Polymerization of 1,4-bis(tetrahydrothiopheniomethyl)-2-cyano-5-methoxybenzene dibromide: synthesis of electronically 'push–pull' substituted poly(*p*-phenylene vinylene)s

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The base-induced polymerization of 1,4-bis(tetrahydrothiopheniomethyl)-2-cyano-5-methoxybenzene dibromide in aqueous acetonitrile yields a soluble polyelectrolyte which may be thermally eliminated to give the electronically 'push–pull' substituted poly(2-cyano-5-methoxy-1,4-phenylene vinylene). Ultraviolet–visible and infra-red spectral studies showed production of the conjugated polymer, with a band gap of ca. 2.6–3.0 eV (410–480 nm) that varied somewhat as a function of elimination conditions. Elemental analysis indicates some retention of tetrahydrothiophenium side groups in the polyelectrolyte polymer, despite the use of a variety of elimination conditions. The retention of side chains in this synthesis is possibly due to a significant degree of irregularity in the positions of the cyano and methoxy substituents in the eliminated polymer, resulting from non-regioselectivity in this polymerization. This reaction demonstrates the potential in the Wessling process for polymerization of *p*-xylylenes that have electronically very asymmetric ('push–pull') substitution patterns.

(Keywords: polyelectrolyte; poly(*p*-phenylene vinylene); asymmetric substitution)

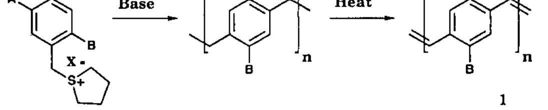
INTRODUCTION

Poly(*p*-phenylene vinylene)s (PPVs) are highly conjugated polymers of considerable interest as optoelectronic materials. Among the areas of practical application for PPVs are as doped conducting polymers[1–4], non-linear optical materials[5–7], and light-emitting display materials[8–10]. Considerable effort has been expended in the development of practically useful means to synthesize a number of PPV variants in the expectation of controlling in a rational fashion the electronic and other properties of the final polymers. For instance, by use of appropriate substituents, PPVs can be rendered soluble, their band gaps altered, and their ability to be doped substantially enhanced.

Among the various means by which PPVs may be synthesized, the so-called Wessling method[11,12] (*Scheme 1*) has been intensively employed. This aqueous-phase, base-induced polymerization of 1,4-bis(dialkylsulfoniomethyl)benzene salts allows production of high-molecular-weight polyelectrolyte precursor polymers, which are in many cases readily film-cast and processed to give films and fibres of PPVs[1,2,4,13,14]. The convenience of the Wessling method lies in the ready storage and thermolysis of the polyelectrolyte precursor polymers – properties that allow the typically insoluble, intractable PPVs to be readily processed.

A drawback of the Wessling method is that it is not universally applicable. The method requires water-soluble precursor monomers that are insensitive to fairly strong base. In addition, we have shown in other work[15] that the delicately balanced series of equilibria producing the actual polymerizing species – a *p*-xylylene – is greatly affected by the substituents attached to the precursor monomer species. As a result, it has not been clear how broad the applicability of the Wessling process is for general PPV synthesis.

As part of our studies of electronically unusual conjugated polymers, we were interested in the electronically 'push–pull' substituted poly(2-cyano-5-methoxy-1,4-phenylene vinylene) (2-CN-5-OMe-PPV) **1**.



1
(A = OMe, B = CN)

Scheme 1

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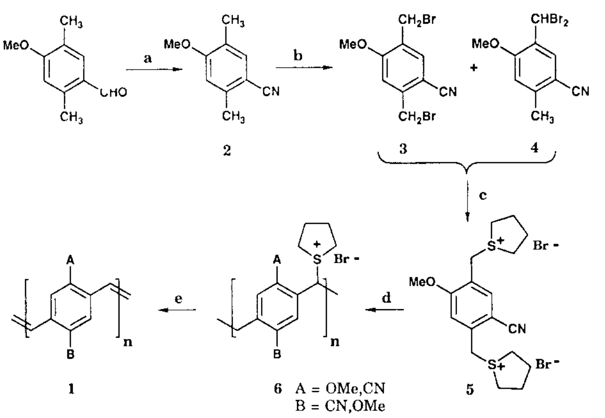


Scheme 2 Synthesis of polymer **1**: (a) $EtNO_2$, C_5H_5NHCl, heat; (b) *N*-bromosuccinimide, CCl_4, benzoyl peroxide catalyst, heat; (c) tetrahydrothiophene, MeOH, heat; (d) Me_4NOH, 4:1 H_2O/MeCN; (e) heat, vacuum

We previously reported[15] the synthesis of the monomeric precursor to this polymer, and its behaviour, in studies aimed at understanding the variation in *p*-xylylene production as a function of substitution in the Wessling process. In this contribution, we describe the synthesis of 1,4-bis(tetrahydrothiopheniomethyl)-2-cyano-5-methoxybenzene dibromide, its polymerization to polyelectrolyte under Wessling conditions, and characterization of the PPV obtained from thermal elimination of the polyelectrolyte.

EXPERIMENTAL

General considerations

All chemicals and solvents were reagent grade (Aldrich Chemical Company) and were used as received, unless otherwise stated. All melting points reported are uncorrected.

Ultraviolet–visible spectra were obtained on a Shimadzu UV-260 spectrophotometer. Infra-red spectra were obtained using an IBM 9000 *FT*i.r. spectrophotometer. ^1H n.m.r. spectra were obtained using either an 80 MHz IBM NR-80A or a 200 MHz Bruker HX-200 spectrometer. Thermogravimetric analysis (t.g.a.) was carried out using a Perkin–Elmer TGA-7 analyser. Gel permeation chromatography (g.p.c.) experiments were carried out on a Waters instrument consisting of a model 590 pump, a model 410 differential refractometer detector, and a Waters data module.

*2-Cyano-5-methoxy-*p*-xylene 2*

Following the method of Dauzonne *et al.*[16] (*Scheme 2*), pyridinium hydrochloride (13.3 g, 0.12 mol) was quickly added to a solution of 4-methoxy-2,5-dimethylbenzaldehyde (16.4 g, 0.10 mol) in 8.2 ml (0.12 mol) of nitroethane. The reaction mixture became homogeneous and was heated under reflux for 2.5 h, then cooled to room temperature. The reaction was diluted with 200 ml of 0.1 M aqueous HCl, extracted with 200 ml of dichloromethane, and then further extracted with three more 40 ml portions. The combined organic phases were washed with three 100 ml portions of water, then passed through a short column of silica gel. The solvent was evaporated and the residue was kept under vacuum overnight to give 15.6 g (97%) of **2** as a yellowish solid with m.p. 75–76°C. Calculated for $C_{10}H_{11}NO$: C, 74.50; H, 6.88; N, 8.69. Found: C, 74.25; H, 6.80; N, 8.72. I.r. (KBr, cm^{-1}): 2220 (sharp, C≡N stretch). ^1H n.m.r. ($CDCl_3$, ppm): 2.16 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 6.70 (s, 1H, ArH), 7.32 (s, 1H, ArH).

1,4-Bis(bromomethyl)-2-cyano-5-methoxybenzene 3

To a solution of **2** (10.0 g, 0.062 mol) in 50 ml of carbon tetrachloride was added *N*-bromosuccinimide (22.6 g, 0.127 mol) and 0.6 g of benzoyl peroxide. The mixture was heated at reflux under an argon atmosphere and irradiated with a sun lamp for 2.5 h. The resultant floating suspension was filtered hot, and the solid material was rinsed with hot carbon tetrachloride (three 40 ml portions). The combined carbon tetrachloride solutions were evaporated under reduced pressure to give an orange solid, which was redissolved in 60 ml of carbon tetrachloride. This solution was left to stand at room temperature for 2 h after which a white precipitate had formed, which ^1H n.m.r. showed not to be the desired product **3** but instead the asymmetric bromination product 2-cyano-5-methoxy-4-(dibromomethyl)toluene **4**. Removal of the solvent from the filtrate under reduced pressure yielded 17.4 g of a honey-like oil, the ^1H n.m.r. spectrum of which showed a mixture of brominated products containing substantial amounts of the dibromide **3**. Repeated efforts to isolate pure **3** through recrystallization and chromatography failed; however, this crude material could be used as is in the next synthetic stage.

1,4-Bis(tetrahydrothiopheniomethyl)-2-cyano-5-methoxybenzene dibromide 5

The crude bromide **3** (15.0 g) was suspended in a solution of tetrahydrothiophene (12.4 g, 0.14 mol) in 160 ml of methanol at 60°C. After heating for 15 h, the reaction was cooled to room temperature and filtered. The solid product was washed with three 30 ml portions of dry hexane and evacuated overnight at room temperature for 12 h to yield 6.5 g of **5** as a white solid. Calculated for $C_{18}H_{21}Br_2NOS_2$: C, 43.65; H, 5.09; Br, 32.26; N, 2.83; S, 12.94. Found: C, 43.63; H, 5.09; Br, 32.12; N, 2.86; S, 12.74. ^1H n.m.r. ($CDCl_3$, ppm): 2.23 (m, 8H, $SCH_2C\underline{H}_2$), 3.40 (m, 8H, $SC\underline{H}_2CH_2$), 3.89 (s, 3H, OCH_3), 4.38 (s, 2H, CH_2Br), 4.59 (s, 2H, CH_2Br), 7.27 (s, 1H, ArH), 7.81 (s, 1H, ArH).

Wessling polymerization of monomer 5 to polymer 6

The sulfonium monomer **5** was polymerized using the procedure of Garay and Lenz[17]. Generally, a solution of known concentration in a given solvent system was thoroughly degassed with argon, covered with an equal volume of degassed pentane, cooled to 0°C, placed under an argon atmosphere, and treated with a basic solution with brisk stirring.

In a typical reaction, 2.0 g (4.0 mmol) of monomer **5** were dissolved in 27 ml of a 4:1 (v/v) acetonitrile/water solvent to make a 0.15 M solution. The solution was filtered to remove any insoluble material, placed under argon, and covered with a layer of pentane equal in volume to the aqueous acetonitrile layer. The stirred, two-layer system was cooled to 0°C and purged for 1 h with argon. An aqueous solution of tetramethylammonium hydroxide (Aldrich, 25% in water) was similarly pre-cooled and purged. After purging, the two-layer system was treated with 1.62 ml of tetramethylammonium hydroxide solution added

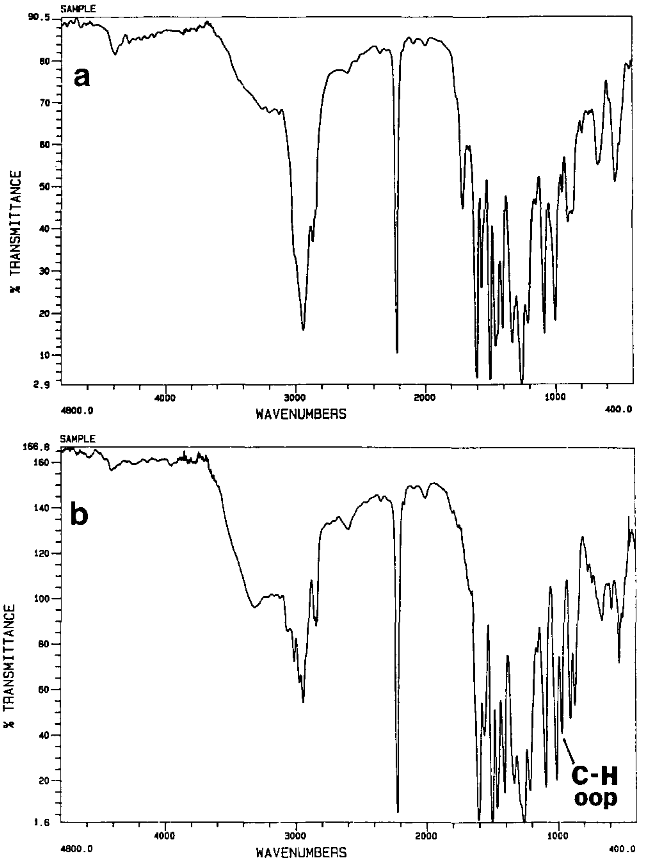


Figure 1 Fourier transform infra-red spectra for (a) polyelectrolyte **6** and (b) eliminated polymer **1**. The indicated peak in (b) is assigned to the olefininc out-of-plane bending mode of the vinylene linkage (oop C–H) in **1**

swiftly by syringe. The reaction mixture instantly turned yellow for a few seconds, then became light brown. The reaction mixture was stirred under argon at 0°C for 1 h, then quenched with sufficient dilute aqueous hydrochloric acid to obtain a neutral aqueous layer containing polymer **6**.

The solution of precursor polymer was dialysed against distilled water (Spectropore I, molecular weight cut-off 6000–8000) to give a solution appropriate for film casting and other studies. The polymer **6** could be cast on quartz or KBr plates under an inert atmosphere and/or evacuation to give somewhat brittle yellow films, usable for spectroscopy or thermal elimination. *Figure 1a* shows the *FT*i.r. spectrum of polymer **6** I.r. (neat film, cm^{-1}): 3400 (broad, OH contaminant), 2940 (OMe and tetrahydrothiophenium C–H stretch), 2220 (sharp, $C\equiv N$ stretch), 1604 (sharp, aryl C=C stretch), 1269 (C–O stretch). U.v.–visible (neat film, λ_{max} nm): 250, 340 (weak, broad shoulder).

The gel permeation chromatographic method of Machado *et al.*[18] was used to obtain molecular weight and polydispersity data for the polymers obtained under various conditions. The solutions of **6** (undialysed except in one case) were treated with sodium thiophenolate as described in ref. 18. *Table 1* shows the g.p.c. results for a number of solvent systems and concentrations used.

Thermal elimination of polymer 6

The optimal conditions for rapid elimination of polymer **6** to yield **1** without pyrolytic degradation of the final material were determined by thermogravimetric analysis. Thin films of polymer **6** cast on quartz plates clamped between two 0.125 inch thick Teflon sheets (Small Parts Inc.) were subjected to the elimination reaction by heating at 240 ± 10°C for 7 h under a vacuum of 0.030 mmHg. The resultant films were orange or yellow-orange. *Figure 1b* shows the *FT*i.r. spectrum of polymer **1**. Calculated for $C_{10}H_7NO$: C, 76.44; H, 4.46; N, 8.91; S, 0.00. Found: C, 63.01; H, 4.39; N, 7.29; S, 1.62. I.r. (neat film, cm^{-1}): 3009 (aryl C–H stretch), 2841 (OMe C–H stretch), 2222 ($C\equiv N$ stretch), 1603 (aryl C=C stretch), 1261 (O–C stretch), 966 (=CH out-of-plane bend). The u.v.–visible spectra of neat films of **1** varied somewhat with the elimination conditions, showing a long-wavelength cut-off of 410–480 nm.

RESULTS AND DISCUSSION

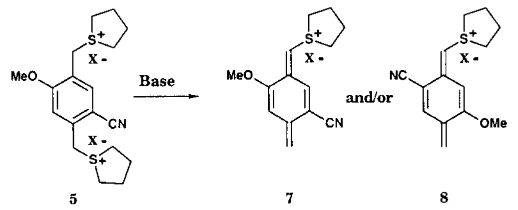
The synthesis of monomeric precursor salt **5** is fairly straightforward, with the exception of the Ziegler bromination of the aryl methyl groups by *N*-bromosuccinimide. When there is a substantial difference in activity of the two methyl groups in the *p*-xylene, owing to one group being *ortho* to the electron-donating methoxy group with the other being *ortho* to the electron-withdrawing cyano group, one may obtain considerable amounts of the product with double bromination on the methyl group *ortho* to the electron donor. Various efforts to defeat this tendency within this reaction scheme failed to eliminate this product. Fortunately, the *asym*-dibromo compound could be crystallized out of a crude mixture containing the desired *sym*-dibromo compound and monobrominated impurities. The impure *sym*-dibromide **3** could be treated with tetrahydrothiophene to produce the salt **5**, which was isolated in pure form for polymerization. We have in general had difficulty in symmetrically dibrominating *p*-xylenes bearing substituents of greatly differing electronic nature.

Polymerization of **5** under aqueous conditions was not very effective, and gave rise to material with a weight-average molecular weight of only 1100 by the assay method previously[18] developed here. The reason for this failure was suggested by our previous study of *p*-xylylene formation[15], in which virtually no xylylene was detected by u.v.–visible spectroscopy under purely aqueous conditions. However, we found that in an aqueous acetonitrile solvent system the u.v.–visible spectrum associated[15] with the presumed *p*-xylylenes **7** and **8** (*Scheme 3*) is readily observed. We assume in *Scheme 3* that both xylylenes are present, although it is not completely clear that this must be so[19]. Under higher

Table 1 G.p.c. molecular weight data for polymerization of **5** in different solvent systems

Polymerization solvent system[a]	Monomer concentration (mol l^{-1})	Base[b]	M_n/M_w[c]
H_2O/pentane	0.2	NaOH	900/1100
H_2O/dimethyl sulfoxide	0.2	NaOH	20 000/37 000
H_2O/acetonitrile (1:4)	0.12	NaOH	35 700/77 000
H_2O/acetonitrile/ pentane (1:4:5)	0.15	NaOH	39 000/66 900

[a] Volume/volume solvent ratios
[b] Base used for polymerization by procedure in the text
[c] G.p.c. results by the method of ref. 18



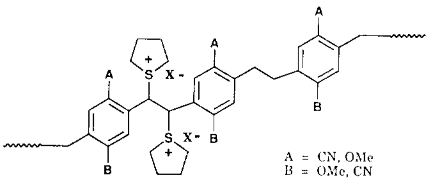
Scheme 3

concentration conditions appropriate to polymerization (rather than the dilute conditions used for u.v.–visible studies), a polymer of $M_w = 77\,000$ was obtained in a 1:4 (v/v) water/acetonitrile system. The degree of polymerization obtained as a function of solvent conditions rose from a minimum of about 4 in pure water to about 173 when using aqueous acetonitrile by the method of Garay and Lenz[17], yielding polydispersities ranging from 1.2 to 2.2 under the conditions used by us. The improvement in the degree of polymerization, shown by the solvent variations given in *Table 1*, demonstrates the usefulness of our earlier published u.v.–visible spectroscopy based method[15] for optimizing PPV formation by the Wessling method.

The films of polyelectrolyte **6** cast after dialysis with distilled water were typically somewhat brittle, but otherwise fairly strong. These films can be redissolved after film casting, showing that crosslinking does not occur. Pyrolytic elimination of sulfide side groups from **6** under a variety of conditions suggested by thermogravimetric analysis studies gave deep yellow to orange-yellow films that showed the usual ethylenic out-of-plane bending mode in the *FT*i.r. spectrum at 966 cm^{-1} (*Figure 1*). U.v.–visible solid-film studies also showed a strong red shift relative to the spectrum of the polyelectrolyte, from a spectrum dominated by benzenoid absorbance to an extremely broad, featureless absorption that cut off in the 410–480 nm range, depending upon the elimination conditions.

The spectral data show the formation of substantial conjugation in the pyrolysis of **6**, as expected for the formation of 2-CN-5-OMe-PPV **1**. In addition, major loss of the cyano group does not occur with pyrolysis, as shown by retention of the cyano stretching absorption in the i.r. spectrum of **1**. However, elemental analyses of the products obtained from a wide variety of elimination conditions always showed some retention of sulfur in the final product (1.6–5.5%) and a deficit in carbon, even at the maximum elimination temperatures usable in our pyrolysis apparatus. These trends are consistent with incomplete elimination of the sulfide groups from the polyelectrolyte films. The variation in sulfur retention also correlated with the observed u.v.–visible spectral cut-off (band gap) in the pyrolysed samples, in that samples exhibiting higher amounts of retained sulfur showed lower wavelength (higher energy) cut-offs. This result constitutes a means to control the band gaps of samples of **1** subjected to the elimination reaction under different conditions. A similar strategy of varied, partial elimination was used by Burroughs *et al.*[8] to control the effective conjugation length of other PPV derivatives.

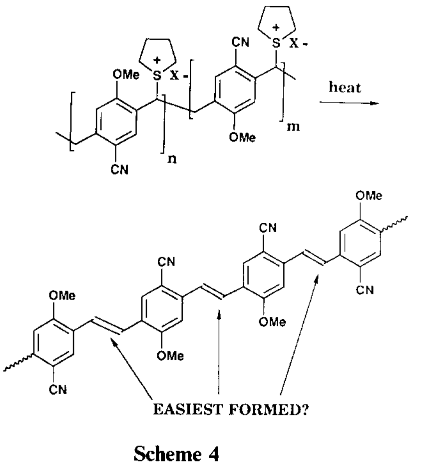
Apparently, a number of sulfonium side groups in the polyelectrolyte are not readily eliminated by pyrolysis without sample degradation. This result could be due to a lower activity of some sulfonium groups caused by the highly electron withdrawing cyano groups, or more likely due to a particular regiochemical connectivity that inhibits elimination in some segments of the polymer. For instance, if a substantial number of head-to-head linkages are formed in the polyelectrolyte, these linkages would not be amenable to easy formation of ethylenic, conjugating linkages by pyrolysis. The homopolymerization of **7** and/or **8** may occur with the formation of a number of head-to-head or tail-to-tail linkages as follows.



Such a result would be in contrast to the excellent regiospecificity of polymerization for symmetrically substituted PPV precursors, in which elimination of sulfur is near total in many cases, implying that only head-to-tail polymerization occurs.

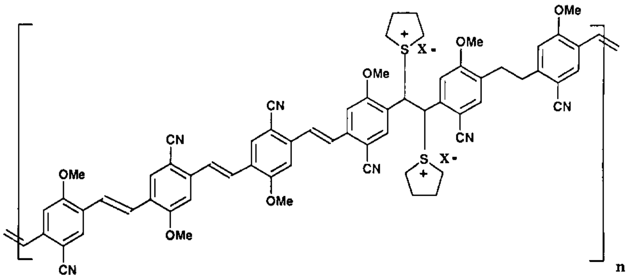
There is some additional evidence supporting the idea that cyano groups affect the inherent elimination chemistry of the Wessling synthesis. In other work in our laboratory[20] we have found that poly(2,5-dicyano-1,4-phenylene vinylene) (2,5-di-CN-PPV) has substantial retention of sulfur and carbon deficits by elemental analysis when made by the Wessling route. *FT*i.r. spectroscopy shows that 2,5-di-CN-PPV also retains a very high intensity cyano absorption, counterindicating loss of the cyano moiety. Apparently, the cyano group alters the usually facile elimination of sulfonium groups from the polyelectrolyte precursor in a manner that is unusual for these reactions (*Scheme 4*).

Related to the issue of incomplete elimination of sulfonium groups from polyelectrolyte **6** is the issue of regiospecificity in this reaction. The difference in activation of the benzylic protons owing to the proximity of either the electron-donating OMe group or the electron-accepting CN group could in principle lead to a substantial favouring of one of the two *p*-xylylenes **7** or **8** produced in *Scheme 3* above. The Wessling reaction is known to involve an ylid intermediate in at least some cases[12,21], so it was believed that the benzylic position *ortho* to the cyano group would be preferentially activated and be more likely to yield an ylid than the benzylic position *ortho* to the methoxy group, thereby favouring production of **7** in the reaction. The breadth of the



Scheme 4

u.v.–visible spectrum observed[15] after treatment of **5** with base suggests, however, that both **7** and **8** are actually formed in this process. Hsieh has argued along similar lines[19] for the formation of two xylylenes in another Wessling reaction with asymmetric ring substitution (A = H, B = CN in *Scheme 1*). Under the conditions of our reaction, it is possible that there is little difference in the likelihood of formation between **7** and **8**. At the present time an unequivocal method to differentiate the possible connectivity isomers of **1** is unavailable, and so we cannot tell whether any one of the following possible modes of connection is dominant.



We continue to work towards methods to distinguish between different types of linkage in PPV samples in which multiple regiochemical outcomes are possible, and hope to be able to comment more fully in future work on the exact nature of **1** and analogous asymmetric PPVs synthesized through the Wessling process.

CONCLUSIONS

The monomeric precursor appropriate for the Wessling synthesis of electronically 'push–pull' substituted 2-CN-5-OMe-PPV **1** is readily made, and can be homopolymerized under conditions that may be optimized by use of u.v.–visible model studies to give a degree of polymerization of about 170. The resultant polyelectrolyte product can be film-cast and subjected to an elimination reaction under conditions similar to those used for previously studied analogues. Spectral studies indicate that pyrolysis of the polyelectrolyte gives the conjugated PPV*. Elemental analysis shows defects in elimination to the final PPV product, with a significant number of sulfonium sites remaining uneliminated.

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 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.

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*As this paper was under review, Kim *et al.*[22] appeared with a description of u.v.–visible spectra for copolymers of parent PPV and 2-CN-5-OMe-PPV; however, synthetic details were not given in this report