methylene-1′-vinyl]-1,3-dioxa-4(*R*),5(*R*)-cyclopentanedicarboxylate, 116377-51-6; 1-(*tert*-butyldimethylsiloxy)-2(*Z*)-(2′-methoxy)ethylidene-5,5-dimethyl-3-methylidenecyclopentane, 116377-52-7; 1-(*tert*-butyldimethylsiloxy)-2-(*Z*)-(2′-methoxy)ethylidene-5,5-dimethyl-3(*E*)-(1′-trimethylsilyl)methylidenecyclopentane, 116377-53-8; 1-(*tert*-butyldimethylsiloxy)-2(*Z*)-butylidene-5,5-dimethyl-3-methylidenecyclopentane, 116377-54-9; 1-(*tert*-butyldimethylsiloxy)-2-butylidene-5,5-dimethyl-3-(2′-methoxyethoxymethoxypropylidene)cyclopentane, 116377-55-0; 1-(*tert*-butyldimethylsiloxy)-2(*Z*)-butylidene-3(*E*)-(carbomethoxymethylidene)-5,5-dimethylcyclopentane, 116377-56-1; 1-(*tert*-butyldimethylsiloxy)-9-(2′-methoxy)ethylidene-8-methylidenebicyclo[4.3.0]nonane, 116377-57-2; 20(*S*)-methyl-21-(*tert*-butyldimethylsiloxy)-21-[[4,4-bis(carbomethoxy)-2-methylidene-1(*E*)-cyclopentylidene]methyl]-4-pregnen-3-one, 116377-58-3; dimethyl 3(*E*)-(2-hydroxy-3-methylbutylidene)-4(*E*)-(acetoxymethylidene)cyclopropanedicarboxylate, 116377-60-7; dimethyl 3(*E*)-(2-hydroxy-3-methylbutylidene)-4-methylidenecyclopentanedicarboxylate, 116405-79-9.

Supplementary Material Available: Experimental procedures and spectral data (3 pages). Ordering information is given on any current masthead page.

Polymerization of α,α′-Bis(dialkylsulfonio)-*p*-xylene Dihalides via *p*-Xylylene Intermediates: Evidence for a Nonradical Mechanism

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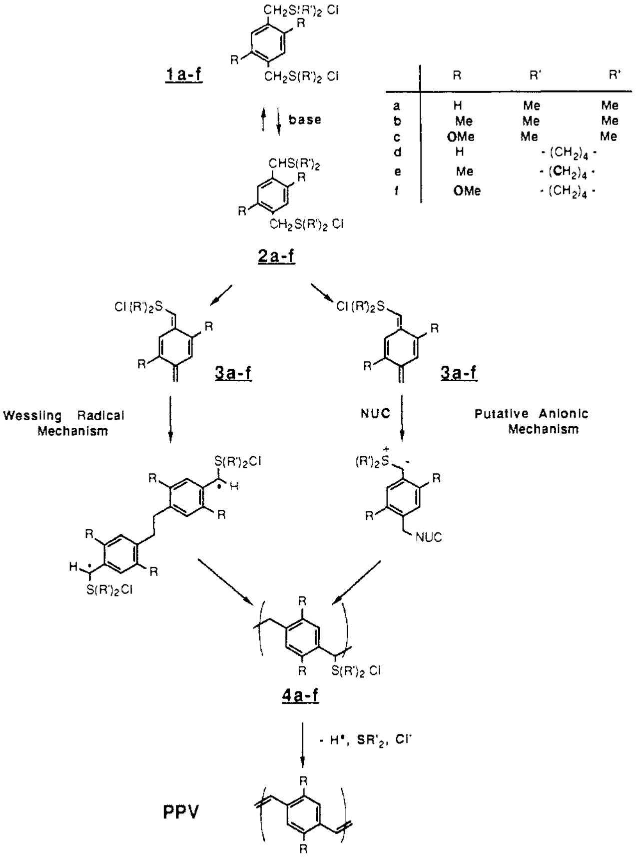
Simple *p*-xylylenes (PX's) require fairly low-temperature conditions for direct solution state observations, although stabilization can be achieved through appropriate substitution.[1] Recent advances in polymer chemistry have increased interest in functionalized PX's as useful monomers,[1,2] which one may in principle generate as reactive monomers that polymerize in situ.[3] Wessling[3b,c] has postulated that basic treatment of bis(dialkylsulfonio) salt derivatives of **1** yield polymerization to **4** by the route indicated in Figure 1. Since the Wessling polymerization is of particular importance in current work involving the production of the important conducting polymer precursor poly(*p*-phenylenevinylene)[4] (PPV), understanding its mechanism is of much potential use in controlling efficient syntheses of various substituted PPV's. In the investigations described below, we spectroscopically observed PX's **3a–f** but found no direct evidence favoring intervention of radical intermediates. We propose a modified polymerization mechanism, whereby PX's under typical reaction conditions polymerize by an anionic chain rather than a radical chain mechanism.



	R	R′	R′
a	H	Me	Me
b	Me	Me	Me
c	OMe	Me	Me
d	H	-$(CH_2)_4$-	
e	Me	-$(CH_2)_4$-	
f	OMe	-$(CH_2)_4$-	

Figure 1. Two possible polymerization mechanisms forming poly(*p*-xylylenes) **4**. Wessling mechanism from ref 3c, anionic mechanism from this paper.

At -12 °C, treatment of **1a**[5] in basic methanol yields a new UV–vis band at 317 nm (Figure 2) that reaches maximum intensity within 10 min and then gradually fades within 1 h. Similar treatment of **1b**[5] and **1c**[5] yields transient UV–vis absorptions at 322 and 330 nm, in reasonable agreement with model INDO-CI[6] computations predicting transitions for **3a–c** at 293, 334, and 325 nm, respectively. Similar absorptions are observed upon similar treatment of **1d–f**[5] and analogous tetrafluoroborate salts. The common position and transience of absorbance in all these reactions is consistent with formation of PX's **3a–f**.

Line-broadening effects in the ^1H NMR spectrum ($CD_3OD/NaOCD_3$) show exchange deuteriation of the methylene positions in **1a** via ylid **2a** at -50 °C.[7a] At >-40 °C the spectrum

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(1) Mulvaney, J. E. In *New Monomers and Polymers*; Culbertson, W. M., Pittman, C. V., Jr., Eds.; Plenum Press: New York, NY, 1974; Vol. 25.

(2) Szwarc, M. *J. Chem. Phys.* **1948**, *16*, 128.

(3) (a) Cf., for instance: Errede, L. A.; Hoyt, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 436. (b) Wessling, R. A.; Zimmerman, R. G. U.S. Patents 3 401 152 (1968); 3 404 132 (1968); 3 532 643 (1970); 3 705 677 (1972). Wessling, R. A.; Settineri, W. J. U.S. Patents 3 408 525 (1968); 3 697 398 (1972). (c) Wessling, R. A. *J. Polym. Chem., Polymer Symp.* **1985**, *72*, 55.

(4) (a) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Synth. Met.* **1987**, *17*, 639; *Polym. Comm.* **1984**, *25*, 327. (b) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 333. (c) Karasz, F. E.; Capistran, J. D.; Gagnon, D. R.; Lenz, R. W. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 327. (d) Antoun, S.; Gagnon, D. R.; Karasz, F. E.; Lenz, R. W. *Polym. Bull.* **1986**, *15*, 181. (e) Gagnon, D. R.; Capistran, J. D.; Karasz, F. E.; Lenz, R. W. *A.C.S. Polym. Prepr.* **1984**, *25*, 284. (f) Montando, G.; Vitalini, D.; Lenz, R. W. *Polymer* **1987**, *28*, 837.

(5) (a) Salts **1a–f** are obtained by boiling the corresponding 1,4-di(α-chloromethyl) compounds[5b] in a methanolic solution of the appropriate dialkyl sulfide. We thank Dr. Sharon Palmer for furnishing us with purified samples of the chloromethyl precursors of **1b–c,e,f**. Full experimental details of syntheses of **1a–f** and ^1H NMR spectral data for these compounds is described in the Supplementary Material. (b) Syntheses of the chloride precursors to **1a–f** that are not commercially available are described more fully by Lenz et al. (Lenz, R. W.; Han, C.-C.; Lux, M., submitted for publication).

(6) Zerner, M. C.; Ridley, J. E. *Theor. Chim. Acta* **1973**, *32*, 11; **1976**, *42*, 233.

(7) (a) In further support of this process, vacuum pyrolytic elimination of tetrahydrothiophene (THT) from **4d** produced from **1d** in CH_3OD/CH_3ONa yields unsubstituted PPV with an IR spectrum showing substantial deuterium incorporation at the vinyl positions (2229 cm^{-1} for C–D stretch, decreased intensity of vinyl C–H out-of-plane at 968 cm^{-1}, new band at 910 cm^{-1} assigned to vinyl C–D out-of-plane). Assignments were made in typical fashion, e.g., as in Dolphin and Wick (Dolphin, D.; Wick, A. E. *Tabulation of Infrared Spectral Data*; Wiley: New York, NY, 1977). (b) Polymers **4a,d** when synthesized under conditions similar to these have been characterized by ^1H NMR and IR spectroscopy (see Supplementary Material). The molecular weight (MW) of **4d** produced thusly is difficult to measure due to frequent clogging of GPC columns but is measured in the range 500 000–2 000 000. See: Machado, J. M.; Denton, F. R., III; Schlenoff, J. B.; Karasz, F. E.; Lahti, P. M. *J. Polym. Sci. Phys.*, in press. As a result of the difficulties in finding routine MW's for these polymers, investigation of the effects of anionic inhibitors, added inert nucleophile initiators, etc., upon the polymer MW remains for future mechanistic work.

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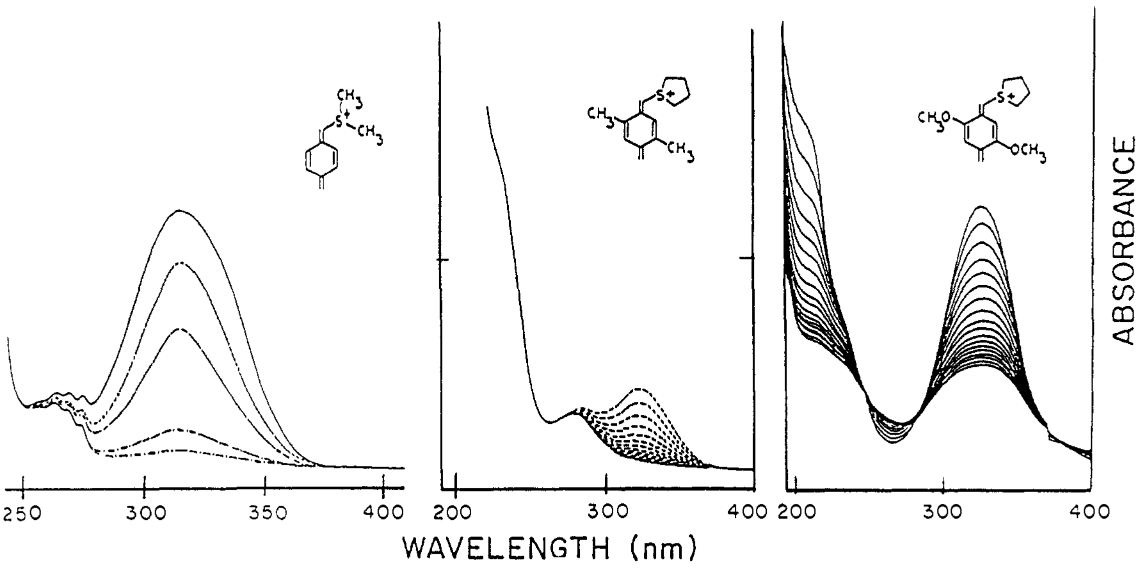

Figure 2. UV–vis spectra assigned to *p*-xylylenes **3a,e,f**. All spectra show decrease of spectral intensity as a function of time at fixed temperature, after attainment of maximum absorbance in the region of 300 nm.

shows disappearance of the precursor coincident with growth of both eliminated dimethyl sulfide (R'_2S, δ 2.07) and oligomeric **4a**.[7b] Upon further warming to room temperature, elimination of **4a** to oligomeric PPV[8] occurs if there is excess base (aromatic singlet at δ 7.48 ppm). Use of **1b** yields similar results but slower reaction times. Methoxy derivative **1f** shows a transient set of peaks in the vinylic region δ 6.0–6.5 ppm *coincident with elimination of tetrahydrothiophene*, which disappears upon warming above −20 °C to yield the spectrum of oligomeric **4f**. By comparison to the known ^1H NMR spectrum of *p*-xylylene itself (ring H δ 6.49, exocyclic H δ 5.10),[9] we have tentatively assigned these peaks to the ring hydrogens of PX **3f**.[10] Although further experiments are required to confirm this ^1H NMR assignment, the sequence of spectral changes as a function of temperature is consistent with our assignment and with the observed thermal behavior of the UV–vis absorption likewise attributed to **3f**.

In accordance with Wessling's proposed mechanism, we also sought evidence for radicals. We carried out the reaction with **1d** (CH_3OH, $NaOCH_3$, N_2 3-fold freeze–thaw degassing, −10 °C) in the cavity of an ESR spectrometer in the presence of 0.1–1.0 equiv of the standard radical trap TEMPO.[11] No decrease in ESR signal intensity for TEMPO was observed, despite obvious production of the characteristic yellow color of polymerization. Under similar conditions with 0.1–1.0 equiv of phenyl-*N*-(*tert*-butyl)nitrone to trap transient radicals as stable nitrosyl radicals,[12,13] no ESR signal was produced during polymerization. In the presence of styrene, polymerization proceeded as usual without apparent polystyrene formation, whereas under radical conditions, one would expect some production of polystyrene and a readily noticeable qualitative effect on the polymerization efficiency and yield for **4a**.

None of these experimental tests produce conclusive evidence requiring the presence of radicals in this polymerization. We therefore propose a putative anionic chain polymerization as a reasonable modification of the Wessling mechanism (see Figure 1). The sulfonium moieties polarize PX's **1a–f** and should favor exocyclic nucleophile attack and anionic polymerization, as observed with related but more stable *p*-xylylenes.[14] The anionic mechanism of Figure 1 seems most reasonable under the typical basic, highly polar reaction conditions, which are conversely not particularly conducive to radical mechanisms.

In conclusion, we report conditions for convenient electronic spectral observation of PX derivatives **3a–f**. NMR and IR studies are consistent with the Wessling mechanism for formation of *p*-xylylenes as reactive intermediates formed by 1,6-elimination from ylids. ESR and trapping studies, however, show no evidence requiring the radical polymerization postulated by Wessling. Proposal of our alternative anionic polymerization mechanism seems in good accord with all data presently available, when compared to the chemistry of related substituted *p*-xylylenes.[14] Work is ongoing in efforts to further clarify the nature of this polymerization and will be reported in due course.

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Supplementary Material Available: Experimental procedures for synthesis and polymerization of **1a–f** under UV–vis, ^1H NMR, and ESR conditions (where applicable) and interpretations of ^1H NMR experimental data (20 pages). Ordering information is given on any current masthead page.

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(8) The PPV formed in these reactions may be characterized by infrared spectroscopy (see Supplementary Material) and elemental analysis. A typical elemental analysis for PPV from **4a** (**4a** first dialyzed to remove NaCl) yields theoretical C, 94.1; H, 5.9. Found: C, 92.5; H, 5.7; S, 0.7; Cl, 0.4; O, 0.3. The slow production of conjugated PPV units during our dilute UV–vis polymerizations of **1a** can be monitored under extended reaction times with excess base, by production of long wavelength absorption at >400 nm, as previously noted[3c] but is not seen under our typical conditions and reaction times.

(9) Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1970**, *92*, 1436.

(10) The exocyclic hydrogens of **3f** under these conditions would be obscured by previous exchange of the methylene protons of **1f** with deuterium via the ylid **2f**.

(11) For data showing the utility of stable nitrosyl radicals in bimolecular coupling with alkyl radicals, cf.: Ingold, K. U. In Landolt–Boernstein *Numerical Data and Functional Relationships in Science and Technology*; *Subvolume C, Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Springer-Verlag; New York, NY, 1983; Vol. 13.

(12) For a brief review of PBN and related spin traps, see: Evans, C. A. *Aldrich. Acta* **1979**, *12*, 23.

(13) Controls established the stability of PBN and TEMPO to the reaction conditions over the time intervals studied.

(14) (a) Iwatsuki, S.; Itoh, T.; Sato, T.; Higuchi, T. *Macromolecules* **1987**, *20*, 2651. (b) Brandt, M. W.; Mulvaney, J. E.; Hall, H. K., Jr. *Macromolecules* **1988**, *21*, 1553.