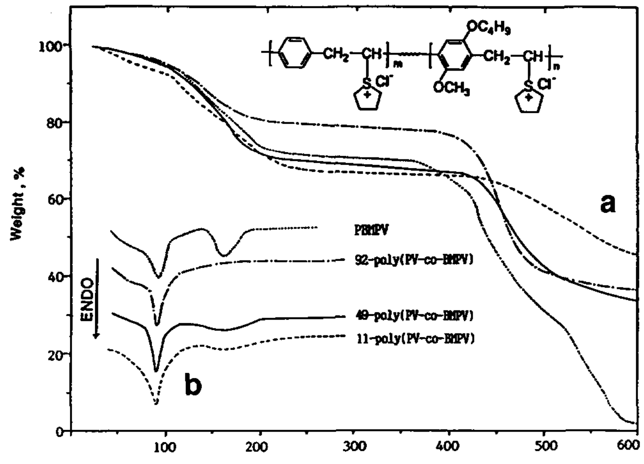


Figure 1 T.g.a. (a) and d.s.c. (b) thermograms for the precursor polymers of PBMPV and *n*-poly(PV-*co*-BMPV)s: (···) PBMPV; (–·–·–) 92-poly(PV-*co*-BMPV); (——) 49-poly(PV-*co*-BMPV) and (– – –) 11-poly(PV-*co*-BMPV). *n* indicates the number of BMPV units in the final copolymer as determined by elemental analysis

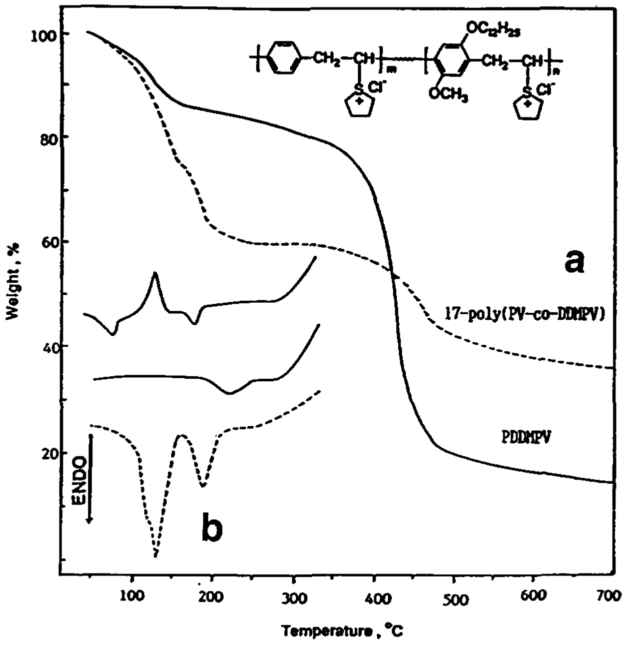


Figure 2 T.g.a. (a) and d.s.c. (b) thermograms for the precursor polymers of PDDMPV and 17-poly(PV-*co*-DDMPV): (——) PDDMPV and (– – –) 17-poly(PV-*co*-DDMPV). D.s.c. thermograms of PDDMPV: upper curve, 1st heating cycle and lower curve, 2nd heating cycle, obtained for a sample previously heated to 142°C and then cooled to room temperature

stretched film exhibits only a very weak and broad diffraction peak, which is centred at approximately $2\theta = 4.2°$ ($d = 21$ Å). This destruction of an ordered structure must be due to changes in the chemical structure of the main chain, together with thermal disordering of the layered morphology, experienced by the precursor polymer during its final elimination to the final polymer, which takes place at 200°C over a prolonged period of time. Although wide angle X-ray diffractograms of the same samples are not shown, the precursor polymer of PDDMPV, which was obtained at room temperature by casting from an aqueous solution under reduced pressure, exhibited only one, very broad diffraction peak centred at approximately $2\theta = 21.5°$ ($d = 4.1$ Å), corresponding to an interchain distance. However, both stretched and annealed films showed an additional, relatively sharp peak at $2\theta = 9.26°$ ($d = 9.6$ Å), which may relate to a second-order diffraction resulting from the layer structure alluded to above, or be due to an as-yet unidentified regular structure occurring in the polymers.

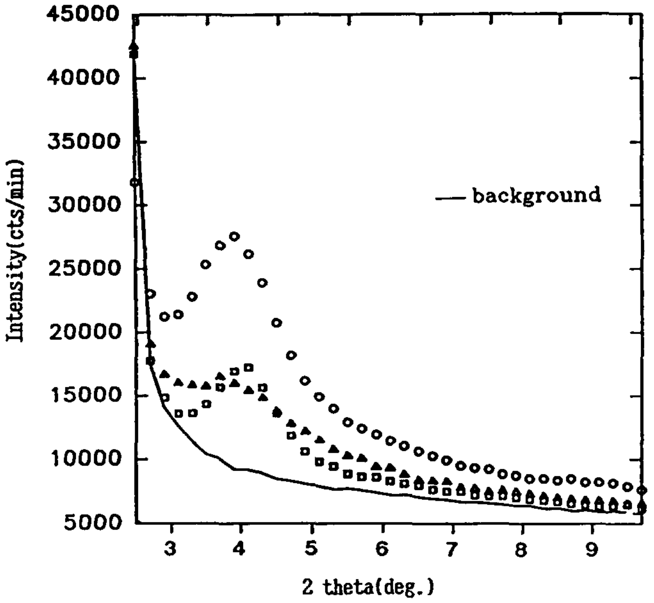


Figure 3 SAXS diffractograms of PDDMPV precursor polymers: (○) sample heated to 142°C (heating rate = 10°C min^{-1}) and then cooled to room temperature; (□) sample stretched ($L/L_0 = 10$) at 80°C followed by cooling to room temperature and (▲) sample unstretched, at room temperature

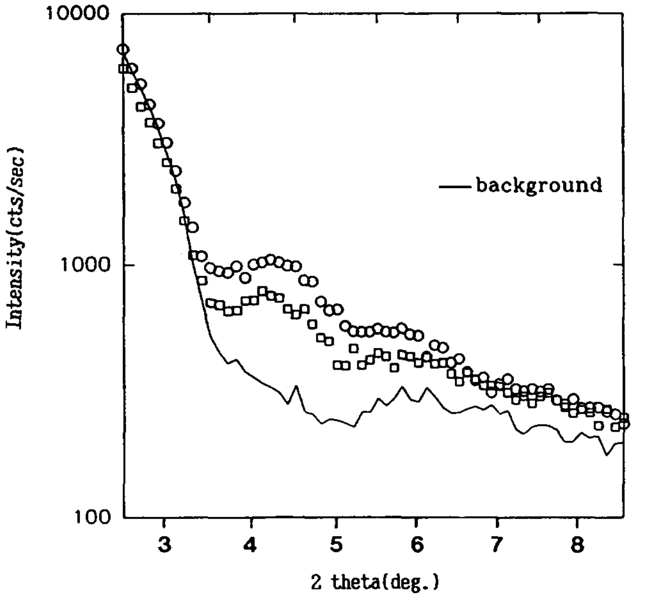


Figure 4 SAXS diffractograms of final PDDMPV films obtained from: (○) a stretched ($L/L_0 = 10$) precursor polymer and (□) from an unstretched precursor polymer. Both films were obtained by thermal elimination of the precursor polymer by treatment at 35°C for 8 h, at 150°C for 3 h, at 180°C for 7 h, and finally at 200°C for 1 h

The unstretched and eliminated final PDDMPV film, however, did not show the same peak, whereas the stretched PDDMPV film showed a much weaker, but nevertheless definite, diffraction peak at the same position. It should be noted that none of the copolymers revealed any similar structural ordering; this can be ascribed to the structural irregularity along the chain and the irregular distances between the adjacent alkoxy substituents.

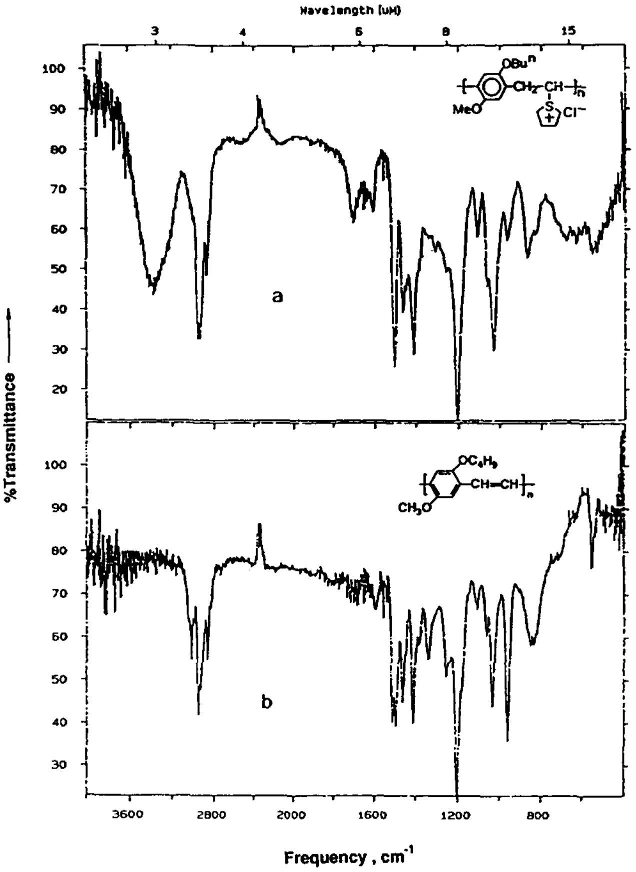


Figure 5 *FT*i.r. spectra of: (a) the precursor polymer of PBMPV and (b) the final PBMPV film

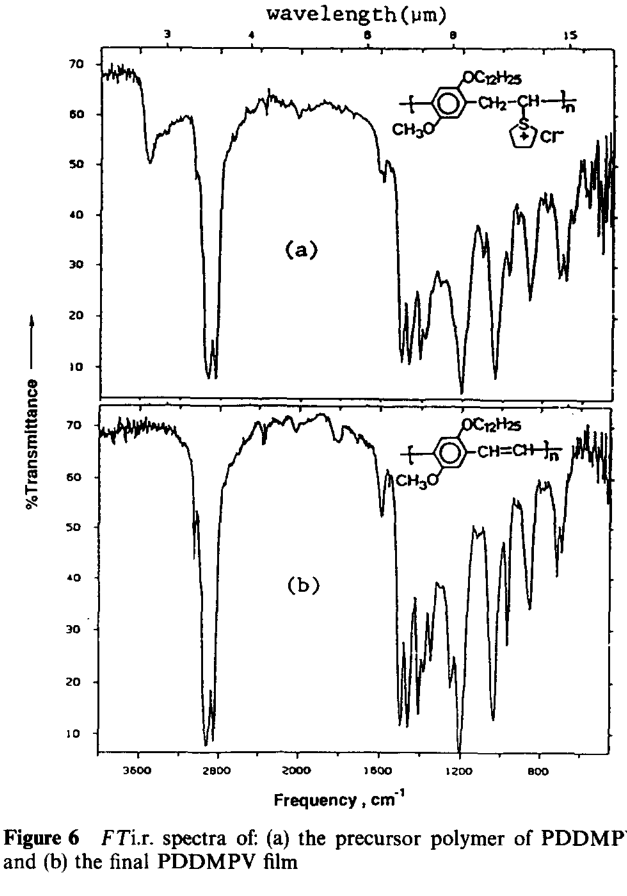


Figure 6 *FT*i.r. spectra of: (a) the precursor polymer of PDDMPV and (b) the final PDDMPV film

The *FT*i.r. spectra of the final PBMPV and PDDMPV films, compared with those of the precursor polymer films, are shown in *Figures 5* and *6*, respectively. The precursor polymers exhibit a broad absorption at 3100–3600 cm^{-1}, due to absorbed water, which disappears in the spectra of the eliminated films. A strong absorption peak appears at 968 cm^{-1}, after elimination, indicating that the vinylene C=C bonds that are formed are of a *trans* configuration[3,29]. The spectra of the precursor polymers also show a small absorption peak, appearing as a shoulder, at the same position. This results from a premature elimination reaction which occurs during film casting. The copolymers show all of the corresponding absorption peaks of the homopolymers, although their spectra are not given in this present paper.

Figures 7 and *8* show the u.v.–vis. spectra of thin films of fully eliminated PBMPV, PDDMPV and some of their copolymers. The maxima of the longest wavelength absorption for π–π transitions and the edges of these absorptions, estimated from the intersects between the base lines and the peaks are 426/519, 490/600 and 447/582 nm, for PPV, PBMPV and PDDMPV, respectively. The maximum absorption positions of PBMPV and PDDMPV are shifted to the longer-wavelength region when compared with that of PPV. In general, the λ_{max} position of the copolymers increases with an increasing content of BMPV or PPDMPV units in the chain. The bathochromic shift brought about by the two alkoxy groups on the phenylene rings is significant, and can be explained by the electronic effects of the electron-donating substituents[30].

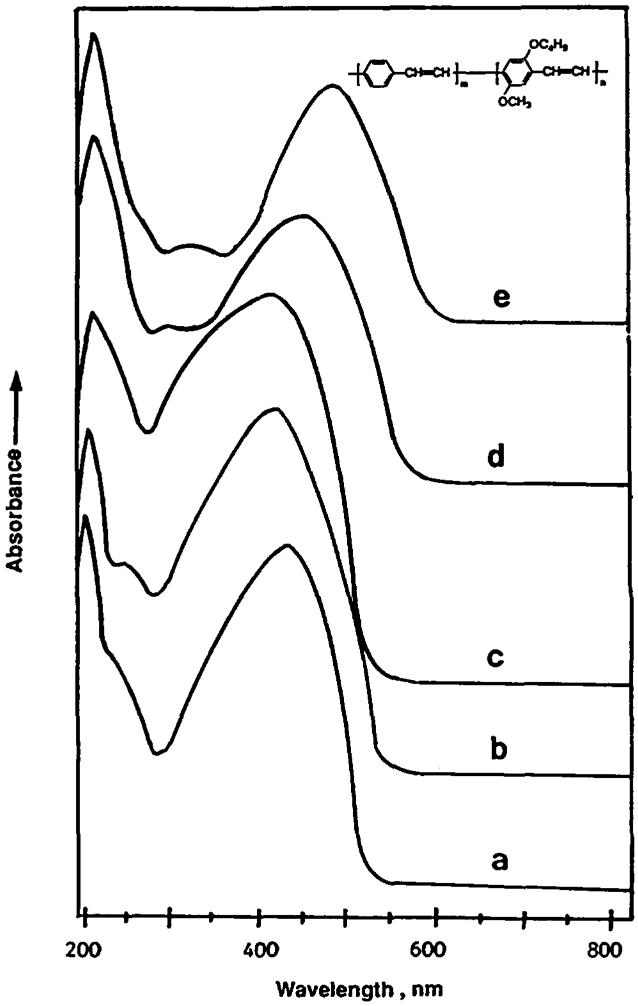


Figure 7 U.v.–vis. spectra of: (a) PPV; (b) 11-poly(PV-*co*-BMPV); (c) 49-poly(PV-*co*-BMPV); (d) 92-poly(PV-*co*-BMPV) and (e) PBMPV. The numbers 11, 49 and 92 indicate the content of BMPV units in the final copolymer as determined by elemental analysis

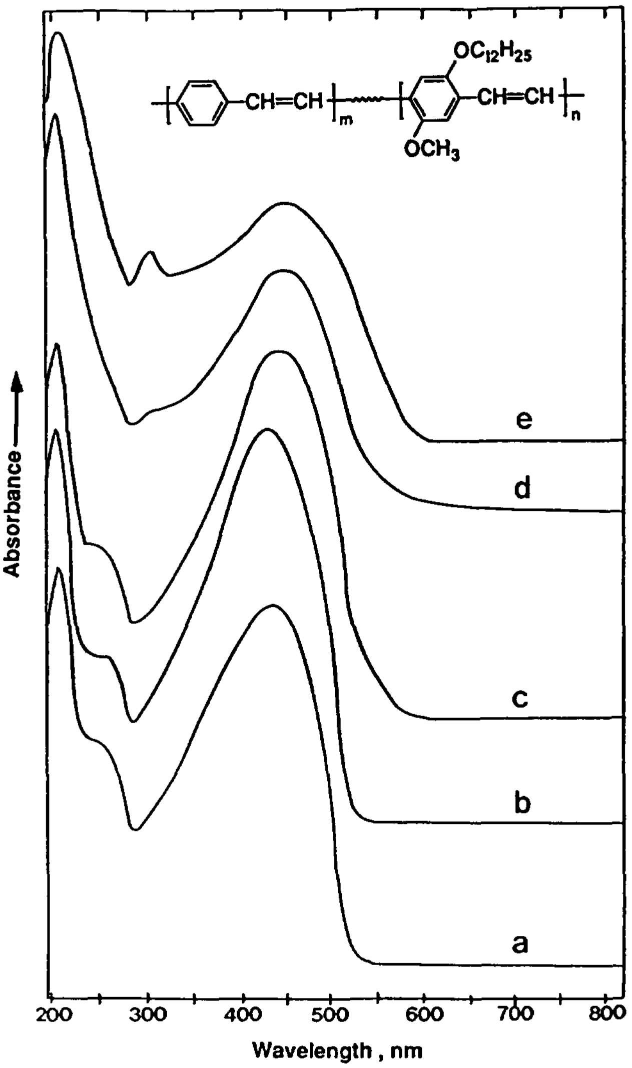


Figure 8 U.v.-vis. spectra of: (a) PPV; (b) 7-poly(PV-*co*-DDMPV); (c) 37-poly(PV-*co*-DDMPV); (d) 66-poly(PV-*co*-DDMPV) and (e) PDDMPV. The numbers 7, 37, and 66 indicate the content of DDMPV units in the final copolymer as determined by elemental analysis

Electrical conductivity

The electrical conductivities of the polymers and copolymers were measured using a standard four-in-line-probe technique. The maximum conductivity values for both oriented and unoriented polymers, plus the degrees of doping are given in *Tables 3–5*. Films of poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMPV), are known to be easily doped with I_2 or $FeCl_3$, giving materials with electrical conductivities as high as 10^2 S cm^{-1} (refs 8, 9, 17 and 28). PDMPV films, however, cannot easily be obtained in a uniaxially oriented form because the precursor polymer films are not readily stretched. Uniaxial orientation is known to significantly improve the electrical conductivity along the stretching direction[5,17,31]. In contrast, PBMPV and its copolymer films could be easily stretched up to a draw ratio of 4 (ref. 10). A slight structural modification of PDMPV, to produce an unsymmetrical structure with longer alkoxy groups on the phenylene rings, facilitates the stretching of the precursor polymer films prior to the final thermal elimination reaction[6,10,32].

Table 3 Maximum electrical conductivities of I_2- and $FeCl_3$-doped PBMPV and PBMPV copolymers

		Conductivity ($S\,cm^{-1}$)		Degree of doping[b,c]	
Copolymer[a]	Dopant	Undrawn film	Drawn film, 4 L_0	I_3^-/RU	$FeCl_4^-$/RU
11-Poly(PV-*co*-BMPV)	I_2	5×10^{-1}	35	0.03(0.05)	
	$FeCl_3$	9×10^{-3}	1×10^{-1}		0.02(0.02)
21-Poly(PV-*co*-BMPV)	I_2	6	88	0.09(0.08)	
	$FeCl_3$	7×10^{-2}	2		0.06(0.05)
49-Poly(PV-*co*-BMPV)	I_2	4	44	0.20(0.19)	
	$FeCl_3$	8×10^{-2}	3		0.14(0.17)
76-Poly(PV-*co*-BMPV)	I_2	12	131	0.35(0.37)	
	$FeCl_3$	6	73		0.24(0.24)
92-Poly(PV-*co*-BMPV)	I_2	25	266	0.43(0.49)	
	$FeCl_3$	27	256		0.28(0.29)
PBMPV[d]	I_2	100	590	0.57(0.78)	
	$FeCl_3$	240	2160		0.44(0.47)

[a] The numbers 11, 21, etc. indicate the content of BMPV units in the final copolymer as determined by elemental analysis

[b] Values for drawn films are shown in parentheses

[c] RU = average repeat unit

[d] Values taken from ref. 10

Table 4 Maximum electrical conductivities of doped PDDMPV homopolymer films

Draw ratio, L/L_0	Dopant	Degree of doping, dopant/repeat unit[a]	Conductivity ($S\,cm^{-1}$)
1	I_2	0.45	4.4
	$FeCl_3$	0.16	2.3
	$Fe(ClO_4)_3$	0.12	1.1
5	I_2	0.51	46
	$FeCl_3$	0.21	25
	$Fe(ClO_4)_3$	0.15	5.1
5[b]	I_2	0.49	27
	$FeCl_3$	0.21	18
	$Fe(ClO_4)_3$	0.14	2.9
10	I_2	0.54	91
	$FeCl_3$	0.24	55
	$Fe(ClO_4)_3$	0.21	13

[a] I_3^- and $FeCl_4^-$ were assumed to be present as counterions in the doped samples

[b] Sample of fully eliminated PDDMPV film uniaxially drawn at 150–160°C to a draw ratio of 5

A rapid increase in conductivity was observed on exposure of the PBMPV films to the dopants (see *Table 3*). Conductivities as high as 590 $S\,cm^{-1}$ were measured for the I_2-doped stretched homopolymer films, and 2160 $S\,cm^{-1}$ for the $FeCl_3$-doped stretched materials[10]. The copolymers containing both PV and BMPV units show a very sensitive dependence of electrical conductivity on composition. A rapid increase in the conductivity values of the copolymers is initially observed with increasing content of BMPV units, after which the extent of increase then diminishes. The degrees of doping presented in *Tables 3* and *4* were obtained from the weight gain after doping treatment. In general, the polymer films having the highest conductivities show a higher degree of doping. It is rather surprising to note that the copolymer containing only 11 mol% of BMPV units can be easily doped with I_2 to give a material with an electrical conductivity of 5×10^{-1} $S\,cm^{-1}$, in spite of the fact that PPV itself can hardly be doped at all with the same dopant. As observed for doped PPV and other related polymers, the conductivities of oriented films along the stretching direction are consistently higher than those of unoriented ones. It is conceivable that the inclusion of BMPV units in the copolymer chain brings about morphological changes, thus making it easier for the dopant molecules to approach and oxidize the conjugated π backbone. Electronic effects of the two alkoxy groups should also play an important role in the easier doping and the increased conductivity.

Table 4 shows the maximum conductivity values that are obtained for the PDDMPV films when they are doped with I_2, $FeCl_3$ or $Fe(ClO_4)_3$. The values of the I_2- or $FeCl_3$-doped PDDMPV homopolymer films are much lower than those of the corresponding doped PBMPV films. The presence of insulating, long dodecyloxy substituents is likely to be the major reason for this lower conductivity. Ferric perchlorate, $Fe(ClO_4)_3$, is the least effective of the three dopants examined, and, in fact, the polymer films disintegrated when they were kept longer than 2 min in a solution (0.2 M) of $Fe(ClO_4)_3$ in nitromethane.

Fully eliminated PDDMPV films could be uniaxially drawn at 150–160°C to a draw ratio of 5. As shown in *Table 4*, the electrical conductivity (27 $S\,cm^{-1}$ for an I_2-doped sample) of the drawn film after thermal elimination is comparable to that of a PDDMPV film prepared from preoriented polyelectrolyte precursor polymer (46 $S\,cm^{-1}$, see *Table 5*). As far as we know, this is the first example of a PPV derivative that exhibits such a thermal deformation behaviour. This polymer could also be hot-pressed as mentioned earlier. The presence of the long dodecyloxy substituent on the phenylene ring is almost certainly responsible for these properties.

Table 5 compares the electrical conductivities of the poly(PV-*co*-DDMPV) materials after being doped with I_2 or $FeCl_3$. The conductivity of the copolymers increases steadily with increasing content of DDMPV units, finally reaching that of the PDDMPV homopolymer. In general, DDMPV copolymers show lower electrical conductivities than the corresponding BMPV copolymers, again most probably due to the presence of the long insulating

Table 5 Maximum electrical conductivities of I_2- and $FeCl_3$-doped PDDMPV and PDDMPV copolymers

		Conductivity ($S\,cm^{-1}$)		Degree of doping[b,c]	
Copolymer[a]	Dopant	Undrawn film	Drawn film, 4 L_0	I_3^-/RU	$FeCl_4^-$/RU
7-Poly(PV-*co*-DDMPV)	I_2	1.5×10^{-5}	–[d]	0.02	
	$FeCl_3$	7.1×10^{-3}	1.5×10^{-1}		0.04(0.03)
17-Poly(PV-*co*-DDMPV)	I_2	9.1×10^{-5}	1.4×10^{-3}	0.05(0.05)	
	$FeCl_3$	6.2×10^{-3}	5.7×10^{-2}		0.05(0.05)
37-Poly(PV-*co*-DDMPV)	I_2	1.4×10^{-1}	4.6×10^{-1}	0.17(0.18)	
	$FeCl_3$	4.7×10^{-3}	6.1×10^{-3}		0.12(0.12)
66-Poly(PV-*co*-DDMPV)	I_2	9.5×10^{-1}	2.2	0.36(0.36)	
	$FeCl_3$	1.0×10^{-2}	1.3×10^{-2}		0.21(0.23)
PDDMPV	I_2	4.4	46[e]	0.45(0.51)	
	$FeCl_3$	2.3	25[e]		0.16(0.21)

[a] The numbers 7, 17, etc. indicate the content of DDMPV units in the final copolymer as determined by elemental analysis

[b] Values for drawn films are shown in parentheses

[c] RU = average repeat unit

[d] This film could not be doped even after treatment with the dopant for 3 weeks

[e] Values given are those for films uniaxially stretched to 5 times their original length, i.e. $L/L_0 = 5$

dodecyl substituents attached to the backbone of the former. Another interesting phenomenon that is observed regarding the influence of uniaxial stretching on the electrical conductivities of poly(PV-*co*-DDMPV) films is the fact that the conductivities of stretched copolymers containing higher levels of DDMPV units, for example, 37- and 66-poly(PV-*co*-DDMPV), are similar to those of the unstretched species (see *Table 5*). In contrast, the copolymers containing low levels of DDMPV units reveal significantly enhanced electrical conductivities for the drawn specimens. This difference can be explained by an easier thermal relaxation of the chain orientation of the copolymers which contain higher contents of DDMPV structure taking place at an elevated temperature during the elimination reaction. The irregular occurrence along the chains of long alkoxy substituents in high concentrations certainly imparts a higher mobility when heated, which is expected to lead to chain relaxations destroying the chain alignment previously attained by uniaxial stretching of the precursor polymer films.

CONCLUSIONS

Copolymers of PPV containing 2-n-butoxy-5-methoxy-1,4-phenylenevinylene (BMPV) or 2-n-dodecyloxy-5-methoxy-1,4-phenylenevinylene (DDMPV) units were prepared via water-soluble, polyelectrolyte precursor polymers. The precursor polymer of PDDMPV was found to be able to form an ordered structure, induced thermally and by stretching, where the long dodecyloxy group is positioned in an ordered fashion and most probably with an extended *trans* conformation. This ordered structure appears to be at least partially retained even after thermal elimination to the final polyconjugated polymer, PDDMPV, particularly in the preoriented film. This conclusion is derived from the results of d.s.c., and WAXD and SAXS diffraction analyses. None of the precursor polymers of PBMPV, or the BMPV or DDMPV copolymers, however, exhibited this similar ordering process.

The vinylene groups in the final polyconjugated polymers were found to have a *trans* configuration, as deduced from their i.r. spectra. Showing quite different behaviour to unsubstituted PPV, all of the present polymers could be readily doped with I_2 and $FeCl_3$. The electrical conductivities of I_2- and $FeCl_3$-doped BMPV copolymers initially increase rapidly with increasing content of BMPV units, after which the extent of increase then diminishes to finally reach that of the PBMPV homopolymer. PDDMPV and DDMPV copolymers showed lower electrical conductivities when compared to PBMPV and BMPV copolymers, which can be ascribed to the insulating property of the long dodecyloxy substituent.

All of the copolymers of PBMPV and PDDMPV exhibited absorptions in their u.v.–vis. spectra representing π–π^* transitions which occurred at longer wavelengths than those observed for PPV. This bathochromic effect of the two electron-donating alkoxy substituents on the phenylene ring certainly results in a reduction of the band-gap between the valence band and the conduction band, which, in turn, promotes easier doping (or oxidation by dopants), leading to an improved electrical conductivity. Morphological changes resulting from the alkoxy substituents must also be another important contributing factor in the improved doping ability.

Finally, PDDMPV is unique in that its film could be stretched at 150–160°C to a draw ratio of 5 as a result of the plasticizing effect of the long dodecyloxy group in this polymer. Moreover, this polymer is soluble in solvents such as *p*-xylene.

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