Synthesis and Characterization of Ring-Halogenated Poly(1,4-phenylenevinylenes)

Ray K. McCoy and Frank E. Karasz

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

Ananda Sarker and Paul M. Lahti*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

Received April 16, 1991. Revised Manuscript Received July 23, 1991

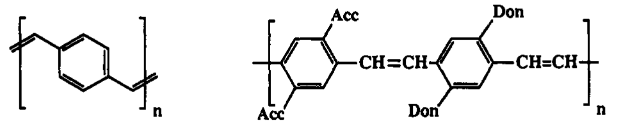
The synthesis and physical characterization of halogenated poly(1,4-phenylenevinylenes) (PPVs) is described. The mechanical properties of the PPV films thermally cast from water-soluble polyelectrolyte precursors in this methodology were found to be quite dependent upon the purity of the monomeric 1,4-bis(tetrahydrothiopheniomethyl)benzene dihalide starting materials, as was the molecular weight of the polyelectrolytes. The UV-vis spectra of the halogenated PPVs were blue-shifted relative to the parent PPV, suggesting an increased bandgap consistent with the net electron-withdrawing nature of the halogenated substituents.

Introduction

In the past several years, the highly conjugated organic polymer poly(1,4-phenylenevinylene) (PPV, 1) and its derivatives have been the subject of intense investigation because of both their conductive properties and, more recently, their nonlinear optical (NLO) properties. A majority of recent syntheses and investigations of PPVs has involved derivatives with alkyloxy or other electron-donating groups on the aromatic rings of the system. Electron-acceptor-substituted PPVs have not been investigated to the same extent. In an early patent,[1] investigators at Dow Chemical Corp. reported the synthesis of 2,5-dichloro-PPV (2) and 2,5-dibromo-PPV (3) but did not report specific synthetic procedures or properties. Murase and co-workers[2] have reported the synthesis of 2, as well as its conductivity upon doping with SO_3 and its thermal degradation at temperatures above 350 °C, but the report lacks significant detail concerning polymer characterization and molecular weight. A perchlorinated PPV has been synthesized by a fairly specific synthetic route and its impressive thermal stability noted.[3] We are not aware of other reports[4] in the literature that detail synthesis by Wessling's method[1] of PPVs bearing only halogens or other electron-acceptor groups on their aromatic rings.

There is much potential interest in PPVs containing electron-acceptor substituents in the production of electronically novel blends or copolymers of these with structural moieties containing electron-donor groups. For example, work on smaller molecular systems has shown the importance of dipole separation in achieving NLO activity.[5] For NLO-active materials, it is structurally desirable to obtain conjugated π-systems containing both resonance-donor and resonance-acceptor types of substituents. PPV offers a highly conjugated, typically planar[6] π-system that would seem ideal for NLO activity, if appropriate substitution could be designed. Third-order NLO activity has been shown for the parent PPV homopolymer 1.[5] In principle, in analogues of PPV where resonance electron-donor and -acceptor substituents alternate, second-order NLO activity might be induced (Scheme I). For example, a PPV copolymer with substantial incorporation of alternating electron π-donor and π-acceptor substituents would fulfill the structural desiderata of high conjugation and presence of "push-pull" π-substitution patterns. Various schemes attempted by us to incorporate the strong resonance electron-acceptor cyano and nitro substituents into high molecular weight PPVs have so far been unsatisfactory. However, the electronic nature of halogens as π-donors and inductive acceptors[7] made them appropriate secondary choices for the development of synthetic methodology for electron deficient PPVs. Eventually, we hope to show that production of $\chi^{(2)}$ NLO activity in PPVs is a plausible strategy through copolymerization as shown in Scheme I. Optimizing the synthesis of electron-deficient PPV homopolymers is a logical first step in this plan. Although halogen substituents have poor electronic resonance properties for production of strong $\chi^{(2)}$ activity, their substantial difference in electronic nature from electron-rich PPV monomers that have been extensively studied to date makes them useful targets for our planned studies of PPV copolymerization a lâ Scheme I. As part of the

Scheme I



1

$\chi(3)$ activity

Acc = electron acceptor
Don = electron donor

$\chi(2)$ activity (?)

---

[1] Wessling, R. A.; Zimmerman, R. G. U.S. Patent 3,401,152, 1968; 3,706,677, 1972.

[2] Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Synth. Met.* **1987**, *17*, 639.

[3] Ballester, M.; Castaner, J.; Riera, J. *J. Am. Chem. Soc.* **1966**, *88*, 957.

[4] A ring-nitrated PPV copolymer has been reported: Jin, J.-I.; Shim, H.-K.; Park, C.-K.; Kang, H.-J.; Yu, S. H.; Kim, J.-C. *Int. Conf. Sci. Technol. Synth. Met.*; Abstracts Vol. 1.; Tubingen, Germany, Sept 2-7, 1990; Abstract POL 21.8, p 176. Few details are included.

[5] *Cf.*, for instance: Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690. Dalton, L. R. In *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum: New York, 1988; p 243.

[6] Masse, M. A.; Martin, D. C.; Karasz, F. E.; Thomas, E. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.)* **1987**, *57*, 441. Masse, M. A.; Schlenoff, J. B.; Karasz, F. E.; Thomas, E. L. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 2045.

[7] *Cf.* the discussion in: March, J. *Advanced Organic Chemistry: Reactions, Mechanism, and Structure*, 2nd ed.; McGraw-Hill: New York, 1977; pp 459-461.

* To whom correspondence should be addressed.

0897-4756/91/2803-0941$02.50/0

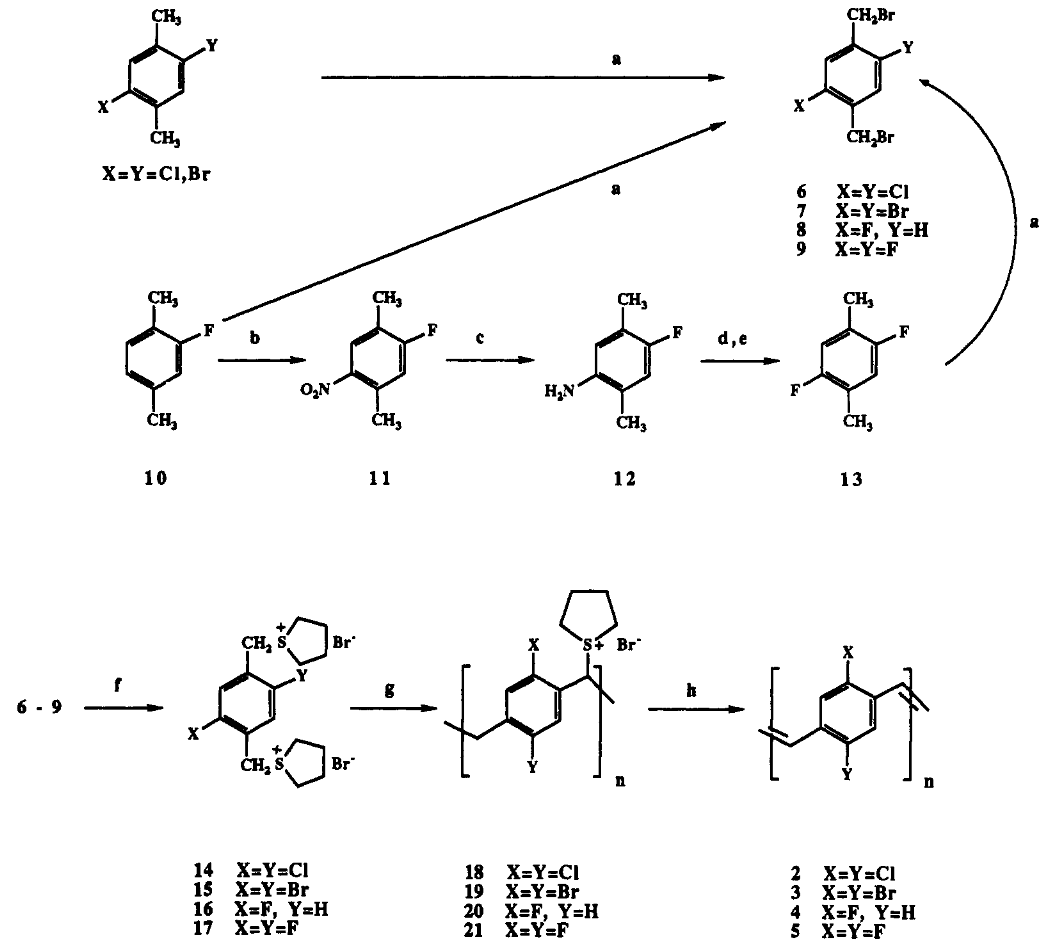


Figure 1. Synthesis of poly(1,4-phenylenevinylenes) **2–5**. (a) *N*-bromosuccinimide/benzene or CCl_4/heat. (b) Fuming nitric acid/−15 °C. (c) 60 psi hydrogen/PtO_2/EtOH/2.5 h. (d) 48% fluoroboric acid/$NaNO_2$/H_2O/0 °C. (e) Dry pyrolysis. (f) Tetrahydrothiophene/48% $HBr_{(aq)}$. (g) 10% Me_4NOH/0 °C/H_2O-pentane. (h) Pyrolytic vacuum elimination.

initial phases of these studies, we have undertaken the synthesis of the halogenated PPV homopolymers **2–5** (Figure 1) by the so-called soluble precursor (polyelectrolyte) route to PPVs.[8] In this paper, we report full synthetic details and characterization of these homopolymers.

Synthetic Methodology for Halogenated PPV Homopolymers

The basic method of forming PPV via the soluble precursor route has been published.[8] Figure 1 shows a schematic summary of our syntheses of PPV homopolymers **2–5**. *p*-Xylene-derived starting materials whose structures are shown in Figure 1 are commercially available and were used for synthesis of ring-halogenated intermediates **6** and **7** via benzylic bromination. Synthesis of fluorinated intermediates **8** and **9** was more involved. Monofluoro intermediate **8** was made by a standard sequence involving transformation of commercially available 2,5-dimethylaniline via its diazonium salt to 1,4-dimethyl-2-fluorobenzene (**10**), followed by benzylic bromination. Intermediate **9** was made by nitration of **10** to **11**, followed by reduction to **12**, repetition of the synthetic sequence for transformation of an amino group into the fluoro group to give difluoride **13**, benzylic bromination. In the synthesis of **9**, placement of one fluorine atom at a time produced much higher yields than did efforts to fluorinate 1,4-diamino-2,5-dimethylbenzene via diazotization, as others have similarly noted.[9]

With the benzylic bromides **6–9** in hand, we proceeded to synthesize the monomeric bisbenzylic tetrahydrothiophenium salt precursors **14–17** by treatment with excess tetrahydrothiophene (THT) in concentrated hydrobromic acid.[10] The monomeric salts were purified by repeated precipitation from dry acetone and stored in well-sealed bottles at −25 °C. The stability of **14–17** was fairly good, and these monomeric precursors could be stored in the freezer for weeks without apparent decomposition or subsequent loss of efficacy in the polymerization stage of the syntheses.

Polymerization of **14–17** was carried out under argon at 0 °C using the two-phase solvent system described by Garay and Lenz.[11] Basic aqueous reaction conditions were employed for actual polymerization of the monomeric salts, while an overlying immiscible organic layer was used to extract the byproduct tetrahydrothiophene, bringing the polymerization reaction toward completion. Polyelectrolyte solutions of **18–21** obtained in this way could be dialyzed against distilled water or precipitated into isopropyl

---

(8) (a) A review that includes a description of the soluble precursor method and a variety of leading references: Bradley, D. D. C. *J. Phys. D: Appl. Phys.* **1987**, *20*, 1389. (b) Cf. also references cited in: Denton, F. R., III, Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1990. (c) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1984**, *25*, 327. Gagnon, D. R.; Capistran, J. D.; Karasz, F. E.; Lenz, R. W.; Antoun, S. *Polymer* **1987**, *28*, 567.

(9) *Cf.*, for instance, the 38% yield of 1,4-difluorobenzene from 1,4-phenylenediamine in: Bergmann, E. D.; Berkovic, S.; Ikan, R. *J. Am. Chem. Soc.* **1956**, *78*, 6037.

(10) Rempfler, H.; Bosshard, H.; Weber, K. U.S. Patent 4,016,203, 1977.

(11) Garay, R.; Lenz, R. W. *Makromol. Chem. Suppl.* **1989**, *15*, 1.

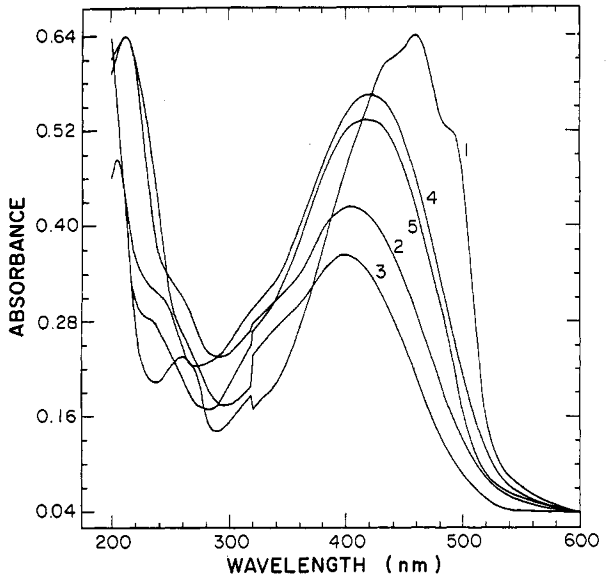


Figure 2. UV–vis spectra for poly(1,4-phenylenevinylenes) 1–5. Abscissa is in nanometers, ordinate is in absorbance units, with the individual spectra scaled arbitrarily in fit the single figure.

Table I. Gel Permeation Chromatographic Analysis of PPV Polymer Precursors

polymer	[monomer],[a] M	M_n/M_W[b]	degree of polymerization[c]
2, X = Y = Cl	0.5	53 000/155 600	553
	0.2	62 300/138 900	494
	0.2[d]	191 100/979 300	4613
3, X = Y = Br	0.1	260 500/656 800	1775
	0.05	93 600/269 200	727
4, X = H, Y = F	0.2	85 700/342 600	1488
5, X = Y = F	0.05	5 900/171 500	1166

[a] Concentration of monomeric salt used in polymerization (see Experimental Section). [b] Analysis of thiophenoxide-derivatized samples of polyelectrolytes 18–21 according to the method described in ref 12. [c] Computed via division of M_W divided by equivalent weight of monomer. [d] Highly purified monomeric precursor 14 used in polymerization.

alcohol, the products stored conveniently either as refrigerated dialyzed solutions or as damp, fibrous masses after precipitation. Aqueous solutions of 18–21 could then be cast into films by evaporation and thermally eliminated under vacuum to give the desired homopolymers 2–5. Optimal elimination conditions were determined by thermal gravimetric analysis (TGA). Required temperatures were, on the one hand, sufficiently low to avoid rapid degradation of the polymer (as determined by the sample's continuous weight loss after initial losses due to elimination of tetrahydrothiophene) but, on the other hand, high enough to allow elimination at a reasonable rate, typically 4–6 h. Individual thermal elimination conditions for 18–21 are given in the Experimental Section. Films of 2–5 produced in this way were also quite acceptable for analysis by infrared and UV–vis spectroscopy. UV–vis spectra are shown in Figure 2, along with the spectrum of a thin film of PPV 1 produced under similar conditions.

Molecular Weight Analysis

Gel permeation chromatography (GPC) was used to determine the molecular weights of homopolymers 2–5. Calibration of molecular weights was done relative to polystyrene standards, with tetrahydrofuran as the eluting solvent. Actual measurements were not carried out on the extremely insoluble PPVs themselves but on thiophenoxide-derivatized samples of polyelectrolytes 18–21, using a method developed by some of us in related work.[12] We refer the reader to this reference for procedures but note that the derivatization involved is used to render the water-soluble polyelectrolytes soluble in organic solvents such as tetrahydrofuran. Table I shows typical GPC results for derivatives of polyelectrolytes 18–21, which were used to make 2–5. Under our variable monomer concentrations, no large changes in polymer molecular weight occurred. However, when sufficient monomeric salt precursor was available to allow multiple precipitation and purification—as was tested for homopolymer 2—a dramatic increase in molecular weight was observed. We have noted a similar effect for parent PPV 1 polymerizations, namely, that reactions that gave low molecular weights often were found to involve preparations that had pernicious impurities of some sort in the monomer salts. This point is further addressed in the Discussion. For our present studies, the degrees of polymerization achieved in Table I were sufficient, despite the fact that they represent substantially lower degrees of polymerization than those achievable by the presently available techniques for PPV 1.[10]

Discussion

As mentioned, our interest in electron-acceptor ring-substituted PPVs is complementary to our studies of electron-donor-substituted PPVs for making potentially NLO-active copolymers and homopolymer blends. High molecular weight PPVs with highly electron-donating amino substitution are not presently available, but alkoxy-substituted PPVs have been made[13–15] and are presently the subject of substantial interest as dopable conducting polymer precursors. Highly electron-accepting substituents that have resonance properties appropriate for potential NLO use include the nitro and cyano groups. Both nitro and cyano groups strongly deactivate the benzylic positions on substituted *p*-xylenes to free radical bromination (see Figure 1), and hence the strategy we eventually used for the ring halogenated PPVs was not efficient for these more strongly electron-withdrawing substituents. Efforts to make a 2-nitro-PPV via an alternative synthesis based on nitration of commercially available 1,4-bis(chloromethyl)benzene failed when the corresponding tetrahydrothiophenium bis-salt from this material failed to give any identifiable high molecular weight product when subjected to the typical soluble precursor polymerization conditions. This result was consistent with our failure to observe by UV–vis spectroscopy a *p*-xylylene intermediate at λ_{max} near 300 nm under these polymerization conditions. All successful PPV syntheses based on the soluble precursor methodology have shown such corresponding *p*-xylylene intermediates,[16–18] so our inability to observe one

---

(12) Machado, J. M.; Denton, F. R., III; Schlenoff, J. B.; Karasz, F. E.; Lahti, P. M. *J. Polym. Sci. B: Polym. Phys.* **1989**, *27*, 199.

(13) Han, C.-C.; Lenz, R. W.; Karasz, F. E. *Polymer* **1987**, *28*, 261. Antoun, S.; Gagnon, D. R.; Karasz, F. E.; Lenz, R. W. *Polym. Bull.* **1986**, *15*, 181. Jen, K.-Y.; Cava, M. P.; Huang, W.-S.; MacDiarmid, A. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1502. Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1987**, *28*, 227, 230. Also, work on monomethoxy ring-substituted PPV has been carried out: Liang, W.; Lenz, R. W.; Karasz, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 2867–2875.

(14) Momii, T.; Tokito, S.; Tsutsui, T.; Saito, S. *Chem. Lett.* **1988**, 1201.

(15) Askari, S. H.; Rughoopath, S. D.; Wudl, F. *Synth. Met.* **1989**, *29*, 129. Asakari, S. H.; Rughoopath, S. D.; Wudl, F. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.)* **1988**, *59*, 1068. Asakari, S. H.; Rughoopath, S. D.; Wudl, F.; Heeger, A. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *39*, 157.

(16) Hörhold, H.-H.; Palme, H.-J.; Bergmann, R. *Faserforschung und Textiltechnik Zeitscrift fur Polymerforchung*, **1978**, *29* (5), 299; *Chem. Abstr.*, **1978**, *78*, 110456y.

in this case suggests that the mechanism responsible for the desired polymerization was suppressed. The different behavior of the nitro-substituted systems is not completely unexpected, based on other well-known reports of anomalous behavior of nitro-substituted benzylic systems.[20] Accordingly, we designated the ring-halogenated PPVs our electron-acceptor-substituted polymers, at the same time realizing that they would not be ideal in terms of their limited electron-acceptor ability compared to cyano an nitro groups. Although other synthetic methodologies may make these more desirable groups available in the future, we felt that synthesis of the halogen-substituted PPVs would constitute an extension of the soluble precursor methodology to electron-deficient PPV systems of high molecular weight. It is also liable to provide a basis for eventual evaluation of the electronic properties of future copolymers and homopolymer blends between **2**–**5** and electron-rich PPVs such as 2,5-dialkoxy-PPVs or poly(2,5-thiophenevinylene)[19] derivatives.

Our results show 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 were noted. Formation of the monomer precursor salts **14**–**17** required use of more vigorous conditions with heated concentrated hydrobromic acid and neat THT, rather than the milder use of THT in boiling methanol for parent PPV synthesis, due to the low reactivity of **6**–**9** in the milder conditions. The actual polymerizations to polyelectrolytes **18**–**21** were feasible with conditions fairly similar to those for parent PPV.[8] Thermal elimination of the films of **18**–**21** to **2**–**5** 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 was followed by steady loss of sample weight, indicating polymer degradation. If temperatures were too low or elimination times too short, polymer degradation was avoided, but at the cost of incomplete elimination of volatiles, as shown by the presence of residual sulfur in elemental analyses of eliminated films. To date we have been unable to achieve complete elimination of polyelectrolytes **18**–**21** to PPVs **2**–**5**, and we have detected residual sulfur in elemental analysis of 0.2–1.0%. This is still inferior to the best results that have been achieved for parent PPV, but it nonetheless still implies a very high average degree of conjugation in each chain, with very few interruptions in the sequence of conjugated units.

The average molecular weights obtained in analysis of functionalized **18**–**21** by GPC were substantially lower than those obtained for the precursor polyelectrolyte to PPV **1**.[12] Whereas we routinely found the precursor to **1** to have a GPC M_w of $(1-2) \times 10^6$ under optimized conditions, the M_w's for **18**–**21** were typically $(1-6) \times 10^5$, depending upon the concentration of starting material used in the polymerization. In general, high molecular weight material was favored by high concentrations of monomer precursors **14**–**17** during polymerization, where monomer/polymer solubility and solution viscosity conditions permitted it. An impressive increase of average degree of polymerization was realized for one polymerization of **14** to **18** at 0.2 M, where **14** was subjected to unusually rigorous purification (see Table I). When **14** was precipitated several times—rather than the typical one or two times—from dry acetone, the observed M_w was on the order of 10^6, similar to that achieved for parent PPV **1**. While such purification measures are quite expensive and time consuming (unless on a scale where acetone may be recycled), it is clear that they substantially increase the degree of polymerization in these reactions and are necessary where very high M_w material is needed. We presume that molecular weights for our PPVs **2**–**5** may be routinely increased to the M_w = 500 000–1 000 000 range when sufficient quantities of monomer precursor salts **14**–**17** are available to allow the inevitable losses associated with stringent purification. In particular, we have noted that the presence of small (even 1–2%) amounts of monohalogenated side products generated during synthesis of dihalides such as **6**–**9** apparently led to formation of monosulfonium salt impurities in the polyelectrolyte monomer bissulfonium salt, which in turn appear to inhibit chain growth at the actual polymerization stage.[18]

The UV–vis spectroscopy of PPVs **2**–**5** in Figure 2 seems consistent with the net electron-acceptor nature of the halogen substituents. This is most readily seen by comparing these spectra with those for parent PPV **1**[21] and 2,5-dimethoxy-PPV.[22,23] All of the PPVs **2**–**5** have their longest wavelength absorption maxima in the range 400–412 nm. Figure 2 shows the spectrum for a film of PPV **1** prepared under the same conditions used for **2**–**5**, with long-wavelength transitions at 440–460 nm. Finally, the spectrum for the dimethoxy-PPV variant in other experiments (not shown in Figure 2) indicates band onset at 610 nm[22] with maxima at 485–510 nm.[23] There is a noticeable red shift proceeding along the series in the order presented corresponding to a decrease in bandgap. This is consistent with the simplistic picture that alkoxy substitution decreases the bandgap E_g (which correlates with the long-wavelength absorption maxima) relative to PPV **1** by electron donation, while the halogens all increase E_g by electron withdrawal. One would expect, as a result, that the halogenated polymers would be inefficient as p-dopable conducting polymers. This is consistent with the observation of Murase et al.[2] of poor conductivity for doped samples of **2**.

We are presently carrying out further physical studies of PPVs **2**–**5** aimed at determination of their NLO properties. We also are investigating homopolymer blends of **2**–**5** with other PPV derivatives and analogues, as well as reactions aimed at producing copolymers of ring-halogenated PPV monomers with other PPV analogues. Comparison of these investigations with the results for homopolymers **2**–**5** will be described upon completion of the studies.

Conclusions

We find that synthesis of ring-halogenated PPVs **2**–**5** may be carried out by minor modification of the standard soluble precursor route for PPVs. The molecular weight magnitudes and distributions for these polymers are readily studied by methods previously described by us for other PPVs and indicate that further improvement in

---

(17) Denton, F. R., III; Lenz, R. W.; Karasz, F. E.; Lahti, P. M. *J. Am. Chem. Soc.* **1988**, *110*, 7258.

(18) Denton, F. R., III; Lahti, P. M. Unpublished results.

(19) Jen, K. Y. A.; Elsenbaumer, R. L.; Shacklette, L. W. U.S. Patent 894,172 (pending); *Chem. Abstr.* **1987**, *109*, 191098g. Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Cummun.* **1987**, *28*, 227, 230. Yamada, S.; Tokito, S.; Tsutsui, T.; Saito, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1448. Gregorius, R.; Karasz, F. E. Unpublished results.

(20) Cf. for instance the study of reactions between strong base and 4-nitrobenzylsulfonium tosylate in: Closs, G. L.; Goh, S. H. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2103; *J. Chem. Soc., Perkin Trans. 2* **1972**, 1473.

(21) Obrzut, J.; Karasz, F. E. *J. Chem. Phys.* **1987**, *87*, 6178.

(22) Jen, K.-Y.; Shacklette, L. W.; Elsenbaumer, R. L. *Synth. Met.* **1987**, *22*, 179.

(23) Obrzut, J.; Karasz, F. E. Unpublished results. *Cf.* also the spectroscopy of the 2,5-dihexyloxy-PPV described in the first citation of ref 15.

degrees of polymerization beyond those described herein may be achieved if efficient high-purification procedures can be defined for the monomeric precursor salts **14–17**. UV–vis spectroscopy indicates a net electron-withdrawing character for the halogen substituents on homopolymers **2–5** and will provide a convenient benchmark for comparison to experiments already in progress that are aimed at synthesis of copolymers between ring-halogenated and otherwise substituted PPVs and PPV analogues.

Experimental Section

Melting point determinations were made using a Fisher-Johns melting point apparatus; all temperatures are uncorrected. Elemental analysis was performed by the University of Massachusetts Microanalytical Laboratory; methodological interference between chlorine and bromine caused us in some cases to omit certain elemental determinations. Unless otherwise noted, UV–vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrometer; infrared spectra were recorded on an IBM 9000 FTIR spectrometer, and proton nuclear magnetic resonance (NMR) spectra were recorded on Varian XL-200 and XL-300 FT-NMR spectrometers. Proton NMR spectrum resonance positions are reported relative to the tetramethylsilane standard on the δ scale in parts per million (ppm). TGA was carried out on a Perkin-Elmer TGA-7 analyzer. GPC experiments were carried out on a Waters GPC setup consisting of a Model 590 pump, a Model 410 differential refractometer detector, and Waters data module. Unless otherwise stated, starting reagents were obtained from Aldrich Chemical Co. and were used as received.

General Procedure for Preparation of 1,4-Bis(bromomethyl)benzenes 6–9. Following the general procedure of Greenwood et al.,[24] in a typical run 0.10 mol of the appropriate substituted *p*-xylene was dissolved in 100 mL of spectral grade benzene or carbon tetrachloride in a 250-mL round-bottom flask equipped with boiling stones and a condenser. *N*-Bromosuccinimide (0.20 mol) was added along with 0.01 g of benzoyl peroxide or 2,2′-azobisisobutyronitrile as initiator. The mixture was heated under reflux under nitrogen atmosphere for several hours, and the resulting suspension suction filtered to remove succinimide byproduct. The solvent was then removed from the filtrate under reduced pressure, and the crude product benzylic bromides recrystallized from an appropriate solvent. *Caution*: Benzylic bromides can be powerful lachrymators and should be used with adequate ventilation and precautions against skin contact or ingestion!

1,4-Bis(bromomethyl)-2,5-dichlorobenzene (6). Compound **6** was obtained from 2,5-dichloro-*p*-xylene (175.1 g, 1.00 mol) by the general procedure described for bromination, using benzene as solvent. The crude product was recrystallized from ethanol to give 162 g (49%) of white solid **6** with mp 124–125 °C (lit.[25] mp 112–114 °C). ^{1}H NMR ($CDCl_3$) δ 7.48 (s, 2 H, aromatic C–H), 4.51 (s, 4 H, CH_2Br). Anal. Calcd for $C_8H_6Br_2Cl_2$: C, 28.87; H, 1.82; Br, 48.01; Cl, 21.30. Found: C, 28.64; H, 1.81.

1,4-Bis(bromomethyl)-2,5-bromobenzene (7). Compound **7** was obtained from 2,5-dibromo-*p*-xylene (100.3 g, 0.38 mol) by the general procedure described for bromination, using carbon tetrachloride as solvent. The crude product was recrystallized from ethanol to give 62 g (38%) of white solid **7** with mp 161–162 °C (lit.[25] mp 145–147 °C). ^{1}H NMR ($CDCl_3$) δ 7.66 (s, 2 H, aromatic C–H), 4.51 (s, 4 H, CH_2Br). Anal. Calcd for $C_8H_6Br_4$: C, 22.78; H, 1.43; Br, 75.78. Found: C, 22.93; H, 1.40; Br, 75.68.

1,4-Dimethyl-2-fluorobenzene (10). Following the method of Valcanas,[26] 2,5-dimethylaniline (24.2 g, 0.20 mol) was added dropwise to a 500-mL beaker containing stirred 48% fluoroboric acid (168.0 g, 120 mL, 0.92 mol) at or below 0 °C. Care must be taken not to allow the white suspension that forms to clump together, so mechanical stirring is recommended. Sodium nitrite (14.0 g, 0.20 mol) dissolved in 30 mL of water was added dropwise to the stirred suspension, maintaining the temperature at or below 0 °C. After addition of the nitrite solution, the mixture was allowed to stir for 45 min with continued cooling. The resultant precipitate was suction filtered and washed with cold water, cold methanol (50 mL), and cold anhydrous diethyl ether (75 mL). The product, 2,5-dimethylbenzenediazonium tetrafluoroborate, was obtained as a beige solid that was dried under high vacuum to give 38.0 g (86%) of material with mp 69–71 °C (dec) (lit.[26] mp 70–72 °C). This material was used directly in the following decomposition step.

2,5-Dimethylbenzenediazonium tetrafluoroborate (28.0 g, 0.13 mol) was placed in a 500-mL round-bottom flask equipped with a condenser. The flask was carefully heated in an oil bath at 85 °C until gas evolution began, at which time the heat source was removed and the salt allowed to decompose under the condenser. *Caution*: Due to the rapid evolution of gas, large-scale preparations by this method require appropriate precautions such as use of a blast shield and cautious heating. After evolution of gas ceased, 250 mL of water was added to the reaction flask and crude products distilled in steam into a 500-mL flask containing 50 mL of diethyl ether. The distillate was separated, and the aqueous layer extracted with 50 mL of diethyl ether. The combined organic layers were washed with 50 mL of saturated aqueous sodium carbonate and then with brine and then dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure and distillation of the product gave 12.5 (77%) of colorless liquid 1,4-dimethyl-2-fluorobenzene (**10**), bp 145–146 °C (lit.[26] 137–138 °C/730 mmHg). ^{1}H NMR ($CDCl_3$) δ 7.00 (pseudo t, 1 H, J = 8 Hz, aromatic C–H), 6.75–6.81 (m, 2 H, aromatic C–H), 2.27 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3).

1,4-Bis(bromomethyl)-2-fluorobenzene (8). Compound **8** was obtained from 1,4-dimethyl-2-fluorobenzene (**10**, 12.0 g, 0.10 mol) by the general procedure described for bromination, using carbon tetrachloride as solvent and heating with a 275-W sunlamp placed 3 cm from the reaction for 8 h. The crude product was recrystallized from hexanes to give 13.5 g (48%) of white crystalline **8** with mp 99–101 °C. ^{1}H NMR ($CDCl_3$) δ 7.35 (pseudo t, 1 H, J = 8 Hz, aromatic C–H), 7.15 (m, 2 H), 4.48 (s, 2 H, CH_2), 4.42 (s, 2 H, CH_2Br). Anal. Calcd for $C_8H_8Br_2F$: C, 34.10; H, 2.50; Br, 56.70; F, 6.70. Found: C, 34.25; H, 2.59; Br, 56.76; F, 6.40.

2-Fluoro-5-nitro-*p*-xylene (11). To 30 g (0.24 mol) of **10** in a 150-mL beaker was added dropwise 30 mL of fuming nitric acid at a temperature of –15 to –20 °C (Dry Ice/acetone) over 1.5 h. After addition, the reaction was stirred for 30 min at –15 °C. The dark brown reaction mixture was allowed to warm to room temperature and then heated to 40 °C for 2 h. The reaction was then poured onto cracked ice, extracted with diethyl ether, and separated. The organic layer was washed with 5% sodium bicarbonate, water, and brine, and then dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure and recrystallization from methanol gave 20 g (50%) of yellow needles of **11**, mp 59–60 °C (lit.[27] mp 61.5 °C). ^{1}H NMR ($CDCl_3$) δ 7.91 (d, 1 H, J = 6.2 Hz, aromatic C–H), 6.95 (d, 1 H, J = 11.0 Hz, aromatic C–H), 2.57 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3). Anal. Calcd for $C_8H_8FNO_2$: C, 56.82; H, 4.73; N, 8.28; F, 11.24 Found: C, 56.71; H, 4.68; N, 8.16; F, 10.88.

2-Fluoro-5-amino-*p*-xylene (12). Compound **11** (17.0 g, 0.1 mol), was dissolved in 140 mL of absolute ethanol and reduced in a Parr shaker under hydrogen at 60 psi for 2.5 h in the presence of 200 mg of PtO_2. Filtration and removal of the solvent under reduced pressure gave 13.6 g (98% yield) of **12** as a slightly reddish solid, which was pure enough for the subsequent conversion to **13** described next. An analytical sample was obtained by recrystallization from 1:1 ether:hexane, mp 76–78 °C (lit.[27] mp 80–80.5 °C). ^{1}H NMR ($CDCl_3$) δ 6.71 (d, 1 H, J = 10.0 Hz, aromatic C–H), 6.46 (d, 1 H, $J \approx$ 7.1 Hz, aromatic C–H), 3.39 (br s, 2 H, NH_2), 2.16 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3). Anal. Calcd for $C_8H_{10}NF$: C, 69.06; H, 7.19; N, 10.07; F, 13.68. Found: C, 68.82; H, 7.31; N, 9.90; F, 13.90.

2,5-Difluoro-*p*-xylene (13). Compound **12** (12.5 g, 0.09 mol) was added to 40 mL of 48% HBF_4 (0.22 mol), followed by dropwise addition of 6.3 g (0.09 mol) of $NaNO_2$ in 12 mL of H_2O to the reaction maintained at 0 °C. Following addition, the reaction was stirred at 0 °C for 15 min more. The resultant precipitate

---

(24) Greenwood, F. L.; Kellert, M. D.; Sedlak, J. *Org. Synth. Coll. 4*, **1963**, 108.

(25) Blum, J.; Zimmerman, M. *Tetrahedron* **1972**, 275.

(26) Valcanas, G. *J. Chem. Soc.* **1963**, 5554.

(27) Saito, S.; Ferraris, J. P. *J. Chem. Soc., Chem. Commun.* **1979**, 1027.

was filtered and then washed with ice water, cold 1:1 ether-methanol, and finally cold diethyl ether. After 3 h of drying under vacuum, 2-fluoro-5-*p*-xylenediazonium tetrafluoroborate was isolated (13.2 g, 61.5%, mp 93–94 °C (dec)). This material is pure enough for use in the next step.

A 250-mL round-bottom flask was charged with powdery diazonium salt, followed by connection to the reaction setup of a distillation head with condenser attached. The reaction flask was cautiously heated in an oil bath until nitrogen evolution ceased. *Caution*: Due to the rapid evolution of gas, large-scale preparations by this method require appropriate precautions such as use of a blast shield and cautious heating. The decomposition residue was then distilled in steam and extracted with diethyl ether. The organic layer was washed with 5% sodium bicarbonate and then dried over anhydrous magnesium sulfate. After removal of solvent, the crude product was distilled (bp 80 °C/33 mmHg) and finally recrystallized from pentane. White crystals of compound **13** (4.5 g, 35%) were obtained with mp 37–39 °C (lit.[27] mp 3 –40 °C). ^{1}H NMR (CDCl$_3$) δ 6.79 (pseudo t, 2 H, J = 8.0 Hz, aromatic C–H) 2.20 (s, 2 H, CH$_3$). Anal. Calcd for $C_8H_8F_2$: C, 67.61; H, 5.63; F, 26.76. Found: C, 67.56; H, 5.45; F, 26.50.

1,4-Bis(bromomethyl)-2,5-difluorobenzene (9). Compound **9** was obtained from 2,5-difluoro-*p*-xylene (**13**, 8.6 g, 0.61 mol) by the general procedure described above for benzylic bromination, using carbon tetrachloride as solvent and heating with a 275-W sunlamp placed 3 cm from the reaction flask for 4 h. The crude product was recrystallized from hexanes to give 7.5 g (42%) of white crystalline solid **9** with mp 102–104 °C (lit. mp 107–108 °C,[27] 53–55 °C[27]). ^{1}H NMR (CDCl$_3$) δ 7.13 (pseudo t, 2 H, J = 7.6 Hz, aromatic C–H), 4.44 (s, 4 H, CH$_2$Br). Anal. Calcd for $C_8H_6Br_2F_2$: C, 32.02; H, 2.00; Br, 53.30; F, 12.67. Found: C, 31.90; H, 1.90; Br, 53.45; F, 12.32.

General Procedure for Preparation of 1,4-Bis(tetrahydrothiopheniomethyl)benzene Salts. Following the procedure described by Rempfler et al.[10] the appropriate 1,4-bis(bromomethyl)benzene was added to a condenser-equipped flask along with 30% molar excess of tetrahydrothiophene and 30% molar excess of 48% hydrobromic acid. The mixture was stirred in an oil bath at 70 °C for 24 h. The condenser was removed, and the flask connected to an aspirator trap to remove excess acid, water, and sulfide; this stage must be carried out with care due to foaming and potential loss of product. Once most of the volatiles were removed, the flask was opened and the dark liquid residue dissolved in a minimum amount of distilled water. The solution was filtered, and the filtrate poured slowly into a chilled (–20 °C) amount of HPLC-grade acetone 10-fold greater in volume than the volume of the filtrate. The salt began precipitating almost immediately, and after allowing a few minutes for coagulation, the salt was suction filtered, placed in a desiccator, and dried overnight under high vacuum. If necessary, the salt can be redissolved in water and reprecipitated from acetone for material of higher purity. Once the salt is dried, it should be stored in the cold (–25 °C).

1,4-Bis(tetrahydrothiopheniomethyl)-2,5-dichlorobenzene Dibromide (14). Compound **14** was prepared from **6** (15.0 g, 0.045 mol), tetrahydrothiophene (10.5 g, 0.12 mol), and 48% hydrobromic acid (19.8 g, 0.12 mol) by using the general procedure for salt formation above. The product was 20.1 g (88%) of an off-white powder with mp 160–161 °C (dec). ^{1}H NMR (D$_2$O, acetone reference) δ 7.74 (s, 2 H, aromatic C–H), 4.75 (s, 4 H, benzylic CH$_2$), 3.45 (m, 8 H, SCH_2H$_2$), 2.36 (m, 8 H, SCH$_2$CH_2). Anal. Calcd for $C_{16}H_{22}S_2Br_2Cl_2$: C, 37.74; H, 4.36; S, 12.59. Found: C, 37.57; H, 4.37; S, 12.32.

1,4-Bis(tetrahydrothiopheniomethyl)-2,5-dibromobenzene Dibromide (15). Compound **15** was prepared from **7** (42.2 g, 0.10 mol), tetrahydrothiophene (20.3 g, 0.23 mol), and 48% hydrobromic acid (38.8 g, 0.23 mol) by using the general procedure for salt formation above. The product was 23.3 g (38%) of an off-white powder with mp 165–168 °C. ^{1}H NMR (D$_2$O, acetone reference) δ 7.89 (s, 2 H, aromatic C–H), 4.72 (s, 4 H, benzylic CH$_2$), 3.46 (m, 8 H, SCH_2CH$_2$), 2.34 (m, 8 H, SCH$_2$CH_2). Anal. Calcd for $C_{16}H_{22}S_2Br_4$: C, 32.13; H, 3.71; Br, 53.44; S, 10.72. Found: C, 31.79; H, 3.84; Br, 53.22; S, 10.40.

1,4-Bis(tetrahydrothiopheniomethyl)-2-fluorobenzene Dibromide (16). Compound **16** was prepared from **8** (5.0 g, 0.02 mol), tetrahydrothiophene (5.0 g, 0.06 mol), and 48% hydrobromic acid (5.0 g, 9 mL, 0.06 mol) by using the general procedure for salt formation above, with the difference that the crude product was dissolved in methanol—not water—following vacuum removal of volatile residues. The methanol solution of crude product was precipitated into 20 volumes of HPLC-grade acetone to give 7.0 g (86%) of an off-white powder with mp 148–150 °C. ^{1}H NMR (CD$_3$OD) δ 7.84 (pseudo t, 1 H, J = 7 H, aromatic C–H), 7.62–7.70 (m, 2 H, aromatic C–H), 4.83 (s, 2 H, benzyl CH$_2$), 4.75 (s, 2 H, benzyl CH$_2$), 3.60 (m, 8 H, SCH_2CH$_2$), 2.48 (m, 8 H, SCH$_2$CH_2). Anal. Calcd for $C_{16}H_{22}Br_2FS_2$: C, 41.95; H, 5.02; Br, 34.88; F, 4.15; S, 14.00. Found: C, 41.60; H, 5.22; Br, 35.36; F, 3.87; S, 13.74.

1,4-Bis(tetrahydrothiopheniomethyl)-2,5-difluorobenzene Dibromide (17). Compound **17** was prepared from **9** (3.3 g, 0.037 mol), tetrahydrothiophene (3.3 g, 0.04 mol), and 48% hydrobromic acid (6 mL, 0.04 mol) by using the general procedure for salt formation above with a reaction temperature of 65 °C for 20 h. The deep violet crude product was dissolved in minimal methanol and precipitated into HPLC-grade acetone to give 3.0 g (54%) of a **17** as a white powder with mp 130–133 °C. ^{1}H NMR (D$_2$O) δ 7.57 pseudo (t, 1 H, J = 8 Hz, aromatic C–H), 4.69 (s, 4 H, benzyl CH$_2$), 3.53 (m, 8 H, SCH_2CH$_2$), 2.43 (m, 8 H, SCH$_2$CH_2). Anal. Calcd for $C_{16}H_{22}Br_2F_2S_2$: C, 40.34; H, 4.62; Br, 33.58; F, 7.98; S, 13.47. Found: C, 40.36; H, 4.71; Br, 33.54; F, 7.67; S, 13.24.

General Procedure for Polymerization and Elimination of Bis-Sulfonium Salts to PPVs 2–5. The general procedure of Garay and Lenz[11] was followed for the polymerizations of **14–17**. The appropriate bis-sulfonium salt was dissolved in distilled water to the desired concentration (typically 0.05–0.2 M), degassed by bubbled nitrogen or argon, and added under inert atmosphere to a nitrogen-purged aqueous 10% solution (1 equiv) of tetramethylammonium hydroxide stirred under an equivolume layer of pentane at 0 °C for 1 h by using an inert atmosphere of argon or nitrogen. Separation of the pentane layer and dialysis of the aqueous layer against deionized water was then carried out typically for 3 days using Spectropor 1 dialysis tubing with a molecular weight cutoff of 6000–8000. Where necessary, the dialyzed aqueous polyelectrolyte solutions of **18–21** could be stored indefinitely in a refrigerator. Dialyzed polymer yields were not quantitated. Upon completion, dialyzed solutions were cast on poly(methyl methacrylate) (PMMA) sheets and evaporated in a PMMA box under a stream of nitrogen.

Films of **18–21** made by the procedure above could be thermally eliminated by placing in a vacuum heating apparatus in which the film was clamped between Teflon sheets in a tube heated by wrapped nichrome wire under a vacuum of about 0.0001 mmHg for 4–5 h. (*Caution*: Corrosive volatiles are produced!)

The optimal temperature for elimination of each polymer was roughly determined by multiple TGA on a Perkin-Elmer TGS-7 at different temperatures. Under the best conditions, weight loss through extrusion of tetrahydrothiophene and HBr is complete within the desired 4–5 h, with minimal evidence of thermal degradation of the product PPV evinced by a falling baseline weight. Typical analyses used 3–4 mg of sample polyelectrolyte heated at 20 °C min^{-1} from 40 to 600 °C to establish temperature of elimination, followed by isothermal runs to test maximum time desirable for elimination. Efficiency of elimination under a particular set of conditions was checked by elemental analysis for trial eliminations, using time periods suggested by TGA short enough to ensure minimal degradation. Optimal conditions were taken as those yielding minimal residual elemental sulfur.

2,5-Dichloro-PPV (2). Polymerization of a 0.2–0.5 M aqueous solution of monomeric salt **14** by the procedure described above resulted in a yellow solution of polyelectrolyte **18**. Film casting at 260 °C for 4.5 h as described above gave films that were rather brittle, although very concentrated solutions of the product polyelectrolyte yielded stiffer films. IR (neat film, cm^{-1}) 3059 (aromatic C–H str), 959 (trans vinyl C–H out-of-plane bend). UV (λ_{max}, nm) 212, 410. Anal. Calcd for $C_8H_4Cl_2$: C, 56.18; H, 2.35; Cl, 41.46; S, 0.00. Found: C, 55.17; H, 2.60; Cl, 39.04; S, 1.26.

2,5-Dibromo PPV (3). Polymerization of a 0.05 M aqueous solution of monomeric salt **15** by the procedure described above resulted in a nearly colorless solution of polyelectrolyte **19**. Use of a 0.10 M monomer solution resulted in precipitation of the polyelectrolyte after a few minutes of reaction—it can be readily redissolved by addition of water. Film casting at 260 °C for 4 h as described above gave films that were quite brittle under all conditions attempted by us. IR (neat film, cm^{-1}) 3059 (aromatic C–H str), 957 (trans vinyl C–H out-of-plane bend). UV (λ_{max}, nm) 218, 400. Anal. Calcd for $C_8H_4Br_2$: C, 36.98; H, 1.55; Br, 61.48; S, 0.00. Found: C, 36.89; H, 1.53; Br, 61.19; S, 0.23.

2-Fluoro PPV (4). Polymerization of a 0.2 M aqueous solution of monomeric salt **16** by the procedure described above results in a colorless solution of polyelectrolyte **20**. Film casting at 180 °C for 4 h as described above gave films that were flexible and slightly tacky. IR (neat film, cm^{-1}) 3042 (aromatic C–H str), 961 (trans vinyl C–H out-of-plane bend). UV (λ_{max}, nm) 200 (end absorption), 236 (shoulder), 420. Anal. Calcd for C_8H_5F: C, 79.99; H, 4.20; F, 15.82; S, 0.00. Found: C, 79.04; H, 4.29; F, 14.05; S, 0.44.

2,5-Difluoro PPV (5). Polymerization of 2 g of monomeric salt **15** in 21 mL of H_2O (0.2 M) by the procedure described above resulted in a slightly yellow solution of polyelectrolyte **21**. Film casting at 250 °C for 4.5 h as described above gave reddish films that were somewhat brittle. IR (neat film, cm^{-1}) 3100 (aromatic C–H str), 1260, 1155 (Ar–F str), 960 (trans vinyl C–H out-of-plane bend). UV (λ_{max}, nm) 240, 420 nm. Anal. Calcd for $C_8H_4F_2$: C, 69.57; H, 2.92; F, 27.51; S, 0.00. Found: C, 69.35; H, 2.89; F, 27.28; S, 1.08.

Acknowledgment. This research was supported by the Air Force Office of Scientific Research under the University of Massachusetts Initiative Program Contract F4962087C0027. R.K.M. thanks Mr. Roberto Gregorius for many helpful discussions.

Registry No. **6**, 19036-27-2; **7**, 35335-16-1; **8**, 69857-33-6; **9**, 35335-08-1; **10**, 696-01-5; **11**, 1736-88-5; **12**, 1737-69-5; **13**, 452-94-8; **14**, 135789-45-6; **15**, 135789-46-7; **16**, 135789-47-8; **17**, 135789-48-9; **18**, 135789-55-8; **19**, 135789-57-0; **20**, 135789-58-1; **21**, 135789-59-2; 2,5-dichloro-*p*-xylene, 1124-05-6; 2,5-dibromo-*p*-xylene, 1074-24-4; 2,5-dimethylaniline, 95-78-3; 2,5-dimethylbenzenediazonium tetrafluoroborate, 2192-32-7; tetrahydrothiophene, 110-01-0.

Preparation of Nickel Carbide Ultrafine Particles by Metal Vapor Methods

Paul Hooker,[1a] Beng Jit Tan,[1b] Kenneth J. Klabunde,*,[1a] and Steve Suib[1b]

Departments of Chemistry, Kansas State University, Manhattan, Kansas 66506, and University of Connecticut, Storrs, Connecticut 06268

Received May 14, 1991. Revised Manuscript Received July 24, 1991

Highly reactive nanoscale nickel particles were prepared by nickel atom clustering in low-temperature pentane. During this process some carbonaceous material was incorporated due to attack on pentane of the highly reactive growing clusters. These nickel particles could be converted cleanly and completely to Ni_3C by treatment with additional carbon sources (e.g., octene, octane, or methyl methacrylate) at 200 °C. Similar results have been observed with palladium. Comparisons with other activated forms of nickel (or palladium) reveal that the metal vapor method is most satisfactory. Active forms of both Ni and C are necessary for metal carbide formations.

Introduction

Metal vapor synthesis (MVS) has proven to be a good method for the production of nanoscale metal particles that have shown fascinating physical, magnetic, chemical, and catalytic properties.[2] This procedure involves the low-temperature clustering of metal atoms in organic media. As matrices of metal atoms trapped in alkanes or aromatics are warmed, a competition between two processes is set up:[2b,3] cluster growth vs. reaction of the forming clusters with the low-temperature organic host. Depending on the metal, the organic host (solvent), dilution effects, and rate of warmup, control of the size, composition, and properties of the resultant metal clusters/particles can be achieved. All the extremes have been realized, from formation of organometallic cluster compounds[4,5] to colloidal particles[6-8] to catalysts[2d] to large crystalline metal particles.[9]

In some cases the forming metal clusters are so reactive that even relatively "inert" organic hosts react at low temperature. Examples include nickel, cobalt, iron, and chromium alkane deposits.[2,10] In these cases the final product is a black, pyrophoric "pseudoorganometallic" powder that contains about 2–8% by weight carbonaceous fragments. These fragments are mainly C_1 species distributed throughout the nanoscale metallic particles but are not in the form of interstitial carbidic carbon.[2b]

The picture that has evolved for these extremely reactive materials is that of nearly amorphous metal particles interspersed with CH_3, CH_2, CH plus other reactive carbon species, leading to the conclusion that both "activated" metal and "activated" carbon exist simultaneously. The question arises as to whether these materials could be of use in the preparation of ultrafine particles of metal carbides with a small distribution in particle size. Such materials could be very useful in a variety of technological areas. The work described herein deals with this possibility for the nickel and palladium cases.

---

(1) (a) Kansas State University. (b) University of Connecticut.

(2) (a) Davis, S. C.; Klabunde, K. J. *J. Am. Chem. Soc.* **1978**, *100*, 5973. (b) Davis, S. C.; Severson, S. J.; Klabunde, K. J. *J. Am. Chem. Soc.* **1981**, *103*, 3024. (c) Kernizan, C.; Klabunde, K. J.; Sorensen, C., Hadjapanayis, G. *Chem. Mater.* **1990**, *2*, 70. (d) Klabunde, K. J.; Li, Y. X.; Tan, B. J. *Chem. Mater.* **1991**, *3*, 30.

(3) Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic Press: New York, 1980.

(4) Klabunde, K. J.; Groshens, T. J.; Brezinski, M.; Kennelly, W. *J. Am. Chem. Soc.* **1978**, *100*, 4437.

(5) Schneider, J. J.; Nolte, M.; Kruger, C. *J. Organomet. Chem.* **1991**, *403*, C4.

(6) Bradley, J. S.; Hill, E.; Leonowicz, M. E., Witzke, H. *J. Mol. Catal.* **1987**, *41*, 59.

(7) Andrews, M. P.; Ozin, G. A. *Chem. Mater.* **1989**, *1*, 174.

(8) Cardenas-Trivino, G.; Klabunde, K. J.; Dale, E. B. *Langmuir* **1987**, *3*, 986.

(9) Klabunde, K. J.; Tanka, Y. *J. Mol. Catal.* **1983**, *21*, 57.

(10) Klabunde, K. J.; Jeong, G. H.; Olsen, A. W. In *Selective Hydrocarbon Activation*; Davies, J. A., Watson, P. L., Greenberg, A., Liebman, J. F., Ed.; VCH: New York, 1990, p 433.

0897-4756/91/2803-0947$02.50/0