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SYNTHESIS AND PROPERTIES OF PHENYL-SUBSTITUTED ARYLENE VINYLENE POLYMERS AND COPOLYMERS

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ABSTRACT

Poly(phenyl-1,4-phenylene vinylene) (PhPPV) and a series of arylene vinylene copolymers containing phenyl-monosubstituted arylene units and either unsubstituted or 2,5-dialkoxy 1,4-phenylene vinylene units was prepared from water-soluble, sulfonium salt precursor polymers. The conversions of the respective precursor polymers to the conjugated polymers were studied by thermogravimetric analysis, and the arylene vinylene polymers so formed were characterized by elemental analysis and by FT-IR and UV-Vis spectroscopy. The substituted polymers could be drawn above their softening points even though some degree of crosslinking occurred during the thermal elimination step. Doping of the polymer films with either iodine or antimony pentafluoride vapor led to conductivities in the $10^{-4} \text{ S} \cdot \text{cm}^{-1}$ range. The low level of conductivity observed may be a result of morphological perturbations that inhibit the interchain hopping of the charge carriers.

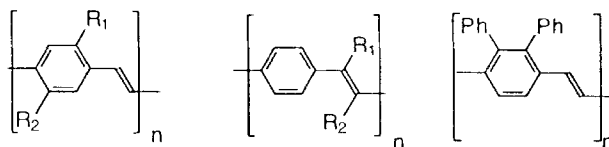
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INTRODUCTION

Among the highly conjugated organic polymers that display unusual electro-optical properties, poly(*p*-phenylene vinylene) (PPV), **1a**, is of special interest because of its ability to form free-standing or self-supported films of very good optical quality [1]. This property makes PPV a candidate for various electro-optical applications. Moreover, both films [2] and fibers [3] of PPV can also be obtained with high degrees of molecular orientation and excellent mechanical properties. However, the processing of PPV can only be achieved through a precursor polymer route [4] that involves several synthetic steps because the final conjugated polymer is insoluble and infusible. Some degree of success has been achieved in the synthesis of soluble PPV derivatives [5] by substituting long alkyl side chains on the main chain phenylene groups of the conjugated polymer, but much less effort has been applied to obtaining meltable PPV derivatives.

Phenyl-substituted monomers have been used with excellent results to decrease the melting transitions of wholly aromatic, liquid crystal polyesters [6]. In these systems a useful compromise has been reached between the lowering of the melting point of the liquid crystal polymers and the loss of mechanical properties caused by the decrease in crystallinity by the bulky substituent.

Meltable copolymers of phenyl-substituted PPV, with and without flexible units, have been reported [7], but these copolymers also contained approximately 40% of their vinylic groups in the *cis* configuration in addition to the flexible units. In an early study [8], Hörhold described the synthesis of 2,5-diphenyl-PPV, **1c**, and although the thermal properties of the polymer were not reported, it is well known that symmetric substitution in the aromatic ring of the polymer main chain generally is not effective in disrupting the crystalline order [9], which is probably the reason why this polymer was found to be insoluble. In contrast, the polymer with structure **2b** was found in that study to dissolve in many common organic solvents.



1a $R_1 = R_2 = H$

2a $R_1 = Ph, R_2 = H$

3

1b $R_1 = Ph, R_2 = H$

2b $R_1 = R_2 = Ph$

1c $R_1 = R_2 = Ph$

Another phenyl-disubstituted poly(arylene vinylene) [10], **3**, and a phenyl-monosubstituted polymer, poly(phenyl-1,4-phenylene vinylene) (PhPPV) [11], **1b**, have been synthesized by the Wittig polymerization reaction and the Heck Pd-catalyzed condensation reaction, respectively. Although these synthetic routes are of general use in the synthesis of conjugated polymers, very often the polymers are of low molecular weight, as it was in the case of polymer **1b**, and unable to form continuous films, which are desirable to eliminate the resistance to conductivity caused by grain-grain interfaces in pressed powders. The synthesis of **3** by the

precursor route has been reported [10], but the thermal properties of **3** were not described in the communication.

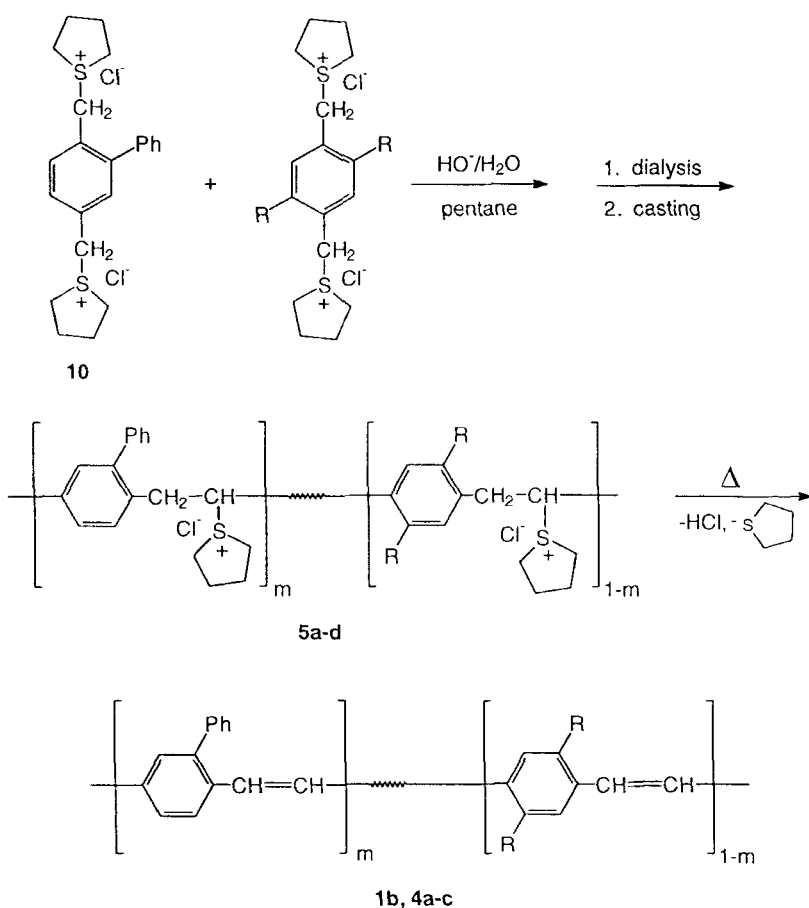
Electric conductivity of conjugated polymers seems to be very sensitive to any distortion of the planar conformation of the conjugated polymer chains. Thus the phenyl substitution on the vinylic carbons of polymers **2a** and **2b** led to a significant decrease in the electrical conductivity of these systems after doping [12]. In this regard, therefore, it is uncertain whether a single phenyl group substitution on the aromatic ring of the units PPV will yield a meltable polymer without a significant degree of distortion of the backbone, which could prevent the doped polymer from reaching the metallic regime of electric conductivity. Another report [13] also casts doubt on the feasibility of melt processing polyarylene vinylene polymers because of the likelihood of crosslinking of the vinylene units during the thermal elimination reactions.

The present contribution is concerned with the synthesis and properties of phenyl-monosubstituted PPV, **1b**, and related copolymers **4a–c** through high-molecular-weight precursor polyelectrolytes **5a–d** as shown in Scheme 1. Copolymers with this monomeric unit and with unsubstituted and alkoxy-substituted aromatic units were prepared by the same synthetic route, and films of all of these conjugated polymers were characterized in terms of physical properties and conductivity.

EXPERIMENTAL

Polymer Characterization

^1H - and ^{13}C -NMR spectra were recorded on a Varian XL300 spectrometer in CDCl_3 solutions with CHCl_3 at 7.24 ppm as the internal standard and in D_2O solutions with HDO at 4.67 ppm as the internal standard. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory. Melting points reported are not corrected. IR spectra were taken on freestanding polymer films using an IBM IR30-S FT-IR spectrophotometer. DSC and TGA measurements were recorded on Perkin-Elmer DSC2 and TGA2 instruments with a scan rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ with a dry N_2 flow. UV/Vis spectra were obtained on thin polymer films, which were cast and eliminated on quartz plates, using a Perkin-Elmer Lambda 9 spectrophotometer. Optical observations were made with a Carl Zeiss polarized-light microscope equipped with a Mettler FP-2 hot stage. Wide-angle x-ray diffraction patterns were obtained on flat films using a Statton camera. Viscosities of the precursor polymers were measured at 25°C with a Cannon viscometer (Model 75/J76) in a mixed solvent of MeOH and H_2O (volume ratio 1:4) containing 0.05 M Na_2SO_4 . Dialyses of solutions of the precursor polymers were performed in the Macro HF dialysis set (Spectrum Co.) by passing deionized water through a cellulose fiber bundle, which had a molecular weight cut-off of 6000 Da, immersed in the stirred polymer solution to remove unreacted bisulfonium salts, sodium chloride, and other possible impurities and oligomers. Films of the precursor polymers were obtained by casting in vacuo on flat polypropylene dishes. The precursor films were heated in vacuo (10^{-2} torr) at about 230°C for 22 hours for conversion to the arylene vinylene films. The eliminated films were drawn in vacuo at 290 – 320°C by attaching a small piece of the eliminated film of PhPPV (typically 5 mm width and $20\ \mu\text{m}$ thickness) to a small weight (typically 18 g) at the lower end of the



homopolymer **1b**, **5a**; $m = 1$

copolymers **4a**, **5b**; $m = 0.80$, $R = \text{H}$

4b, **5c**; $m = 0.87$, $R = \text{MeO}$

4c, **5d**; $m = 0.78$, $R = \text{n-BuO}$

SCHEME 1.

film. This assembly was hung inside a glass vessel, and after evacuation at 10^{-2} torr for 2 hours, the container was immersed into a salt bath maintained at 315°C . Conductivity measurements were carried out using the conventional four-probe technique by evacuating the doping chamber to a pressure of less than 10^{-2} torr and then opening the system to either the I_2 or SbF_5 source at room temperature until a minimum electrical resistance was obtained.

Monomer Synthesis

Reagent-grade solvents were dried over molecular sieves. α - α -Dichloro-*p*-xylene and tetrahydrothiophene were purchased from Aldrich. 1,4-Bis(chloromethyl)-2,5-

dimethoxybenzene and 1,4-bis(chloromethyl)-2,5-dibutoxybenzene were prepared from their dialkoxy-benzene derivatives by chloromethylation according to the procedure of Wood and Gibson [14]. 1,4-Dimethoxybenzene (Aldrich) was used as received. 1,4-Dibutoxybenzene was synthesized from the reaction of hydroquinone (Aldrich) with *n*-butyl bromide (Aldrich) by the Williamson synthesis. The unsubstituted and dialkoxy-substituted bisulfonium salts were synthesized by procedures described previously [15] by reacting either 1,4-bis(chloromethyl)benzene or its 2,5-dialkoxy-substituted analogues with an excess of sulfide (three equivalents) in methanol at 50°C for 24 hours. 1,4-Dimethylphenylbenzene (**6**), Scheme 2, and phenylterephthalic acid (**7**) were prepared according to the procedure reported by Jadhav et al. [16].

1,4-Bis(hydroxymethyl)-2-phenylbenzene (8). A solution of LiAlH₄ (4.0 g, 0.105 mol) in THF (50 mL) was added dropwise into a solution of **7** (14.7 g, 0.061 mol) in THF (300 mL) during 30 minutes. The mixture was refluxed for an additional 14 hours. The stirred reduction mixture was treated by a successive dropwise addition of water (4 mL), a 15% sodium hydroxide solution (4 mL), and water (12 mL). After cooling, the mixture was filtered, and the filter cake was washed with THF (2 × 50 mL). The volume of the combined THF phases was reduced to about 100 mL, and CHCl₃ (200 mL) was added. The organic layer was washed with brine (2 × 50 mL), evaporated, and dried under reduced pressure for 6 hours at room temperature to yield **8**, a white precipitate (10.7 g, 82%). This product was used without further purification in the next synthetic step.

¹H NMR (CDCl₃, δ): 7.26–7.61 (m, 8H, aromatic C–H), 4.75 (s, 2H, CH₂), 4.64 (s, 2H, CH₂), 1.90 (br s, 2H, OH).

1,4-Bis(chloromethyl)-2-phenylbenzene (9). A solution of SOCl₂ (13.0 g, 0.109 mol) in CHCl₃ (50 mL) was added dropwise to a solution of **8** (10.6 g, 0.05 mol) dissolved in pyridine (5 mL) and CHCl₃ (100 mL). The solution was heated at 60°C for 2 hours, washed with 3 N HCl (50 mL) and water (2 × 50 mL), and dried over Na₂SO₄; the solvent was evaporated. The remaining oil solidified overnight. An attempt to recrystallize the product in hexane failed, so it was distilled under reduced pressure at 161°C/1.2 mmHg, affording **9** (9.9 g, 80%).

¹H NMR (CDCl₃, δ): 7.25–7.60 (m, 8H, aromatic C–H), 4.61 (s, 2H, CH₂Cl), 4.51 (s, 2H, CH₂Cl). Analytical calculation for C₁₄H₁₂Cl₂: C 66.95, H 4.82, Cl 28.23%; found: C 67.10, H 4.88, Cl 28.06%.

1,4-Bis(tetrahydrothiophenylmethyl)-2-phenylbenzene dichloride (10). Following the procedure described by Rempfler et al. [17], the dichloride **9** (3.6 g, 14.3 mmol) was stirred with THT (4.5 mL, 51 mmol) and HCl (35%, 10 mL) at 60°C for 14 hours. The unreacted THT and about half of the solvent were removed under reduced pressure. The dark liquid was stirred first with acetone (3 × 65 mL), the solvent was removed by decantation, and the product was treated with MeOH (10 mL) and acetone (130 mL). After stirring for half an hour, the solvent was decanted and the remaining viscous liquid was dried under reduced pressure for 2 hours to yield a highly hygroscopic semisolid material (5.08 g).

¹³C NMR (D₂O, δ): 30.62, 30.94, 45.72, 45.85, 46.22, 47.75, 131.45, 131.79, 131.97, 132.04, 133.18, 133.38, 135.17, 135.53, 140.74, 147.13.

This material was dissolved in distilled water to afford an acidic, transparent brown solution that was stored in the cold. The amount of remaining HCl (7% by weight) in the monomer was calculated by titration of the aqueous solution of the dichloride **10**. The brown color vanished when the neutralization was complete, and a pale yellow solution of **10** was obtained. The concentration of **10** was calculated gravimetrically by forming the water-insoluble tetraphenylborate salt of **10**. A solution of Ph₄BNa in water was added to 2 mL of the dark solution previously diluted with distilled water (5 mL). The white precipitate was filtered and dried under reduced pressure overnight. The concentration of the dichloride salt in the aqueous solution, [**10**] = 0.45 mmol/mL, was calculated from the amount of the tetraphenylborate salt obtained (0.8036 g).

Analytical calculation for C₆₂H₅₂S₂B₂: C 84.35, H 5.94, B 2.45, S 7.26%; found: C 84.21, H 6.03, B 2.51, S 7.08%.

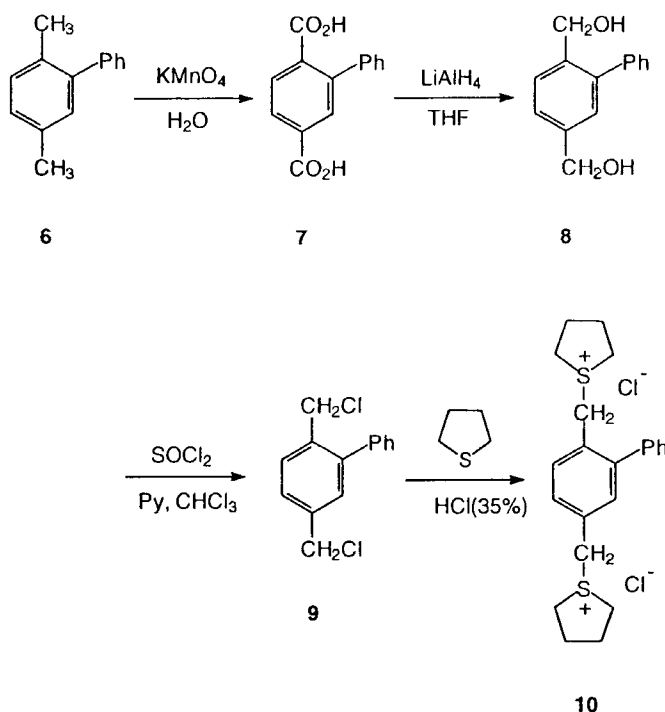
Polymer Syntheses

All polymerization reactions were carried out under similar conditions. The synthesis of the precursor polymer **5a** (see Scheme 1) is described in detail. The polymerization reaction was started by the addition of an argon-purged aqueous solution of NaOH (20 mL) (0.4938 N standard solution, Aldrich) to an argon-purged solution of the bissulfonium salt **10** (10 mL, 4.47 mmol) in water stirred with an amount of pentane such that the volume ratio of the aqueous reacting mixture to the organic solvent was 1:2. Both solutions were first cooled to the desired temperature, and the reaction was allowed to proceed at that temperature under an argon atmosphere for the desired time. The reaction was quenched by adding a known volume of 0.095 N HCl standard solution (Aldrich) with a syringe. The solution was neutralized with 0.095 N NaOH standard solution, most of the pentane was decanted, and nitrogen was bubbled through the solution overnight to eliminate residual pentane, after which the amber transparent solution was dialyzed for 3 days. To measure the polymer yield, 25 mL of the solution was cast into a film, which was transformed into the film of poly(phenyl-1,4-phenylene vinylene), **1b**, by heating in vacuo (10⁻² torr) at 230°C for 22 hours. From the weight of the resulting film and the volume of the polymer solution, the yield (in mol%) of the polymerization was calculated.

RESULTS AND DISCUSSION

Monomer Syntheses

The synthetic strategy described above for the synthesis of monomer **10** is shown in Scheme 2. The preparation of 2,5-bis(bromomethyl)phenyl benzene was first attempted by using the benzylic bromination of 1,4-dimethylphenylbenzene (**6**) with *N*-bromosuccinimide. Because of difficulties in the isolation of a pure compound in good yield from the complex mixture of brominated compounds, this direct route was abandoned. Instead, the sequence of oxidation, reduction, and halogenation on the benzylic carbon atoms shown in Scheme 2 afforded the dichloride **10**.



SCHEME 2.

Compared with the synthesis of the parent, unsubstituted sulfonium salt monomer, the formation of the phenyl-substituted monomer, **9**, required use of more vigorous conditions with concentrated hydrochloric acid as solvent. The use of methanol as the solvent led to only partial substitution by the sulfide of the benzylic chlorine in the *ortho* position to the phenyl substituent. This difficulty can be attributed to steric hindrance of the substitution reaction caused by the phenyl group rather than to the influence of electronic effects. All efforts to crystallize or precipitate the dichloride **10** using a variety of conditions failed, and it could not be isolated. The phenyl-substituted sulfonium salt was then isolated as the water-insoluble tetraphenylborate salt derivative, and it was characterized as such. However, the ^{13}C -NMR spectra of an aqueous solution of **10** showed only the carbon signals expected, so this solution was used directly for the polymerization reactions.

Precursor Polymer Synthesis

All the precursor polymers **5** prepared from the bisulfonium salt monomers formed stable aqueous solutions. Data for monomer conversions in the polymerization reactions, polymer yield, and intrinsic viscosities for the polymerizations are collected in Table 1. The free-standing precursor polymer films, which were obtained after dialysis of the solutions, were homogeneous in appearance and could be uniaxially drawn after immersion in silicone oil under a nitrogen atmosphere at

TABLE 1. Polymerization Conditions and Polymer Yields for the Polymerization and Copolymer Reactions

Polymer	Comonomer substituent R	r^a	Temperature, °C ^b	Monomer conversion, % ^c	Polymer yield, %	$[\eta]$, ^d dL·g ⁻¹
P1	—	—	11	59	58	2.15
P2	H	1/4	11	97	99	1.70
P3	MeO	1/9	0	70	50	0.90
P4	BuO	1/4	0	98	99	0.61

^aRatio of comonomer to Ph-substituted monomer in the feed.

^bPolymerization reaction temperature.

^cCalculated on the basis of the titration result.

^dIntrinsic viscosity in H₂O/MeOH (v/v 4:1) containing 0.05 M Na₂SO₄.

90°C when held in a vertical position with a small weight attached to their lower end.

The precursor polymer films were converted into the final conjugated polymers by thermal elimination. The observed and calculated elemental analyses for the conjugated polymers are presented in Table 2. The elemental analyses of the eliminated films showed low contents of sulfur and chlorine, so the compositions of the alkoxy-substituted units in copolymers **4b** and **4c** could be calculated from the ratio of carbon to oxygen. Nevertheless, corrections to account for the presence of low levels of saturated units and sodium chloride were made. For copolymer **4a**, the almost quantitative polymer yield obtained assured that the unsubstituted units were incorporated into the copolymer film in the same ratio as the feed ratio.

The use of an improved polymerization procedure [18] with pentane as a cosolvent led to polymer yields that were good to excellent, as shown in Table 1. However, the intrinsic viscosities of the polymers synthesized in this study were lower than those obtained for the precursor polymer of PPV itself obtained under similar reaction conditions, and these intrinsic viscosity values were undoubtedly a reflection of the lower molecular weight of the precursor polymer **5a** rather than an effect of differences in the hydrodynamic volumes of the two polymers in solution. The lower molecular weight could have been caused by a lower reactivity of the phenyl-substituted quinonedimethane intermediate which is formed during the reaction according to the accepted mechanism for this polymerization reaction [19]. This intermediate was detected by a transient absorption at 330 nm in the UV/Vis spectra of an aqueous basic solution of the monomer **10**.

If the polymerization reaction is regioselective such that the active center has the ring-substituted phenyl group in the *ortho* position, then the lower reactivity of the intermediate could be due either to steric hindrance by the *ortho*-phenyl group or to resonance stabilization by delocalization of either the unpaired electron for a radical mechanism or the electron pair for an ylid polymerization reaction by the *ortho*-phenyl group.

The use of pentane as an extraction solvent in the synthesis of the copolymers also led to the incorporation of comonomer units into the polymers in ratios very

TABLE 2. Elemental Analyses of Poly(Arylenes Vinylenes)

Polymer ^a	PhPPV units, ^b mol%	Elemental analysis											
		C		H		S		Cl		Na		O	
		Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
CP1	100	92.81	94.35	5.51	5.65	<0.1		0.61		0.19		0.67	0.00
CP2	—	93.48	94.31	5.60	5.69	0.29		0.41		<0.1		0.33	0.00
CP3	87	91.27	92.50	5.71	5.71	0.32		0.42		0.15		2.03	1.80
CP4	78	89.32	90.01	6.12	6.51	0.26		0.62		0.1		3.71	3.34

^aCP*n* is derived from the polyelectrolyte obtained in the polymerization P*n* of Table 1.

^bBased on monomer composition.

close to the feed ratios, as can be concluded from the results of the elemental analyses of the conjugated polymer films shown in Table 2.

It has been observed previously that the alkoxy-substituted bissulfonium salt monomers showed a higher tendency to be incorporated into the polymers than did the unsubstituted bissulfonium salt [15]. As discussed below, the question of whether the polymers formed are either random or block copolymers, or a blend of homopolymers, could not be conclusively answered, but the UV evidence is in favor of a random copolymeric structure for copolymers **4a-c**.

Preparation and Thermal Behavior of Poly(Arylene Vinylenes)

The eliminated films which were obtained by thermal treatment of the poly-electrolyte films were all transparent. The films were either yellow (polymers **1b** and **4a**) or orange, the latter for the samples containing alkoxy units (polymers **4b** and **4c**). It has been observed that the thermal elimination of the precursor polymer of PPV at 220°C for 22 hours or at 290°C for 4 hours yields polymers with a sulfur content of <0.1% [20], but sulfur contents of about 0.3% were found when the above conditions were applied to PhPPV derivatives. However, almost complete elimination of the sulfide was achieved by carrying out the elimination at 230°C for 22 hours. The thermal elimination properties of these polymers are shown by their thermogravimetric analysis (TGA) thermograms in Figs. 1 and 2.

The transformation of the precursor films to the conjugated polymers was determined by TGA measurements at a heating rate of 20°C·min⁻¹. The TGA

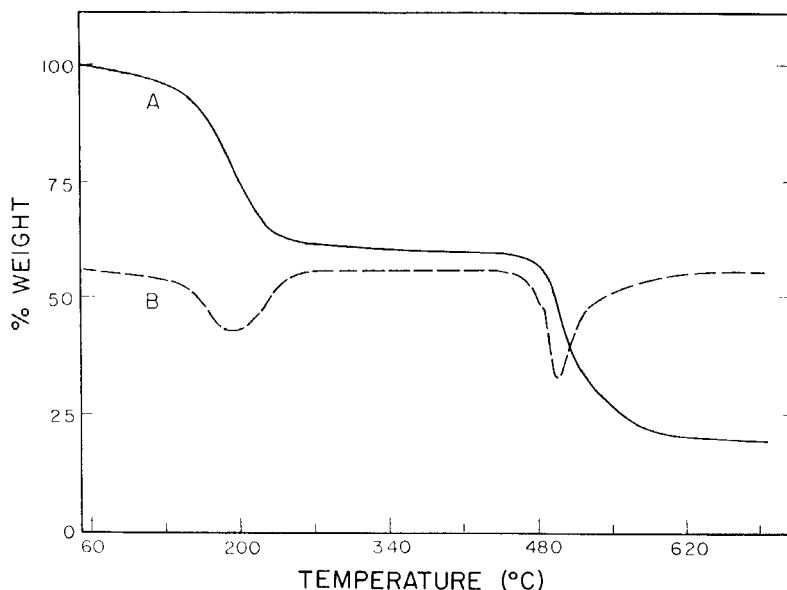


FIG. 1. TGA (A) and differential TGA (B) thermograms of the precursor polymer of PhPPV (**5a**); heating rate, 20°C·min⁻¹.

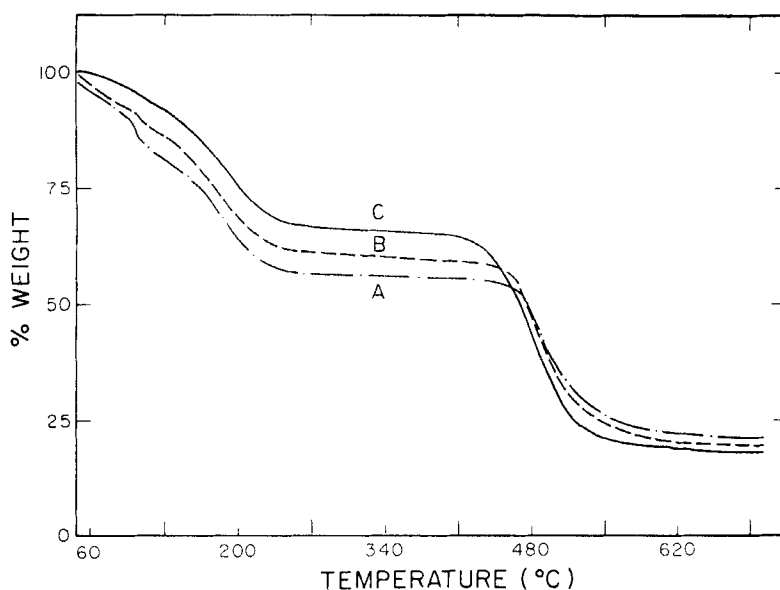


FIG. 2. TGA thermograms of the precursor polymers measured at a heating rate of $20^{\circ}\text{C}\cdot\text{min}^{-1}$: (A) copolymer **5b**; (B) copolymer **5c**; (C) copolymer **5d**.

thermogram of the precursor polymer of phenyl-substituted PPV (**5a**) in Fig. 1 shows a substantial rate of elimination that starts at 50°C with the maximum rate of elimination at 180°C . This weight loss corresponds to the volatilization of entrapped water and the conversion of the precursor polymer to the conjugated polymer. The products of the thermal elimination, hydrogen chloride and the cyclic sulfide, were formed at higher temperatures than those from the unsubstituted precursor polymer (about 150°C), a result suggesting that the phenyl substituent in the precursor polymer **5a** decreased the rate of elimination of the sulfonium salt by steric hindrance. Indeed, as stated above, it was necessary to increase the elimination temperature from 220 to 230°C to decrease the sulfur content in the eliminated films beyond the elemental analysis detection limit ($<0.1\%$).

Figure 2 shows the TGA thermograms of copolymers **5b-d**. An additional small step in the weight loss can be seen in the temperature range from 100 to 130°C . This step can be assigned to the elimination of the sulfonium group of either the unsubstituted units (**5b**) or the dialkoxy units (**5c** and **5d**) present in the copolymer samples. For polymer **5a**, the final weight loss began at 465°C , with the maximum weight loss at about 500°C . These values are approximately 100°C lower than those for unsubstituted PPV at 510 and 590°C . The introduction of dialkoxy units into the polymer decreased further the thermal stability of the conjugated polymer film. The corresponding temperatures for copolymers **5b-d** were found to be 455 and 500°C , 450 and 480°C , and 400 and 470°C , respectively.

Figure 3(A) shows the FT-IR spectrum of a film of PhPPV, **1b**, prepared by the thermal elimination of the precursor polyelectrolyte **5a**. Overall, the spectrum obtained is in good agreement with that previously reported for PhPPV prepared

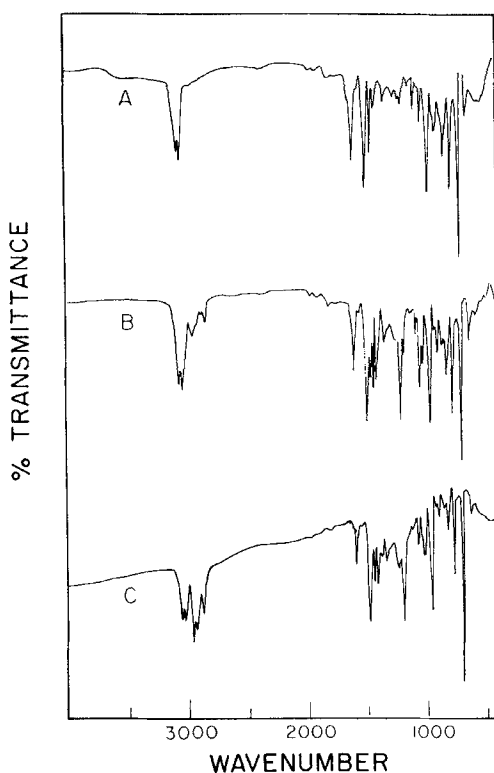


FIG. 3. FT-IR spectra of eliminated films: (A) polymer **1b**; (B) copolymer **4b**; (C) copolymer **4c**.

by the Heck olefination reaction [21]. The more sharply defined aromatic CH stretch mode at 3054 cm^{-1} in the spectrum of the polymer prepared from the precursor polymer is the only appreciable difference between the two spectra. The appearance of the strong band at 961 cm^{-1} after the thermal treatment may be assigned to an out-of-plane CH bending mode, which is characteristic of the *trans* configuration for the vinylene group. The strong bands at 700 and 770 cm^{-1} were already present in the precursor polymer and can be assigned to the CH out-of-plane bending modes of the aromatic rings. The corresponding mode for the *cis* configuration would be expected in the $730\text{--}650\text{ cm}^{-1}$ range, and no additional bands are seen in this range. It is concluded, therefore, that the thermal elimination reaction produced phenyl-substituted PPV with the *trans* configuration.

The strong band at 1597 cm^{-1} , almost absent in PPV, corresponds to the "quadrant stretching" mode and is caused by the loss of symmetry at the ring center of PhPPV from the introduction of the phenyl substituent [22].

The FT-IR spectrum of **4a** (not reported here) resembled that of PhPPV in which the absorption band pattern was dominated by the maxima corresponding to the PhPPV moiety. The FT-IR of the polymers **4b** and **4c** are shown in Figs. 3(B) and 3(C). Both spectra show clear evidence of the presence of alkoxy groups by bands at 2831 , 1205 , and 1045 cm^{-1} caused by the presence of dimethoxyphenylene

units for sample **4b** and by bands at 2957, 2932, 2870, and 1202 cm^{-1} derived from the dibutoxyphenylene units for copolymer **4c**.

Observations on all the polymer films obtained by the thermal elimination reactions were made on samples placed on a hot stage on a polarizing microscope stage. Areas with strong birefringence were observed for all samples in addition to the dominant black field. These areas may be due to strain orientation because of the reduction of the film volume which occurred during the elimination reaction of the clamped samples. This birefringence faded and finally disappeared when the samples were heated on the hot stage at a heating rate of $2^\circ\text{C}\cdot\text{min}^{-1}$. No development of birefringence was observed in the subsequent cooling and reheating cycles from 20°C above the temperature at which the field was completely dark. This clearly reflects a local relaxation although, as already mentioned, no characteristic glass transition phenomenon could be observed calorimetrically. The corresponding temperatures for polymers **1b** and **4a-c** were found to be 210, 240, 205, and 200°C , respectively.

Softening points were detected for polymers **1b** to **4a-c** by visual observation of the behavior of a piece of film of the thermally converted polymers placed between two heated glass slides. Corresponding temperatures for polymers **1b** to **4a-c** were found to be 310, 300, 290, and 260°C , respectively. The rubbery appearance of the polymers persisted until the polymers darkened because of a degradation process occurring in air at $60\text{--}70^\circ\text{C}$ above its softening points, but no shear flow was observed up to 380°C . Furthermore, analysis by DSC over a $50\text{--}400^\circ\text{C}$ temperature range of the fully eliminated polymers indicated that no glass or melt transitions were observable. Samples heated to 30°C above their softening points did not show a rubbery appearance in subsequent heating cycles.

In the case of low molecular weight PhPPV obtained in another study by the Heck olefination reaction, irreversible solidification was reported to occur in the molten state on annealing $20\text{--}50^\circ\text{C}$ above its softening point (reported as 155°C) [21]. The four polymers prepared in that study were found to be insoluble in a wide variety of solvents and temperature conditions, although indications of swelling were occasionally observed. For example, in dichlorobenzene at 60°C the films became tacky and elastic, but the solvent became yellow and strongly fluorescent upon irradiation with 366 nm wavelength light. Apparently, in the present case, a smaller degree of crosslinking occurred during thermal elimination reaction of the precursor polymers, and the physical and thermal properties of the conjugated polymers were influenced to a lesser extent.

Films of the conjugated polymers could be drawn to varying degrees under uniaxial stress when heated under dynamic vacuum. For polymer **1b**, draw ratio values, L/L_0 , of 2 to 3 were achieved at 315°C , whereas films of copolymer **4b** started to elongate at 290°C and were easily drawn to L/L_0 values of 3 at 305°C . The introduction of unsubstituted phenylene units hampered this process, and copolymer **4a** could only be slightly drawn ($L/L_0 = 1.2$).

Although to date no study by the polarized IR technique has been carried out to determine whether some molecular orientation occurred during the drawing process, observations of films of the drawn polymers under cross-polarization in a polarized-light microscope showed extinction positions at 90°C , a result indicating that some alignment of the polymer molecules took place. Nevertheless, unstretched and stretched films of polymer **1b** showed similar x-ray patterns and exhibited a

broad halo centered at about 3.4\AA , a result consistent with an amorphous structure, without any indication of crystallinity or orientation of the polymer chain.

Optical Properties and Electrical Conductivity of Poly(Arylene Vinylenes)

UV/Vis spectra of thin films of the conjugated polymers are shown in Fig. 4. For PhPPV, **1b**, the maxima of the broad, longest wavelength absorptions, which are due to the energetically lowest $\pi \rightarrow \pi^*$ transition of the conjugated system and the edge of these absorptions calculated as the onset to the baseline, were found to be 415 and 497 nm, respectively (2.49 eV). These results indicate that the optical band gap (E_{opt}) of PhPPV increased with respect to that of the parent PPV by about 0.1 eV.

The increment in the E_{opt} , which results from the phenyl substitution in the phenylene ring, is not as high as the increase observed when the phenyl group is

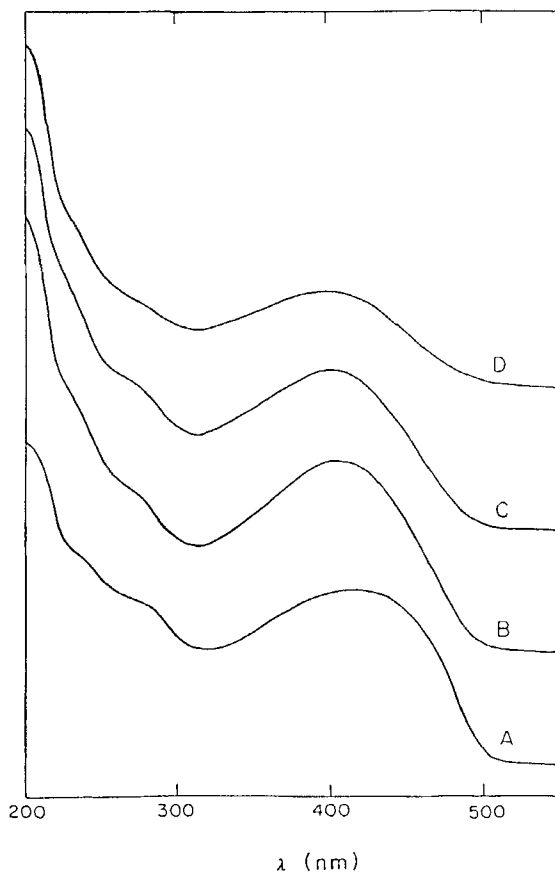


FIG. 4. UV/Vis spectra of eliminated films: (A) polymer **1b**; (B) copolymer **4a**; (C) copolymer **4b**; (D) copolymer **4c**.

introduced into the vinylene unit. In the latter case, the distortion produced a broadening of the band gap from 2.39 to 2.8 eV [23]. The UV/Vis spectra of the polymers obtained when the phenyl-substituted bisulfonium salt was copolymerized with unsubstituted (**4a**), methoxy disubstituted (**4b**), or dibutoxy monomer (**4c**) are shown in Figs. 4(B), 4(C), and 4(D), respectively. For these polymers, the absorption edge and the position of the broad absorption band in the visible region had almost similar values, and they showed no significant differences compared with PhPPV.

It was previously reported that PPV films containing either 30 or 50 mol% dimethoxy-substituted units showed a UV/Vis spectra with a "PPV-like" appearance [15]. This behavior was taken as an indication of the copolymeric nature of these polymers. Recently, a detailed IR spectroscopic study [24] of the absorption bands corresponding to the *trans* vinylene groups in a series of poly(arylene vinylenes) established that the copolymerization of bisulfonium salts having either phenylene or dichlorophenylene cores with thiophene units yielded random copolymers, whereas the copolymerization of bisulfonium salts with dimethoxyphenylene and with thiophene cores afforded a mixture of homopolymers. The lack of resolved absorption frequencies precludes such a distinction by IR spectroscopy in the present system, but for copolymers **4a-c**, the "PhPPV" appearance of their UV/Vis spectra can be taken as an indication of their copolymeric microstructures.

Conductivity measurements were performed on doped films of PhPPV. No measurable conductivities ($\sigma < 10^{-6} \text{ S}\cdot\text{cm}^{-1}$) were detected in PhPPV films doped with H_2SO_4 , MeSO_3H , FeCl_3 , I_2 , or SbF_5 . The conductivity values obtained after doping of the polymers **1b** and **4a-c** with I_2 and SbF_5 are presented in Table 3. Undoubtedly, the perturbation of the conjugation of the π -system by the steric effect of the *ortho*-substitution in the phenylene ring plays a major role in the low level of conductivity exhibited by PhPPV. It is, however, difficult to rationalize the conductivity results solely on the grounds of steric or electronic effects due to the *ortho*-substitution. The polymer **2a** bearing the phenyl substituent on the vinylene unit had an optical band gap of 2.8 eV and showed a conductivity value in the order of $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ on SbCl_5 doping [12], but polymer **1b** ($E_{\text{opt}} = 2.49 \text{ eV}$) was not able to reach this conductivity level when it was exposed to the vapors of the same oxidizing agent.

TABLE 3. Conductivities of Poly(Arylene Vinylenes)

Polymer	Dopant	
	I_2	SbF_5
CP1	$< 10^{-6}$	$< 10^{-6}$
CP2 (20) ^a	$< 10^{-6}$	1.1×10^{-4}
CP3 (13) ^b	4.4×10^{-5}	2.8×10^{-4}
CP4 (22) ^b	3.3×10^{-4}	3.5×10^{-4}

^aMol percentage of phenylene units in parentheses.

^bMol percentage of dialkoxy units in parentheses.

It is well established that conductivity depends both on the ability of the conjugated polymer to be oxidized and on the ability for the charge carriers to move through the solid polymers, that is, on the solid-state morphology. Figure 5 shows a molecular representation of the spatial arrangements of the polymers substituted either in the aromatic ring (polymer **1b**) or in the vinylic group (polymer **2a**). Presumably, polymer **2a** could adopt a more closely packed, ribbon- or rodlike configuration, thereby producing a more ordered solid-state structure after doping than does polymer **1b**.

The effect of the molecular structure on the electronic and conducting properties of a variety of poly(arylene vinylenes) is compared in Table 4. Interestingly, polymers with a high E_{opt} (entries 4 and 5) show orders of conductivity that are comparable to or higher than those shown by polymers with lower E_{opt} but that have substituents or structures that could lead to less ordered morphologies (entries 2 and 3). Therefore, the low levels of conductivity exhibited by this series of polymers may be due to morphological perturbations that restrict the interchain hopping of the charge carriers.

After doping with I_2 to saturation, the copolymer films with 13% (**4b**) and 22% (**4c**) alkoxy-disubstituted units became black, and the conductivity of these films ranged from 10^{-5} to $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ (see Table 3). The introduction of phenylene units in the copolymer was almost as effective as the introduction of dialkoxy-substituted aryl units to improve the conductivity of SbF_5 -doped PhPPV films, although the unsubstituted units did not increase the conductivity of I_2 -doped PhPPV to a measurable level. Drawn PhPPV films showed no appreciable conductivity increase (at least less than $10^{-6} \text{ S}\cdot\text{cm}^{-1}$) when treated with SbF_5 , and undrawn and drawn films of copolymer **4b** showed the same order of conductivity values.

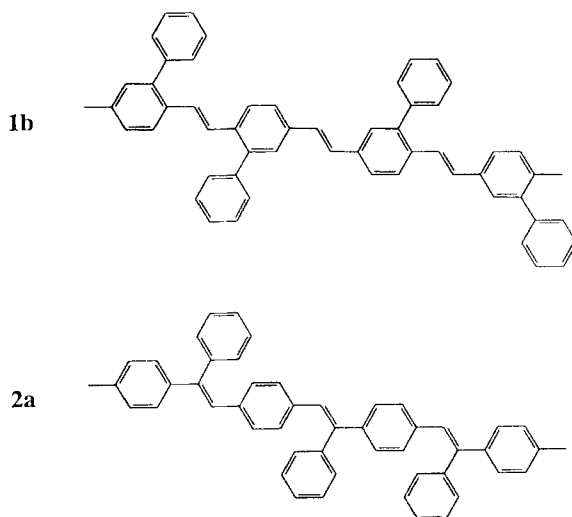
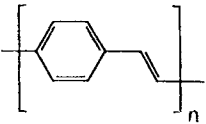
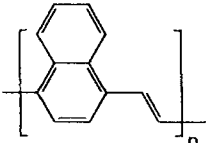
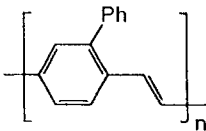
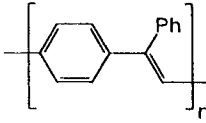
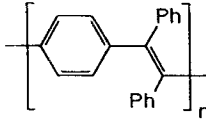


FIG. 5. Possible spatial arrangement of the units in polymers **1b** and **2a**.

TABLE 4. Effect of Molecular Structure on Electronic and Conducting Properties of Arylene Vinylene Polymers

Polymer	E_{opt} , eV ^a	E_{ox} , eV ^b	Conductivity, S·cm ⁻¹ [dopant]
	2.39	0.80 ^c	58 [SbF ₅]
	2.05 ^d	0.75 ^d	3×10^{-2} [AsF ₅] ^e
	2.49	—	$< 10^{-6}$ [SbF ₅]
	2.80	1.2	10^{-4} [SbCl ₅] ^f
	2.88	1.17	10^{-4} [SbF ₅] ^g

^aOptical band gap, calculated as the onset to the baseline from UV/Vis spectra.

^bElectrochemical oxidation potential vs SCE electrode.

^cRef. 25.

^dRef. 26.

^eRef. 27.

^fRef. 23.

^gRef. 28.

CONCLUSION

A series of homopolymers and copolymers derived from the basic polyphenylene vinylene structure and synthesized by an analogous precursor scheme has been described. These polymers are all film forming, exhibit softening points, and could be partially drawn, but their electrical conductivities, after doping with either iodine or antimony pentafluoride, are several orders of magnitude lower than that of the parent polymer. Possible explanations for this difference are adduced.

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