

# Poly(hetero)arylene Vinylenes, Synthesis Via Soluble Precursor Polymers, Characterization, Mechanism and Application: A Review

Ali Akbar Entezami\* and Massoumeh Bagheri\*\*

Laboratory of Polymer Chemistry, Faculty of Chemistry, Tabriz University, Tabriz 51664, I.R. Iran

Received 9 July 2001; accepted 12 January 2002

## ABSTRACT

Poly(arylenevinylene)s are considered to be promising candidates for electrical and/or optical materials. Most of these polymers are neither fusible nor soluble in common solvents, making it difficult to process them into shaped articles. The synthetic procedures have mostly involved the preparation of a precursor polymer which is processible, usually in solution, and which can then be converted into the desired poly(arylenevinylene); alternatively, these conjugated polymers can be rendered soluble and therefore processible in organic solvents by attaching large lipophilic groups to the arylenevinylene moiety. The precursor route involves producing a polymer in which the arylene units are connected by ethylene units. The saturated units contain a group which not only solubilizes the macromolecule and allows processing, but which can under suitable conditions also act as a leaving group, thus affording the saturated vinylene units of a fully conjugated polymer. In this article the synthesis of poly(hetero)arylene vinylenes via a soluble precursor polymers, characteristics, mechanism of polymerization and their application together with some properties are reviewed.

## CONTENT

1. Introduction
2. Preparation of poly(hetero)arylene vinylenes
3. Poly(hetero)arylene vinylenes prepared via a soluble precursor polymers
  - 3.1. PPV and its derivatives
  - 3.2. Poly(naphthalene vinylene)
  - 3.3. Poly(9,10-anthrylene vinylene)
  - 3.4. Poly(4,7-benzofuran vinylene) and Poly(4,7-benzothiophene vinylene)
  - 3.5. Poly(2,5-thienylene vinylene)
  - 3.6. Poly(2,5-furylene vinylene)
  - 3.7. Poly(*p*-phenylene vinylene) copolymers
  - 3.8. Polyblends of PPV
4. Mechanism of base-induced polymerization
5. Effect of different factors on polymer properties
  - 5.1. Sulphonium structure
  - 5.2. Nature of the anion
  - 5.3. Polarizer and leaving group
6. Applications
7. Summary

(\*) Corresponding author; E-mail: aentezami@yahoo.com

(\*\*) Present address: Tabriz Teacher Training University of Azarbaijan, Tabriz, I.R. Iran

## 1. INTRODUCTION

The possibility of using polyconjugated macromolecules for semiconductors or, indeed, conducting devices has opened a wide and stimulating new field of both fundamental and applied research that has recently overflowed into other areas such as non-linear optics and photoluminescence. Two main types of synthetic methods have been reported for the conducting polymers. One of the most widely used is electrochemical polymerization method. Aniline [1], thiophene [2], pyrrole [3],  $\alpha$ -naphthyl amine [4], carbazole and its derivatives [5] have been electrochemically polymerized and electrochemical behaviours, conductivity and the other characteristics have been studied. In other methods, acetylene [6], aniline [7], thiophene [8] and its derivatives have been chemically polymerized with various methods and conductivity of obtained polymers has been studied.

Highly conjugated polymers are generally insoluble and infusible because of the stiffness of their backbones. This makes it difficult to process these materials into useful objects such as fibres and films. A solution to this problem is the synthesis of these polymers via precursor polymers (Figure 1). The precursor polymers, which are soluble, can be processed by conventional methods and are converted in a last reaction step to the fully conjugated chain.

Poly(arylene vinylene)s represent a class of conjugated organic polymers that are intermediate in structure between polyacetylene and the polyarylenes and that may exist in a many large number of structural variations. Because of the combination of environmental stability, processibility, good physical and mechanical properties of these polymers, poly(*p*-phenylene vinylene) (PPV) and its derivatives have been evoked considerable interest as a good electrical conductor and as a materials for non-linear optics [10, 11, 12].

In 1968, investigation by R.A. Wessling and

R.G. Zimmerman has resulted in a novel approach to the synthesis of high molecular weight Poly(*p*-phenylene vinylene) via a water soluble polyelectrolyte [12]. An appropriate thermal treatment of the intermediate polymer yields PPV in the forms of films, fibres, coating, and foams with good mechanical properties. The processibility of high molecular weight conducting polymers has been achieved by the development of soluble precursor polymers for polyacetylene, polyphenylene, poly(*p*-phenylene vinylene), poly(thienylene vinylene) (PTV), and other polymers [13–15].

In this review the preparation of poly(hetero)-arylene vinylenes via soluble precursor polymer, characteristics, mechanism of polymerization and their application together with some properties are reviewed.

## 2. PREPARATION OF POLY(HETERO)-ARYLENE VINYLENES

Various approaches have since been developed for the synthesis of poly(hetero)arylene vinylenes. The Wittig condensation, typically involving the dialdehyde and the corresponding phosphonium salt, has been applied to the preparation of PPV [16, 17], PTV [18] and copolymers [19–21] but intractable products were obtained that could not be fabricated into useful products. Dehydrohalogenation of 2,5- dialkoxy-*p*-xylylene dihalides has been also applied to the synthesis of PPV polymers [16]. Another way of preparing poly(hetero)arylene vinylenes calls upon a completely different approach such as the mutual condensation of methyl and aldehyde moieties in a basic medium (Figure 2) [9].

Other synthetic procedures, commonly used in C–C bond formation such as McMurry, Yamamoto and Suzuki [22], Knoevenagel [16], and Horner-type [23] condensation, Heck [16, 24, 25] reaction, Still

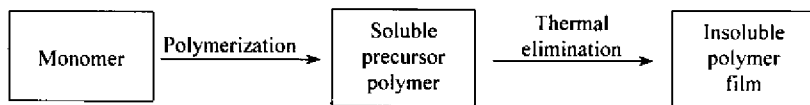
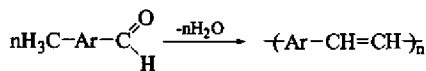


Figure 1. The soluble precursor approach [9].



**Figure 2.** The 'aldol-crotonic' condensation (with Ar= 1,4-phenyl; 2,5-furyl; or 2,5- thienyl) [9].

reaction using potassium *t*-butoxide [18, 27] and the employment of a phase-transfer catalyst (PTC) [27] coupling reaction [26], a strong base-promoted have been applied to PPV polymer preparation.

Also, electrochemical oxidative polymerization has been widely applied to the synthesis of conductive polymer films containing heteroaromatic and dissymmetric diheteroaromatics with ethylenic spacer [28–30].

The sulphonium route presented an opportunity to develop some novel fabrication techniques [31]. The use of soluble precursor, which is at the origin of the developments of PPV, has been extended to heterocyclic homologues. The route involving a soluble precursor is certainly very interesting for casting films or spinning fibres. Three precursor routes, namely the sulphonium precursor route, the halogen precursor route, and the xanthate precursor route have been used for synthesis of a wide range of PPV derivatives [32].

### 3. POLY(HETERO)ARYLENE VINYLENES PREPARED VIA A SOLUBLE SULPHONIUM PRECURSOR POLYMERS

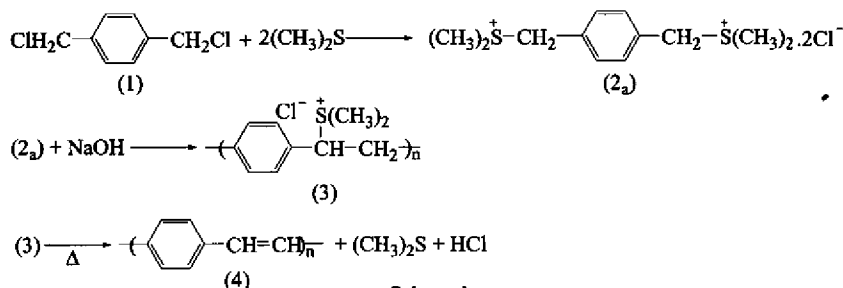
#### 3.1. PPV and its Derivatives

The synthesis of PPV is carried out in a two-stage

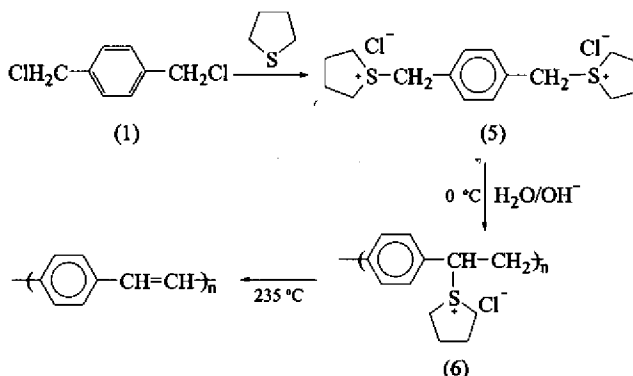
route. Initially a high molecular weight, soluble and non-conjugated precursor polymer is produced that could be easily solution-cast into films, then a thermal conversion stage is followed to obtain a final conjugated polymer [33, 34]. In this way, high molecular weight films of PPV can be prepared by a relatively simple and high yield series of reactions [33–44]. This synthesis was reported by Wessling and Zimmerman and later it was studied more in detail by Murase and Gagnon et al. [33].

The synthesis of the aryl sulphonium salt monomers (2) has been performed by the reaction of the bis(chloromethyl)arylene compound (1) with dimethylsulphide in the presence of polar solvents such as methanol, acetone, DMF or water [45]. Then the base catalyzed polymerization of *p*-xylene-sulphonium salts (2) into a water soluble sulphonium salt precursor has been carried out [12, 31, 34, 36, 46, 47]. The polyelectrolyte (3) could be processed into films, foams and fibres. The sulphonium groups solubilize the polymer in protic solvents such as water and methanol and, furthermore, they can be eliminated during the conversion into the conjugated polymer. Heating a cast film of (3) at 200 °C or 300 °C for more than 2 h resulted in a yellow, free-standing film of PPV. However, rapid heating at 220 °C provided a flexible foam structure, since at 200 °C two gaseous molecules [(CH<sub>3</sub>)<sub>2</sub> S and HCl] were being eliminated from each monomer unit (Scheme 1) [48].

A major problem in the conversion of (3) to PPV is the incomplete loss of all the sulphur and chlorine producing a polymer with sp<sup>3</sup> hybridized carbon atoms in the main chain. This reduces the overall conjugation. The optimum condition for the preparation of (3) and,



**Scheme 1**



Scheme II

in turn, for the conversion of (3) to PPV with minimum amount of sulphur has been determined by heating beyond 380 °C [49]. In the reports of Wessling et al. [31, 33, 38, 47, 50, 51] and other investigators [36, 39, 40, 52–56], the dimethyl and diethyl sulphonium salts, with either the chloride or bromide counter ions have been prepared from the reaction of the  $\alpha, \alpha'$ -dihalide of *p*-xylene with the dialkyl sulphide, and used for polymerization reactions.

Films of PPV have been prepared via pyrolysis of a water-soluble sulphonium polyelectrolyte precursor polymer (6) derived from *p*-xylylene bis (tetrahydrothiophenium chloride) (5) (THT) [27] according to the Kanbe [57] and Wessling [58] procedures, which was later modified by Lenz et al. [59] (Scheme II).

The solution of the reaction has been submitted to dialysis in order to eliminate all the under-products or non-reactant residues as well as the low-molecular-weight products ( $<10^4$ ). In the preparation of PPV, THT gives a lower pyrolysis temperature, higher polymerization rate, minimizes the side-reaction and higher polymer yield than dimethylsulphide [33, 60]. The pyrolysis of these films under an inert atmosphere in the temperature range 180–280 °C gives rise to the elimination of sulphide and halogen acid, and leads to the final product of PPV [60].

Conversion of polyelectrolyte to poly(arylene vinylene) has been followed by IR spectroscopy and thermal gravimetric analysis, TGA, and the films

change in appearance from colourless to red or yellow but remain transparent [53, 61]. The thermal elimination of dimethylsulphide and HCl proceeds via an  $E_1\text{CB}$  mechanism giving a transconfiguration of the double bond as evidenced by the strong IR absorbance at 970  $\text{cm}^{-1}$ . The thermal analysis of the elimination reaction by TGA and DSC has shown three major coinciding weight losses and endotherm transitions centered at 102 °C, 124 °C and 184 °C probably corresponding, respectively, to the loss of water and two stages of the elimination reaction. The only other defined TGA transition noted in this sample was the final decomposition point at between 575 °C and 600 °C. The residual sulphur ( $<2\%$ ) in the film indicates that some saturated units still remain ( $>90\%$  of the units are unsaturated). Further studies have been shown that by optimizing the elimination temperature, this residual sulphur can be more completely removed, and the conjugation length increases to give higher conductivities [36, 45, 53]. Molecular weight for polymer (3) has been obtained by low-angle laser scattering and was reported to be 990,000 for weight average and 500,000 for number average with a polydispersity of 2.0 [62].

Exposure of the PPV films to gaseous  $\text{H}_2\text{SO}_4$  or  $\text{AsF}_5$  has resulted in maximum conductivity of 100 and 10 S/cm, respectively [33, 36, 39, 40, 42, 53]. Further, films could be stretch oriented and conductivities after  $\text{AsF}_5$  and  $\text{SO}_3$  doping reached 2780 and

685  $\text{cm}^{-1}$ , respectively [40, 48]. Doping with iodine in either the vapour or in solution form has been resulted in no appreciable increase in conductivity [33, 12, 53, 63]. Murase and co-workers have been reported a conductivity of  $10^{-3}$  S/cm for iodine doped PPV films after orientation [42]. N-type doping with sodium naphthalide yields as  $\sigma_{\text{max}}$  of  $2 \times 10^{-4}$  S/cm. The doped material is metallic in appearance with the nature of conduction determined to be electronic [12].

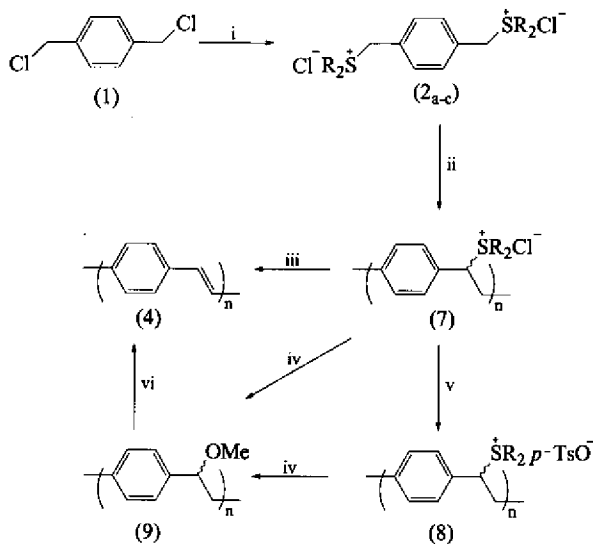
Following the doping procedure of Pron' et al. [59] for polyacetylene and poly(*p*-phenylene), the PPV films have been doped by  $\text{FeCl}_3$  in dry nitro-methane. The room temperature electrical conductivity and the final dopant content in the doped films depend on the concentration of  $\text{FeCl}_3$  in the doping solution and the doping time [64]. The conductivity of  $\text{FeCl}_3$ -doped PPV films reaches almost the same conductivity as films doped with  $\text{SO}_3$ ,  $\text{AsF}_5$ , and  $\text{H}_2\text{SO}_4$  [40].

A second precursor route where the solubilizing and leaving group is an alkoxy group, usually methoxy, has been developed and gives polymers

which are soluble in polar aprotic solvents such as chloroform, dichloromethane, and tetrahydrofuran [65] (Scheme III).

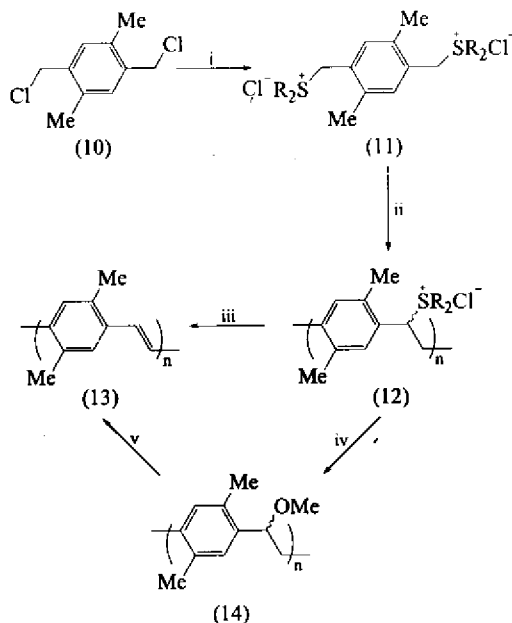
It has been shown that all the different precursor polymers give PPV. However, the structural and hence electronic properties can vary quite dramatically depending on which precursor polymer is utilized [65]. In both precursor polymer routes (sulphonium and methoxy) there is evidence for some elimination of the leaving groups, either the sulphonium leaving group by thermal elimination, or the methoxy leaving group by thermal elimination under acid catalysis. The conjugation can be seen both in the IR and  $^1\text{H}$  NMR spectra by a decrease in the signal due to the methoxy leaving group and an increase in the signals due to the conjugated units.

The sulphonium group precursor polymers have been converted into the conjugated polymers by heating thin films at typically 220–250  $^\circ\text{C}$  for 12 h under vacuum. Heat treatment of methoxy precursor polymer has given rise to a thermally stable partially



(i)  $\text{Me}_2\text{S}$ ,  $\text{S}[\text{CH}_2]_3\text{CH}_2$  or  $\text{S}[\text{CH}_2]_4\text{CH}_2$ ,  $\text{MeOH}$ , 50  $^\circ\text{C}$  [ $\text{R}=\text{Me}$  or  $\text{R}_2=(\text{CH}_2)_4$  or  $(\text{CH}_2)_3$ ]; (ii)  $\text{NaOH}$ ,  $\text{MeOH-H}_2\text{O}$ , 0  $^\circ\text{C}$ ; (iii) 220 or 300  $^\circ\text{C}$ , vacuum; (iv)  $\text{MeOH}$ , 52  $^\circ\text{C}$ ; (v),  $p\text{-TsO}^- \text{Na}^+$ ; (vi) 220  $^\circ\text{C}$ ,  $\text{Ar-HCl}$ .

Scheme III



(i)  $\text{Si}(\text{CH}_2)_3\text{CH}_2$ , MeOH,  $55^\circ\text{C}$  [ $\text{R}_2=(\text{CH}_2)_4$ ]; (ii) NaOH, MeOH-H<sub>2</sub>O,  $0^\circ\text{C}$ ; (iii)  $220^\circ\text{C}$ , vacuum; (iv) MeOH,  $52^\circ\text{C}$ ; (v)  $220^\circ\text{C}$ , Ar-HCl.

Scheme IV

conjugated precursor polymer. To prepare the fully conjugated PPV it was necessary to heat the precursor polymer at  $200^\circ\text{C}$  under flowing hydrogen chloride-argon.

The substituted PPV, made by the precursor polymer route employing sulphonium salts, has previously been reported by Wessling and Zimmerman [34]. They have reported the preparation of methyl substituted (on the *p*-phenylene ring) PPV using the same precursor polyelectrolyte sulphonium polymer procedure that they used for the parent PPV. The prepared systems contained 2,5-dimethyl- and 2,3,5,6-tetramethyl-*p*-phenylene groups.

Poly(2,5-dimethyl-1,4-phenylene vinylene) (PDMePV) has been obtained from both sulphonium and methoxy leaving group precursor polymers [65] (Scheme IV).

As expected, on electronic grounds (the two

methyl groups on the aromatic ring are inductively electron-donating), it has been observed that the reactivity of the precursors to PDMePV are indeed intermediate in reactivity between those for PPV and PDMeOPV which will be discussed later.

Studies of the 2,5-dimethyl derivatives show fairly low conductivities, after doping with  $\text{I}_2$  or  $\text{SO}_3$ , to be  $2 \times 10^{-4}$  S/cm and  $10^{-4}$  S/cm, respectively [31], and with  $\text{AsF}_5$ ,  $3.2 \times 10^{-2}$  S/cm [36].

Poly(2,5-dimethoxy-1,4-phenylene vinylene) (PDMeOPV) [53] has previously been made by the dehydrohalogenation reaction [61], and this low-molecular weight oligomer showed a conductivity of  $4.1 \times 10^{-4}$  S/cm, when doped with  $\text{AsF}_5$ .

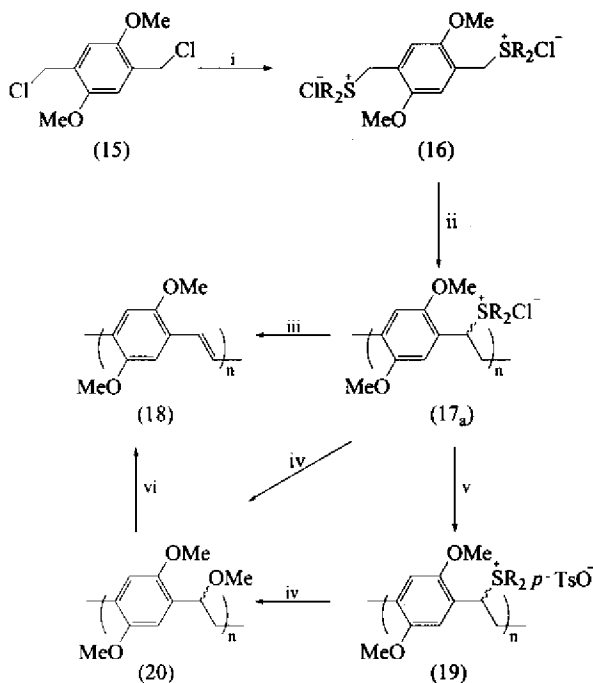
Lenz and Karasz [36], Murase [42], and Elsenbaumer et al. [53] have prepared polymer (18) by the precursor polymer route from the sulphonium polymers (17<sub>b</sub>) and (17<sub>a</sub>). The chemistry involved in

# Archive of SID

the preparation of PDMeOPV is governed by the increased reactivity of the intermediates due to the two methoxy groups attached to the aromatic ring [65] (Scheme V).

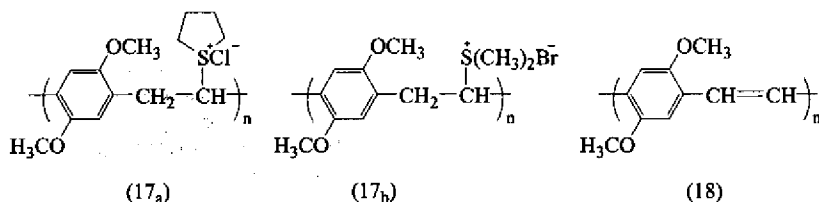
Unstability and decomposition of the bis-sulphonium salt monomer and sulphonium precursor polymer in contrast to the PPV monomer and precursor polymer are probably due to the two methoxy groups on the benzene ring activating the benzylic

positions towards substitution by nucleophiles such as water or chloride. This reactivity of the benzylic position can be utilized advantageously by taking an aqueous solution of the sulphonium precursor polymer and exchanging the chloride anion with the toluene-*p*-sulphonate anion. Unlike the PPV precursor polymer, reaction required no heating and the sulphonium precursor polymer underwent substitution at room temperature.



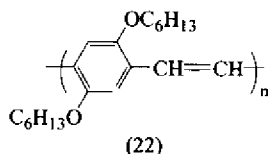
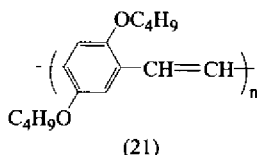
(i)  $\text{S}[(\text{CH}_2)_3\text{CH}_2]$ , MeOH, 50 °C [ $\text{R}_2=(\text{CH}_2)_4$ ]; (ii) NaOH, H<sub>2</sub>O, 0 °C or  $[\text{Bu}_4\text{N}]^+\text{OH}^-$ , MeOH, 0 °C; (iii) 300 °C, vacuum; (iv) MeOH, 25 °C; (v) *p*-TsO<sup>-</sup>Na<sup>+</sup>; (vi) 220 °C, Ar-HCl.

Scheme V



The films (18) were tough and transparent and doping with  $I_2$ ,  $FeCl_3$ ,  $SO_3$ ,  $AsF_5$ ,  $H_2SO_4$  or electrochemically gave a conducting polymer with four-probe conductivities as high as 500 S/cm [46, 53, 67]. Poly(2,5-dimethoxy phenylene vinylene) can be doped with iodine to give electrical conductivities in the order of  $10^0$ – $10^1$  S/cm [53–55, 64], while iodine doping of unsubstituted PPV, and even of poly(2,5-dimethyl phenylene vinylene) results in only weak conductivities (approximately,  $10^{-7}$  S/cm) [45–47, 53, 68, 69].

When the poly(2,5-dialkoxy-1,4-phenylene vinylene) has butoxy (21) [70] or hexyloxy (22) [71] groups as substituents, not only are the polyelectrolyte precursor polymers from which they are made soluble and processable but, because of the long-chain alkyl substitution, so are the conjugated polymers (21) and (22) themselves. When unstretched and stretch-aligned (draw ratio of 7) films have been doped with  $I_2$  the maximum conductivities were 3–4 and 200 S/cm, respectively [71].



Another route to polymer (21) has been developed by the initial replacement of the sulphonium moiety by butoxy to produce neutral polymer (24), which is now soluble in organic solvents [70]. This neutral polymer (24) can either be eliminated thermally or with a weak acid. When a strong acid has been used, the polymer (21) was produced in the doped state [70] (Scheme VI). Polymer (21) is said to be freely soluble in solvents such as chloroform, tetrahydrofuran,

chlorobenzene, nitrobenzene, and toluene.

Poly(2,5-diheptyl-1,4-phenylene vinylene) (28) has been prepared by the sulphonium salt pyrolysis procedure. Tough films of (27) have been obtained by pyrolysis of sulphonium salt precursor film (Scheme VII). The bis (sulphonium salt) from THT were unstable and gradually decomposed into bis-chloromethylated compound and THT at room temperature. Dimethylsulphide afforded the stable bis (sulphonium salt). This is attributable to steric hindrance between bulky THT and heptyl groups [46].

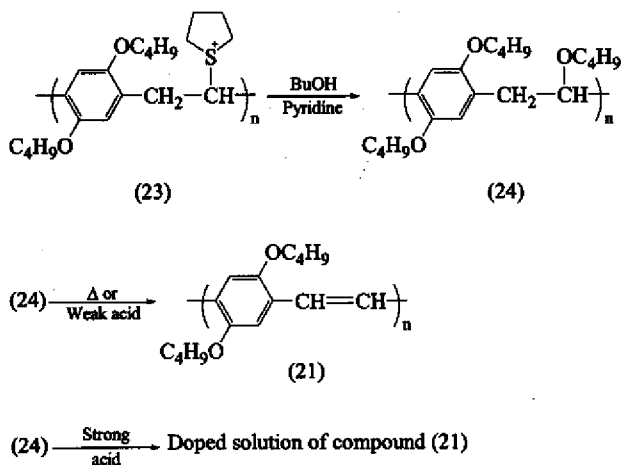
IR Spectrum of a film of poly(2,5-diheptyl-1,4-phenylene vinylene), (28) has shown the strong peak at  $963\text{ cm}^{-1}$  which is assigned to *trans* double bonds, but, it was not clear from the IR spectrum whether *cis* double bonds are present in (28). The peak of  $^1\text{H-NMR}$  spectrum at  $\delta=7.25$  and  $6.75$  have been assigned to the olefinic hydrogens of the *trans* and *cis* repeating units, respectively. The ratio of *trans* to *cis* olefinic units has been found to be 93:7 from the integrals of the peaks. This ratio is 71:29 for poly(2,5-dihexyl-1,4-phenylene vinylene) has been prepared by the McMurry's method [72]. The present data clearly indicate the sulphonium salt decomposition process is suitable for the preparation of *trans*-PPV derivatives.

The peak at  $\delta=2.77$  and the smaller one at  $\delta=2.43$  have been assigned to the arylmethylenes. The ratio of their integrals has been found to be 9:1. These two peaks should be due to two kinds of stereochemically different arylmethylenes. The possible structures are shown by structures 29 and 30. The peak at  $\delta=2.77$  is due to the regular structure and the peak at  $\delta=2.43$  can be assigned to the more crowded structure. The conjugated system would deviate from the coplanar configuration due to the steric effect of the heptyl groups. This effect causes a blue shift but is balanced with their electron-donating one, which causes a red shift.

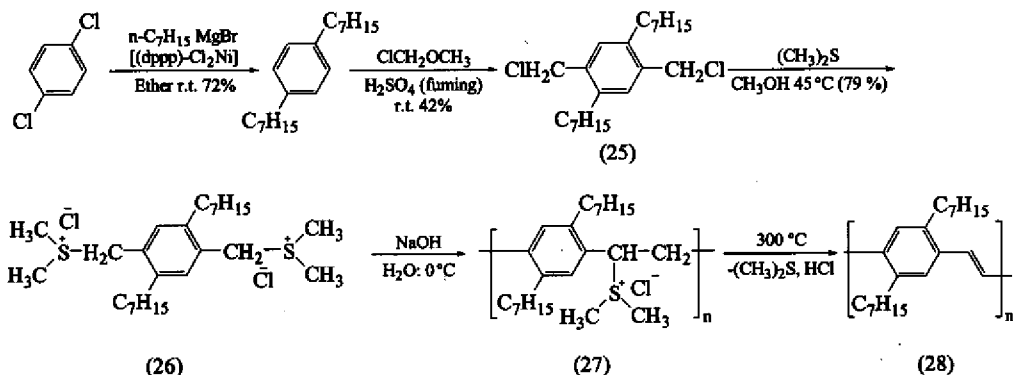
Muras and co-workers [73] have reported the synthesis of 2,5-dichloro PPV as well as its conductivity upon doping at temperature above  $350^\circ\text{C}$  with  $SO_3$  and its thermal degradation.

Synthesis of poly(2-methoxy-5-methylthio phenylene vinylene), (PMTPV) also has been reported [74] (Scheme VIII).

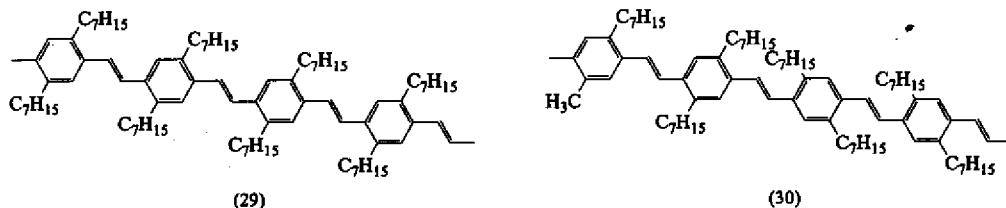


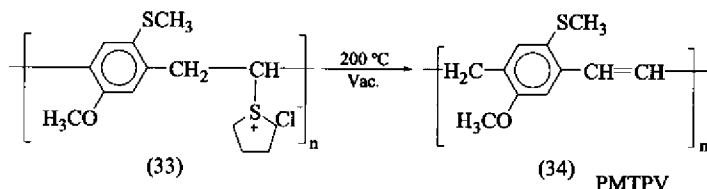
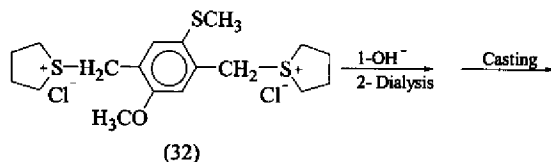
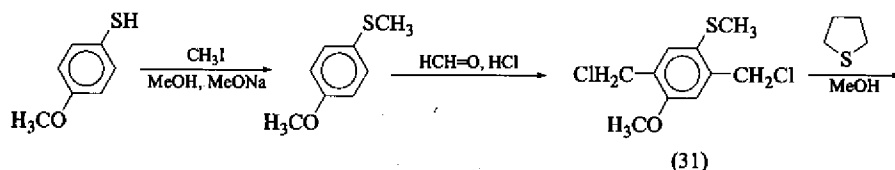


Scheme VI



Scheme VII





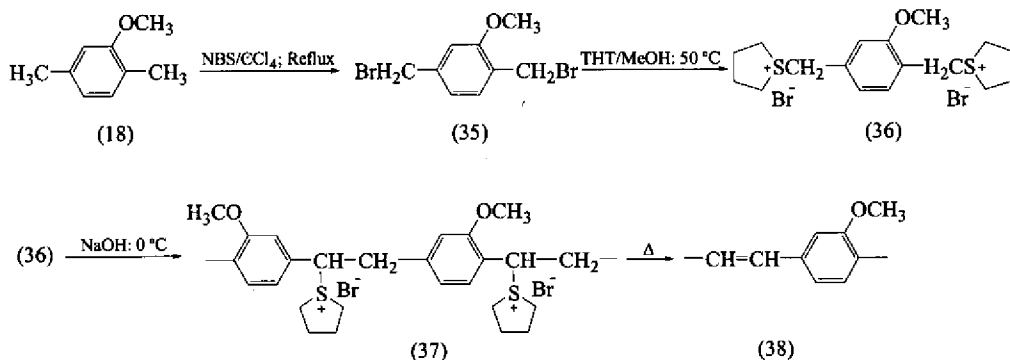
Scheme VIII

Thermal analyses of the elimination reaction of the precursor polymers of PMTPV have been studied by TG and DSC [75]. DSC analyses, however, exhibit two major endothermic processes at about 100 °C and 150–180 °C. The low temperature endotherm corresponded to the loss of water, and the higher temperature one to the elimination of THT and HCl. The weight losses above 350 °C are attributed to decomposition of the polymers [76]. FTIR Spectrum of PMTPV film is compared with that of the precursor polymer film [74]. The precursor polymer film exhibits a broad absorption at 3100–3600  $\text{cm}^{-1}$  due to absorbed water, which disappears in the spectrum of the eliminated film. A strong absorption peak appears at 968  $\text{cm}^{-1}$  after eliminated indicating that the vinylenic C=C bonds formed were entirely of *trans* configuration [33, 39, 76]. Presence of small, but sharp absorption peak at the same position, due to a premature elimination reaction occurred during film casting. UV-Vis spectra of polyconjugated polymer films of PMTPV have been compared with that of the PPV and PDMPV films. The

maxima of the longest wavelength absorption for  $\pi \rightarrow \pi^*$  transitions and the edges of these absorption have been found to be 426/519 nm for PPV, 477/596 nm for PDMPV, and 428/534 nm for PMTPV, respectively. The bathochromic shift by the two methoxy groups on the phenylene rings is significant and this can be explained by the electronic effects of the substitution [76].

The absorption maximum of poly(PMTPV-co-PPV), containing 77.6 mol % of MTPV unit is practically the same as those for PPV and PMTV. This fact strongly indicates that the presence of the methylthio substituent *para* to the methoxy group nullify the bathochromic effect of the methoxy group on the  $\pi \rightarrow \pi^*$  transitions. Absorption edge of the copolymer lies between those of PPV and PMTPV. The absorption maximum and edge of poly(MTPV-co-DMPV) containing 68.8 mol % of MTPV unit are greater than those of PMTPV, but lower than those of PDMPV, which coincide with expectations.

Undoped polymer films had conductivities less



Scheme IX

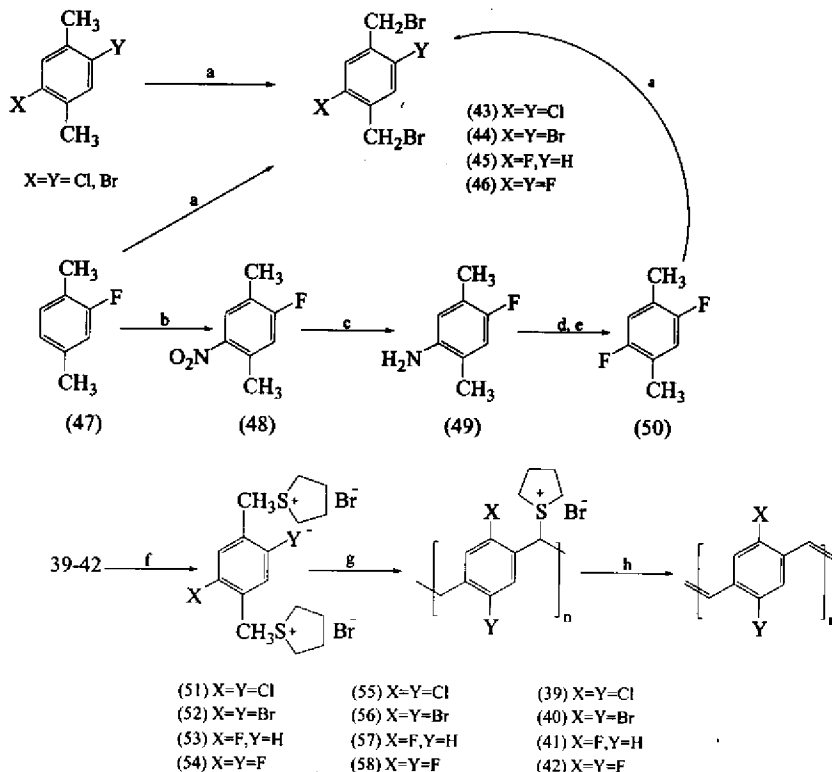
than 10 S/cm. In doping with I<sub>2</sub>,  $\sigma_{\max}$ , for oriented and unoriented polymer with drawn ratio (L/L<sub>0</sub>) 75 are measured  $1.0 \times 10^{-4}$  and  $1.2 \times 10^{-3}$  S/cm for degree of doping 3.0 and 3.1, respectively.

Synthesis of an asymmetrically substituted PPV, poly(2-methoxy phenylene vinylene) has been also reported [77]. Synthetic route for the preparation of poly(2-methoxy phenylene vinylene) (38) is shown (Scheme IX).

It has been found that the monomer salt based on a bromide counterion was less hygroscopic compared to the monomer previously used, *p*-xylene-bis(dimethylsulphonium chloride). Unlike the closely related unsubstituted and symmetrically disubstituted arylene polymers, poly(2-methoxy phenylene vinylene) and its precursor polymer are essentially copolymers in the sense that an asymmetric ring substitution and an expected random head-to-head and head-to-tail arrangement of units in the polymer chain exists. The undoped polymer is an insulator with a conductivity of less than  $10^{-11}$  S/cm for the planar isotropic, fully eliminated film. For the fully eliminated polymer films, conductivity increase of more than 10 orders of magnitude was obtained by AsF<sub>5</sub> doping, and at room temperature a value of about 100 S/cm was achieved. As a result I<sub>2</sub>-doped PMDV exhibits a lower electrical conductivity (~1.0 S/cm) than I<sub>2</sub>-doped PDMPV does.

Synthesis of the ring halogenated PPV (39–42) (Scheme X) has been reported by minor modification

of the standard soluble precursor route for them [33, 68]. Halogenation polymers are inefficient as *p*-dopable conducting polymer as Muras et al. [42] observed poor conductivity for doped samples of (39). The results have shown the general applicability of the soluble precursor strategy to the ring-halogenated PPVs. Some complications relative to the synthetic transformations in the electron-rich PPVs have been noted. Formation of the monomer precursor salts (51–54) required the use of more vigorous conditions with heated concentrated hydrobromic acid and neat THT, rather than milder use of THT in boiling methanol for parent PPV synthesis, due to the low reactivity of (43–46) in the milder conditions. The actual polymerization to polyelectrolytes (55–58) was feasible with conditions fairly similar to those for parent PPV [33, 68]. Thermal elimination of the films of (55–58) to (39–42) required optimization of heating conditions by TGA of test runs under isothermal conditions. If temperatures much exceeded 250 °C for elimination, initial rapid elimination of volatiles could be followed by dramatically drop of temperatures and very short elimination times, and so polymer degradation would be avoided, but at the cost of incomplete elimination of volatiles, as shown by the presence of residual sulphur in elemental analyses of eliminated films. The UV-vis spectra of the halogenated PPV (39–42) were blue-shifted relative to the parent PPV, suggesting an increased band gap consistent with the net electron-



(a) *N*-Bromosuccinimide/benzene or  $\text{CCl}_4$ /heat, (b) Fuming nitric acid/ $^\circ\text{C}$ , (c) 60 psi hydrogen/ $\text{PtO}_2$ /EtOH/2.5 h, (d) 48 % Fluoroboric acid/ $\text{NaNO}_2$ / $\text{H}_2\text{O}$ / $0^\circ\text{C}$ , (e) Dry pyrolysis, (f) Tetrahydrothiophene/48  $\text{HBr}_{(\text{aq})}$ , (g) 10 %  $\text{Me}_4\text{NOH}$ / $0^\circ\text{C}$ / $\text{H}_2\text{O}$ .pentane, (h) Pyrolytic vacuum elimination.

#### Scheme X

withdrawing nature of the halogenated substituents [78].

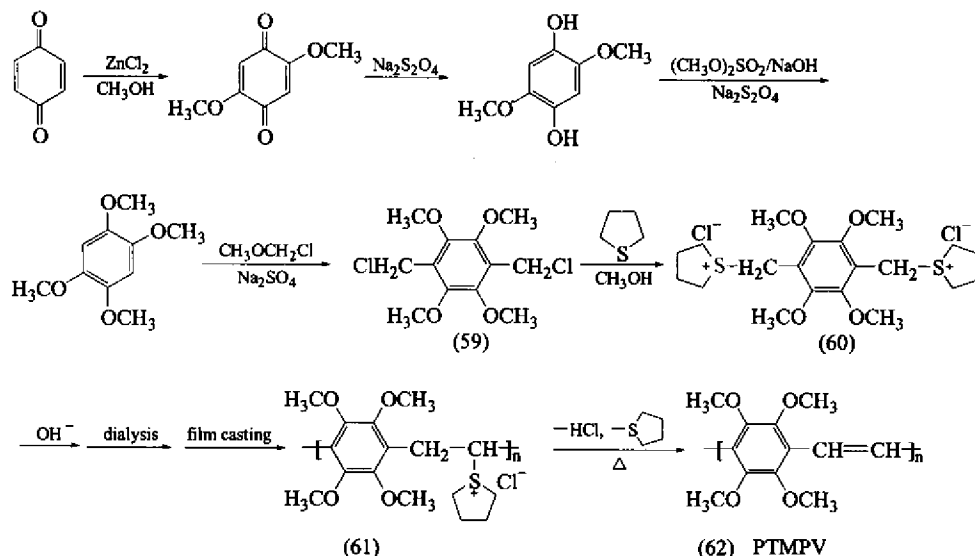
All of the PPVs have their longest wavelength absorption maxima in the range of 400–412 nm.

Poly(2,3,5,6-tetramethoxy-1,4-phenylene vinylene) (PTMPV) has been successfully synthesized via water soluble polyelectrolyte precursor (Scheme XI). Although the chloromethyl groups (59) are surrounded by two adjacent methoxy groups, its reaction with THT proceeded smoothly to give (60) in

a high yield. It is conjectured that the cyclic structure of THT makes the reaction system free from the severe steric hindrance of the four-methoxy substituents flanking the two-chloromethyl groups [79].

Table 1 summarizes the draw ratio, the degree of doping, and the maximum conductivity values obtained for the oriented as well as unoriented polymer films [79].

The synthesis of poly(2-bromo-5-methoxy-1,4-phenylene vinylene) (PBrMPV) and its copolymers



Scheme XI

has been reported [80]. One of the unsatisfactory structural features of PBrMPV and its copolymers resides in the fact that the electron withdrawing power of the bromo group is not sufficiently high. An attempt was followed to prepare poly(2-methoxy-5-nitro-1,4-phenylene vinylene)s (PMNPV). Scheme XII shows the synthetic route utilized for synthesis of PMNPV (66).

Table 1. Draw ratio, degree of doping and the maximum conductivity values for oriented and unoriented films.

Maximum conductivities of I <sub>2</sub> - and FeCl <sub>3</sub> -doped polymers [79]				
Polymer	Dopant	Draw ratio, L/L <sub>0</sub>	Deg. of doping dopant/repeat unit (I <sub>2</sub> or FeCl <sub>3</sub> /RU)	Conductivity (Scm <sup>-1</sup> )
PTMPV	I <sub>2</sub>	1	a	a
		10	a	a
	FeCl <sub>3</sub>	1	0.08	6.8×10 <sup>-4</sup>
		10	0.08	1.1×10 <sup>-2</sup>

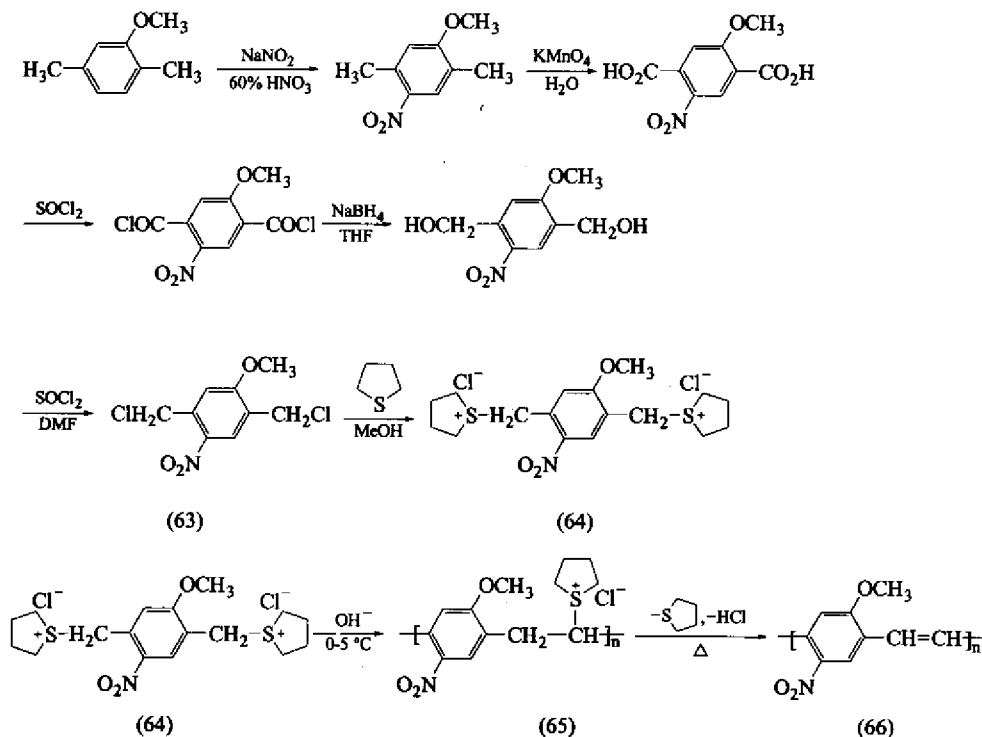
a The film was not doped even after treatment with dopant for 3 weeks.

All of the undoped polymer films had conductivities less than 10 S/cm. The maximum conductivity values and degree of doping are listed in Table 2.

By using the sulphonium precursor route, another soluble poly(2,3-diphenyl-1,4-phenylene vinylene) (DP-PPV, an isomer of PPV-DP) has been developed from bis(chloromethyl) derivative (67) [81] (Scheme XIII).

The PPVs with acceptor cyano and nitro groups on the 2,5-phenylene positions have been synthesized, as well as a "push-pull" substituted PPV derived from 2-cyano-5-methoxy-bis(tetrahydrothiopheniummethyl)-benzene dibromide [82]. It has been found that variation of substitution on PPV precursor monomers substantially affects yield and degree of polymerization to polyelectrolytes. The details for synthesis of 2-nitro-PPV and 2,6- dicyano-PPV have been reported [82].

The base-induced polymerization of 1,4-bis-(tetrahydrothiopheniummethyl)-2-cyano-5-methoxybenzene dibromide in aqueous acetonitrile has yielded a soluble polyelectrolyte (72) which may be thermally eliminated to give the electronically push-pull substi-



Scheme XII

tuted poly(2-cyano-5-methoxy-1,4-phenylene vinylene) (73) [83] (Scheme XIV).

Cyano-substituted polyelectrolytes has been given particular problems in elimination to the PPVs. Alternatively, cyano-substituted polyelectrolytes may have substantial degrees of head-to-head (H, H) and tail-to-tail (T, T) connectivity in the final polymer, making elimination to the  $-C=C-$  group at these sites unsatisfactory by comparison to elimination at the more usual head-to-tail (H, T) connectivity sites [82].

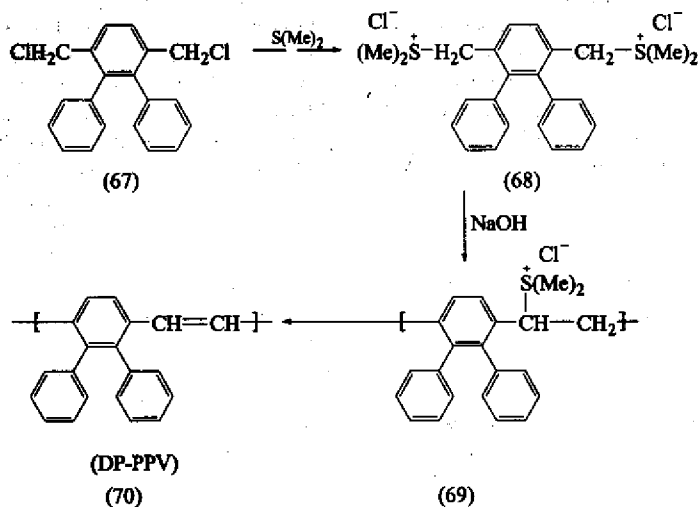
The application of the Wessling process to the synthesis of PPVs and analogues with regiospecific placement of strongly asymmetric substitution patterns may be difficult to achieve in some cases because of the possibility for production of more than one type of

polymerizable *p*-xylylene monomer under these reaction conditions. Unless overwhelmingly preferential formation or polymerization of one *p*-xylylene occurs in a reaction of this type, some degree of randomization of substituent placement can be expected to occur, forming sites which may not be

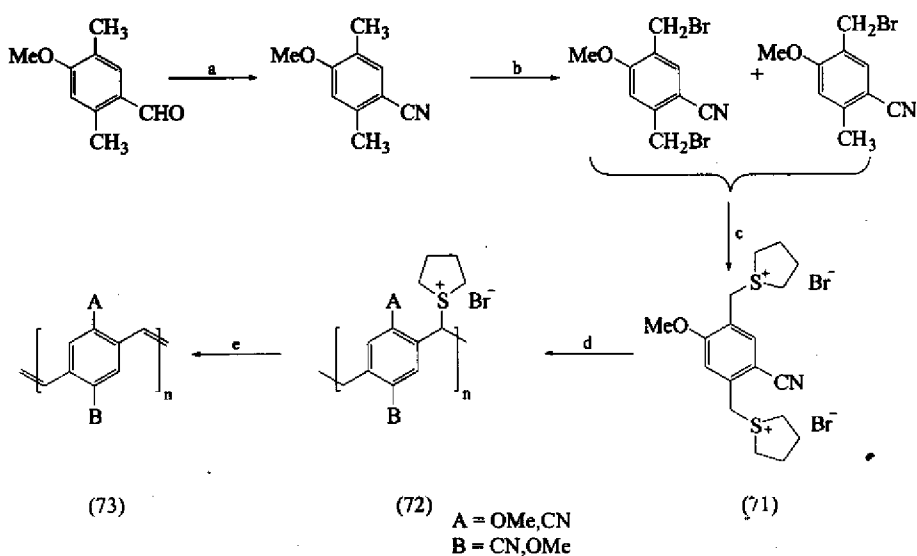
Table 2. Maximum conductivities of  $I_2^-$  and  $FeCl_3^-$ -doped PMNPV [80].

Max. conductivity ( $S\text{cm}^{-1}$ )		Degree of doping <sup>b</sup>	
$I_2^-$	$FeCl_3^-$	$I_2^-$	$FeCl_3^-$
$1.38 \times 10^{-7}$	$1.15 \times 10^{-5}$	0.07	0.14

(a) The values in parentheses are those for uniaxially stretched ( $L/L_0=5$ ) films along the stretch direction; (b)  $I_2^-$  or  $FeCl_3^-$  per average repeating unit estimated from the weight gain on doping.



Scheme XIII



Scheme XIV

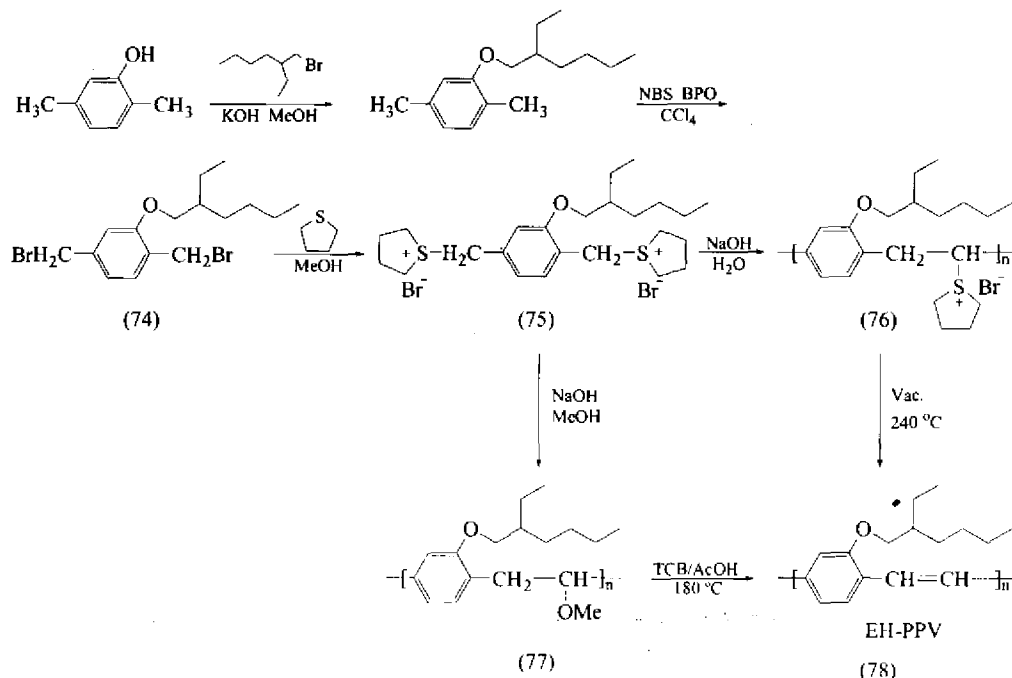
(a)  $EtNO_2$ ,  $C_6H_5NHCl$ , heat; (b)  $N$ -bromosuccinimide,  $CCl_4$ , benzoyl peroxide catalyst, heat; (c) tetrahydrothiophene, MeOH, heat; (d)  $Me_4NOH$ , 4:1  $H_2O/MeCN$ ; (e) heat, vacuum.

readily eliminated to give ethylenic units. Although these limitations need not be critical to the practical use of PPV-based materials in some applications, they should be taken into account in planning new syntheses. If complete control of substituent placement asymmetry is desired in PPV synthesis, it may prove preferable in some cases to choose synthetic routes that give lower molecular weights and less flexibility in processing, but better control of bond placement in the final products [83].

Branched monoalkyl-substituted poly[2-(2-ethylhexyloxy)-1,4-phenylene-vinylene] (EH-PPV) has been prepared in thin films via the water-soluble precursor technique and solution elimination method (Scheme XV). These precursor polymer films could be stretched up to 8 times, and the drawn films of the EH-PPV could be doped with  $I_2$  and  $FeCl_3$  to give conductivities of  $5.28 \times 10^{-3}$  and 0.56 S/cm, respectively [84].

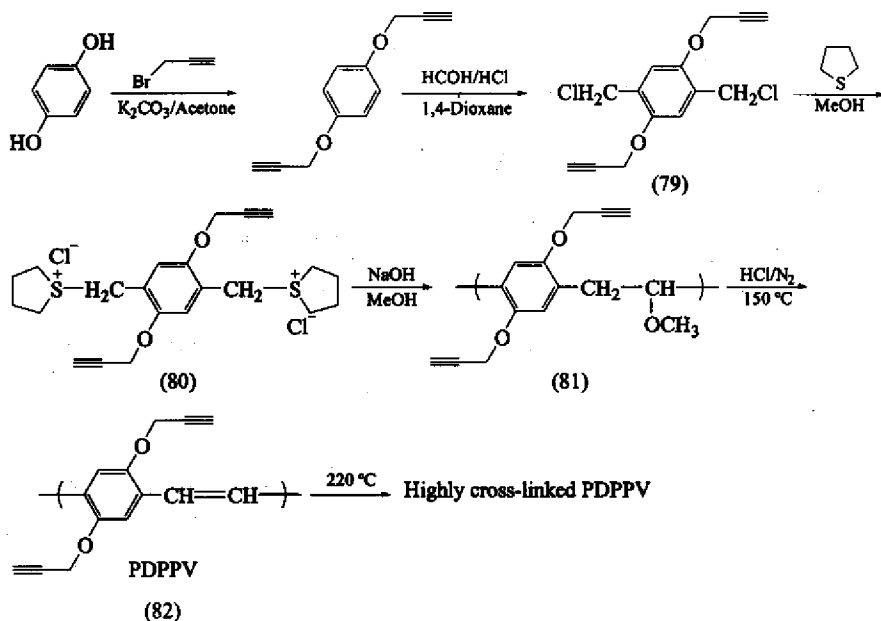
The syntheses of poly(2,5-dipropargyloxy-1,4-phenylenevinylene) (PDPPV) as thin film via the organic-soluble and water-soluble precursor routes have been described in detail [85] (Scheme XVI). Elimination and cross-linking reactions could be controlled by temperature. Cross-linked PDPPV is stable up to 450 °C. The conductivity values of undrawn and drawn  $FeCl_3$ -doped PDPPV films are  $5.0 \times 10^{-2}$  and  $2.0 \times 10^{-1}$  S/cm, respectively. Third-order non-linear optical susceptibility measurements have been studied.

Recently, syntheses of a new poly(1,4-phenylenevinylene) derivative containing Disperse Red 1 as a side chain of the phenylene ring, named poly(2-butoxy-5-(2'-ethyl [4'-(4'-nitrophenylazo)] phenyl) aminoethoxy)-1,4-phenylene vinylene) (PBDR1PV) has been reported [86] (Scheme XVII). The amino group could be used as a powerful electron donor group of dipoles and the nitro group as an electron

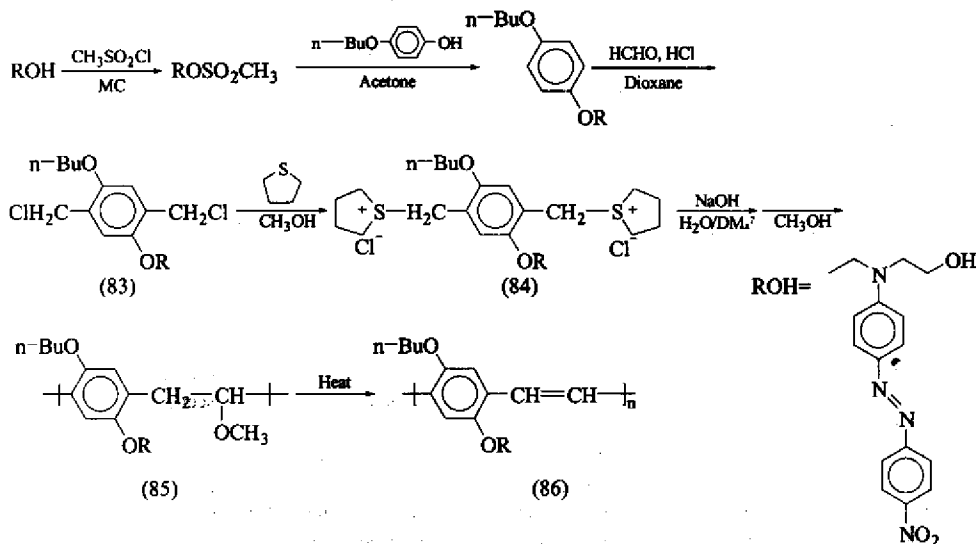


Scheme XV

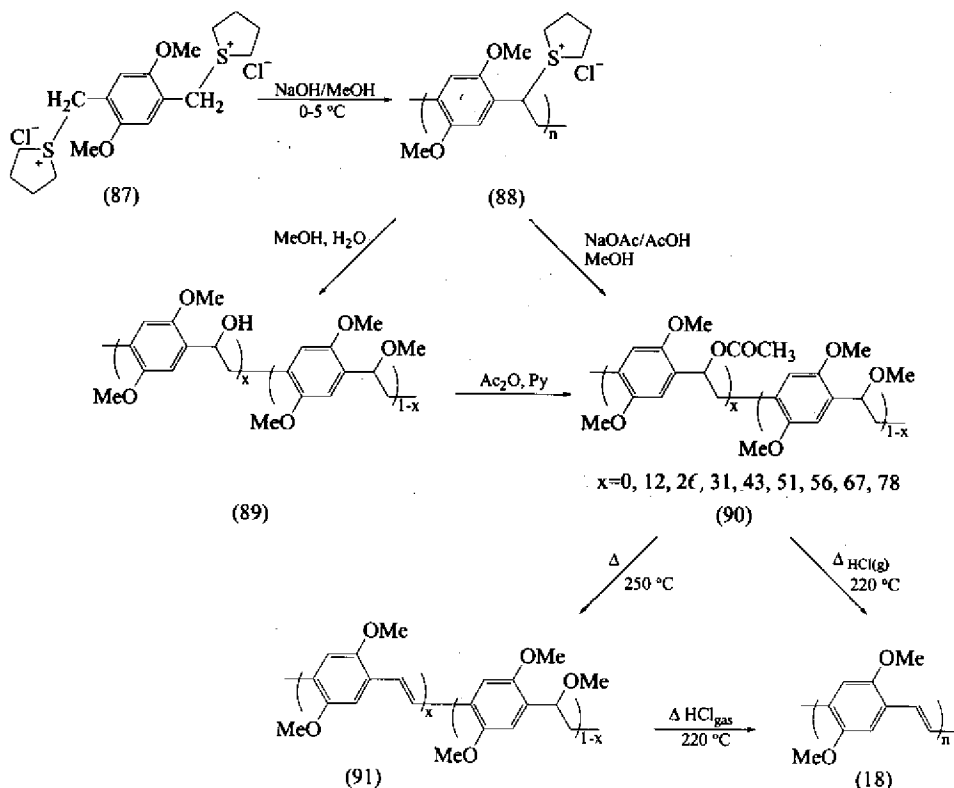




Scheme XVI



Scheme XVII



Scheme XVIII

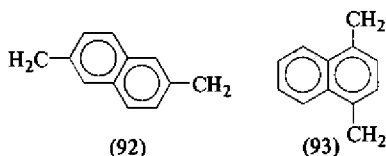
acceptor. The higher  $\beta$  value and the rigidity of the PPV backbone were expected to exhibit a large second-order non-linear optical susceptibility and temporal stability of non-linearity.

Recently, poly(2,5-dimethoxy-*p*-phenylenevinylene) (PDMeOPV) of varying conjugation length has been synthesized by selective elimination of organic soluble precursor polymers that contained two eliminable groups, namely, methoxy and acetate groups [87] (Scheme XVIII). These precursor copolymers have been in turn synthesized by competitive nucleophilic substitution of the sulphonium polyelectrolyte precursor (generated by standard Wessling route) using methanol and sodium acetate in acetic acid. The

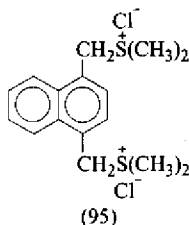
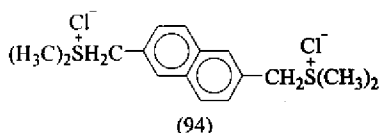
composition of the precursor copolymer, in terms of the relative amounts of methoxy and acetate groups, has been controlled by varying the composition of the reaction mixture during nucleophilic substitution. The facile elimination of the acetate groups, leaving the methoxy groups intact, permitted a controlled variation of the conjugation length, which is evident in both their UV-visible and photoluminescence spectra.

### 3.2. Poly(naphthalene vinylene)

Prior to producing the monomers, the precursors chloromethylnaphthalene (92) and (93) had to be synthesized by reaction of dimethylnaphthalene [12, 88].

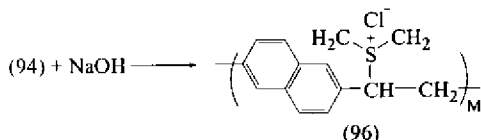


Bis-sulphonium salts of naphthalene derivatives (94) and (95) have been synthesized in good yield via the reaction of dimethylsulphide with primary naphthalenechloride under mild condition [88].

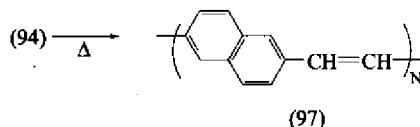


The sulphonium salts (94) and (95) are relatively unstable and undergo some degradation within 24 to 48 h with the loss of dimethylsulphide. However, their aqueous solutions are rather stable at room temperature indicating the aqueous stabilization of the pendant sulphonium ion group.

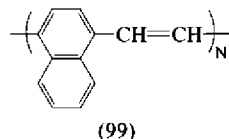
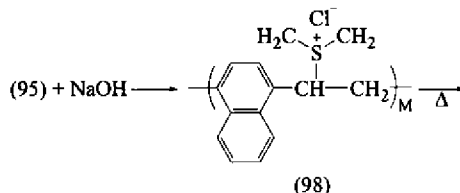
Polymerization of (94) in aqueous base gave the poly(2,6-naphthalene dimethylene- $\alpha$ -dimethylsulphoniumchloride) polyelectrolyte (96) [12, 45], which exhibited UV fluorescence presumably because of a partial base-induced elimination to form short arylene vinylene sequences in the polymers [39].



Because the mechanism of this reaction is essentially the same as that of initial step in the polymerization reaction, being apparently much slower, it is very difficult to prevent it completely [39, 53]. Heating of these films results in the elimination of  $(\text{CH}_3)_2\text{S}$  and HCl yielding PNV with the idealized structure (97).



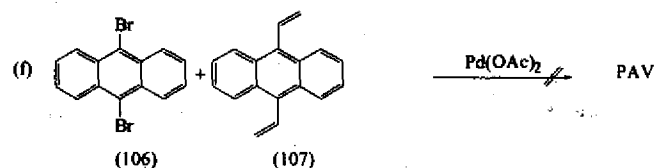
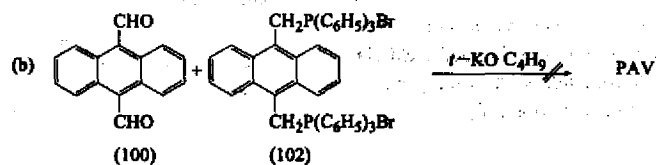
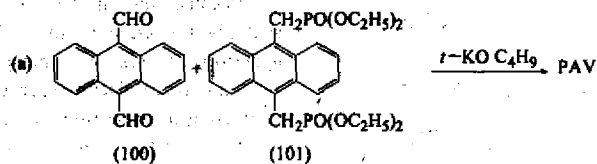
The polymer containing 1,4-naphthalene vinylene units (99), also, have been prepared by polymerization of their bis(sulphonium salts) through a base elimination reaction in solution [36, 45].

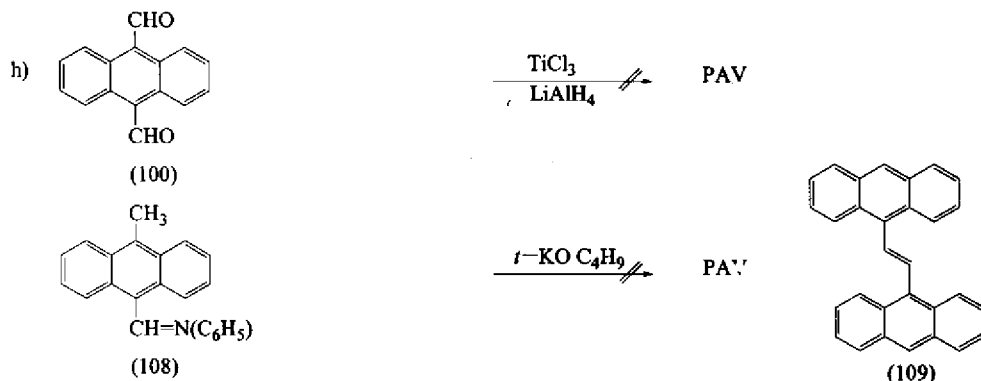


Films of this polymer was cast from aqueous solution and chemically doped with  $\text{AsF}_5$  vapour, maximum conductivity of films were  $3.2 \times 10^{-2} \text{ S/cm}$  [36].

### 3.3. Poly(9,10-anthrylene vinylene)

Some reactions for the synthesis of PPV are examined for their capability to form poly(9,10-anthrylene vinylene), (PAV), [67]. Of all the reactions (Scheme XIX) merely the Horner-Emmons modification of the Wittig (Scheme XIX<sub>a</sub>) results in structurally uniform, but very low molecular weight products ( $\bar{P}_n = 3-4$ ) other polymerization experiments led either undefined material (Scheme XIX<sub>b,c,d,h,i</sub>) or to a product in which





Scheme XIX

no polymerization took place (Scheme XIX<sub>e,f,g</sub>).

The reason for the absence of the tendency toward polymerization in all cases mentioned lies in the steric crowding at the reaction center, the C-atoms neighbouring the (108) and (109) positions, respectively, in anthracene.

Soluble oligomers with up to seven anthracene units have been synthesized [67]. The dimer, *trans*-1,2-di (9-anthryl)ethylene (109), has been known for some time [73]. It can be synthesized via Wittig or McMurry reaction from the respective reactions. The synthesis of further oligomers (trimer up to heptamer) via Wittig, Horner-Emmons, and McMurry reactions, among others, have been used.

### 3.4. Poly(4,7-benzofuran vinylene) and Poly(4,7-benzothiophene vinylene)

The reaction of bis (4,7-tetrahydrothiopheniummethyl) benzofuran dibromide with aqueous tetramethylammonium hydroxide has been lead to a water-soluble polyelectrolyte which can be film cast and thermolytically eliminated to give poly(4,7-benzofuran vinylene) (PBFV). Subjection of bis (4,7-tetrahydrothiopheniummethyl) benzothiophene dibromide to the same reaction sequence has been given poly(4,7-benzothiophene vinylene) (PBTv) [89] (Scheme XX). These systems are pi-isoelectronic with PNV, but

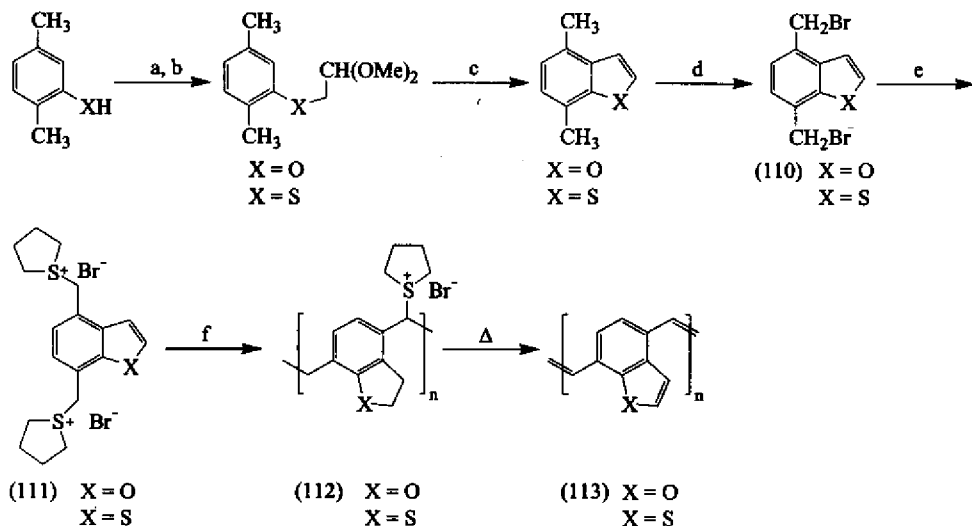
incorporate heteroatom-containing pseudoaromatic fused rings, and so after wider possibilities for functionalization than those of PNV itself.

Thermal elimination of the precursor polymers to PBFV and PBTv was readily accomplished within 6–8 h at 250–270 °C. IR and UV-vis spectroscopy demonstrated the conjugation obtained in the final eliminated polymers. UV-Vis studies show that PBFV has a band gap of 2.76 eV, while PBTv has a band gap of 2.92 eV, which are somewhat smaller than the band gap of PPV itself ca. 3.1 eV.

### 3.5. Poly(2,5-thienylene vinylene)

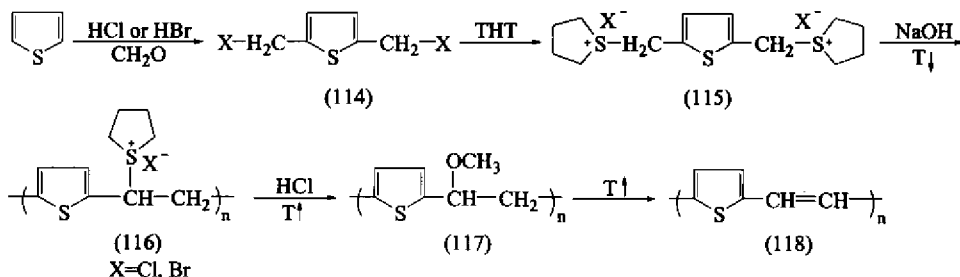
PTV is conjugate polymer regarded as an alternating copolymer of thiophene and acetylene. In 1986, Kosmehl [39,90] reported the synthesis of PTV using a Wittig condensation reaction. This procedure formed intractable, low molecular weight polymer with low conductivities. Then in 1987, the facile preparation of high molecular weight PTV via a processible precursor polymer and its oxidative behaviour has been reported [14, 91].

PTV film has been prepared according to a modified Kanbe [50] and Wessling [34] processability of PTV can be improved by an adaptation of the synthesis, leading to a methoxy precursor which can be converted to the final conjugated polymer by



(a) NaOEt/EtOH; (b) BrCH<sub>2</sub>-CH(OMe)<sub>2</sub>, reflux; (c) P<sub>4</sub>O<sub>10</sub>-H<sub>3</sub>PO<sub>4</sub>, heat; (d) *N*-bromo-succinimide, CCl<sub>4</sub>, reflux; (e) MeOH, tetrahydrothiophene, 50 °C, 48 h; (f) Me<sub>4</sub>NOH (aq.), 0 °C, 1 h.

Scheme XX



Scheme XXI

reaction with strong acid at room temperature. Synthesis route to poly(thienylene vinylene) through methoxy precursor polymers is shown in Scheme XXI [92]. Although a precursor polymer soluble in DMF was obtained, partial elimination of the sulphonium salt group during polymerization could be avoided. Rapid heating of the cast prepolymer results in low density foams of PTN while gentle warming with a slow increase in temperature results in more dense

shine gold films.

These films were stable and flexible, which were converted to highly conducting tough films on iodine doped [91]. Undoped films exhibit low levels of conductivity ( $10^{-6}$ – $10^{-5}$  S/cm) much like *trans*-polyacetylene [93]. A remarkably rapid conducting increase was observed on exposure of 25 μm thick films of PTV to different oxidizing dopants (Table 3). Air exposure causes a significant rise in conductivity

**Table 3.** Conductivities of doped PTV [93].

Dopant	$\sigma_{\text{room temperature}} (\text{ohm.cm})^{-1}$
I <sub>2</sub>	62
NOSbF <sub>6</sub>	25
FeCl <sub>3</sub>	56
NaPF <sub>6</sub> <sup>a</sup>	37
Air	10 <sup>-4</sup>

(a) Electrochemical oxidation.

[14] ( $10^{-4}$  to  $10^{-3}$  S/cm). The doped film was very stable in air; this conductivity was retained for more than a month.

### 3.6. Poly(2,5-furylene vinylene)

Kossmehl et al. [94] have reported the synthesis of poly(2,5-furylene vinylene), (PFV), using a condensation reaction. Only low molecular weight intractable polymers were formed which reached low conductivities on doping ( $10^{-3}$ – $10^{-2}$  S/cm).

The facile synthesis of high molecular weight, free-standing films of PFV by a similar route to that used to prepare PTV (Scheme XXII) has been reported [13]. The elimination of HCl and THT (or dimethylsulphide) occurred less readily from the precursor of PFV than from that of PTV.

A remarkably rapid conductivity increase was observed on exposure of 10–15  $\mu\text{m}$  thick films of PFV to different oxidizing dopants (Table 4) [13].

Undoped films exhibited low levels of

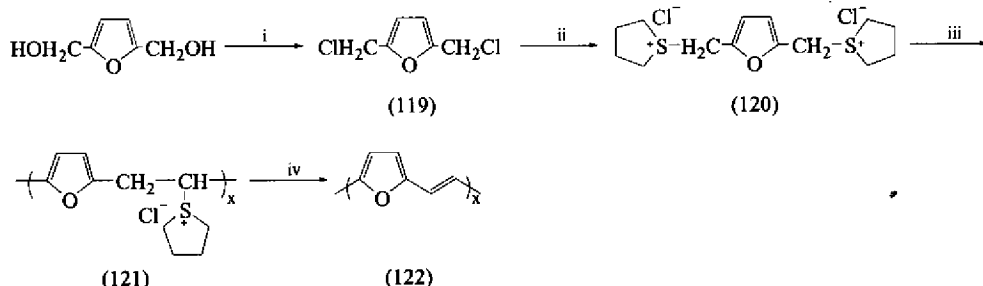
conductivity ( $\sim 10^{-2}$ – $10^{-6}$  S/cm) much like *trans*-polyacetylene [95]. Air exposure caused a significant rise in conductivity, which saturated at  $10^{-4}$  to  $10^{-3}$  S/cm [13]. PFV also was prepared by thermal treatment of films cast from THF or CH<sub>2</sub>Cl<sub>2</sub> solution of methoxy precursor polymer. Scheme XXIII summarizes the variation steps [92, 96].

In this method, the Wohl-Ziegler halogenation of 2,5-dimethylfuran is explored, which is a relatively unknown approach [97]. The Wohl-Ziegler reaction is also applicable to other methyl furan derivatives [98].

The resulting PFV film was either vapour-doped by smoking sulphuric acid or iodine, or dip-doped by iron trichloride in nitromethane. The maximum obtained conductivity in function of doping time is given in Table 5 together with the conductivity which remained as the samples were kept in loosely capped under laboratory condition for 14 days.

### 3.7. Poly(*p*-phenylene vinylene) Copolymers

Several investigations have examined the possibility of combining the different physical properties of copolymerizing the known producing methods [15, 41, 76, 74]. A series of copolymer containing both PPV and 2,5-dimethoxy-PPV units have been prepared in high molecular weight by a two-stage route [33, 14, 34], and these also had electrical conductivity ranging from 300–400 S/cm when doped with I<sub>2</sub> [34]. Moreover, the conductivity of the I<sub>2</sub>-doped films along the polymer chain direction can be



(i) SOCl<sub>2</sub>–CHCl<sub>3</sub>–pyridine; (ii) tetrahydrothiophene (excess)–MeOH, room temp.; (iii) OH<sup>−</sup> (aq., 1 equiv.), 0 °C, argon; (iv) heat to 60 °C; then to 150 °C under reduced pressure.

**Scheme XXII**

**Table 4.** Conductivities of doped poly(2,5-furylene vinylene) films [13].

Dopant	Conductivity (S/cm)
I <sub>2</sub>	36
FeCl <sub>3</sub>	25
Electrochemical (PF <sub>6</sub> <sup>-</sup> )	4
Air	10 <sup>-4</sup>

greatly enhanced if the precursor films are uniaxially drawn during the second stage thermal elimination reaction [99].

Synthetic methods for PMTPV copolymers have been reported, which is the same as shown earlier for the homopolymer PMTPV [56] (Scheme XXIV).

Copolymers containing either 1,4-phenylene vinylene or 2,5-dimethoxy-1,4-phenylene vinylene units combined with 2,5-thienylene vinylene units were prepared in film form from precursor polymer films of the respective sulphonium salt polymers which, in turn, were synthesized by the copolymerization of the respective bis (sulphonium salt) monomers. The structures of the monomers and copolymers prepared and characterized are shown in (Scheme XXV) [15].

The solution viscosities show that reasonably high molecular weights were obtained in the polymerization reaction. Although the copolymerization mechanism is not yet clear, it appears that thiophene

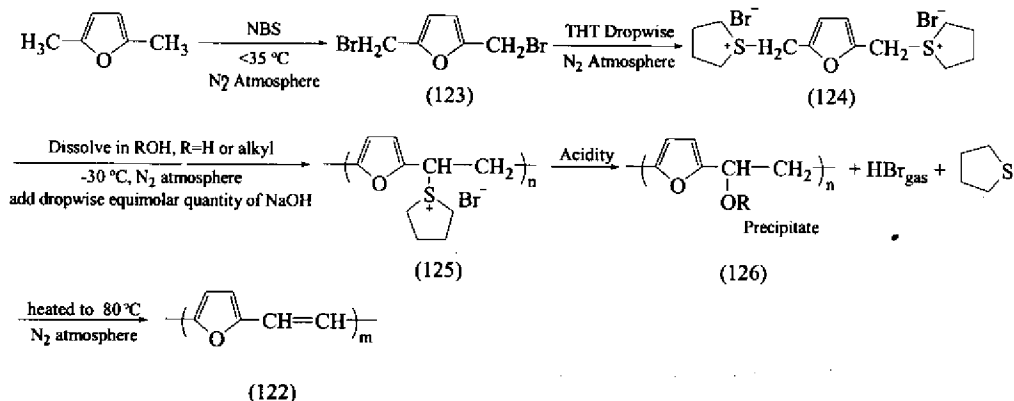
**Table 5.** Maximum conductivity ( $\Omega^{-1}\text{cm}^{-1}$ ) and corresponding doping time (min) of precursor made PFV films together with rest conductivity after 14 days [92].

Dopant	Maximum conductivity ( $\Omega^{-1}\text{cm}^{-1}$ )	Corresponding doping time (min)	Conductivity after 4 days ( $\Omega^{-1}\text{cm}^{-1}$ )
FeCl <sub>3</sub>	6	3	1
I <sub>2</sub>	20	4	$\leq 10^{-5}$
Smoking H <sub>2</sub> SO <sub>4</sub>	14	1	0.01

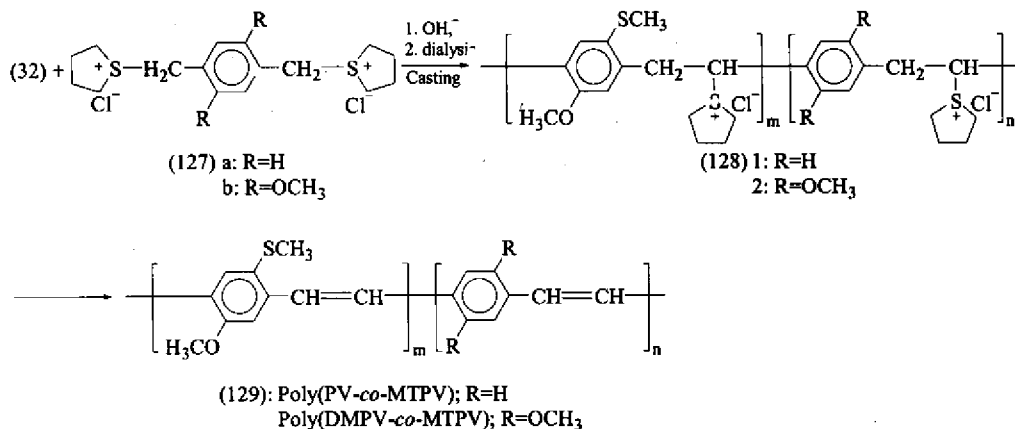
based monomer may have an inherent termination and/or chain transfer reaction in its polymerization, which limits the molecular weight attainable.

On doping with I<sub>2</sub> the copolymer films became black and highly electroconductive, as shown by the data in Table 6 [15]. The higher the content of the thiophene units in the copolymers (131<sub>a</sub>), the higher conductivity was obtained. In general, the oriented films displayed higher conductivities along the stretch direction than did the unoriented films. The iodine-doped films of the copolymers (131<sub>b</sub>), both oriented and unoriented, are even more highly conductive than the corresponding doped films (131<sub>a</sub>).

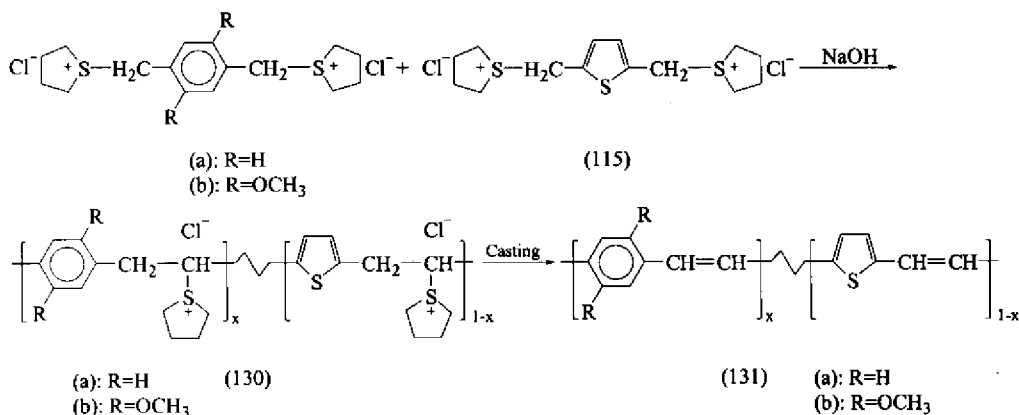
Thermal analyses of the elimination reaction of the precursor copolymer (130<sub>a</sub>) to poly(1,4-phenylene-co-2,5-thienylene) (131<sub>a</sub>) by TG and DSC indicated that major weight losses have occurred at two

**Scheme XXIII**





Scheme XXIV



Scheme XXV

different temperatures, at about 100 °C and 190 °C [74]. The low temperature endotherm in the DSC curve corresponded to the loss of water, and the higher temperature endotherm to the elimination of HCl and thiophene. The film of the copolymers (131) has exhibited a strong IR absorption at 965 cm<sup>-1</sup>, indicating that the vinylenes C=C bonds formed in the elimination were entirely of the *trans* configuration. A premature elimination reaction probably has occurred during film casting of the precursor copolymers

(131<sub>2</sub>). The IR spectrum of one of the precursor copolymers has sharp absorptions at 3022 cm<sup>-1</sup> and 950 cm<sup>-1</sup>, which correspond to the stretching mode and the out-of-plane bending mode of *trans*-vinylenes C-17 groups, respectively.

These absorption bands must result from the preliminary elimination of HCl and THT to form vinylenes structure during film casting, as suggested above. The precursor and the final polymers show sharp C-C stretching absorptions at 1660 and 1514 cm<sup>-1</sup>. The

**Table 6.** Conductivities of the iodine-doped copolymer films 131 [15].

Copolymer		Draw ratio <sup>a</sup> $L/L_0$	Colour of film after doping	Max. doping level in 1 atom/structural unit	Max. <sup>b</sup> conductivity (S/cm)
131 <sub>a</sub>	PPV <sup>c</sup>	1	yellowish green		$10^{-5}$
	CP-3	1	dark red		1.0
		5			20
	CP-4	1	dark red	1.1 (13) <sup>d</sup>	0.7
		6.5			14
	CP-10	1	red	0.43 (7) <sup>d</sup>	0.2
		6			0.3
	CP-20	1	light red	0.075 (3) <sup>d</sup>	0.1
131 <sub>b</sub>		6			0.02
	MeO-PPV <sup>c</sup>	1	dark red		40
	MeO-CP-10	1	dark red		80
		2.1			120
	MeO-CP-20	1	dark red		60
		1.5			85

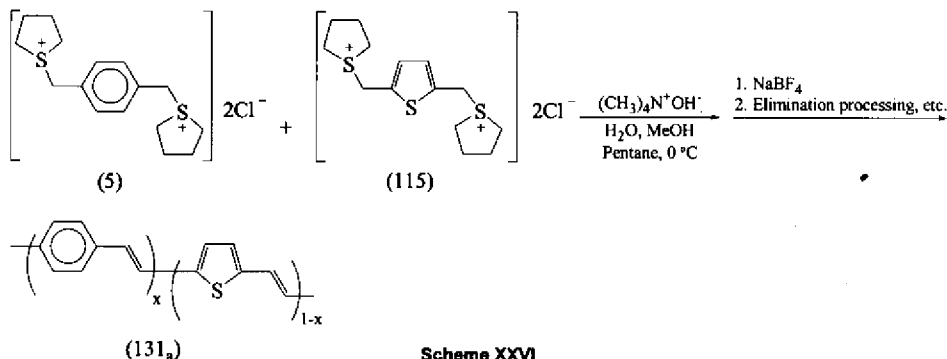
(a)  $L_0$  and  $L$  are the lengths of the film before and after orientation; (b) Maximum conductivity achieved before the film was exposed to air; (c) Homopolymers; (d) Days required to reach the maximum doping levels are given in brackets.

first of these originated from thiophene rings and the second from benzene rings. The final polyconjugated polymer clearly showed an absorption at  $837\text{ cm}^{-1}$  for the out-of-plane bending mode of O-H groups in the phenylene ring, and another at  $809\text{ cm}^{-1}$  due to the same type of bending vibration of C-H in the thienylene rings.

The copolymer series poly(PV-co-XTV) have been prepared by using a modified Wessling process

(Scheme XXVI) and have been fully described elsewhere.

The conductivity of the poly(PV-co-TV) system is dependent on the size of the block of contiguous PTV repeat units. Iodine doping, and the associated high levels of conductivity, does not occur unless the bulk sample's oxidation potential is lowered by an interchain correlation provided by at least four TV systems. A substantial increase in

**Scheme XXVI**

parallel conductivity was observed for poly(PT-co-TV) copolymers that were uniaxially oriented by drawing as anticipated. The lower net increase in conductivity for copolymers with lower TV content could be a function of the higher oxidation potentials due to the shorter (fewer than four TV units) interchain TV correlation. Alternatively, the lower net increase in conductivity could be a reflection of the lower *p*-interaction TV correlation that is expected from copolymers with low PTV content. For poly(PV-co-TV), however, a noticeable diminution of the effects of orientation on conductivity was observed. This suggests that the interchain correlation of TV segments is important in uniaxially drawn samples, where drawing results in molecular orientation but not in crystallite lateral packing or registered TV segments; these latter two arrangements attenuate the effect of orientation on conductivity, especially for copolymers with low TV content.

The copolymers containing both unsubstituted (1,4-phenylenevinylene, PV) and 2-methoxy-1,4-phenylenevinylene (MPV) units have been prepared in thin films from their water-soluble sulphonium salt precursor polymers [95] (Scheme XXVII).

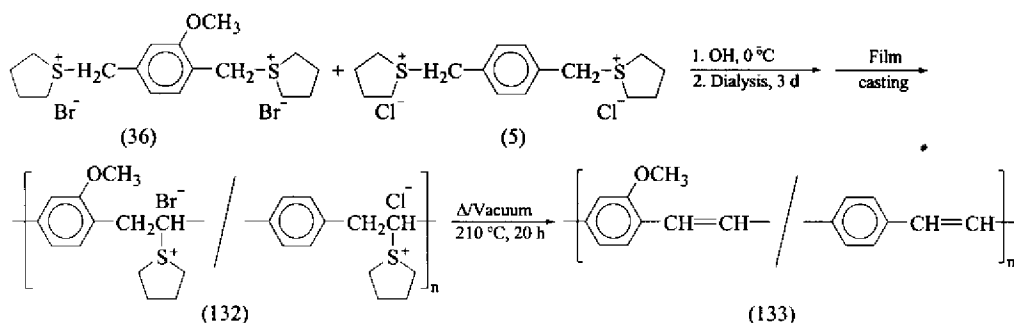
The degree of monomer conversions (55–75%) to the precursor polymers and the polymer yields (17–40%) after dialysis is comparable to those reported for other similar polymerization systems [100]. All the precursor polymer films cast from aqueous solutions appeared homogeneous and transparent. They could be oriented by drawing before or during the final elimination process. Symmetrically ring-

substituted PDMPV could not be drawn, whereas asymmetrically ring-substituted PMPV could be drawn up to a draw ratio of 6. The content of the MPV units incorporated in the copolymers was significantly higher than that in feed, suggesting that the MPV monomer is more reactive than the PV monomer.

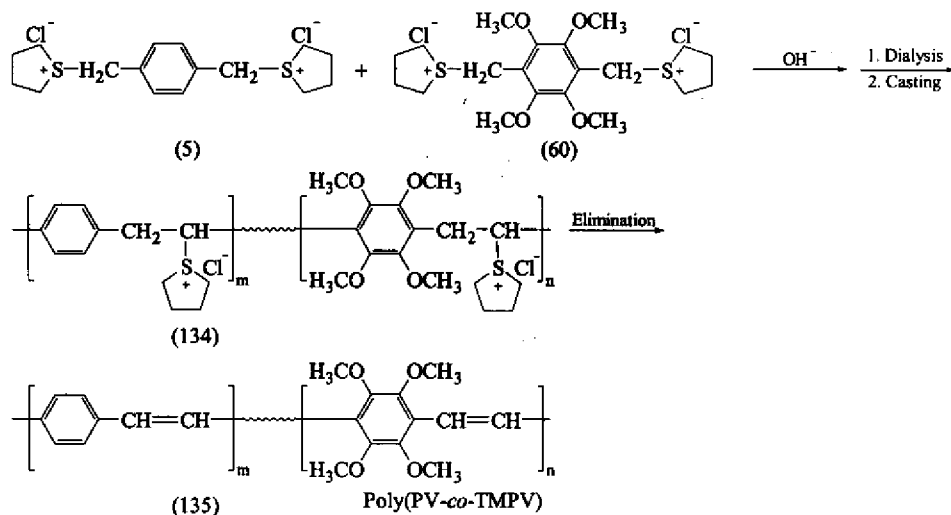
Thermal analyses of the elimination reaction of the precursor homopolymer by TGA and DSC with a heating rate of 10 °C/min have indicated that major weight losses occur at two different temperatures, at about 100 °C and 190 °C. The low temperature endotherm in the DSC curve corresponds to the loss of water, and the higher temperature one to the elimination of HCl and tetrahydrothiophene. The conductivity of FeCl<sub>3</sub>-doped copolymer films has ranged from 10<sup>0</sup> to ca. 10<sup>2</sup> S/cm depending on the composition. The conductivity gradually decreases with decreasing temperature.

Random copolymers containing both 2,3,5,6-tetramethoxy-1,4-phenylene vinylene and 1,4-phenylene vinylene units have been successfully synthesized via water soluble polyelectrolyte precursors [81]. Synthetic route to poly(PT-co-TMPV) are shown in Scheme XXVIII. The content of TMPV units-incorporated the copolymers is consistently and significantly higher than those in the monomer feed mixtures, suggesting that the reactivity of TMPV monomer (60) is greater than unsubstituted PV monomer and the presence of electron-donating methoxy groups in structure (60) facilitates chain propagation.

Table 7 summarizes the draw ratio for the degree



Scheme XXVII



Scheme XXVIII

Table 7. Maximum conductivities of  $\text{I}_2^-$  and  $\text{FeCl}_3$ -doped polymers [81].

n-Poly(PV-co-TMPV)	Dopant	Draw ratio, $L/L_0$	Degree of doping of dopant/repeat unit ( $\text{I}_3^-$ or $\text{FeCl}_4^-$ RU)	Conductivity ( $\text{Scm}^{-1}$ )
75-poly(PV-co-TMPV)	$\text{I}_2$	1	a	a
		10	a	a
	$\text{FeCl}_3$	1	0.07	$9.8 \times 10^{-4}$
		10	0.10	$2.0 \times 10^{-1}$
37-poly(PV-co-TMPV)	$\text{I}_2$	1	0.11	$7.2 \times 10^{-4}$
		10	0.13	$5.2 \times 10^{-2}$
	$\text{FeCl}_3$	1	0.14	$9.5 \times 10^{-2}$
		10	0.27	11
13-poly(PV-co-TMPV)	$\text{I}_2$	1	0.09	$2.9 \times 10^{-2}$
		10	0.13	$5.2 \times 10^{-1}$
	$\text{FeCl}_3$	1	0.16	38
		10	0.40	$7.2 \times 10^2$
12-poly(PV-co-TMPV)	$\text{I}_2$	1	0.06	$9.8 \times 10^{-3}$
		10	0.11	$3.7 \times 10^{-1}$
	$\text{FeCl}_3$	1	0.14	6.3
		10	0.31	$6.3 \times 10^2$
6-poly(PV-co-TMPV)	$\text{I}_2$	1	a	a
		10	a	a
	$\text{FeCl}_3$	1	0.06	19
		10	0.09	$4.2 \times 10^2$

(a) The film was not doped even after treatment with dopant for 8 weeks.

of doping, and the maximum conductivity values obtained for the oriented as well as unoriented polymer films.

Thermal analyses of the elimination reaction of PTMPV (62) and 13-poly(PV-co-TMPV) have been studied by DSC and TG. DSC thermograms exhibit two major endothermic processes at about 110 and 150 °C. The low temperature endotherm corresponds to evaporation of absorbed water, and the higher temperature endotherm to the elimination of THT and HCl. A major weight loss up to about 130 °C is mainly due to the loss of absorbed water, and elimination of THT and HCl occurs from 130 to about 230 °C [81]. The FTIR spectra of PTMPV, 75-poly(PV-co-TMPV) and 12-poly(PV-co-TMPV) has been compared. All of them reveal a strong absorption at 964 nm due to the out-of-plane bending vibration of *trans*-vinylene C-H band and another absorption at 882 cm<sup>-1</sup> that is known to be due to the *cis*-vinylene C-H out-of-plane bending mode [94]. With increasing the content of TMPV moieties in the copolymers increase the amount of *cis*-vinylene structure. The presence of four methoxy groups on the phenylene rings certainly restricts conformational rotation around C-C bonds of incipient vinylenes groups being formed during the elimination process and, thus, brings about the formation of *trans*-as *cis*-vinylene groups; and the *cis*-vinylene structure. Once formed, it is not easily isomerized to the *trans*-vinylene structure even at an elevated temperature [81].

UV-Vis spectra of thin films of PTMPV and copolymers have been presented. The profile of the absorption spectra and the maximum absorption positions of these polymer films are similar to those of PPV [33]. It is well known that the bathochromic shift by the two electron-donating methoxy groups on the phenylene ring in PDMPV is significant [101]. But, contrary to the expectations of the present PTMPV and copolymers they are slightly, but definitely shifted to shorter wavelength relative to PPV. This suggests that four methoxy groups in the TMPV unit reduce the effective  $\pi$ -conjugation between the phenylene and vinylenes units. Molecular model clearly demonstrates that methoxy oxygens are in too close proximity to vinylenes protons if the phenylene

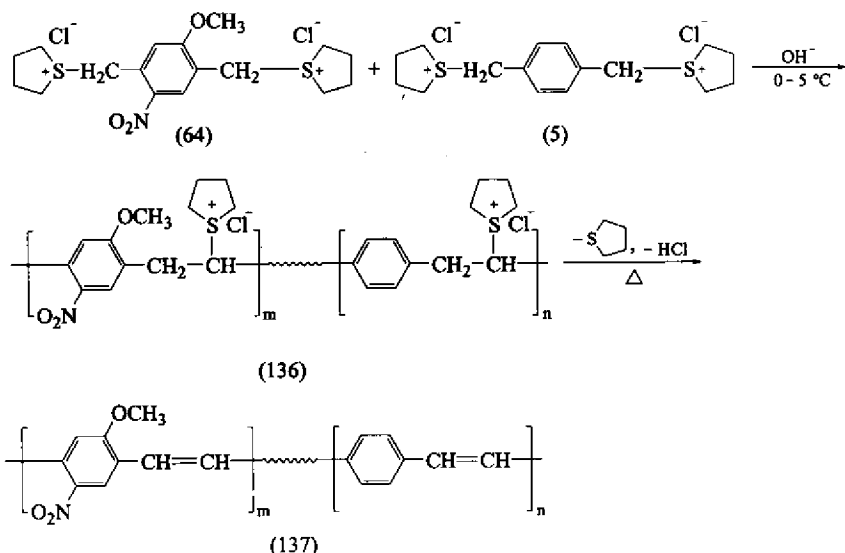
and vinylenes units were assumed to be coplanar. To avoid such steric crowding the phenylene rings have to twist around to a certain degree in relation to each other and the  $\pi$ -system loses the coplanar overlapping and would diminish the effective  $\pi$ -delocalization, resulting in a blue shift in the UV-vis spectra.

The synthesis of poly(2-bromo-5-methoxy-1,4-phenylene vinylene), (PBrMPV), and its copolymers containing, PV units has been reported [80]. Attempts to prepare poly(2-methoxy-5-nitro-1,4-phenylene vinylene), (PMNPV), and a series of poly(1,4-phenylene vinylene-co-2-methoxy-5-nitro-1,4-phenylene vinylene)s [poly-(PV-co-MNPV)s] have been prompted. It was previously demonstrated [102] that PPV copolymer containing comonomer units having a nitro substituent on the phenylene ring could be synthesized by a slightly modified synthetic method. This polymer could be synthesized via the water-soluble polyelectrolyte precursor route. Scheme XXIX shows the synthetic route utilized for synthesis of poly(PV-co-MNPV)s.

The monomer (64) retards the chain propagation or facilitates chain termination or both. However, earlier it was observed that the presence of the electron-withdrawing nitro (NO<sub>2</sub>) group not only reduces the reactivity of the bis-sulphonium salt monomer, but also causes a significant decrease in the molecular weight of the obtained copolymers. The maximum conductivity values and degree of doping are listed in Table 8. Uniaxial stretching of polymer films increased conductivity further due to improved chain orientation and, thus, interchain contacts.

Thermal analyses of the elimination reaction of the precursor polymers of 55-poly(PV-co-MNPV) and 35-poly(PV-co-MNPV) by TGA and DSC indicate that two major weight losses occur from about 80 to 140 °C and again from about 150 to 200 °C. The low-temperature endotherm on the DSC thermogram corresponds to the loss of absorbed water, and the higher temperature endotherm corresponds to the elimination of THT and HCl. Preliminary tests suggested that the elimination reaction at higher temperature may lead to considerable side reactions, resulting in lower electrical conductivity after doping.

Too severe thermal treatment of precursor polymer films at a higher temperature can lead



Scheme XXIX

adverse side reactions of vinylene groups, resulting in disappearance of vinylene C=C bonds [61].

The FTIR spectrum of a copolymer containing 35 mol % of MNPV units, 35-poly(PV-co-MNPV) has been compared with the corresponding precursor film. The precursor polymer film has exhibited a very broad and strong absorption at 3100–3700  $\text{cm}^{-1}$  due

to the presence of absorbed water, which disappears in the spectrum of the eliminated film. A strong and sharp absorption peak appears at 960  $\text{cm}^{-1}$  after elimination, indicating that the vinylene C=C bonds formed have the *trans* configuration [103]. This absorption is known to be characteristic of the *trans*-vinylene C–H out-of-plane bending mode. The IR

Table 8. Maximum conductivities of  $\text{I}_2$ - and  $\text{FeCl}_3$ -doped poly(PV-co-MNPV) [80].

Polymer	Maximum conductivity ( $\text{Scm}^{-1}$ )		Degree of doping <sup>b</sup>	
	$\text{I}_2$	$\text{FeCl}_3$	$\text{I}_2$	$\text{FeCl}_3$
PMNPV	$1.38 \times 10^{-7}$	$1.15 \times 10^{-5}$	0.07	0.14
55-poly(PV-co-MNPV)	$1.9 \times 10^{-7}$	$6.0 \times 10^{-1}$	0.05	0.16
35-poly(PV-co-MNPV)	$7.4 \times 10^{-5}$	$4.4 \times 10^{-1}$	0.16	0.30
		(1.7)		
8-poly(PV-co-MNPV)	$2.5 \times 10^{-4}$	$3.0 \times 10^1$	0.14	0.27
		( $1.5 \times 10^2$ )		
4-poly(PV-co-MNPV)	$5.2 \times 10^{-3}$	$2.2 \times 10^1$	0.14	0.26
		( $3.8 \times 10^2$ )		
PPV	$5.8 \times 10^{-6}$	$1.7 \times 10^{-5}$	0.09	0.02

(a) The values in parentheses are those for uniaxially stretched ( $L/L_0=5$ ) films along the stretch direction; b)  $\text{I}_2$ - or  $\text{FeCl}_3$ - per average repeating unit estimated from the weight gain on doping.

spectrum of the precursor films has shown a small absorption at the same position, which can be ascribed to premature partial elimination of THT and HCl during film casting.

UV-Vis spectra of PMNPV and poly(PV-co-MNPV)s has been compared with that of the PPV films [104]. Although it was not included, the non-eliminated precursor film of 35-poly(PV-co-MNPV) was displayed. A weak absorption band of about 325 nm has been shifted to a  $\lambda_{max}$  of about 435 nm and its intensity has increased after elimination. The positions of  $\lambda_{max}$  and  $\lambda_{edge}$  clearly have been demonstrated that the presence of nitro and methoxy substituents on the phenylene rings cause a hypsochromic shift. As the content of MNPV units in the copolymers increase, the position of maximum absorption ( $\lambda_{max}$ ) gradually shifted from 422 nm for PPV to the shorter wavelength of 292 nm for PMNPV. This spectroscopic change must be arising from a combination of electronic and steric effects of the two substituents. The strong electron-withdrawing power of the nitro group may overwhelm the electron-donating power of the methoxy group. It also appears highly probable according to a molecular model that the two bulky substituents, i.e.; the nitro and methoxy groups, presence in the phenylene rings hinder the polymer chains from attaining a perfectly coplanar  $\pi$ -configuration. Disturbance coplanarity in the  $\pi$ -system should cause a blue shift. At the same time, the band onset, i.e., the  $\lambda_{edge}$  position, also decreases from 525 nm of PPV to 468 nm of PMNPV, which indicates a steady increase in band-gap with increasing content of MNPV units.

Poly[2-(2-phenylethyl)-1,4-phenylene]vinylene] (PPEPV), poly[(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene]vinylene] (PMPEPV), and their copolymers containing 1,4-phenylenevinylene (PV) units [poly(PEPV-co-PV)s and poly(MPEPV-co-PV)s] have been synthesized via water soluble, polyelectrolyte precursor polymers [105] (Schemes XXX and XXXI).

The polymerization results are summarized in Table 9. The data in Table 9 clearly show that the copolymers contain consistently higher levels of the 2-phenylethenyl substituted monomer unit than the mole fraction of the methoxy substituted monomer in

the feed. This suggests that the methoxy-substituted monomer is more reactive than the unsubstituted monomer. This is in line with that of the electron-donating substituents on the phenylene ring of the bis(sulphonium salt) monomers enhance the reactivity in copolymerizations [105]. In general, film quality such as uniformity and integrity was superior when the copolymers contained higher levels of the unsubstituted 1,4-phenylenevinylene units.

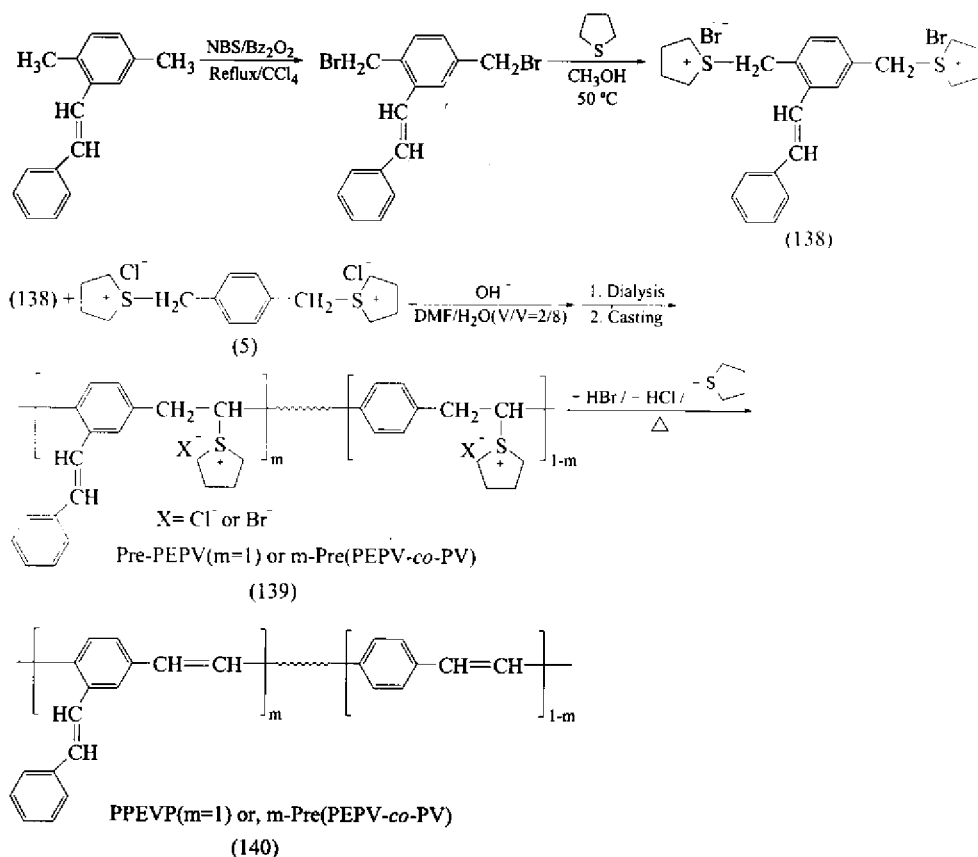
The cross-conjugation between the main chain and the pendant 2-phenylethenyl ( $\beta$ -styryl) unit is insignificant. Electrical conductivities of FeCl<sub>3</sub>-doped PPEPV and PMPEPV are on the order of  $10^{-4}$  S/cm, which are lower than those of copolymers containing PV units. This is ascribed to the charge-transfer interactions between the dopants and styryl units in the side branch. The MPEPV copolymer containing about 93 mol % of PV unit, however, has been exhibited an electrical conductivity of about 5 S/cm, when it has been doped with FeCl<sub>3</sub>. The PEPV copolymer containing 85 mol% PV unit has shown to have an electrical conductivity ( $0.24 \text{ cm}^{-1}$ ) of 1 order of magnitude lower. In general, doping with I<sub>2</sub> resulted in lower electrical conductivities than with FeCl<sub>3</sub>.

### 3.8. Polyblends of PPV

A series of polyblends of PPV and PDMPV were prepared in film form from precursor polyblends of the respective sulphonium salt polymers, separately prepared from the bis (sulphonium salt) monomers and blended in aqueous solution in varying molar ratios and cast into films, as shown at the Scheme XXXII [102].

The blend films were doped with I<sub>2</sub> at room temperature to obtain a wide range of electrical conductivities ( $10^{-2}$  to  $10^2$  S/cm) depending on the blend composition. The conductivities were reduced as the content of PDMPV decreased.

The DSC thermogram of a film of polyblend of PPV and PDMPV contains a strong endothermic peak at 105 °C and a broad, weaker second at 120–240 °C [102]. The first peak corresponds to the loss of water present in the cast film, and the second to the thermolysis of the precursor polymers with the loss of



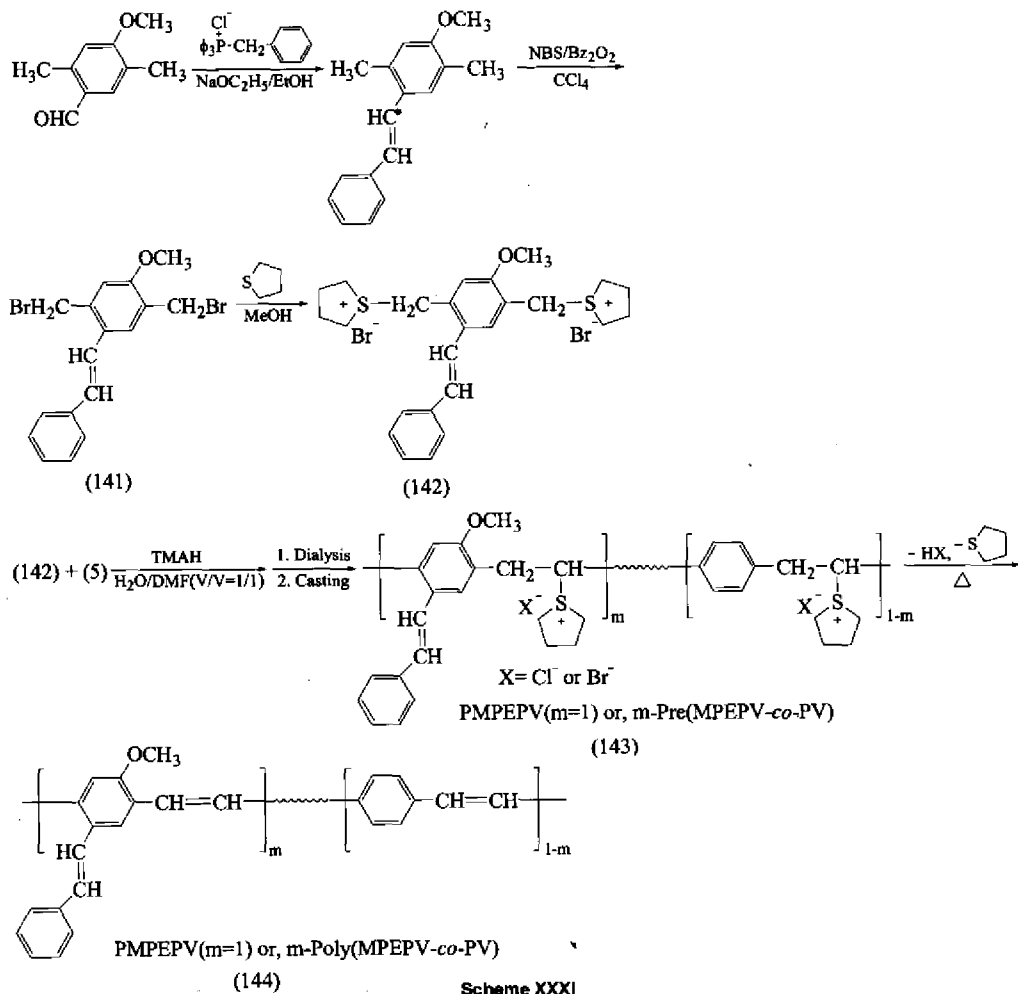
Scheme XXX

HCl and THT. According to the TGA thermogram of the same blend an initial fast weight loss began at about 93 °C, followed by a gradual weight loss of about 35 %. Polymer chain degradation apparently begins near 400 °C. The DSC and TGA results agree closely. Premature elimination reactions can be resulted from the comparison of weight loss of about 35% observed and theoretically expected value of 52.8 % for the amount of water, which occurred during film casting. This suggestion has been supported by the observation that the as-cast blend films were yellow to reddish yellow in colour with

increasing PDMPV content. Furthermore, their IR spectra have shown a sharp absorption at 960 cm<sup>-1</sup>, which corresponds to the presence of a vinylene C-H out-of-plane vibration mode.

It has been also reported recently that an I<sub>2</sub>-doped polyblend film of PPV and PTV displayed remarkably high electro-conductivities [39]. As expected, bulk conductivity of the blend samples is dependent on the concentration of the dopable component. It suggests that the interchain correlation of the PTV chains play a role in the conductivity of such blend samples, especially at low PTV content, and leads to





conductivities that were initially independent of TV content.

#### 4. MECHANISM OF BASE-INDUCED POLYMERIZATION

Since the Wessling polymerization is of particular

importance in the current work involving conducting polymer precursor PPV and so understanding its mechanism is of much potential use in controlling the efficient syntheses of various substituted PPVs. Wessling has postulated that basic treatment of bis (dialkyl sulphonio) salt derivatives of (145) results in polymerization to (148) by the route indicated in (Scheme XXXIII) [147]. NMR and IR studies are

**Table 9. Synthesis of PPEPV and poly(PEPV-co-PV) [105].**

Polymer <sup>a</sup>	Feed ratio <sup>b</sup> 3:4	Actual ratio <sup>b</sup> m:1-m	Monomer conversion (mol %)	$\eta_{inh}^c$ (dL/g)	Polymer <sup>d</sup> yield (%)
PPEPV	100:0	1.00:0	85.7	0.65	47
57-poly(PEPV-co-PV)	50:50	0.57:0.43	78.3	2.46	44
38-poly(PEPV-co-PV)	25:75	0.38:0.62	68.1	4.57	34
15-poly(PEPV-co-PV)	10:90	0.15:0.85	66.4	8.40	35

(a) The numbers in the expression of copolymer indicate the mole percent of the PEPV unit incorporated into the final polymers. (b) Mole ratios. (c) The viscosity of precursor polymers was measured for aqueous solutions of 2 g/dL at 30 °C in the presence of NaSO<sub>4</sub>. (d) The values were estimated from the weight of the final polyconjugated polymers obtained after thermolysis of the dialyzed precursor polymers.

consistent with the Wessling mechanism for formation of *p*-xylylene as respective intermediates formed by 1,6-elimination [106, 107] from ylids. ESR and trapping studies, however, show no evidence requiring the radical polymerization postulated by Wessling. Therefore it has been proposed a putative anionic chain polymerization, a reasonable modification of the Wessling mechanism (Scheme XXXIII).

The sulphonium moieties polarize PX's 145<sub>a-f</sub> and should favour exocyclic nucleophilic attack and anionic polymerization, as observed with corresponding of much more stable *p*-xylylene. Proposal of their alternative anionic polymerization mechanism seems in good accord with all the data presently available, when compared to the chemistry of related substituted *p*-xylylenes.

According to the literature of Garny and Lenz the polymerization mechanism of this Wessling route can be divided into two steps (Scheme XXXIV)

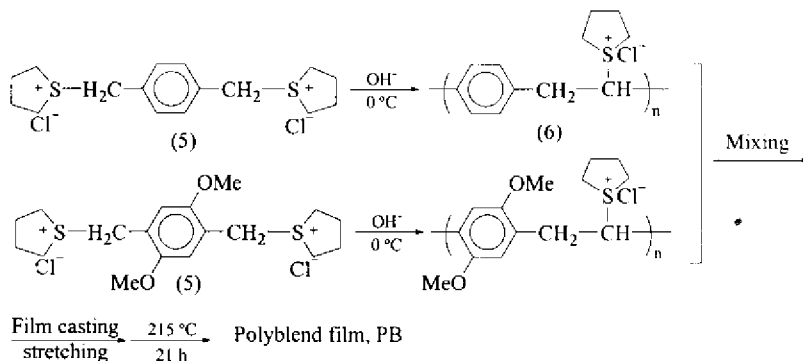
[106]. In the first step, an anion (150) is formed through an acid-base equilibrium. Secondly, this anion undergoes a 1,6-elimination reaction of a <sup>+</sup>HT to the quinoid structure (151), which polymerizes to the water-soluble precursor polymers (151).

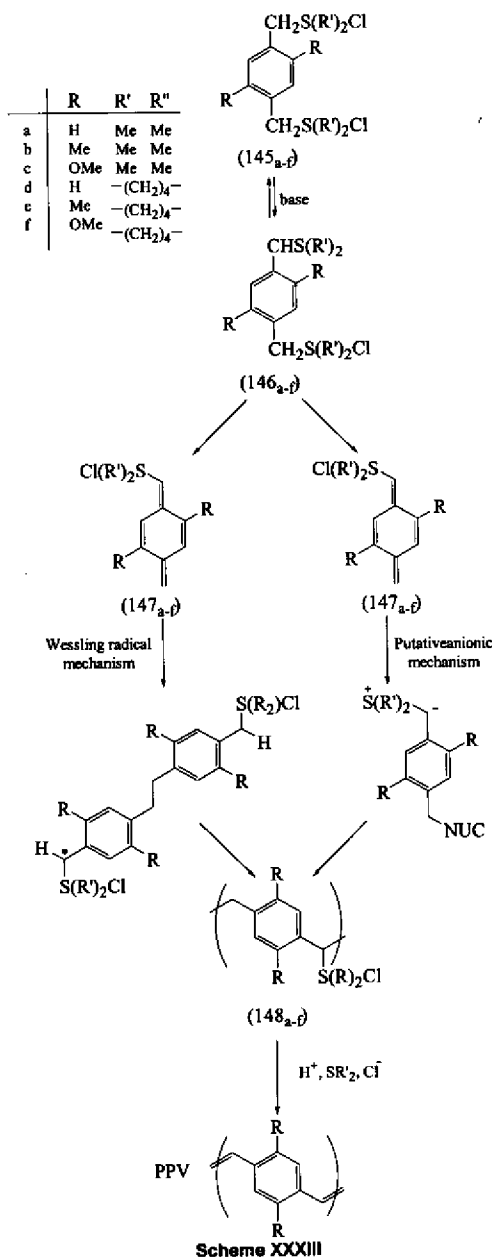
Scheme XXXIV can be generalized in the acid-base equilibrium, one needs to have a polarizer group (P) which stabilizes the anion (150) and in the 1,6-elimination reaction there is a need for a leaving group (L), to form the quinoid structure (151) [108, 109].

## 5. EFFECT OF DIFFERENT FACTORS ON POLYMER PROPERTIES

### 5.1. Sulphonium Structure

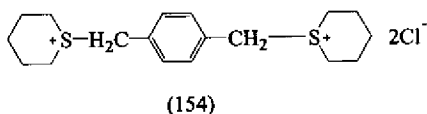
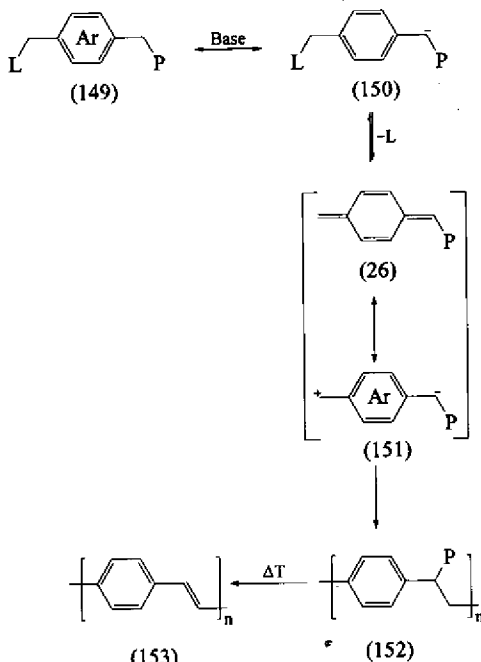
The effect of altering sulphonium was studied by examining the diethyl (2<sub>a</sub>), tetramethylene (5), and

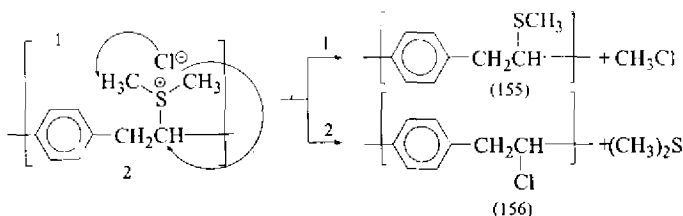
**Scheme XXXII**



penta methylene (154), xylene sulphonium salt derivatives, and the precursor polymers derived from them. These were subsequently compared to dimethyl sulphonium derivatives (2a) and (3). Better yield of PPV with higher molecular weight has been obtained in all three cases, with the cyclic sulphonium precursor polymers, (5) and (154) being the best [36].

The rate of the sulphide group elimination reactions at higher temperatures was determined for the polymers with dimethyl and diethyl sulphonium groups, and for the polymers with the THT sulphonium groups, and THP sulphonium groups by TGA. The observed TGA weight loss and DSC endotherm represent both the loss of water of hydration and the thermal elimination reaction of the





sulphide groups and HCl in each polymer.

Indeed elemental analysis showed very little residual sulphur and chlorine compared to the larger amounts after thermal elimination [36]. The PPV from (6) shows a slightly longer wavelength absorption maximum corresponding to longer conjugation lengths. This is consistent with the observation of considerably less sulphur and chlorine and hence fewer sp hybridized carbon atoms, and therefore greater conjugation lengths in polymers. The UV-vis spectrum of (6) shows photon side band attributed to narrower distribution of crystallite sizes [110].

The limiting conductivities obtained for each are given in Table 10 [59]. The data show that the undrawn phenylene vinylene films obtained from the intermediate polymers containing cyclic sulphonium groups gave much higher conductivities than those from the polymers containing dialkyl sulphonium groups, presumably because of the much more efficient conversion of polyelectrolyte to PPV for the former. That is, the smaller the extent of side reactions leading to units of (155) and (156), the longer will be the sequences of conjugated phenylene

vinylene units in the polymer.

Also fewer extraneous units may permit higher degree of orientation and order in PPV polymer. Both of these factors may be responsible for the higher conductivities obtained when the films of the polymers from (6) and (154) were "doped" with AsF<sub>5</sub>.

## 5.2. Nature of the Anion

The influence of the nature of the anion on the solution behaviour of the poly(xylylene tetrahydrothiophenium) is investigated. It is found that the effect of the anions on the water structure beyond their first hydration shell,  $\Delta S_{1st}^+$ , determines whether or not the polyelectrolyte precipitates. For anions with negative  $\Delta S_{1st}^+$  value, the polyelectrolyte stays in solution. Anions with a positive value will precipitate the polyelectrolyte. Then, the solution behaviour of the polyelectrolyte is dependent on the nature of the added salt. After introduction of BF<sub>4</sub> [111] or *p*-toluene sulphonate [112] the polymer would be insoluble in water but soluble in polar organic solvents. Mixing the polyelectrolyte solution with sodium salts of I<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup> and AsF<sub>6</sub><sup>-</sup> results in new precursor polymers [113, 114]. The anion exchange is very efficient; no residual chlorine could be detected in elemental analysis. Elimination of poly-electrolyte AsF<sub>6</sub><sup>-</sup> film results in a black and conducting film.

The elimination process of the precursor polymer with different counter ions is followed by thermogravimetry and mass spectrometry. Most of the anions did not have a great influence on the elimination process. Substantial differences are found in the elimination temperature of the counterion which has been active in a substitution reaction. If the acetate ion acts as counterion, the polyelectrolyte is stable to 250 °C. Probably the THT ion is replaced by

**Table 10.** Electrical conductivity of polymer films obtained from different types of sulphonium polymers [59].

Monomer	Elimination temperature (°C)	Film thickness (μm)	Conductivity <sup>a</sup> (Ohm <sup>-1</sup> cm <sup>-1</sup> )
2 <sup>a</sup>	260	10	7
	200	7	15
154	210	23	44
	220	6	180

(a) Highest conductivity achieved after multiple cycles of exposure to AsF<sub>5</sub> at 200 torr and -78 °C and evacuation.

the acetate ion which eliminates at higher temperatures. The polyelectrolyte  $-\text{IO}_3^-$ ,  $-\text{BrO}_3^-$  and  $-\text{ClO}_3^-$  films eliminate at one temperature only i.e., the decomposition temperature of the anion. Then, if the substitution reaction does take place, the elimination temperature depends on the leaving group capacity of the anion. The elimination of a polyelectrolyte-Br film occurs in one step at 70 °C. To eliminate a polyelectrolyte-Cl<sup>-</sup> or  $-\text{F}^-$  film, it is necessary to heat it to 200 °C.

### 5.3. Polarizer and Leaving Group

The  $\alpha$ -chloro  $\alpha'$ -alkyl (aryl) sulphinyl- and  $\alpha$ -chloro  $\alpha'$ -alkyl (aryl) sulphonyl-*p*-xylenes can be polymerized according to a general route adopted from the Wessling bisulphonium salt route. The motivation for this choice lies in the leaving group capacity of Cl<sup>-</sup> and in the polarization property of the sulphinyl and sulphonyl groups.

The gel permeation chromatography (polystyrene as standard) shows that the molecular weight increases with a better polarizer, i.e., providing the anion results in easier stabilization.

If the polarizer is a sulphinyl group, the polymer, which is soluble in organic solvents (such as  $\text{CHCl}_3$ , DMF and THF) and is relatively stable, can be converted to *trans*-PPV. On the other hand, if the polarizer is a sulphonyl group the result is a polymer with a rather high thermal stability [106].

## 6. APPLICATIONS OF POLY(ARYLENE VINYLENES)

The discovery of electrical conductivity of conjugated organic polymers has opened a novel and a very important field of modern material science. The first electronic device of a field-effect transistor (FET) with a conjugated polymer as an active new component, reported by Tsumura et al. [61], showed that conducting polymers are very promising materials for electronic devices.

The possibility of using polyconjugated macromolecules or, indeed, conducting devices has opened a wide and stimulating new field of both fundamental and applied research that has recently overflowed into

other areas such as non-linear optics [85, 86], photoluminescence [105, 115], gas sensors [116–118], controlled release of drugs [119], and liquid crystal [120], etc.

Many types of conjugated polymers are now actively researched. Among them, the interests in PPV and its derivatives have been increased in recent decades because of their possible application to electronic and photonic devices. PPVs are one of the important series of conjugated polymer for their environmental stability and outstanding photo- and electroluminescent properties [87]. Research on electroluminescence (EL) polymers has become an active area since EL in PPV was described in 1990 by Burroughes et al. [121]. Many EL-active polymers have been synthesized, and emission colours reported have covered the whole range of the visible spectrum with increasing quantum efficiencies. PPV is the first conjugated polymer reported for the application in light-emitting diodes [122–124]. Today, PPV and its derivatives remain the most popular conjugated polymer class for this application. The reason was by good processibility, high efficiency of radiative decay process and easy tuning of emitting colour than inorganic materials [84]. At first, Friend and colleagues [125] reported that PPV could be used to fabricate light emitting diodes (LEDs). Most of the devices studied to date use PPV or modified PPV as a whole transporter and/or emitter layer in the LEDs. Fully conjugated PPV and its derivatives are of interest for optical devices, because they can be readily prepared in high molecular weight through both of the water-soluble and organic-soluble precursor routes [85]. Conjugated polymers containing extensive  $\pi$ -electron delocalization have emerged as an important class of third-order non-linear optical materials, especially PPV derivatives, for they are amorphous polymers with good processibility, large third-order non-linear optical susceptibility and good optical quality, etc. [126].

## 7. SUMMARY

Polyarylene vinylenes, its derivatives and related

copolymers can be readily prepared in high molecular weight through the water-soluble precursor route. These water-soluble and non-conjugated precursor polymers are cast into films and the converted into extended  $\pi$ -conjugated structures by thermal elimination reaction. Polyarylene vinylene and its derivatives, thus prepared, display very high electrical conductivities after doping with a variety of oxidants and reductive dopants, and they also possess very good non-linear optical properties. Soluble PPV shows great promise as semiconducting molecular material for use in high emitting diodes and photoconducting of photo-reactive devices. Since the phenylene ring can be subjected to various chemical modifications to carry many different types of substituents, therefore, substitution on the phenyl ring of PPV with different types of electron-donating or electron-withdrawing group has a significant influence on the electronic structure of the resulting polymer and thus affects the electrochemical and optical properties. A base-induced 1,6-elimination from a *p*-xylene derivative leads to the in situ formation of a *p*-quinodimethane system. In a second step this intermediate polymerizes spontaneously and rapidly to yield high molecular weight PPV precursor polymers. The conjugated structure is obtained directly or after thermal treatment depending on the specific chemical structure of the starting monomer and the polymerization condition.

The poly(hetero)arylene vinylenes are a very interesting group of materials with much potential, and will provide the focus for considerable future research. Structural modifications based on the inclusion of various substituents at C-3 and C-4 in order to attain solubility and examination of the optical and liquid crystalline properties of oligomers and polymers can be done in this context.

## REFERENCES

1. Diaz A.F., Kanazawa K.K. and Gardini G.P., "Electrochemical polymerization of pyrrole", *J. Chem. Soc. Chem. Commun.*, **14**, 635 (1979).
2. Tourillon G. and Garnier F., "New electrochemically generated organic conducting polymers", *J. Electroanal. Chem. Interfacial Electrochem.*, **135**, 1, 173 (1982).
3. Diaz A.F., Castillo J.L., Logan J.A. and Lee W.Y., *J. Electroanal. Chem.*, **129**, 115, 1981.
4. Entezami A., Golabi S.M. and Raouf D.J., "Electrochemical behaviour of electroactive/conductive poly( $\alpha$ -naphthylamide) in aqueous media", *Iran. J. Polym. Sci. & Tech.*, **1**, 1, 7 (1992).
5. Entezami A. and Hosseini S.H., "Synthesis of conducting polypyrrole and polycarbazole containing hydroxamic acid groups", *Eur. Polym. J.*, **31**, 635-641 (1995).
6. Shirakawa H., Louis E.J., MacDiarmid A.G., Chiang C. and Heeger A., "Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene,  $(CH)_x$ ", *J. Chem. Soc. Chem. Commun.*, **16**, 578 (1977).
7. MacDiarmid A.G., Chiang J.C., Richter A.F. and Somasiri N.L.D., "Polyaniline: Synthesis and characterization of the emeraldine oxidation state by elemental analysis", *Conduct. Polym; Proc. Workshop*, 105 (1987).
8. Dadras Marani A. and Entezami A.A., "New synthesis method of polythiophenes", *Iran. Polym. J.*, **3**, 1, 2 (1994).
9. Gandini A. and Meales C., "Poly(heteroarylene vinyl-ene)s-a new family of polyconjugated materials", *TRIP*, **2**, 4 (1994).
10. Bradley D.D.C., "Precursor-route poly(*p*-phenylenevinylene): Polymer characterization and control of electronic properties", *J. Phys. D: Appl. Phys.*, **20**, 11, 1389 (1987).
11. Hoerhold H.H. and Helbig M., "Poly(phenylenevinylene)s-synthesis and redox chemistry of electroactive polymers", *Makromol. Chem. Macromol. Symp.*, **12**, 229 (1987).
12. Capistran J.D., Gagnon D.R., Antoun S., Lenz R.W. and Karasz F.E., "Synthesis and electrical conductivity of high molecular weight poly(arylene vinylenes)", *Polym. Prepr.*, **25**, 2, 282 (1984).
13. Jen K.Y., Jow T.R. and Elsenbaumer R.L., "Facile preparation of high molecular weight highly conductive poly(2,5-furylene vinylene)", *J. Chem. Soc., Chem. Commun.*, **14**, 1113 (1987).
14. Jen K.Y., Maxfield M.R., Shacklette L.W. and Elsenbaumer R.L., "Highly-conducting, poly(2,5-thienylene vinylene) prepared via a soluble precursor polymer", *J. Chem. Soc., Chem. Commun.*, **4**, 309 (1987).
15. Shim H.K., Lenz R.W. and Jin J.L., "Synthesis and electrical conductivity of poly(1,4-phenylene vinylene-co-2,5-thienylene vinylene)", *Makromol. Chem.*, **190**, 2, 389 (1989).
16. Babudri F., Cicco S.R., Iannola G.M. and Naso F., "Synthesis, characterization and properties of a soluble polymer with a poly(phenylenevinylene) structure", *Macromol. Rapid Commun.*, **17**, 905 (1996).

17. Saito H., Ukai S., Iwatsuki S., Itoh T., and M. Kubo, "Synthesis of soluble poly(arylenevinylene)s carrying various heterocycles as arylene units", *Macromolecules*, **28**, 8363 (1995).
18. Jen K.Y., Eckhardt H., Jow T.A., Shacklette L.W., Elsenhaumer R.L., "Optical, electrochemical and conductive properties of poly(3-alkoxy-2,5-thienylvinylene)s", *J. Chem. Soc., Chem. Commun.*, 215 (1988).
19. Jin S.H., Sun Y.K., Sohn B.H. and Kim W., "Synthesis and electro-optical properties of electroluminescent polymers containing carbazol unit" *Eur. Polym. J.*, **36**, 957 (2000).
20. Wang M. L.H., Kang E.-T., Huang W., "Synthesis, spectroscopy, and electrochemical properties of a novel p-n diblock poly(p-phenylenevinylene)-related copolymer containing bipyridine", *Polymer*, **42**, 3949 (2001).
21. Xue M., Huang D. and Liu Y., "Design and synthesis of poly(p-phenylenevinylene) derivative with triphenylamine segments on polymer backbone", *Synth. Met.*, **110**, 203 (2000).
22. Cacialli F., Daik R., Feast W.J., Friend R.H. and Lartigue C., "Synthesis and properties of poly(arylene vinylene)s with controlled structures", *Optical Materials*, **12**, 315 (1995).
23. Pfeiffer S., Rost H. and Horhold H.H., "Investigation of poly(arylenevinylene)s", *Macromol. Chem. Phys.*, **42**, **200**, 2471 (1999).
24. Pan M., Bao Z., and Regiospecific I. Yu, "Functionalized poly(phenylenevinylene) using the heck coupling reaction", *Macromolecules*, **28**, 5151 (1995).
25. Xie H.Q., Gao G.H., Lin J.M. and Guo J.S., "Synthesis and properties of three kinds of phenylenevinylene copolymers with dialkoxyphenylene units", *J. Appl. Polym. Sci.*, **68**, 937 (1998).
26. Akagi K., Oguma J., Shibata S., Toyoshima R., Osaka I. and Shirakawa K., "A family of liquid crystalline polyarylenevinylene", *Synth. Met.*, **102**, 1287 (1999).
27. Leung L.M. and Chik G.L., "Phase transfer catalysed synthesis of disubstituted poly(phenylene vinylene)", *Polymer*, **34**, 24 (1993).
28. Entezami A. and Rahmatpour A., "Electropolymerization of disymmetric diheteroaryl ethylenic containing n-methyl pyrrole, pyrrole, thiophene and furan units", *J. Polym. Mater.*, **14**, 91 (1997).
29. Entezami A.A. and Rahmatpour A., "Electropolymerization of disymmetric diheteroaryl ethylenes containing n-methyl pyrrole, pyrrole and thiophene", *Eur. Polym. J.*, **34**, 5/6, 871, (1998).
30. Shilabin A.G. and Entezami A.A., "Electrochemical behaviour of conducting polyfuran derivatives containing pyrrole, thiophene and ethylenic spacers", *Eur. Polym. J.*, **36**, 2005, (2000).
31. Wessling R.A., "The polymerization of xylylene bisdialkyl sulphonium salts", *J. Polym. Sci., Polym. Symp.*, **72**, 55, (1985).
32. Wan W.C., Antoniadis H., Choong V.E., Razafitrimo H., Gao Y., Feld W.A. and Hsieh B.R., "Halogen precursor route to poly((2,3-diphenyl-p-phenylene)vinylene) (DP-PPV): synthesis, photoluminescence, electroluminescence, and photoconductivity", *Macromolecules*, **30**, 6567 (1997).
33. Gagnon D.R., Capistran J.D., Karasz F.E. and Lenz R.W., "Synthesis, doping and electrical conductivity of high-molecular-weight poly(p-phenylene vinylene)", *Polymer*, **28**, 4, 267 (1987).
34. *U.S. Patent* 3706677 (1972), Dow Chemical Co., R.A. Wessling, R.G. Zimmerman, "Polyelectrolytes from bisulphonium salts", R.A. Wessling, R.G. Zimmerman, *U.S. Patent* 3401152 (1968), Dow Chemical Co.
35. Liang W.B., Lenz R.W. and Karasz F.E., "Poly(2-methoxy phenylene) synthesis, electrical conductivity, and control of electronic properties", *J. Polym. Sci.: Polym. Chem.*, **28**, 10, 2867, (1990).
36. Gagnon D.R., Capistran J.D., Karasz F.E., Lenz R.W., and Antoun S., "Synthesis, doping, and electrical conductivity of high molecular weight poly(p-phenylene vinylene)", *Polymer*, **28**, 567-573 (1987).
37. Antoun S., Karasz F.E. and Lenz R.W., "Synthesis and electrical conductivity of poly(arylene vinylene). I. poly(2,5-dimethoxy phenylene vinylene) and poly(2,5-dimethyl phenylene vinylene)", *J. Polym. Sci.: Polym. Chem. Ed.*, **26**, 7, 1809 (1988).
38. Lenz R.W., Han C.C., Stenger-Smith J., and Karasz F.E., "Preparation of poly(phenylene vinylene) from cycloalkylene sulphonium salt monomers and polymers", *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 3241 (1988).
39. Karasz F.E., Capistran J.D., Gagnon D.R., Lenz R.W., "High molecular weight poly(phenylene vinylene)", *Mol. Cryst. Liq. Cryst.*, **118**, 327 (1985).
40. Murase I., Ohnishi T., Noguchi Y.T., Hirooka M. and Murakami S., "Highly conductive poly(p-phenylenevinylene) prepared from sulphonium salt", *Mol. Cryst. Liq. Cryst.*, **118**, 333 (1985).
41. Jin, J.-I., Shim H.-K. and Lenz R.W., "Synthesis and electroconductivity of poly(1,4-phenylene-1,3,5-hexatrienylene-1,4-Phenylenevinylene)", *Synth. Met.*, **29**, 1, E53 (1989).

42. Murase I., Ohnishi T., Noguchi T. and Hirooka T.M., "Highly conductive poly(phenylene vinylene) derivatives via soluble precursor process", *Synth. Met.*, **17**, 639 (1987).
43. Murase M., Ohnishi I., Noguchi T. and Hirooka T.M., "Alkoxy-substituted effect of poly(p-phenylene vinylene) conductivity", *Polym. Commun.*, **26**, 362 (1985).
44. Han C.C., Lenz R.W. and Karasz F.E., "Highly conductive, iodine-doped copoly(phenylene vinylene)s", *Polym. Commun.*, **28**, 9, 261 (1987).
45. Antoun S., Gagnon D.R., Karasz F.E.J. and Lenz R.W., "Polymerization of arylene-bissulphonium salts and their derivatives and the preparation of poly(p-phenylene vinylenes)" *Polymer Prepr.*, **27**, 116 (1986).
46. Yoriko S. and Kyoji K., "Preparation of poly(2,5-diheptyl-1,4-phenylene vinylene) by sulphonium salt pyrolysis", *Bull. Chem. Soc. Jpn.*, **65**, 3, 853 (1992).
47. Lahti P.M., Modarelli D.A., Denton F.R., Lenz R.W. and Karasz F.E., "Polymerization of  $\alpha,\alpha'$ -bis(dialkylsulphonio)-p-xylene dihalides via p-xylene intermediates: Evidence for nonradical mechanism", *J. Am. Chem. Soc.*, **110**, 7258 (1988).
48. Skotheim T.A., *Electroresponsive Molecular and Polymeric Systems*, New York, 197 (1991).
49. Diaz A.F. and Hall B., IBM "Synthesis of poly-p-xylylidene from p-xylylenebis(dimethylsulphonium) tetrafluoroborate", *J. Res. Dev.*, **27**, 342 (1983).
50. Kanbe M. and Okawara M., "Synthesis of poly-p-xylylidene from p-xylylene-bis (dimethylsulphonium) tetrafluoroborate", *J. Polym. Sci. part A*, **6**, 1058 (1968).
51. Murase I., Ohnishi T., Noguchi T. and Hirooka M., "Highly conducting poly(2,5-thienylene vinylene) via a precursor route" *Polym. Commun.*, **28**, 229 (1987).
52. Gagnon D.R., Karasz F.E., Tohmas E.L. and Lenz R.W., "Molecular orientation and conductivity in highly drawn poly(p-phenylene vinylene)", *Synth. Met.*, **20**, 85 (1987).
53. Gagnon D.R., Capistran J.D., Karasz F.E., and Lenz R.W., "Conductivity anisotropy in oriented poly(p-phenylene vinylene)" *Polym. Bull.*, **12**, 293 (1984).
54. Granier T., Thomas E.L., Gagnon D.R., Karasz F.E. and Lenz R.W., "Structure investigation of poly(p-phenylene vinylene)", *J. Polym. Sci. Polym. Phys.*, Ed. 24, 2793 (1986).
55. Murase I., Ohnishi T. and Noguchi T., "Highly electro-conductive conjugated polymer composition and process for producing the same", *U.S. Pat.* 4, 528, 118 (1985).
56. Murase I., Ohnishi T., Noguchi T., Hiroka, "Highly conductive poly(p-phenylene vinylene) prepared from a sulphonium salt", *Polym. Commun.*, **25**, 327 (1984).
57. Wessling R.A., "The polymerization of xylylene bisdialkyl sulphonium salts", *J. Polym. Sci., Polym. Symp.*, **72**, 55 (1986).
58. Pron A., Billaud D., Kulszewicz A., Budrowski C., Przyluski J. and Suwalski J., "Synthesis and characterization of new organic metals formed by interaction of ferric chloride with polyacetylene (CH), and poly(para) phenylene (C<sub>6</sub>H<sub>4</sub>)<sub>x</sub>", *Mater. Res. Bull.*, **16**, 10, 1229 (1981).
59. Lenz R.W., Han C.C., Stenger-Smith J. and Karasz F.E., *J. Polym. Sci., Polym. Chem.*, Ed., **26**, 3241 (1988).
60. Tran V.H., Massardier V. and Guyot A., "Interaction in metal-polymer-metal interfaces", *Polymer*, **34**, 15, 3179 (1993).
61. Schaeffgen J.R., *J. Polym. Sci.*, **15**, 230 (1955).
62. Tourillon G. and Garnier F., "Stability of conducting polythiophene and derivatives" *J. Electrochem. Soc., Electrochem. Sci. Techn.*, **130**, 10, 2042 (1983).
63. Wnek G.E., Chien J.C.W., Karasz F.E. and Lillva C.P., "Electrically conducting derivative of poly(p-phenylene vinylene)", *Polymer*, **20**, 12, 1441 (1979).
64. Mertens R., Nagels P., Callaerts R., Vanroy M. and Briers J., "Characterization and DC-conductivity of poly(p-phenylene vinylene) films doped with FeCl<sub>3</sub>", *Synth. Met.*, **51**, 55 (1992).
65. Burn P.L., Bardley D.D.C., Friend R.H., Halliday D.A., Holmes A.B., Jackson R.W. and Kraft A., "Precursor route chemistry and electronic properties of poly(p-phenylene-vinylene), poly([2,5-dimethyl-p-phenylene]vinylene) and poly([2,5-dimethoxy-p-phenylene]vinylene)", *J. Chem. Soc. Perkin Trans.*, **1**, 3225 (1992).
66. Gourley K.D., Lillya C.P., Reynold J.R., and Chien J.C.W., "Electrically conductivity polymers: Arsenic pentafluoride-doped poly(phenylene vinylene) and its analogs", *Macromolecules*, **17**, 5, 1025 (1984).
67. Weitzel H.P., Bohnen A., and Muehlen K., "Polyarylenes and poly(arylenevinylene)s. 3. Oligomeric model compounds for poly(9, 10-anthrylene vinylene)", *Makromol. Chem.*, **191**, 2815 (1990).
68. Bradley D.D.C., "Precursor-route poly(p-phenylene vinylene)polymer characterization and control of electronic properties", *J. Phys. D: Appl. Phys.*, **20**, 1389 (1987).



69. Jin J.L., Park C.K., Shim H.K. and Park Y.W., "Highly conducting poly(2-butoxy-5-methoxy-1,4-phenylene vinylene)", *17*, 1205. (1989).
70. Becker H.D., Hansen L. and Andersson K., "Cis-1,2-bis(9-anthryl)ethylene. Preparation and photochemical properties", *J. Org. Chem.*, **46**, 5419 (1981).
71. Han C.C. and Elsenbaumer R.L., "Protonic acids: generally applicable dopants for conducting polymers", *Synth. Met.*, **30**, 1, 123 (1989).
72. Askari S.H., Rughooputh S.D.D., Wudl F., "Soluble conducting polymers: DHPV.", *Synth. Met.*, **29**, E 129 (1989).
73. Rehan M. and Schluter A.D., *Makromol. Chem., Rapid Commun.*, **11**, 375 (1990).
74. Jin J.L., Park C.K., Shim H.K. and Park Y.W., "Highly-conducting poly(2-butoxy-5-methoxy-1,4-phenylene vinylene)", *J. Chem. Soc. Chem. Commun.*, **17**, 1205 (1989).
75. Park J.J., Chi K. and Shim H.K., "Synthesis and electrical conductivity of poly(1, 4-phenylene vinylene-co-2, 3, 5, 6-tetramethyl-1, 4-phenylene vinylene)s", *J. Polym. Sci. Polym. Chem. Ed.*, **29**, 93 (1991).
76. Machado J.M. and Denton R.R., III; Schlenoff J.B., Karasz F.E. and Lahti P.M., "Analytical methods for molecular weight determination of poly(p-xylylene dialkylsulfonium halide): Degree of polymerization of poly(p-phenylene-vinylene)-precursors", *J. Polym. Sci. Polym. Phys. Ed.*, **27**, 199 (1989).
77. Lenz R., Han C. and Lux M., "Highly conducting iodine-doped arylene vinylene copolymers with dialkoxy phenylene units", *Polymer*, **30**, 1041 (1989).
78. Liang W.B., Lenz R.W. and Karasz F.E., "Synthesis and electroconductivities of poly(2-methoxy-5-methylthio-1,4-phenylenevinylene) and copolymers", *J. Polym. Sci.: Polym. Chem.*, **28**, 2867 (1990).
79. McCoy R.K., Karasz F.E., "Synthesis and characterization of ring-halogenated poly(1,4-phenylene vinylenes)", *Chem. Mater.*, **3**, 941 (1991).
80. Jin J.I. and Lee Y.H., "Synthesis and characterization of poly(2-methoxy-5-nitro-1,4-phenylenevinylene) and poly-(1,4-phenylenevinylene-co-2-methoxy-5-nitro-1,4-phenylenevinylene)s", *Macromolecules*, **26**, 1805 (1993).
81. Jin J.I., Kim J.C. and Shim H.K., "Synthesis and electrical properties of poly(2-bromo-5-methoxy-1,4-phenylene vinylene) and copolymers", *Macromolecules*, **25**, 5519 (1992).
82. Hsieh B.R. and Feld W.A., "A "Dehydrochlorination (DHCL) route to poly(2,3-diphenyl-1,4-phenylene vinylene) (DP-PPV)", *Polym. Prepr. (A.C.S. Div. Polym. Chem.)*, **34**, 2, 410 (1993).
83. Sarker A. and Lahti P.M., "Substituted poly(1,4-phenylene vinylene)s by the soluble precursor method for electro-optic application", *Polym. Prepr. (A.C.S. Div. Polym. Chem.)*, **35**, 1, 790 (1994).
84. Lahti P.M., Sarker A., Garay R.O., Lenz R.W. and Karasz F. E., "Polymerization of 1,4-bis(tetrahydrothiophenylmethyl)-2-cyano-5-methoxybenzene dibromide: Synthesis of electrically push-pull substituted poly(p-phenylene vinylene)s", *Polymer*, **35**, 6 (1994).
85. Jang M.S. and Shim H.K., "Synthesis, electrical and optical properties of multifunctional poly[2-(2-ethylhexyloxy)-1,4-phenylenevinylene]", *Polymer Bulletin*, **35**, 49 (1995).
86. Shim H.K., Hwang D.H. and Yoon C.B., "Synthesis and characterization of poly(2,5-dipropargyloxy-1,4-phenylenevinylene) and its copolymers with 1,4-phenylenevinylene", *Macromol. Chem. Phys.*, **197**, 2393 (1996).
87. Yoon C.B., Moon K.J. and Shim H.K., "Synthesis of a new poly(1,4-phenylenevinylene) derivative containing disperse red 1", *Macromolecules*, **29**, 5754 (1996).
88. Gowri R., Mandal D., Shivkumar B., and Ramakrishnan S., "Synthesis of novel poly[(2,5-dimethoxy-p-phenylene)-vinylene] precursors having two eliminable groups: An approach for the control of conjugation length", *Macromolecules*, **31**, 1819 (1998).
89. Antoun S., "Synthesis of bis-sulfonium salts of naphthalene", *Collection Czechoslovak Chem. Commun.*, **52**, 162 (1987).
90. Sarker A., Lahti P.M. and Karasz F.E., "Syntheses of new poly(arylene vinylene) analogues: Poly(4,7-benzofuran vinylene) and Poly(4,7-benzothiophene vinylene)", *J. Polym. Sci.: Part A: Polym. Chem.*, **32**, 65, 1994. Kossmehl G., Hartel M., and Manecke G., *Makromol. Chem.*, **131**, 15 (1970).
91. Yamada S., Tokito S., Tsutsui T., Saito S., "Electrical properties of poly(2,5-dibutoxyphenylenevinylene) film", *J. Chem. Soc. Chem. Commun.*, 1448 (1987).
92. Eevers W., De Schrijver D., Dierick J., Peten C., Van Der Looy J. and Geise H.J., "Poly(2,5-heteroarylene vinylene) from a precursor polymer soluble in organic solvents", *Synth. Met.*, **51**, 329 (1992).
93. Chiang C.K., Fincher C.R., Park Y.W., Heeger A.J., Shirakawa H., Louis E.J., and Gau S.C., McDiarmid, "Synthesis of highly conducting films of derivatives of polyacetylene (CH)<sub>x</sub>", *Phys. Rev. Lett.*, **39**, 1098 (1977).

94. Kossmehl G. and Yaridjanian A., "Poly(arylenealkylenes) and poly(heteroarylene alkylenes) synthesis of poly(1,4-phenylenevinylene), poly(2,5-thiophendiyl vinylene) and (2,5-furandiyl vinylene) from methyl-substituted aldehydes", *Makromol. Chem.*, **182**, 3419 (1981).
95. Shacklett L.W., Elsenbaumer R.L. and Baughman R.H., "Electrochemical cells employing polyacetylene and poly(p-phenylene) as active materials", *J. Phys. C.*, **44**, 559 (1983).
96. Dierick T., De Schrijver D., Evers W. and Geise H. J., "Poly-(2,5-furanylenevinylene) prepared from a precursor polymer soluble", *Bull. Soc. Chim. Belg.*, **100**, 631 (1991).
97. Nguyen-Hoan, Buu-Hoi, J.L. Lecocq, *Compt. Rend. Hebd. Seances, Acad. Sci.*, **222**, 1441 (1946).
98. Murase, Ichiki, Ootsu, Ohnishi, Toshihiro, Itami and Takanobu, "Gereckter poly(heteroarylenvinylene)-formling, bei seiner herstellung verwendetes vorlaeufer-polymier, verfahren zu seiner herstellung und diesen enthalt tende hoch leitfaehige masse", *Deutsches patent, DE 3704411A1* (1987).
99. Hong-Ku Shim, Chi Kyun Park, Jung-Il Jin, and Robert W. Lenz, "Electrical conductivity of polyblends of poly(1,4-phenylenevinylene) and poly(2,5-dimethoxy-1,4-phenylenevinylene)", *Polym. Bull.*, **21**, 409 (1989).
100. Shim H.K. and Hwang D.H., "Synthesis and Electrical and Optical Properties of Poly(2-methoxy-1,4-phenylenevinylene) and Copolymers", *Makromol. Chem.*, **194**, 1115 (1993).
101. Jin J.L., Park C.K., and Shim H.K., "Synthesis and Electroconductivity of poly(2-methoxy-5-methylthio-1,4-phenylene vinylene) and copolymer", *J. Polym. Sc. Part A Polymer Chem.*, **29**, 93 (1991).
102. Jin J.L., Yu S.H. and Shim H.K., "Synthesis and electrical conductivity of poly(1,4-phenylenevinylene-co-2-nitro-1,4-phenylenevinylene)", *J. Polym. Sci., Polym. Phys. Ed.*, **31**, 87 (1993).
103. Jin J.L., Kang H.J. and Shim H.K., "Synthesis and electric conductivity of poly(1,4-phenylene vinylene-2,3,5,6-tetramethyl-1,4-phenylenevinylene)s", *Bull. Korean Chem. Soc.*, **11**, 415 (1990).
104. Jin J.L. and Lee Y.H., *Macromolecules*, **26**, 1805 (1993).
105. Jin J.L., Lee Y.H., Park C.K., and Nam B.K., "Synthesis and characterization of poly[(2-(2-phenylethenyl)-1,4-phenylenevinylene), poly[(2-methoxy-5-(2-phenylethenyl)-1,4-phenylenevinylene], and their copolymers containing 1,4-phenylenevinylene units", *Macromolecules*, **27**, 19, 5240, (1994).
106. Louwet F., Vanderzande D. and Gelan J., "The synthesis of poly(1,4-phenylene-1,2-ethanediyl) derivatives: an adaptation of the wessling route", *Synth. Met.*, **52**, 125 (1992).
107. Yu Y., Lee H., VanLaeken A. and Hsieh B.R., "A new precursor polymer via a new 1,6-polymerization reaction. A new route to cyano poly(p-phenylene vinylenes), *Macromolecules*, **31**, 5553 (1998).
108. Van Der Borgh M., Adriaensens P., Vanderzande D. and Gelan J., "The synthesis of poly(4,4'-biphenylene vinylene) and poly(2,6-naphthalene vinylene) via a radical chemistry polymerization", *Polymer*, **41**, 2743 (2000).
109. Van Der Borgh M., Vanderzande D. and Gelan J., "Synthesis of high molecular weight poly(4,4'-biphenylene vinylene) and poly(2,6-naphthalene vinylene) via a non-ionic precursor route", *Polymer*, **39**, 4171 (1998).
110. Stenger-Smith J.D., Lenz R.W. and Wegner G., "Spectroscopic and cyclic voltammetric studies of salt precursor polymers", *Polymer*, **30**, 1048 (1989).
111. Han C.C. and Elsenbaumer R.L., "Protonic acids generally applicable dopants for conducting polymers", *Electron. Mater. Process.*, **3**, 419 (1989).
112. Tokito S., Mcmii T., Murata H., Tsutsui T. and Saito S., "Poly(arylenevinylene) films prepared from precursor polymers soluble in organic solvents", *Polymer*, **31**, 1137 (1991).
113. Patil A.O., Rughooputh S.D.V. and Wudl F., "Poly(p-phenylene vinylene): incipient doping in conducting polymers" *Synth. Met.*, **29**, E115 (1989).
114. Wudl F., Patil A.O. and Ikenoue Y., *Functional Polymers*, Plenum, New York, 99 (1989).
115. Zheng M., Bai F., Li F., Li Y. and Zhu D., "The interaction between conjugated polymer and fullerenes", *J. Appl. Polym. Sci.*, **70**, 599 (1998).
116. Hosseini S.H. and Entezami A.A., "Polypyrrole based toxic gas sensors by mass and conductivity measurements", *Iran. Polym. J.*, **8**, 3 (1999).
117. Hosseini S.H. and Entezami A.A., "Chemical and electrochemical synthesis of homopolymer and copolymers of 3-methoxyethoxythiophene with aniline, thiophene and pyrrole for studies of their gas and vapour sensing", *Polym. Adv. Technol.*, **12**, 524-534 (2001).
118. Hosseini S.H. and Entezami A.A., "Preparation and characterization of polyaniline blends with polyvinyl acetate, polystyrene and polyvinyl chloride for toxic gas sensors", *Polym. Adv. Technol.*, **12**, 482-493 (2001).

119. Massoumi B. and Entezami A.A., "Controlled release of sulfosalicylic acid during electrochemical switching of conducting polymer bilayers", *Eur. Polym. J.*
120. Sluch M.I., Pearson C., Petty M.C., Alim M.H. and Samuel I.D.W., "Photo- and electroluminescence of poly(2-methoxy, 5-(2-ethylhexyloxy)-*p*-(phenylene vinylene) Langmuir-Blodgett films", *Synth. Met.*, **94**, 285 (1998).
121. Yang Z., Hu B. and Karasz F.E., "Polymer electroluminescence using ac or reverse dc biasing", *Macromolecules*, **28**, 6151 (1995).
122. Hsieh B.R., Yu Y., Schaaf G.M. and Feld W.A., "Poly(*p*-phenylene vinylenes) via precursor route and side chain route methodologies involving 1,6-polymerization", *Polym. Prepr. (A.C.S. Div. Polym. Chem.)*, **39**, 1, 72, (1998).
123. Scharfel B. and Hennecke M., "Thermo-oxidative stability of a conjugated polymer by chemiluminescence", *Polym. Deg. and Stab.*, **67**, 249 (2000).
124. Cacialli F., Chuah B.S., Friend R.H., Moratti S.C. and Holmes A.B., "Blue light-emitting diodes from a meta-linked 2,3 substituted alkoxy poly(*p*-phenylenevinylene)", *Synth. Met.*, **111-112**, 155 (2000).
125. Papadim F., Itrakopoulos and Galvin M.E., "The origin of carbonyl moieties during the thermal conversion of poly(*p*-phenylenevinylene)", *Polym. Mater. Sci. Eng.*, **71**, 226, (1994).
126. Sun Z., Yang X., Huang Y., Ding L., Qin L. and Wang Z., "π-Electron density dependence of third-order optical nonlinearities in poly(1,4-phenylene vinylene) derivatives", *Optics Commun.*, **160**, 289 (1999).