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This is a review of conducting polymers that are processable or that are prepared from processable precursor polymers. These include polyacetylene, poly(p-phenylene), poly(arylene vinylenes), polyheterocycles (including polythiophenes and polypyrroles), conducting polymer solutions, polyaniline and blends, composites and latexes of conducting polymers.

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Processable Electronically Conducting Polymers

John R. Reynolds and Martin Pomerantz / The University of Texas at Arlington, Arlington, Texas

I. INTRODUCTION

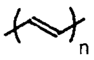
It has now been over 15 years since the discovery that strong, flexible, freestanding films of polyacetylene could be prepared via Ziegler-Natta polymerization on glass surfaces [1]. Even in light of the highly elevated conductivity attained for polyacetylene when redox doped [2], the complete intractability of the material, coupled with its air instability, prevents its acceptance as a useful material.

A significant body of work by chemists, physicists, and materials scientists now exists which provides insights for the basic structural requirements for electronically conducting polymers. Numerous reviews [3] have been written that detail the need for conjugation, the ability to inject charge onto the polymer chain using redox doping techniques, changes in the optical properties during doping, and the numerous potential applications that exist for conducting polymers. As research has progressed, the electronic properties of these polymers have steadily improved. Generally, polyacetylene has led the way as the prototype system. Originally, conductivities of 200-750 S cm^{-1} were found for films synthesized using a $Ti(OBu)_4/AlEt_3$ initiator system. These films have become commonly known as Shirakawa polyacetylene [2]. Improved syntheses, yielding polymers containing fewer defects in their structure, have now led to polyacetylenes having conductivities [4] of 20,000-100,000 S cm^{-1}. These latter conductivities are truly metallic and, when adjusted for the low density of the polymer relative to metals, the conductivity of polyacetylene is approximately the same as that of copper. In addition to polyacetylene, improved syntheses of other conjugated polymers have led to highly conducting materials whose conductivity is a strong function of synthetic conditions. Both poly(*p*-phenylene vinylene) (PPV) and poly(3-methylthiophene) [5] exhibit conductivities in excess of 2000 S cm^{-1} when properly prepared. An additional class of soluble and processable conjugated polymers is produced via the solid-state polymerization of 1,4-disubstituted-1,3-diynes commonly called diacetylenes. The optical properties of these polymers have been thoroughly investigated, as have been the topochemical polymerization mechanism and their electronic properties, and fully reviewed [6]. Attempts to attain highly conductive polydiacetylenes have, in general, been unsuccessful, and thus this class of polymers will not be addressed in detail here.

As is the case with the electronic properties, physical properties are a strong function of the macromolecular structure of conducting polymers. Just as many attempts have been made to improve the electronic properties, so too has considerable effort gone into improving physical properties. These physical properties include processability, stability, and mechanical integrity. Conducting polymers are now available that are soluble and fusible, rather thermally stable, ambient atmosphere stable, and exhibit good mechanical strength. The inducement of processability into these typically intractable polymers has been a major goal of synthetic chemists and is the focus of this manuscript. The techniques employed range from the preparation of processable precursor polymers which are subsequently converted to an intractable conjugated polymer, to the formation of solutions of the polymer in the conducting form, to the use of flexible substituents, copolymerization, and blend and composite formation. The processability now available allows the materials to be used much like common polymers. Films can be extruded, fibers can be spun, and parts can be molded. These material property advances can be traced to the numerous syntheses and polymer preparations developed. It is impossible to acknowledge every contribution to such a broad area but we hope to provide a framework that will stimulate further research.

II. POLYACETYLENE

As the simplest conjugated polymer, polyacetylene [1,$(CH)_x$] has served as a model for developing both the electronic and physical



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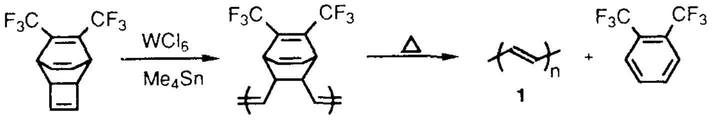
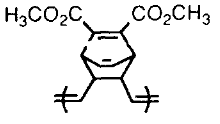
properties of electronically conducting polymers. As mentioned earlier, the complete intractability of $(CH)_x$ can be attributed to the extremely rigid conjugated backbone and strong interchain forces which give rise to crystallinity. Although films can be prepared by the direct polymerization of acetylene, they tend to be highly porous and fibrillar.

The metathesis polymerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (2) by WCl_6 and Me_4Sn shown in Eq. (1) leads to a high-molecular-weight, soluble, precursor



2 **3** (1)

polymer (3) that can subsequently be thermally converted to $(CH)_x$ [7]. The concept of using soluble precursor polymers is now used extensively for the preparation of a variety of conjugated polymers, as will be made evident throughout this chapter. In addition to the bis(trifluoromethyl)benzene precursor polymers, which contain a readily thermally eliminated group, other precursors having groups which can be eliminated and with a range of stabilities have been prepared. These polymers are shown in structures 4, 5, 6, and 7. The thermal instability of polymers 3, 4, and 5 originally precluded any significant characterization in the solution phase. Precursor polymer 6, on the other hand, could be purified by precipitation and was found to have a hydrodynamic volume determined by gel permeation chromatography (GPC) comparable to polystyrene with a number average molecular weight (M_n) of 40,000 and a molecular weight distribution



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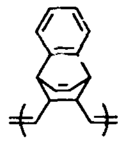

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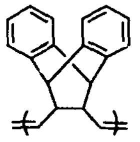

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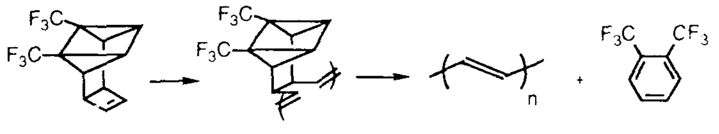
(polydispersity) of $M_w/M_n > 4$. Further discussion of GPC analyses of the soluble polymers, unless otherwise noted, will be relative to polystyrene standards, and so the molecular weights should be taken as approximations only. One of the major benefits of the soluble precursor method is that, after solution casting and careful thermal elimination, the polyacetylene film formed is continuous and space-filling with densities greater than 1 g cm^{-1}. The polyacetylene thus obtained is essentially amorphous.

A trade-off of the thermal instability of the polymers with ease of synthesis motivated Feast and Winter to investigate these soluble precursor syntheses in greater detail [7b]. Their ability to isolate and polymerize 3,6-bis(trifluoromethyl)pentacyclo[$6.2.0.0^{2,4}.0^{3,6}.0^{5,7}$]-dec-9-ene (8) as shown in Eq. (2) yielded the soluble precursor polymer 9, which was quite stable at room temperature and easily

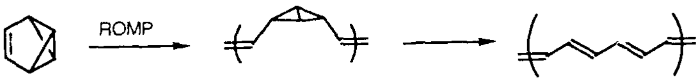


8 9 1 (2)

converted to $(CH)_x$ at 75°C. Unfortunately, the strain energy in this polymer, which is stable only because its thermal reversion to 3 is symmetry-forbidden, caused the conversion reaction to be extremely exothermic and often explosive. Conversion of this polymer to $(CH)_x$ is recommended in thin films only.

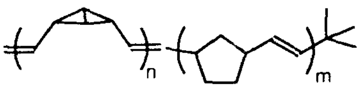
The conversion of polymer 3 to $(CH)_x$, which has become known as the Durham route, and the properties of the resultant materials have been extensively studied. The prepolymer can be significantly oriented and, upon thermal conversion, this orientation is retained and a highly ordered and crystalline $(CH)_x$ is obtained which can be doped to high conductivity [8,9].

A drawback to the Durham precursor method for the synthesis of $(CH)_x$ is the necessary expulsion of a relatively large molecule during the conversion reaction. In addition to representing a relatively large fraction of the overall mass of the precursor polymer, removing these molecules from the bulk of the polymer is difficult, limiting the process to thin films. This has been overcome by the inclusion of strained rings into polymers which can be converted into double bonds. This is exemplified by the work of Grubbs et al. [10], who investigated the ring-opening metathesis polymerization (ROMP) of benzvalene (10) by a tungsten alkylidene initiator system as outlined in Eq. (3). The fact that no molecule is eliminated during conversion suggests this method may be employed in the formation



10 **11** (3)

of relatively thick $(CH)_x$ samples. The isomerization of bicyclobutane rings to 1,3-dienes can typically be accomplished thermally, photochemically, and by transition metals. Interestingly, polybenzvalene (11, PBV) cannot be successfully converted into $(CH)_x$ using either thermal or photochemical methods. Solutions of $HgCl_2$, $HgBr_2$, and Ag^+ salts in tetrahydrofuran (THF) were found to transform films of polybenzvalene into "shiny silvery materials resembling polyacetylene in appearance." IR and NMR spectroscopic analyses showed these films to be $(CH)_x$ with a high density (19%) of saturated defects and ca. 40:60 cis:trans double-bond content. Films of $(CH)_x$ prepared in this manner are strong and flexible with a relatively low extent of crystallinity. Swager and Grubbs [11] extended the homopolymerization of benzvalene in a study of a series of tungsten alkylidenes and concurrently examined the ability of benzvalene and norbornene to form block copolymers having the general structure shown in 12. The homopolymer 11 was found to be quite unstable, undergoing spontaneous detonation with mechanical stress or rapid heating and cross-linking in the solid or gel state. The latter property prevented purification by reprecipitation and dissolution, forcing film casting directly from the polymerization reaction mixture. The ability to carry out living polymerizations of norbornene



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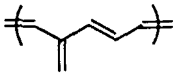
allowed formation of the block copolymers which were more stable and were more soluble than the PBV homopolymer.

Conversion of polybenzvalene (11) to conjugated polymers was accomplished using a variety of catalysts, including $AgBF_4$, ZnI_2, $HgBr_2$, $HgCl_2$, and $Rh(COD)Cl_2$ (COD = 1,5-cyclooctadiene). In addition to the fully conjugated $(CH)_x$, a cross-conjugated polymer 13 containing an exocyclic double bond was expected. It was found that $HgCl_2$ performed best and yielded a silvery black film which exhibited a conductivity of 1 S cm^{-1} when I_2 doped and also was mechanically durable. Infrared spectroscopy showed a small peak at 895 cm^{-1} attributable to the vinylidene moiety, the presence of residual saturation, and a more highly disordered structure when compared to Shirakawa $(CH)_x$. This is also evident in the electronic spectra of the polymer as the $(CH)_x$ formed in this manner has a band gap (absorption onset) at ~1.9 eV (650 nm) and an absorption maximum at 2.8 eV (440 nm) (compared to a band gap of 1.4 eV (885 nm) for Shirakawa $(CH)_x$).



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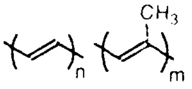
As is the case with Durham $(CH)_x$, orientation can be obtained in this system by stretching the precursor polymer. Polybenzvalene (11) was cast onto a polyethylene support and stretched to orientation draw ratios, l/l_0, of 2.3 and 6.0. After conversion and doping with I_2, these polymers exhibited conductivities of 13 and 49 S cm^{-1}, respectively. Scanning electron microscopy (SEM) showed this form of $(CH)_x$ to have a fibrillar morphology, and the crystallinity of the polymer was increased dramatically with stretching.

Examination of the block copolymers, prior to conversion, by differential scanning calorimetry (DSC) leads to no discernible T_g for the polynorbornene fraction and suggests the material exists as a single phase. Some phase separation occurs upon subsequent conversion of 11 to $(CH)_x$ with the polynorbornene T_g evident at 38°C. The morphologies of these block copolymers are quite smooth and continuous. Elevated conductivities are still found after saturation with I_2 with oriented samples of 50:50 block copolymers reaching ca. 0.4 S cm^{-1}.

The direct formation of copolymers of $(CH)_x$ with a variety of monomers and carrier polymers has also been employed in the preparation of soluble polyacetylenes. The controllable alteration of the electrical conductivity and physical properties of a random acetylene copolymer was demonstrated by Chien et al. [12] with the synthesis of poly(acetylene-co-methylacetylene) (14). Although these copolymers



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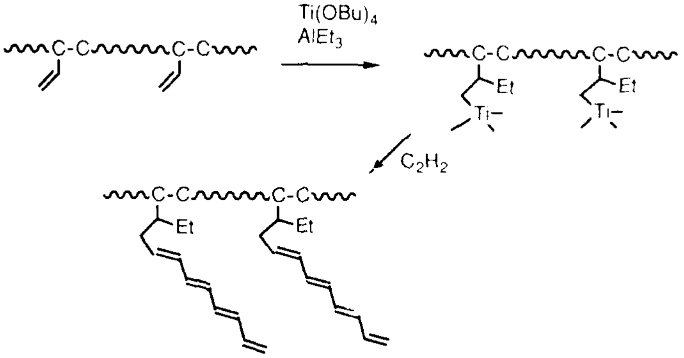
were not soluble, doped conductivities ranging from 10^{-3} to 36 S cm^{-1} were measured and, as the methylacetylene content in the copolymer was increased, the copolymer exhibited a greater propensity to swell in solvent.

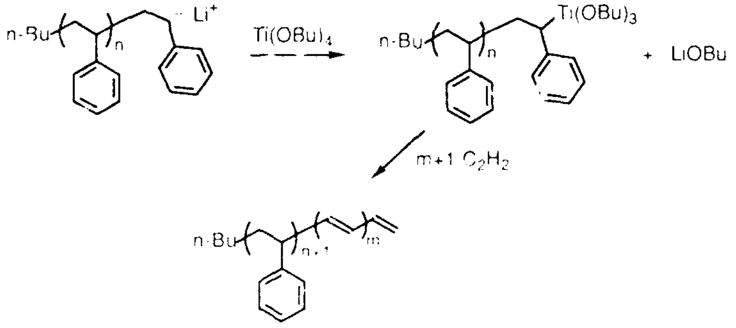
Retention of long domains of unsubstituted $(CH)_x$ chains in soluble materials was accomplished with the application of block and graft copolymer methods [13-23]. A number of synthetic techniques have been utilized to graft $(CH)_x$ chains onto carrier polymers. In general these fall into two classes, where either a growing $(CH)_x$ chain in solution is grafted onto a solubilized carrier polymer, or the $(CH)_x$ chain is polymerized off of the carrier polymer as a side chain. As an example of the former method, Bates and Baker [13,16,17] polymerized acetylene using the $Ti(OC_4H_9)_4/Al(C_2H_5)_3$ system in the presence of modified polyisoprene or polystyrene. They suggest that nucleophilic attack of growing $(CH)_x$ chains on electrophilic sites (previously incorporated) of the carrier polymer leads to termination of the $(CH)_x$ and grafting. Destri et al. [19], on the other hand, utilized an initial reaction between carrier polymer and initiator to subsequently polymerize $(CH)_x$ side chains onto polybutadiene as illustrated in Scheme 1. Using this method, estimations of the extent of grafting were obtained from the relative concentration of 1,2- and 1,4-diene linkages and initiator/vinyl group ratio. In addition, this method allows control of the length of the polyene through monomer concentration and cis:trans ratios through temperature.

Scheme 1



Block copolymers have been prepared by carrying out a living polymerization of one monomer and, after consumption of this monomer, switching to a more reactive second monomer. The number of copolymers possible is broadened by the ability to change the nature of the active site after synthesis of the first block, and subsequently use a different *mechanism* for preparation of the second block. This has been utilized in the preparation of acetylene block copolymers via both anionic to Ziegler-Natta [15,18,20,21] and anionic to metathesis [22,23] methods. This is illustrated in Scheme 2 for the formation of poly(acetylene-b-styrene). An elaborate double-labeling experiment, utilizing ^{14}C and tritium, was employed to show that indeed copolymer was forming and not $(CH)_x$ homopolymer [20]. These PS/$(CH)_x$ block copolymers, which were initially soluble, could be cast into films. Upon subsequent I_2 oxidation however, conductivities $<10^{-6}$ S cm^{-1} were obtained. In an extension of this work, Aldissi and Bishop [21] examined the relationship between the copolymer composition and electrical conductivity. At low levels ($\leq$20%) of PS incorporation, conductivities above 1 S cm^{-1} were obtained which quickly fell off to 10^{-5} S cm^{-1} when the PS level was raised to 40%.

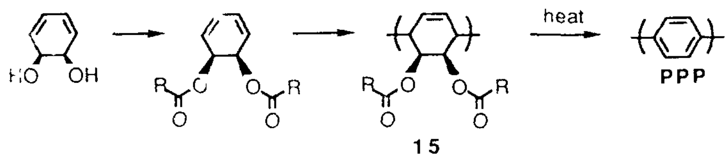
Scheme 2



III. POLY(*p*-PHENYLENE)

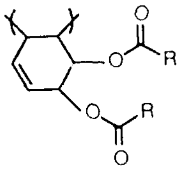
Processable precursor routes have also been developed for the synthesis of the fully conjugated and completely non-processable poly(*p*-phenylene) (PPP). Previous syntheses of this polymer generally yielded poorly characterized oligomers with approximately 10-15 phenylene units in each chain [24-27]. Attempts to improve molecular weight, purity and processability were stimulated by the fact that these oligomers could be oxidized by AsF_5 to form complexes with conductivities as high as 200 S cm^{-1} [28].

The ability to bacterially oxidize benzene, using the microorganism *Pseudomonas putida*, to form 5,6-*cis*-dihydroxycyclohexa-1,3-diene in useful quantities has led researchers at ICI to polymerize it as a PPP precursor as outlined in Eq. (4) [29,30]. The fact that ca. 250 g of the diol was utilized in the conversion to ester in this preparation indicates that relatively large scales are possible in these syntheses. Polymerization of a variety of esters (diacetate, dipivalate, dibenzoate, etc.) was accomplished using common free-radical methods (benzoyl peroxide, 90°C) to yield conversions to 15 greater than 80% in less than 10 min. Using the diacetate as an example, degrees of polymerization of ca. 50-200 and polydispersities M_w/M_n) of 2-4 were obtained for 15 (R = CH_3). These cyclohexene ring containing polymers were processable to films and fibers and could be subsequently thermally converted at 300°C to form PPP. These temperatures could be reduced to 220-260°C by catalyzing the reaction using strong tertiary amine bases and alkali metal salts. Extents of aromatization could be controlled by varying the time and temperature used during conversion with essentially complete aromatization possible.



(4)

Using common synthetic organic methods, McKean and Stille developed a nonenzymatic preparation of the *cis*-dibenzoate and *cis*-dipivalate esters [31]. Polymerizations were carried out using free-radical methods. A close examination of the structure showed that the polymer (R = Ph and *t*-Bu) was not completely 1,4-linked, as desired for full conjugation in the PPP, but contained ca. 10-15% of 1,2-linkages (16). These 1,2-defects should decrease charge mobility along the polymer chain in the conducting complex and would also decrease order by preventing crystallization.



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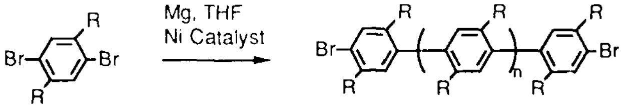
Both groups [29-31] examined the electrical properties of their PPPs upon doping with AsF_5. Although both polymers became highly conducting, the PPP prepared by Ballard exhibited a conductivity of 100 S cm^{-1} while that prepared by Stille was somewhat lower at ca. 1 S cm^{-1}. It should be pointed out that these were initial studies and did not indicate the upper limits possible for the conductivity of these polymers.

Although the precursor polymers described above have high molecular weights and are processable, the PPPs produced are completely intractable. This has been overcome by the synthesis of PPPs that are dialkyl substituted and quite soluble [32,33]. The use of alkyl substitution to improve processability has been used extensively for polyheterocycles and will be discussed in detail later.

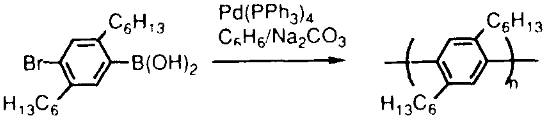
The Grignard coupling reaction of alkyl substituted 1,4-dibromobenzenes was initially employed, as outlined in Eq. (5), where R = C_6H_{13} or C_8H_{17}. These side chains were chosen since



(5)

they were expected to be long enough to induce solubility but not so long that the side chains would crystallize in the solid state. Although these polymerizations were found to produce only para-linked phenylenes, and were thus highly regiospecific, the chain lengths obtained were found to be quite small. Chromatographic analysis yielded an average degree of polymerization (DP) of about 8 with the largest chains containing about 20 repeat units. This low DP was attributed to the loss of chain end functionality during polymerization and difficulty in maintaining stoichiometric balance.

To overcome these problems, an A-B step-growth polymerization system was investigated [33] as shown in Eq. (6). An NMR spectral analysis of the dihexylsubstituted PPP (17) showed essentially complete para linkages and no detectable end groups, suggesting a relatively high molecular weight. Vapor phase osmometry showed the polymer to have a DP of 28. No characterization of the dopability or electrical properties for these soluble PPPs was reported.



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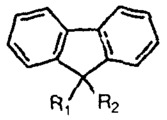
(6)

In addition to the purely para linked polyphenylenes, substituted fluorenes have been used to prepare [34] melt-processable polymers which can be oxidatively doped to conductivities as high as 10^{-3} S cm^{-1}. Polymerization of a series of alkyl-substituted fluorenes 18



$R_1 = H$; $R_2 = C_6H_{13}, C_{16}H_{33}$

$R_1 = R_2 = C_6H_{13}, C_8H_{17}, C_{10}H_{21}, C_{12}H_{25}, C_{16}H_{33}, C_{22}H_{45}$

18

by $FeCl_3$ led to polymers which are expected to contain a conjugated backbone equivalent in structure to poly(*p*-phenylene). The annulated ring system locks the polymer into a stable conformation, and thus the optical band gaps of the mono- and disubstituted species are at approximately the same energy (3.0-3.1 eV). This is in strong contrast to the poly(3-alkylthiophenes), as will be detailed later, where 3,4-disubstitution induces an increase in the band gap via steric interactions. The melting points of the polymers were found to be a strong function of the length of the alkyl group and the extent of substitution. For example, poly(9-hexylfluorene) melts at 140°C which was reduced to 100°C for poly(9,9'-hexylfluorene). It should be pointed out that these melting points were made by visual inspection, and no results on the molecular weights of the polymers were available. As the length of the side chain increases, the observed melting point decreases. In the case of the bis-dodecyl substituted polymer, the melting point is reported to be less than 25°C.

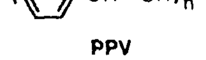
IV. POLY(ARYLENE VINYLENES): PROCESSABLE PRECURSOR POLYMERS

A. Poly(*p*-Phenylene Vinylene)

As previously discussed, one of the important ways to process otherwise intractable materials is via the so-called precursor polymer route. In this, a processable polymer is prepared, processed and then converted in one step to the dopable and ultimately electronically conducting, but intractable, polymer. One area where this has been exploited and has worked extremely well is in the poly(arylene vinylenes) (19) which include both benzenoid and heteroaromatic species as the Ar group.

$\left(\mathrm{Ar{-}CH{=}CH}\right)_n$

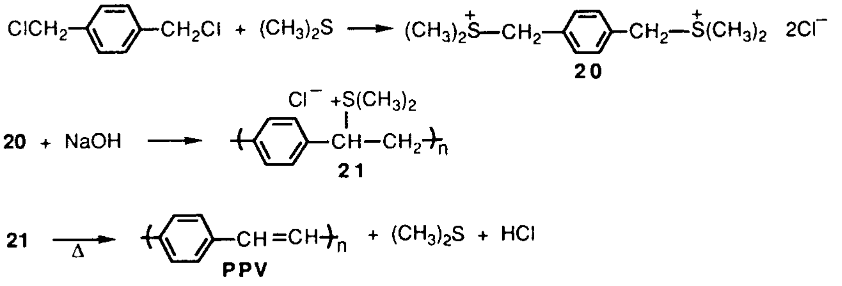
19



PPV

Since the preparation of poly(*p*-phenylene vinylene) (19, Ar = *p*-C_6H_4; PPV) using either a Wittig condensation or a dehydrohalogenation reaction [35] gave oligomers, a different synthetic methodology was examined. In 1984 Karasz and Lenz [36,37] and Murase [38] and their co-workers reported the use of a procedure previously devised by Kanbe [39] and by Wessling and Zimmerman [40] using a soluble precursor polymer for the preparation of PPV which is still being used and has been extended to other poly(arylene vinylenes). The method, shown in Scheme 3, involves preparation of a bis-sulfonium salt such as 20 [*p*-phenylenedimethylenebis(dimethylsulfonium chloride)] for the parent PPV (or the diethylsulfonium chloride) followed by a sodium hydroxide induced elimination-polymerization reaction, at 0°C, to produce an aqueous solution of the polyelectrolyte, precursor polymer 21 (poly[*p*-phenylenedimethylene-α-(dimethylsulfonium chloride)]). This polymer 21 could be processed into films, foams, and fibers [36-40]. Heating a cast film of 21 at 200°C or 300°C for more than 2 h resulted in a yellow, freestanding film of PPV; however, rapid heating at 220°C provided a flexible foam structure. This is not surprising since, at 200°C two gaseous molecules [$(CH_3)_2S$ and HCl] are being eliminated from each monomer unit. These polymers were doped with AsF_5 or H_2SO_4 vapors to yield PPV having conductivities of 10 and 100 S cm^{-1},

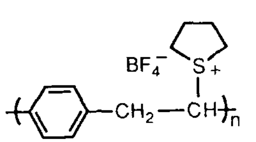
Scheme 3



respectively. Further, films could be stretch oriented and conductivities after AsF_5 and SO_3 doping reached 2780 and 685 S cm^{-1}, respectively. This was considerably higher than had been achieved with other methods [35], where the polymers were made by condensation reactions and were in fact oligomers. A major problem in the conversion of 21 to PPV is incomplete loss of all of the sulfur and chlorine producing a polymer with sp^3 hybridized carbon atoms in the main chain. This reduces the overall conjugation. The optimum conditions for the preparation of 21 and, in turn, for the conversion of 21 to PPV with the minimum amount of sulfur, have been determined by heating above 380°C [41].

Molecular weights for polymer 21 have recently been obtained by low-angle laser light scattering and were reported to be 990,000 and 500,000 for the weight average and number average respectively, with a polydispersity of 2.0 [41].

In a recent paper [42], Karasz and co-workers made an extensive study of the molecular weight of the precursor polymer 22 as the fluoroborate salt and also converted it to a neutral polymer, 23, by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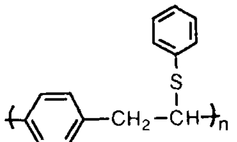
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reaction with thiophenoxide. Using GPC with polystyrene standards and a nonaqueous solvent [22 is soluble in nonaqueous solvents such as dimethylformamide (DMF) and acetonitrile] number average molecular weights for 22 were about 5.5 × 10^6 with a polydispersity of 2.1. For polymer 23 M_n was about 2 × 10^5, M_w about 9 × 10^5 with a polydispersity of about 6. These numbers represent the average of three runs on each polymer and are in qualitative agreement with the low-angle light scattering results for this system of $M_n \approx 5.5 \times 10^5$ and $M_w \approx 1.1 \times 10^6$. Further, ultracentrifugation of polymer 21 gave $M_n = 5.0 \times 10^5$ and $M_w = 9.9 \times 10^5$. Thus all techniques provide similar results and indicate high degrees of polymerization [42].

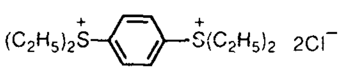
Since precursor polymer 21 could be cast into films and these converted to films of PPV which could then be doped, one could get better conductivities, up to 100 S cm^{-1}, than from the material from the polycondensation reactions. Improvement in the conductivity requires alignment of the polymer molecules, often achieved by stretching a film or fiber. Indeed, as indicated above, 21 (or the diethylsulfonium derivative) could be stretch oriented at elevated temperatures by uniaxial stretching with a draw ratio of up to 15 [37,38,42-44]. This increased the conductivity in the direction of stretching enormously, to well over 10^3 S cm^{-1} with AsF_5 [38,43] dopant and up to 5000 S cm^{-1} with H_2SO_4 dopant [44].

The UV-Vis transition edge, or the band gap, of PPV has been variously reported to be 2.7 eV [45a] and also 2.4 eV [41,45b], intermediate between those of polyacetylene and poly(*p*-phenylene).

X-ray diffraction, electron diffraction, and infrared dichroism studies have shown that the PPV molecules are highly oriented along the stretch axis, and studies have been made of the increase of molecular orientation along the stretch axis as a function of draw ratio [41,43,46]. Further, in stretched precursor polymer 21 the extent of crystallinity of the film increases with extent of conversion to PPV [47].

When the anion in 21 is exchanged for an anion which can produce a dopant molecule, such as $AsF_6^- \rightarrow AsF_5 + F^-$, the thermal elimination gives $(CH_3)_2S$, HF in the case of the AsF_6^- anion, and AsF_5 which then dopes the polymer. This has been referred to as *incipient doping* [48].

The effect of altering the sulfonium structure was studied by examining the diethyl, tetramethylene, and pentamethylene xylene sulfonium salt derivatives, 24, 25, and 26, respectively, and the precursor polymers derived from them, 27, 28, and 29, respectively. These were subsequently compared to the dimethyl sulfonium derivatives 20 and 21. Better yields of PPV with somewhat higher conductivity were obtained in all three cases, with the cyclic sulfonium precursor polymers, 28 and 29, being the best [49]. Indeed elemental analysis showed very little residual sulfur and chlorine compared to the larger amounts observed with the dialkyl sulfonium polymers after thermal elimination [49].



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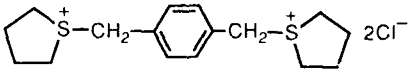

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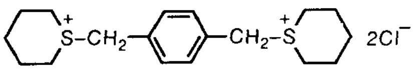

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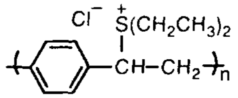

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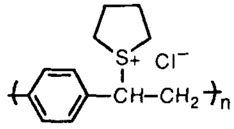

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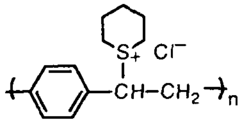

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It is interesting to note that a comparison of properties of PPV formed from precursor polymer 21 with that formed from 28 has revealed that the UV-Vis spectra of the undoped polymers are slightly different [50]. The PPV from 28 shows a slightly longer wavelength absorption maximum corresponding to longer conjugation lengths. This is consistent with the observation of considerably less sulfur and chlorine, and hence fewer sp^3 hybridized carbon atoms, and therefore greater conjugation lengths in the polymers. The UV-Vis spectrum of 28 shows phonon sidebands attributed to a narrower distribution of crystallite sizes [50].

When PPV was examined by DSC, no glass or melt transition was observed between -196 and 500°C. Decomposition began at about 550°C in a nitrogen atmosphere [41]. The thermogravimetric analyses (TGA) of the precursor polymer 21 (and also 27-29) showed weight loss at about 50°C with rapid loss at 100°C to ca. 130°C. There was a second region of slower weight loss up to about 230-240°C with little weight loss, of what is now PPV, up to about 600°C.

Electrochemical oxidation-reduction of PPV in a PPV,PPV^+/$LiAsF_6$, propylene carbonate/Li/Li^+ system was investigated by cyclic voltammetry [51]. Two broad peaks, one anodic and one cathodic, are observed at around 3.85 V. With a sweep rate of 2 mV/s the anodic and cathodic peaks occur at 3.90 V and 3.80 V, respectively. In the absence of impurities such as O_2, N_2, and H_2O PPV can be cycled between oxidized conducting and neutral insulating states hundreds of times over several months without decomposition [51].

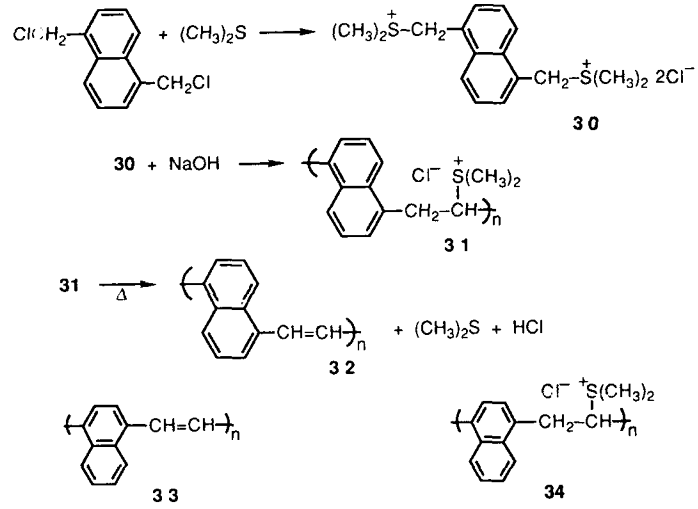
Mechanical testing showed that a drawn film of PPV was significantly stronger and stiffer than an undrawn film. This PPV, formed from the diethylsulfonium precursor polymer 27, drawn fourfold at 90-120°C, and heated 30 min at 300°C, gave an elastic modulus of 9221 MPa, a tensile strength of 274 MPa, and an elongation of 7.0% compared with an elastic modulus of ~1800 MPa, a tensile strength of 71 MPa, and an elongation of 16% for the film which had not been drawn [52].

B. Poly(Naphthylene Vinylenes)

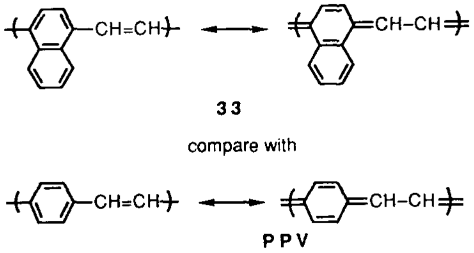
There are a number of other poly(arylene vinylenes), where the arylene group is a benzenoid aromatic moiety, which have been studied, but much less has been done with these systems than with PPV itself. One of the earliest of this type to be prepared was poly(2,6-naphthylene vinylene) (32) also prepared by the precursor polymer route, shown in Scheme 4, from the bis-sulfonium salt 30 via the precursor polymer polyelectrolyte 31 [36]. No properties were reported, however. Another naphthalene derivative, using 1,4-linkages, namely 33, was also prepared by this same methodology [53,54]. Films of the precursor polymer 34 were prepared and thermally eliminated at 300 and 350°C to produce 33. The transition edge (band gap) was at 615 nm or 2.02 eV, which is about 0.5 eV lower than for PPV. This is due to the more effective resonance interaction of the naphthylene with the vinylene unit than the phenylene has with the vinylene unit as shown in Scheme 5.

Electrical conductivity, however, was considerably less than that of PPV. With AsF_5 as dopant a maximum conductivity (for the as-produced film) was 0.032 S cm^{-1} [53].

Scheme 4



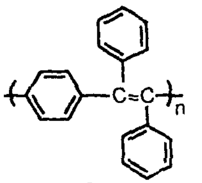
Scheme 5



C. Substituted and Soluble Poly(p-Phenylene Vinylenes) from Processable Precursor Polymers

The earliest report of substituted poly(p-phenylene vinylenes) made by the precursor polymer route employing sulfonium salts was by Wessling and Zimmerman [40]. They reported on the preparation of methyl substituted (on the *p*-phenylene ring) PPV using the same precursor polyelectrolyte sulfonium polymer procedure they used for the parent PPV. The systems prepared contained 2,5-dimethyl- and 2,3,5,6-tetramethyl-p-phenylene groups. More recent studies of the 2,5-dimethyl derivative showed fairly low conductivities after doping with I_2 or SO_3, 2×10^{-4} S cm^{-1} and 10^{-4} S cm^{-1}, respectively [44], and with AsF_5, 3.2×10^{-2} S cm^{-1} [54].

An interesting derivative of PPV that is in fact soluble as the conjugated polymer is poly(p-phenylene-1,2-diphenylvinylene) (35) [55]. It was prepared by a dehalogenation polycondensation reaction of 1,4-bis(phenyldichloromethyl)benzene (36) with chromium(II) acetate and gave material, which after fractionation, showed a number average molecule weight of up to about 80,000 by membrane osmometry. The UV-Vis-near-IR spectra [55,56] showed the long wavelength λ_{max} to be at 350-360 nm with the absorption edge (band gap) at around 425-430 nm (2.9 eV), and this is the same as a cast film or in solution. It is clear from the spectra and the fact that this material is soluble that there is considerable steric distortion in the backbone away from planarity, and hence there is less conjugation. The glass transition temperature (T_g) is reported to be 137°C while TGA (argon atmosphere) shows the polymer to be stable to 550°C then rapidly loses weight. The un-cross-linked polymer 35 does, however, produce a stable highly viscous fluid at about 300°C.



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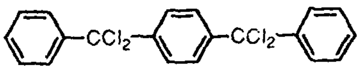

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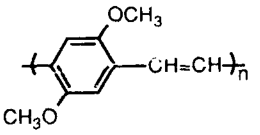
Upon electrochemical oxidation, 35 shows two new Vis-near-IR absorptions at 667 nm and 2500 nm. The electrochemical oxidation is reversible and shows an anodic peak at 1.24 V and a cathodic peak at 1.10 V using CH_2Cl_2 solvent, Et_3BzN $SbCl_6$ electrolyte, and a platinum disk electrode with Ag/AgCl as the reference electrode.

Poly(2,5-dimethoxy-1,4-phenylene vinylene) (37) has been made by the dehydrohalogenation reaction [35], and this low-molecular-weight oligomer showed a conductivity of 4.1×10^{-4} S cm^{-1} when doped with AsF_5. More recently, Lenz and Karasz [54], Murase [44], and Elsenbaumer [57] and their co-workers prepared 37 by the precursor polymer route from the sulfonium polymers 38 and 39, respectively. The incorporation of these electron-donating substituents serve to stabilize the doped cationic form of the polymer and thus lower the ionization potential of the species. Red films of 37 were made by heating polymer 38 to 200°C. Either cast films of 38 were heated or 38 was hot-pressed into a film. The films 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^{-1} [44,54,57]. It should be noted that, while I_2 is a rather poor dopant for PPV itself, it is a good dopant for 37, which is a reflection of the greater ease of oxidizing this polymer compared to PPV. Indeed electrochemical studies suggest the oxidation potential of 37 is comparable to that of polyacetylene [57]. It has also recently been demonstrated that 37 could be doped by protonic acids ($pK_a < 2$) [58] to give conductivities up to about 70 S cm^{-1}.



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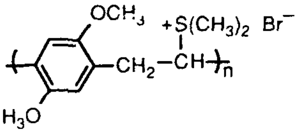

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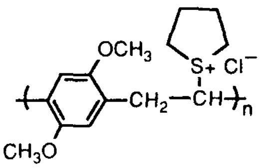
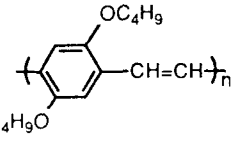


39

The absorption edge of 37 is 610 nm, corresponding to a band gap of 2.0 eV, which is in agreement with the band gap obtained from electrochemical studies of the redox properties of the polymer [57].

When the poly(2,5-dialkoxy-1,4-phenylene vinylene) has butoxy (40) [58] or hexyloxy (41) [59] 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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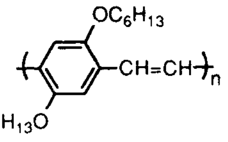
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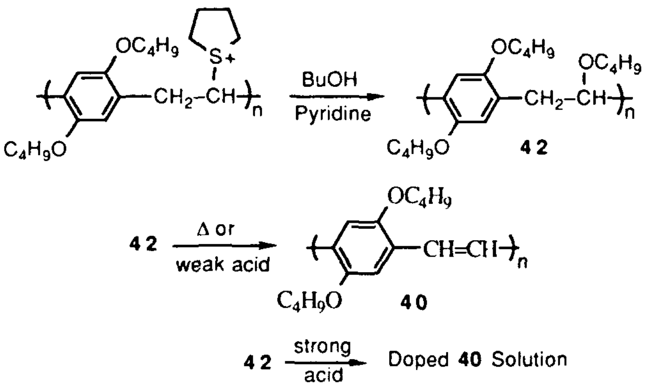
substitution, so are the conjugated polymers 40 and 41 themselves. The *dimethylsulfonium precursor polymer to* 41, *containing* some unsaturation, was gumlike and could be stretched up to 20 times its length. Heating this precursor polymer to 220°C gave 41 as a red soluble material. Prestretched precursor polymer gave 41 which resisted further stretching. The elimination of dimethylsulfide could be carried out in refluxing (214°C) 1,2,4-trichlorobenzene to produce an orange-red solution of 41 from which films could be cast.

The UV-Vis spectrum was similar to that of the dimethoxy polymer 37 and a band gap (transition edge) of 2.08 eV (595 nm) virtually identical to that of 37 was reported [59]. As with many other soluble conjugated polymers, 41 shows both solvatochromism (color change depending on the solvent) and thermochromism (color change with temperature) in 1,2,4-trichlorobenzene solution. When acetonitrile is added to the 1,2,4-trichlorobenzene solution λ_{max} shifts to longer wavelength and in trichlorobenzene as the temperature is increased λ_{max} shifts to shorter wavelength. The reasons for these effects is not clear. When unstretched and stretch aligned (draw ratio of 7) films were doped with I_2 the maximum conductivities were 3-4 and 200 S cm^{-1}, respectively [59].

Another route to polymer 40 has been developed by the initial replacement of the sulfonium moiety (Scheme 6) by butoxy to produce

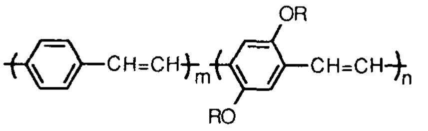
Scheme 6



neutral polymer 42, which is now soluble in organic solvents [58]. This neutral polymer 42 can either be eliminated thermally or with a weak acid. When a strong acid was used, the polymer 40 was produced in the doped state [58]. Polymer 40 is said to be freely soluble in solvents such as chloroform, tetrahydrofuran, chlorobenzene, nitrobenzene, and toluene [58].

D. Copolymers of PPV Prepared from Processable Precursor Polymers

A number of copolymers of PPV have been reported, made from sulfonium precursor polymers. These include polymers 43 where R = CH_3, C_2H_5, and C_4H_9 [60] and 44 [61]. The copolymers 43 were prepared by copolymerizing the two monomeric bis-sulfonium salts followed by thermal elimination at 220°C. The precursor polymers could be stretch oriented before heating. The maximum conductivity for unstretched copolymer (several were studied) was 28 S cm^{-1} compared to dimethoxy PPV homopolymer, which was 51 S cm^{-1}. The stretch-aligned systems, with draw ratios of up to 13, showed maximum conductivities of over 1500 S cm^{-1} using I_2 as dopant. A comparison with PPV homopolymer cannot be made except to note that it does not dope well with I_2. TGA of the precursor copolymers showed sulfide elimination between 50°C and about 200°C, and then all were stable to over 430°C. This latter represents the stability of the copolymers 43. UV-Vis spectra were similar to the parent PPV although λ_{max} for PPV is 440 nm and for dimethoxy PPV homopolymer it is 408 nm.



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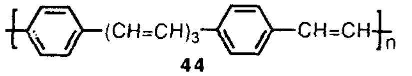

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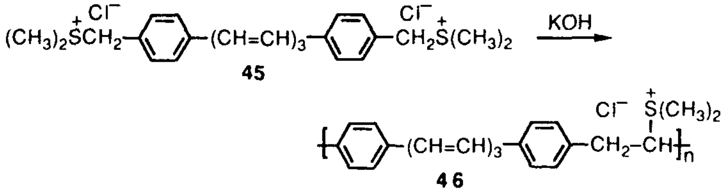
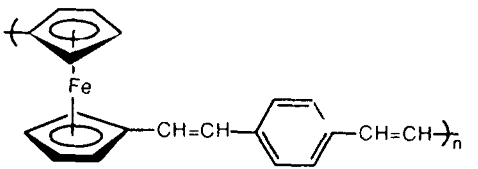
Copolymer 44 was prepared from monomer 45 via precursor



polymer 46 [61]. Doping of 44 with I_2 gave a maximum conductivity of 7×10^{-4} S cm^{-1}. Sulfuric acid doping, however, gave conductivities of up to 0.2 S cm^{-1}. Copolymer 44 is similar to PPV in that H_2SO_4 is a much better doping molecule. X-ray diffraction indicated the polymer was highly crystalline.

Finally, there is a report on the preparation of copolymer 47, by a Wittig reaction, which can be considered a soluble alternating PPV copolymer [62]. The molecular weight of the polymer, which



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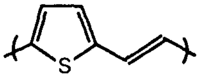
was soluble in DMF, was quite low, ca. 3000. There was also an insoluble component which probably had a higher molecular weight. Pressed pellet conductivities of I_2, Br_2, or AsF_5 doped samples was no higher than 5×10^{-5} S cm^{-1}. Interestingly, I_2 was the best dopant, the doped material was stable in air, and the conductivity actually increased on long exposure to air.

E. Poly(Heteroarylene Vinylenes) from Processable Precursor Polymers

Poly(thienylene vinylene) (48) has been prepared as a film or a foam beginning with bis-sulfonium salts 49 [63] and 50 [64,65] via processable precursor polymers. However, while 49 gave 48



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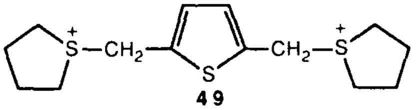

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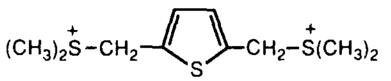

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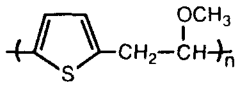
directly [63], 50 gave the organic soluble precursor polymer 51

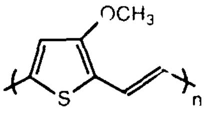


51

when the elimination from 50 was attempted in aqueous methanol. This in turn, upon heating, produced poly(thienylene vinylene) (48). One report [63b] says that 48 can be formed from 50; however, the molecular weight is lower than the polymer prepared from 49. Poly(thienylene vinylene) (48) has a lustrous golden color and is stable in air for long periods of time [63-65]. Doping of cast films of 48 with a number of oxidants including I_2 and $FeCl_3$ gave four-probe conductivities of up to 230 S cm^{-1} [63-65]. Uniaxially stretched film gave over a 10-fold increase in conductivity to values approaching 2700 S cm^{-1}.

The UV-Vis spectrum of 48 showed a maximum at 530 nm [66] (previously reported to be 540 nm [65]) and the band gap was reported to be 1.8 eV from optical spectroscopy. Elsenbaumer et al. report that the absorption maximum is at about 600 nm and the band gap is 1.74 eV [63b]. A band gap of 1.64 eV has also been reported [67]. Cyclic voltammetry of 48 showed a broad oxidation wave with a maximum at 3.61 V and a reversible reduction wave at 3.34 V (versus Li/Li^+) [63a]. A later publication gives the oxidation and reduction maxima as 3.56 V and 3.51 V, respectively [67].

An interesting system prepared recently contains an alkoxy group on the 3-position of poly(thienylene vinylene). Both poly(3-methoxylthienylene vinylene) (52) and poly(3-ethoxythienylene vinylene) (53) have been studied [68,69]. They were not prepared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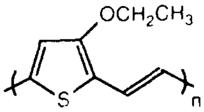
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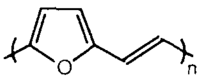
by the processable precursor polymer route but by a Grignard coupling reaction. The oxygen renders the monomers too reactive for the precursor polymer synthesis route but lowers the oxidation potential of the polymers 52 and 53 compared to the parent 48. For comparison, the band gap, based on optical spectroscopy, of 52 is reported to be 1.55 eV (800 nm) [63b] while that of 53 is 1.50 eV (825 nm) [68,69]. This is at least 0.2 eV less than the band gap in 48. The electrochemical half-wave potentials for 52 and 53 are 3.23 V and 3.11 V (versus Li/Li^+), respectively, compared with 3.54 V for 48 [67-69]. The band gap of 53, based on electrochemical n-doping and p-doping, was found to be somewhat lower, 1.32 V [67-69]. Conductivities (pressed pellet) of $FeCl_3$ doped samples were only as high as about 2 S cm^{-1} [68].

Perhaps the most interesting aspect of the chemistry of the poly(3 alkoxythienylene vinylene) is that, upon doping, the absorption band in the visible region of the spectrum decreases significantly while the absorption of the doped state in the infrared region of the spectrum increases. This causes thin films on glass substrates to appear much less colored (faint blue-gray) in the doped state [68,69].

Finally, a poly(furylene vinylene) (54) synthesis has been reported via the processable precursor polymer route. It was prepared from precursor sulfonium polymer 55 in the usual way [63b,69,70]. The properties are similar to those of poly(thienylene vinylene) (48), with a band gap, from optical spectroscopy, of 1.76 eV (700 nm) [63b,69,70]. Upon doping, with, for example, I_2 or $FeCl_3$, conductivities of cast films up to 36 S cm^{-1} have been reported [63b,69,70].



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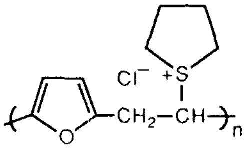

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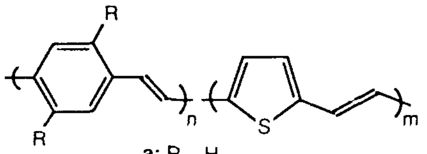
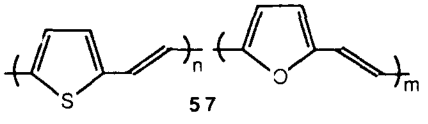
There are reports of copolymers of thienylene vinylene and either phenylene vinylene, 56a, or 2,5-dimethoxyphenylene vinylene, 56b [71], and of thienylene vinylene and furylene vinylene 57 [70]. These have been prepared by copolymerization of mixtures of sulfonium salts which provided processable precursor copolymers 58 [71] and 59 [70].



56 a: R = H
b: R = OCH_3



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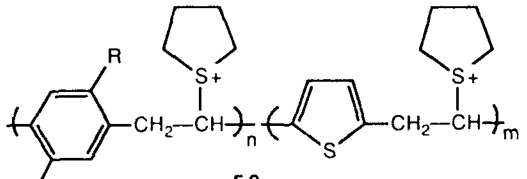
Iodine doping of stretched films of 56 gave fairly high electrical conductivities with the conductivities increasing with the amount of the thienylene vinylene in the copolymer. Copolymer 56a showed a maximum conductivity of 20 S cm^{-1} with a draw ratio of 5 (42% thiophene units) and for 56b it was 120 S cm^{-1} with a draw ratio of 2 (11% thiophene units) [71]. The I_2 doped samples were found to be stable in air for at least several months. Copolymer 57 was reported to have properties intermediate between 48 and 54 [70].



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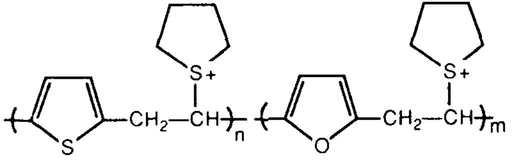


59

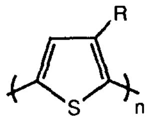
V. PROCESSABLE POLYHETEROCYCLES

A. Poly(3-Alkylthiophenes)

One of the best ways to render an otherwise intractable conjugated polymer processable is to attach long chains of atoms to the backbone. Unfortunately, this frequently causes steric interference with the ability of these polymers to remain planar, and so properties requiring this planarity, such as relatively low band gap and high conductivity of the doped system, are usually compromised. Indeed the steric problems usually get worse with increasing size of these chains.

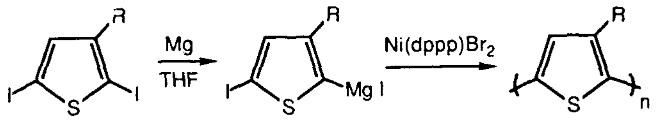
In the case of polythiophene it was found that not only does a long straight-chain substituent render the polymer processable, both soluble and fusible, but there is only a minimal effect on the properties derived from the conjugation of the backbone.

The first reports of the preparation of soluble poly(3-alkylthiophenes) were in 1986 when Sato [72], Elsenbaumer [73,74], Yoshino [75], and co-workers reported their initial results. Sato prepared poly(3-hexylthiophene) (63), poly(3-octylthiophene) (64), poly(3-dodecylthiophene) (66), poly(3-octadecylthiophene) (67), and poly(3-eicosylthiophene) (68) by electrochemical coupling of the appropriate monomers. Elsenbaumer et al. prepared poly(3-methylthiophene) (60), poly(3-ethylthiophene) (61), and poly(3-butylthiophene) (62) along with the octyl derivative 64 by a chemical coupling route involving the nickel-catalyzed coupling of the mono-



60: R = CH_3
61: R = C_2H_5
62: R = C_4H_9
63: R = C_6H_{13}
64: R = C_8H_{17}
65: R = $C_{10}H_{21}$
66: R = $C_{12}H_{25}$
67: R = $C_{18}H_{37}$
68: R = $C_{20}H_{41}$
69 R = $C_{22}H_{45}$

Grignard reagent derived from 3-alkyl-2,4-diiodothiophene as shown in Eq. (7). Yoshino and co-workers used a polymerization method which involved chemical oxidation of the monomers with transition metal halides such as $FeCl_3$, $MoCl_5$, and $RuCl_3$ [Eq. (8)]. Several polymers were prepared, but only poly(3-hexylthiophene) (63) was discussed in detail and the 3-octyl polymer 64 was mentioned. More recently, this and other groups have used this Lewis-acid-induced polymerization of the 3-alkylthiophene monomers, generally using $FeCl_3$ [76-79], as an excellent method for polymer preparation. It should be pointed out that this is a modification of the procedure first reported in 1984 by Yoshino et al. [80].



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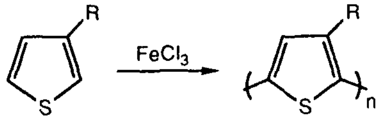


(8)

The room temperature conductivity of these polymers as cast films compares quite favorably with those of polythiophene films produced either chemically or electrochemically. Thus, for example, iodine doped poly(3-butylthiophene) (62), prepared by Grignard coupling [73,74], showed a conductivity of 4 S cm^{-1} and polymers 63, 64, 66, 67, and 68 which were electrochemically prepared and doped showed conductivities of 95, 78, 67, 17, and 11 S cm^{-1} respectively [72]. The $FeCl_3$ produced polymers 63 and 64 had conductivities [75] of over 10 and 11 S cm^{-1} [76] when I_2 was used as the dopant. This is to be compared with chemically produced ($FeCl_3$ oxidant) polythiophene doped with I_2 which showed a conductivity of 14 S cm^{-1} [80], and electrochemically produced and doped polythiophene which was somewhat higher at 190 S cm^{-1} (PF_6^- anion) [81,82].

A further comparison of electrochemically prepared films showed that poly(3-methylthiophene) (60) had a somewhat higher conductivity than polythiophene when doped electrochemically (500 S cm^{-1}; PF_6^- or AsF_6^- anion) [81,82] while poly(3-butylthiophene) (62) was 110 S cm^{-1} (PF_6^- anion) [81]. Other reports of 60 showed electrochemical doping gave a conductivity of 120 S cm^{-1} (ClO_4^- anion) while for iodine doping it was 5 S cm^{-1} [83]. A later report gives a conductivity of up to 750 S cm^{-1} for electrochemically doped 60 (ClO_4^- anion) [84].

There are a number of other, more recent reports of conductivity of the soluble polymers but none are substantially different from these values and are generally within the 1-100 S cm^{-1} range. All of this, of course, shows that there is a very small effect on conductivity due to alkyl substitution in polythiophene, which suggests little twisting of the backbone out of planarity [85].

When branched-chain substituents were incorporated into the poly(3-alkylthiophenes), the conductivity of the electrochemically doped films decreased substantially compared to their linear analogs. When the chain branching was moved away from the ring the conductivity increased, but was still below the analogous straight-chain system [86]. It should also be mentioned that Lemaire et al. [86] report a dependence of the conductivity on the chain length in the poly(3-alkylthiophenes) prepared electrochemically in a similar way. In these polymers the conductivity changes from 450 S cm^{-1} for the methyl system 60 to 2 S cm^{-1} for the octadecyl system 67 (PF_6^- dopant ion) [86]. All values are in reasonable agreement with the other measurements reported above and all polymers show good conductivities.

A study of the effect of film thickness on the conductivity of poly(3-dodecylthiophene) (66) was reported recently [87] and, for thicknesses below 6 μm, the conductivity increases from about 70 S cm^{-1} to over 100 S cm^{-1} at a thickness of 3 μm.

When cast films of poly(3-hexylthiophene) (63) were stretched up to a draw ratio of 5 the conductivity went from 27 S cm^{-1} for unstretched to 200 S cm^{-1} for the iodine-doped, stretched film [88]. It should be noted that whereas polythiophene itself is only slightly stretchable (up to a draw ratio of 1.5 and a 30% conductivity increase upon doping) the poly(3-hexylthiophene) can be stretched about five times [88].

Another interesting feature of conducting polymers is their UV-Vis spectra and band gaps. As was pointed out, the alkyl groups have only a minimal effect on the planarity of the backbone in the poly(3-alkylthiophenes) and so it is not surprising that the band gaps and absorption maxima are only slightly different from that in the parent. This has been incorporated in a recent review of the optical properties of conducting polymers [3k]. The band gap of the parent polythiophene prepared electrochemically is 2.0 eV, while for the 3-methyl and 3-ethyl polymers (60 and 61 respectively) it is 1.96 and 2.06 eV [82,89]. UV-Vis spectra of the soluble poly(3-alkylthiophenes) have been obtained both as films and in solution, and the Vis-near-IR spectra of the doped polymers have likewise been obtained. The spectra of films are similar to those above; all band gaps are around 2 eV [3k,89]. Further, the as synthesized and cast films are also essentially identical to the above polymers both in the neutral state and after doping [3k].

In the doped state the Vis-near-IR spectra of the films are consistent with the appearance of the bipolaron states [3k,81,82]. Further, electron spin resonance studies of doped [with $(NO)^+$ $(PF_6)^-$] poly(3-hexylthiophene) (63) solutions in chloroform coupled with spectroscopic data have indicated that the spinless bipolaron state is the lowest-energy charge storage configuration in dilute solution [90a]. Polarons are formed either because of an odd number of charges on the polymer or, in somewhat more concentrated solutions, as a result of interchain interactions. Gu et al., however, conclude from ESR and spectral measurements that only polaron and no bipolaron states are supported when they used benzonitrile or methylene chloride as solvent [91]. Recently, however, it has been shown that whether polarons or bipolarons are favored in solution depends on the solvent polarity and polymer concentration [90b].

When the spectra are examined in solution several interesting phenomena emerge. First there is a rather large hypsochromic shift from film to solution [75]. Thus, for example, the maximum in the absorption of poly(3-hexylthiophene) (63) moves from around 488 nm as a film [84] to 435 nm in THF solution [90,91] and 430 nm in chloroform solution [92]. Further, the color of the solution can vary with solvent. For example at 30°C the color of a solution of poly(3-docosylthiophene) (69) is red, orange and yellow in methylene chloride, chloroform, and carbon tetrachloride respectively [93a]. Poly(3-hexylthiophene) (63) also changes colors from yellow in a good solvent to magenta when a poor solvent is added [92]. A more recent report [94] confirms the observations on 63 and reports an absorption maximum at 443 nm in chloroform with a bathochromic shift as methanol (a poor solvent), with λ_{max} = 506 nm when there is only 10% chloroform.

Other detailed studies of the solvatochromism [93b] have shown that there is a correlation of the UV-Vis maximum with Taft's solvatochromic π^* parameters with 63 but not with 69. The conclusion was that, for poly(3-hexylthiophene), (63) the solvatochromism is the result of normal solute-solvent interactions where the alkyl groups and the backbone both interact with the solvent. However, for poly(3-docosylthiophene) (69) the large alkyl groups shield the backbone chain from the solvent and so the interaction of solvent is primarily with the side chains [93b].

Further, in addition to this solvatochromism, solutions of poly(3-alkylthiophenes) are also thermochromic [92,93a]. Thus, 63 goes from yellow to magenta when the temperature of a solution in 2,5-dimethyltetrahydrofuran [92] is lowered while 69 in chloroform solution is reported to go from red at 5°C to orange at 30°C to yellow at 50°C [93a]. A very similar phenomenon has been observed with films of poly(3-alkylthiophenes). Thus, for example, the absorption maximum of poly(3-hexylthiophene) (63) moves from 515 nm at room temperature to 419 nm at 190°C [94]. Similar observations have been made with other poly(3-alkylthiophenes) [95]. In addition to the bathochromic shift in λ_{max} as the temperature is lowered and the solvent is changed to a poorer one, two new peaks appear on the long-wavelength side of the band at 607 nm and 560 nm [92,94].

The explanation for the change in absorption maximum from long to short wavelength is that it is the result of reduction in the conjugation length and a change from a more rodlike to a more coil-like conformation [92-95]. By bending or twisting the chain, defects are introduced which shorten the average conjugation length and thus shift the maximum absorption to shorter wavelength. This is what occurs at higher temperature with more thermal energy. The shift to shorter wavelengths as the solvent is changed to a "poorer" one may be a solvent effect or an effect due to aggregation of polymer chains (which could also occur in the films). This has yet to be clarified [96].

It has been suggested that since the thermochromism of the 600-nm band is independent of temperature all spectral changes in the thermochromism and solvatochromism are due to changes in single chains and not to interchain interactions and aggregation [92], although there must be some aggregation at lower temperatures and in the poorer solvents [92]. Inganäs et al. have reported slightly different results and suggest a somewhat different interpretation [94]. They report that the 607- and 560-nm bands do not change position with temperature but do disappear with increasing temperature. However, they disappear at different rates and the band at 607 nm disappears last as the temperature is raised. Thus the two shoulders do not come from the same phase. These phases could be on the same polymer chains but this still requires considerable clarification [94].

It is interesting to note that not only does the absorption maximum shift to shorter wavelength as the temperature is increased but also there is a more rapid decrease in wavelength with temperature around the melting point [96], indicating a more rapid loss of conjugation length at this point. In addition, x-ray photoelectron spectra shows two peaks for the carbon 1s core level at 3.4 and 5.3 eV higher than the main peak growing in as the temperature is raised [96]. Once again this is consistent with shorter conjugation lengths at higher temperatures.

These ideas of shortening conjugation lengths (more rotational defects along the chain) with temperature giving rise to these observations has been supported by quantum mechanical valence effective Hamiltonian calculations which suggest fully coplanar rings along the polymer chain at low temperature (-60°C) and conjugation lengths of only a few rings at high temperatures (190°C) for poly(3-hexylthiophene) (63) [97]. This has been further reinforced by photoelectron spectroscopy [97,98].

An interesting observation is that the thermochromic behavior is nearly reversible when the poly(3-alkylthiophenes) are heated to <200°C. After many days at room temperature the UV-Vis spectrum has not completely returned to what it was before heating although it is close [94]. When heated above 200°C the poly(3-alkylthiophene) spectra show considerable irreversibility.

Recent x-ray studies of poly(3-butylthiophene) (62) and poly(3-hexylthiophene) (63) have revealed partial crystallinity with periodicities of 12.7 Å and 16.8 Å, respectively, and a lamellar structure with an interlayer spacing of 3.8 Å in 63 [99]. There is also considerable interweaving of the side chains from the neighboring polymer chains. The x-ray data on thermally cycled 63 has shown that the crystalline portion of the polymer disappears at the higher temperatures (>160°C) which corresponds to the melting transition. However, the persistence of a broad x-ray peak, even at elevated temperatures, is assigned to retention of appreciable nematic alignment of the polymer chains [99]. Indeed, the data suggests two coexisting regions, crystalline and nematic. In the intermediate temperature range there is hysteresis and the ordering is a slow process during the cooling cycle.

Winokur et al. observed a single low-energy shoulder on the UV-Vis spectrum of a thin film of poly(3-hexylthiophene) (63) which diminished on heating and irreversible changes were noted using infrared spectroscopy after heating to 300°C [99], consistent with the earlier observations.

When poly(3-dodecylthiophene) (66) film was subjected to pressures up to 8 kbar at 116°C the UV-Vis spectrum absorption maximum shifted to longer wavelength. There was also a shift, but smaller, at 32°C [100a]. Similar observations have been made with poly(3-hexylthiophene) (63) in solution; however, at high pressures (up to 8 kbar) a toluene solution of 63 showed two new peaks at longer wavelength at the expense of the main absorption [100b]. It was also noted that the conductivity of undoped 66 film increased with pressure at 70°C [100a]. These results suggest greater order and fewer defects along the polymer chain under pressure.

When the conductivity of the undoped polymer films, poly(3-dodecylthiophene) (66) and poly(3-docosylthiophene) (69) were examined as a function of temperature there was a marked decrease in the conductivity around the melting point. Cooling reversed the trend with some hysteresis [95,100a,101]. This, too, is explained on the basis of shorter conjugation lengths at the higher temperatures, above the melting point [95,100a,101]. This effect cannot be seen in an iodine doped film of 66. The conductivity ($\sim$10 S cm^{-1}) decreases very slightly with decreasing temperature [102], but temperatures near the melting point were not examined. This is presumably because doped poly(3-alkylthiophenes) rapidly degrade at elevated temperatures [103].

The UV-Vis absorbances of films of poly(3-decylthiophene) (65) *shifts to shorter* wavelength upon elongation (draw ratio = 2). This is explained as being due to increased twisting between thiophene rings upon stretching [104].

There have been a number of optical emission studies of the poly(3-alkylthiophenes) both in the solid and in solution as a function of temperature. In solution the emission quantum yield increases with increasing temperature [93a,105]. It has been reported to be fluorescence emission with a lifetime of about 600 ps [105]. The explanation for the increase in luminescence with temperature, which is opposite to that usually observed, is that the number of torsional defects increases in the chains with temperature, and this results in more localized excitations and hence more fluorescence [93a,105]. The same trend is observed in films, increased emission with temperature, up to the melting point. Above the melting temperature the emission intensity decreases with increasing temperature [106]. Here, since the number of defects does not increase very much with increasing temperature, the more typical nonradiative processes, which increase with temperature, take over and give rise to decreasing luminescence [106].

Since these species are all soluble, molecular weights can be determined. The majority of those reported have been obtained by gel permeation (size exclusion) chromatography using polystyrene standards. As noted earlier, these are actually comparisons of hydrodynamic volume, not molecular weight, but the relative values allow comparison of various polymers. Electrochemical polymerization of 3-hexylthiophene provided a weight average molecular weight (M_w) for 63 of about 48,000 (DP ~300) with the peak maximum at about 20,000 and a polydispersity of approximately 2 [89]. This was about an order of magnitude larger than that reported by Elsenbaumer et al. [73]. Hotta and co-workers have reported an M_w of about 250,000 also for 63 but, with the rather high polydispersity of 5.5, the number average molecular weight (M_n) was about 45,000. The peak maximum was at a molecular weight of 110,000 and the 250,000 M_w corresponds to a relative degree of polymerization about 1500 [88]. These samples were prepared either by dehydrohalogenation of 2-halo-3-hexylthiophene or by metal halide polymerization of 3-hexylthiophene. Inganäs, Salaneck, Österholm, and their co-workers have reported M_w = 19,000 and M_n = 8300 for 63 prepared by nickel-catalyzed coupling of the mono-Grignard reagent of 2,5-diiodo-3-hexylthiophene [94]. The poly(3-octylthiophene) (64) prepared by this method gave M_w = 12,500 and M_n = 6250 while 64 produced by $FeCl_3$ polymerization of 3-octylthiophene provided M_w = 178,000 and M_n = 44,000 [77]. Yoshino and co-workers reported molecular weights for $FeCl_3$ prepared polymers 64, 66 and 69. M_n and M_w were, respectively, 23,400 and 147,000 for 64, 20,600 and 109,000 for 66, and 28,600 and 135,000 for 69 [76].

Recently in our laboratories [79,107] we have examined poly(3-butyl-), poly(3-hexyl-), poly(3-octyl-), poly(3-decyl-), and poly(3-dodecylthiophene) (62-66) by GPC using polystyrene standards and have compared the molecular weights obtained with those obtained using a multiangle laser light scattering detector (MALLS). These polymers were prepared by the $FeCl_3$ polymerization of the 3-alkylthiophene in the presence of oxygen (dry air was bubbled through the reaction mixture) [79]. Using a refractive index detector (the results are somewhat different using a UV detector at 254 nm) and polystyrene standards, M_w for 62-66 were, respectively, 68,000, 175,000, 98,000, 127,000, and 121,000. Our preliminary results using a MALLS GPC detector was that the light scattering molecular weights were considerably greater (by factors of 2-5) than when polystyrene was used as a GPC standard. Our results for these samples (62-66) were, respectively, for M_w, 340,000, 398,000, 204,000, 390,000, and 227,000; for M_n (polydispersity in parentheses), 205,000 (1.7), 297,000 (1.3), 136,000 (1.5), 187,000 (2.1), and 99,000 (2.5), and for the position of the peak maximum, 280,000, 320,000, 190,000, 260,000, and 88,000. The peak maxima based on polystyrene standards and using the RI detector for 62-66 were 44,000, 80,000, 48,000, 73,000, and 53,000, respectively. It should be noted that using light scattering, which provides absolute molecular weights, M_n is less accurate than M_w since the lower-molecular-weight species scatter less than the higher ones.

A study of the molecular weights of 66 produced electrochemically as a function of current density has shown that the molecular weight increases with current density and that cross-linking takes place at high current density [87]. In addition, membrane osmometry has demonstrated that 62 prepared by $FeCl_3$ polymerization had a molecular weight of about 70,000 [78].

A number of thermal studies of poly(3-alkylthiophenes) have been carried out. The following are typical. Thermomechanical studies seem to indicate a glass transition for the hexyl derivative 63 of 33°C [88]. The octyl derivative 64 shows good thermal stability by thermogravimetric analysis under nitrogen to well over 300°C and in oxygen decomposition begins around 250°C [77]. With residual iron in the polymer (from the preparation) decomposition in oxygen begins at lower temperatures [77]. Differential scanning calorimetry of 64 revealed a glass transition of -20°C. For 62 T_g has been reported to be 48°C [74].

The melting points of the various poly(3-alkylthiophenes) have been obtained by DSC and have been reported [77,102]. There is a steady decrease in T_m with chain length of the 3-alkyl substituent to the point where the docosyl derivative 69 melts well below 100°C [77,102].

TGA of a film of doped poly(3-methylthiophene) showed decomposition beginning at about 100°C. Using I_2 as the dopant there was a rapid weight loss between 100 and 200°C, while with other dopants the rapid weight loss was at somewhat higher temperatures, between 200 and 300°C for $NOSbF_6$ [73]. A recent study [103,108] has shown that electrochemically or $FeCl_3$-doped thin films of poly(3-hexylthiophene) (63) and poly(3-decylthiophene) (65) rapidly degrade and lose conductivity at elevated temperatures (110°C). Also in the presence of water or oxygen the conductivity rapidly degrades. In all cases this is due to dedoping of the polymer as shown by optical spectroscopy. There is no evidence that oxygen or water attack the polymer. Thermal undoping has also been observed in solution but, unlike the thin-film case, the polymer is redoped on cooling [103,108]. Optical and x-ray photoelectron spectroscopy have shown that this undoping of $FeCl_3$-doped polymer is accompanied by conversion of $FeCl_4^-$ to $FeCl_2$. A tentative model which assumes that the oxidation potential of the polymer increases with increasing twists at elevated temperatures has been postulated [103,108].

Proton and ^{13}C NMR spectra of a number of poly(3-alkylthiophenes) have been reported. The hexyl polymer 63 is reported to show six ^{13}C lines corresponding to each side chain carbon and four-ring carbons [88]. In the 3-decyl polymer 65 we have observed the four thiophene ^{13}C NMR peaks at essentially the same chemical shifts as reported for the hexyl polymer 63 [88], and see only five broadened peaks for the 10 carbons on the side chain [79] at approximately the chemical shifts reported for 63. We have further observed that the monomer ^{13}C NMR spectrum (of 3-decylthiophene) shows all 10 separate ^{13}C side-chain resonances, and the main difference in the spectra of the monomer and polymer is that the two upfield monomer aryl carbons move downfield by about 10 ppm in the polymer [79]. A proton NMR study of several poly(3-alkylthiophenes) has revealed two different α-CH_2 groups (also β-CH_2), indicating there are different thiophene ring conformations in the polymer chains [109].

Cyclic voltammetry on an electrochemically prepared film of poly(3-dodecylthiophene) (66; DP about 90) has revealed differences in films prepared in different ways. The as-grown film showed two anodic and two cathodic peaks, while a film cast from an oxidized polymer solution showed only one anodic and one cathodic peak. Two peaks would suggest two different conjugation lengths or the ability to separate different charged states in the polymer [110].

Small-angle neutron scattering (SANS) studies of both doped and undoped poly(3-butylthiophene) (62; two samples of molecular weight 49,000; polydispersity 1.5 and 22,000; polydispersity 5) in nitrobenzene-d_5 solution have recently been reported [111]. At room temperature a strong-chain-chain-attractive interaction is observed. Even at the lowest concentration which could be studied, 0.1 mg/mL, there were still chain attractions observed, albeit weaker. At 65°C there were also some residual chain-chain interactions; the statistical molecule length was 50-60 Å and suggested a fairly flexible coil. The lateral width was 11-12 Å corresponding to fairly extended butyl groups. Fully extended butyl groups would provide a value of 15 Å. With the 62 of lower molecular weight 22,000, there were negligible chain interactions at 70°C even up to concentrations of 2 mg/mL. Doped solutions of this latter polymer 62, doped by adding $NOSbF_6$ to the polymer solution at room temperature, showed behavior strongly dependent on polymer concentration and that the conformation was very different from that of the neutral polymer. At low concentration and a high doping level a rod conformation was observed with a length greater than 850 Å. When a solution of polymer, at 80°C, was doped and studied at different doping levels the scattering behavior depended on the doping level. The higher the doping level the more rigid the chain. It was also observed that the doped polymers do not behave like common polyelectrolytes [111].

Morphological studies using scanning electron microscopy have shown that when poly(3-octylthiophene) (64) powder was hot pressed the film had a clear uniform surface [76]. For poly(3-butylthiophene) (62) prepared by $FeCl_3$ polymerization, the films cast from THF solution by slow solvent evaporation were dense and showed some fibrillar structure [78]. The films cast by slow evaporation of $CHCl_3$ or CH_2Cl_2 were smoother with no indication of texture and when these solvents were evaporated faster, or a thicker film was grown, the films appeared uniformly porous [78]. We have observed [79] that fibers of poly(3-decylthiophene) (65) pulled from solution show a rather porous surface. However, fracturing a liquid-nitrogen-cooled fiber and examining the cross section by SEM showed the fiber was quite dense and the pores were only on the surface, indicating that the pitting was probably due to bubbles caused by escaping solvent [79].

For poly(3-dodecylthiophene) (66) freestanding films prepared electrochemically, surface projections have been observed by SEM and these continue to grow as the electrochemical polymerization proceeds [87]. A 0.1-μm-thick film (on a substrate) had a smooth looking surface, but at high magnification many irregularities, due to nucleated growth, were observed [87].

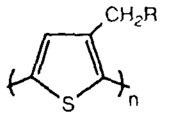
The first report of a melt-spun polythiophene fiber was in 1987 where poly(3-dodecylthiophene) (66) produced a tough, flexible fiber which, after doping with I_2, showed a conductivity up to 55 S cm^{-1} [102]. It showed a somewhat higher conductivity than a hot-pressed film doped under the same conditions with iodine. It was suggested that the higher conductivity was due to alignment of the polymer chains along the fiber [102]. We have produced both melt-spun and solution-drawn fibers [79]. Indeed, solution-drawn fibers (ca. 10 μm) of poly(3-decylthiophene) (65) examined by transmission optical microscopy were red-orange in color. Polarized optical microscopy showed these fibers to be extensively birefringent and suggests that the polymer chains are highly oriented with chain alignment along the fiber axis [79]. Melt-spun fibers of 210 μm diameter were quite flexible and elastic, had a smooth surface, as shown by SEM, and showed no cracks or breaks. TGA, under nitrogen, of the processed fibers was virtually identical to that of the as prepared 65, and by 420°C had only lost about 10% of its weight. Doping of these melt-spun fibers with $FeCl_3$ in CH_3CN occurred extremely rapidly and EDAX studies of a highly conducting fiber which had been fractured under liquid nitrogen showed quite uniform Fe and Cl distributions across the cross section. Even after rather short doping times the doping was quite uniform, demonstrating that the solvent and $FeCl_3$ are able to penetrate the polymer matrix quite rapidly and dope the polymer uniformly [79]. Molded electrically conductive articles can also be prepared from fusible poly(3-alkylthiophenes) [112].

Recently there have been reports of gels being produced from poly(3-alkylthiophenes) where the side chain is shorter than 12 carbon atoms, with the maximum amount of gel being obtained from poly(3-butylthiophene) (62) [113]. These gels expanded in chloroform but shrank by about 100-fold on addition of ethanol and showed drastic color changes. Thermochromism was also observed in these gels, the color going from red when contracted to yellow when expanded. The thermochromism was interpreted as due to changes in conjugation length as discussed previously. When doped (I_2) the conductivity of the expanded state was lower than that of the contracted state and the polymer shrunk upon doping. Dedoping restored the original volume. The nature of the cross-linking in these gels is not clear, but it has been suggested there are enhanced intermolecular interactions of the alkyl side chains in the shrunken state compared to the expanded state [113]. Drawn poly(3-alkylthiophene) gels were prepared by either drawing gel films or irradiating soluble drawn films with x-rays. The drawn films showed very anisotropic changes of length with solvent and temperature. The length perpendicular to the draw direction showed drastic changes, but that parallel to the draw direction was fairly insensitive to these changes. A similar anisotropic length change was observed upon doping. The tentative explanation given was that there was substantial alignment of polymer main chains and that cross-linking occurred between these main chains [114].

A recent paper reports on the photoconductivity of poly(3-alkylthiophenes) both in the solid and liquid states [115]. The photoconduction decreased with increasing temperature in the solid and was interpreted in terms of p-type conduction and increasing twisting of polymer chain at higher temperatures [115].

B. Alkyl-Substituted Poly(3-Alkylthiophenes)

A number of alkyl-substituted poly(3-alkylthiophenes) (70) have been prepared and studied. Substituents, R (70) include R = phenyl [81,84,86,116,117], OCH_3 [118], $OCH_2CH_2OCH_3$ [118],



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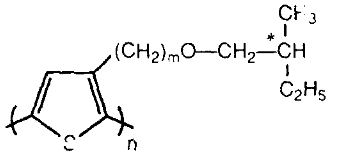
$O(CH_2CH_2O)_2CH_3$ [118], $NHC(O)(CH_2)_{10}CH_3$ [118], $O(CH_2)_6CH_3$ [117], CH_2OCH_3 [117], $CH_2O(CH_2)_5CH_3$ [117], $CH_2O(CH_2)_2OCH_3$ [117], $CH_2(OCH_2CH_2)_2OCH_3$ [117], CH_2OCH_2Ph [117], and $CH_2OSO_2(CH_2)_3CH_3$ [119]. All of these polymers were prepared by electrochemical polymerization. All showed reasonable conductivity, between 0.3 and 1050 S cm^{-1}, with the highest (1050 S cm^{-1}) observed for 70, R = $O(CH_2CH_2O)_2CH_3$ and when doped this polymer is quite soluble [118]. Other studies have shown the similarities of these compounds with the poly(3-alkylthiophenes) discussed above.

Interesting substituted polythiophenes with chiral side groups have also been prepared. These include polymers 71 (m = 2,3) and 72 which have been prepared from optically active monomers



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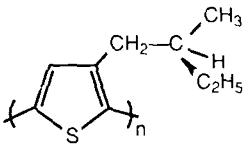

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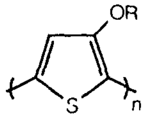
by electropolymerization [117,120]. The former (71) show high specific rotation ($\alpha_D^{22} = \pm 3000°$), reasonable conductivity, and, most significantly, can recognize and distinguish between chiral anions used as dopants [120a]. The latter (72) showed a two-probe conductivity of ca. 0.2 S cm^{-1}. In addition, a clay-polymer composite was prepared but not well characterized [120b].

C. Poly(3-Alkoxy)- and (3-Alkylthiothiophenes)

Poly(3-alkoxythiophenes) (73) and poly(3-alkylthiothiophenes) (74) have been prepared both by chemical and electrochemical methods. Poly(3-methoxythiophene) (73, R = CH_3) has been prepared by electrochemical oxidation of the monomer [121]. Cyclic voltammetry showed one oxidative wave and two broad reduction waves. It is



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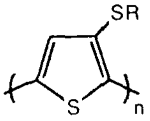

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soluble in a number of organic solvents and produces a deep red solution [121a]. The oxidized form, which is gold in reflected light, is soluble in dimethylformamide and gives a deep blue solution. The low oxidation potential of this polymer relative to other polythiophenes has allowed electrochemical cycling and thus delivery of anions which might be physiologically active. More recent measurements of this system has suggested that it is actually an oligomeric mixture of 5-10 monomer units as determined by GPC [122]. It has been characterized by ^{1}H and ^{13}C NMR, IR and UV-Vis spectroscopy, as well as by electrochemistry and spectroelectrochemistry. The neutral material showed λ_{max} near 470 nm and was *solvatochromic* [123]. The electrochemically or I_2-doped material showed four bands at about 630, 705, 760, and 870 nm, and was solvent-dependent. Further studies including electron paramagnetic resonance (EPR) spectroscopy led to the conclusion that there were at least two different types of species and that the main doped species were bipolarons (dications) in solution [123]. More recent work on higher-molecular-weight material (DP = 75) showed three peaks for the polymer at 550, 820, and 1250 nm, all attributed to bipolaron formation [124]. Conductivity studies have shown that this polymer has a conductivity of 1×10^{-2} S cm^{-1}, which is substantially lower than other poly(3-substituted thiophenes) [125]. An earlier report, however, gives conductivities of 0.33 S cm^{-1} for a PF_6^--doped film and 15 S cm^{-1} after washing with hexane [121b]. Other electrochemically prepared derivatives of 73, where R = C_2H_5 through $C_{15}H_{31}$, all show conductivities for electrochemically prepared, BF_4^--doped material, between 10^{-2} and 10^{-4} S cm^{-1} [125]. With the polyether side chain 73, R = $(CH_2CH_2O)_2CH_3$, the conductivity of PF_6^--doped material is very slightly better, 5×10^{-2} S cm^{-1} [118]. GPC molecular-weight studies of the alkoxy-substituted material gave degrees of polymerization of 5-8 for R = CH_3 through $C_{10}H_{21}$ using a carbon felt electrode and 10-50 for R = $C_{10}H_{21}$ through $C_{15}H_{31}$ using a platinum electrode. All were soluble *in the doped state*.

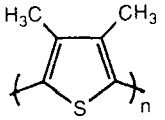
Poly(3-methoxythiophene) (73, R = CH_3) has also been reported to have been prepared by $FeCl_3$ polymerization, and a pressed pellet conductivity of 3 S cm^{-1} was given for the $FeCl_4^-$-doped species [124].

The sulfur-substituted systems 74 with R = CH_3 and C_2H_5 have been prepared and studied. The chemical synthesis (Grignard coupling) shown in Eq. (7) provided a polymer 74, R = CH_3, whose conductivity of I_2-doped material was reported as 0.5 S cm^{-1} [126]. Electrochemical polymerization of 3-(methylthio)thiophene gave a soluble polymer with a degree of polymerization of 7.4 [124]. UV-Vis-near-IR spectroscopy gave peaks at 390, 655, and 1020 nm for the doped (PF_6^-) polymer (74, R = CH_3) in propylene carbonate solution due to bipolarons. Interestingly, after four days in air the blue solution reverted to orange, characteristic of the undoped material.

We have recently reported on the synthesis and properties of the soluble 3-ethylthio derivative of 74 (R = C_2H_5) prepared by the Grignard coupling reaction shown in Eq. (7) [127]. The polymer film exhibited a band gap of 2.0 eV, similar to other polythiophenes, and a solution bandgap of 2.2 eV. Doping with $NOPF_6$ gave two new UV-Vis-near-IR absorptions at about 800 and 1460 nm, consistent with bipolaron formation. It is interesting that in this case the UV-Vis spectrum is not particularly sensitive to changes in solvent [127]. Unfortunately this polymer shows conductivities of only 2×10^{-5} to 1×10^{-3} S cm^{-1}, depending on dopant, and the degree of polymerization is only about 15-20. It is interesting that attempts at electrochemical polymerization of 3-(ethylthio)thiophene failed. Quantum mechanical calculations were in accord with these observations and showed that the spin densities at the two α-carbons of the radical cation, formed by removal of an electron from this monomer, were not high enough to allow polymerization. An extended Hückel calculation gave a theoretical band gap of 1.74 eV, in reasonable agreement with the 2.0 eV observed experimentally [127].

D. Poly[3,4-(Disubstituted) Thiophenes]

Poly(3,4-dimethylthiophene) (75) has been prepared by the Grignard coupling reaction [Eq. (7)] and doping of a film with $NOSbF_6$ gave



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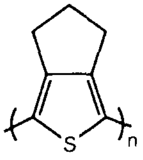
a conductivity of 0.5 S cm^{-1} [73]. Iodine, however, did not dope the polymer. The molecular weight was 26,000, and the yellow color of the undoped polymer suggested less conjugation than in mono-alkyl substituted polymers [73]. It has been reported that poly(3,4-dialkylthiophenes) are not fusible up to 300°C, the band gaps are much larger (due to greater steric hindrance), and the conductivity of doped polymers are much less than the mono-alkyl derivatives [95]. Interestingly, the color is reported to change in an unspecified way upon heating to 150°C [95].

The electrochemically prepared polymer 76 showed, by cyclic voltammetry, that steric hindrance was intermediate between that in poly(3-methylthiophene) (60) and poly(3,4-dimethylthiophene) (75). It gave a conductivity, for electrochemically doped material, of 10-20 S cm^{-1} [128].



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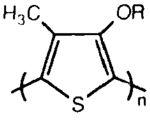

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Other disubstituted systems include monomethyl-monoalkoxy derivatives 77. These systems, prepared and doped electrochemically, showed good conductivity, 5 S cm^{-1} for 77, R = $C_{12}H_{25}$, 30 S cm^{-1} for 77, R = $CH_2CH_2OCH_3$, and 220 S cm^{-1} for 77, R = CH_3. While the undoped polymers are soluble in common organic solvents, the doped polymers are not [124].

Poly[3,4-bis(ethylthio)thiophene] [127] prepared by the Grignard coupling reaction was an ochre-colored material with a GPC number average molecular weight of about 2600 (M_w = 9000). It was soluble in common organic solvents, but when doped with $NOPF_6$ the conductivity was only 2 × 10^{-7} S cm^{-1}, similar to other 3,4-disubstituted polythiophenes [127].

E. Polythiophene Copolymers

There are a number of soluble copolymers of thiophene derivatives that have been prepared. The copolymer of 3-methyl- and 3-butylthiophene where the monomer ratio was 1:1 and of 3-methyl- and 3-octylthiophene where the ratio was 1.5:1 gave conductivities of $NOSbF_6$-doped films of 5 and 20 S cm^{-1}, respectively, while $FeCl_3$ doping of the former gave 50 S cm^{-1} [124].

A report of a copolymer formed electrochemically from 3-benzyl- and 3-hexylthiophene units has recently appeared [129]. Thermal analysis showed it to be quite stable to 300°C. UV-Vis spectra showed the as-synthesized film had λ_{max} = 450 nm while the solution-cast film showed λ_{max} = 490 nm with an increase in the shoulder at 605 nm. This suggests that the precipitated material has more order than the as-synthesized material. There is also a hyposochromic shift, to 440 nm, on dissolution of the copolymer [129].

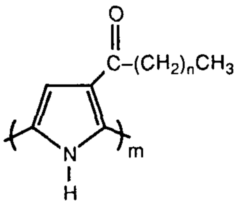
The copolymer of 3-hexyl- and 3-methylthiophene units (using a 2:1 feed ratio) prepared chemically either by dehydrohalogenation of the 2-halogeno-3-substituted thiophenes or by metal halide oxidation of the 3-substituted thiophenes had a GPC weight average molecular weight of 76,000 with a polydispersity of 9.2 and a peak maximum at 84,000. Doping with I_2 gave a film whose conductivity was 55 S cm^{-1} and upon stretching gave a conductivity of 150 S cm^{-1} for a 2.5 draw ratio and 180 S cm^{-1} for a 3.0 draw ratio. These values were higher than those for the homopolymer, poly(3-hexylthiophene) (63), under comparable conditions [88].

Preliminary molecular weight studies in our laboratories on the copolymer of 3-hexyl- and 3-octylthiophene (using a 1:1 feed ratio and $FeCl_3$ polymerization) has shown a GPC weight average molecular weight of 114,000 and the peak maximum at 28,000, while a MALLS detector gave M_n = 159,000, M_w = 442,000 (polydispersity = 2.8), and the peak maximum at 112,000 [107]. Once again, the absolute molecular weights obtained from light scattering are considerably greater than those obtained by GPC using polystyrene standards. The molecular weight of this copolymer is quite high, as reflected by M_w obtained by the MALLS technique.

F. Polypyrroles

In pyrrole there are two positions which can be substituted with groups which can render the polymer soluble and/or fusible, namely the 3 and nitrogen positions. Chemically it is easier to put groups on the nitrogen, but, because of steric hindrance, this often causes adjacent rings to twist relative to one another and thus reduce the conjugation.

A number of poly(3-substituted pyrroles) have been prepared. The long-chain ketopyrrole polymers 78 (n = 10 and 16) have been electrochemically prepared from the respective monomers and give



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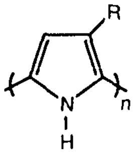
conductivities of PF_6^- doped material of 360 and 10 S cm^{-1} for n = 10 and 16, respectively [118]. It is reported that 78, n = 16, doped with PF_6^- is a transparent conductive polymer [130]. The solubility of these polymers has not been reported. The preparation and study of a variety of poly(3-alkylpyrroles) (79) has been carried out by Rühe and co-workers [131]. They were prepared from the respective



79

monomers electrochemically. Substituents included R = C_2H_5, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{15}H_{31}$, and $C_{18}H_{37}$, and the neutral polymers were partly soluble in common organic solvents such as $CHCl_3$, THF, and o-dichlorobenzene but insoluble in acetonitrile. The solutions were not stable and, upon standing, a black precipitate formed. GPC (polystyrene standards) indicated molecular weights in the range 5000-10,000. The UV-Vis spectra of the dissolved polymers are reported to be similar to those obtained on solid films [131].

The reduction potential of the polymeric films was shifted about 300 mV toward negative values compared to polypyrrole, and the length of the substituent had little effect on the redox potentials up to 10 carbon atoms. However, with 12 or more carbons the redox potential increases significantly [131]. The ClO_4^- doped as-prepared films had conductivities of 10^{-3} to about 10^{-1} S cm^{-1}. However, after pressing the films at 10 kbar/cm^2 the conductivities increased about 10-fold up to 0.03 to 10 S cm^{-1}. There seemed to be a slight dependence on the side-chain length with the longer side-chain polymers showing the poorest conductivities. Studies of the temperature dependence of conductivity showed a marked decrease with decreasing temperature down to about 10 K. For the side chains up to 10 carbons the decrease from the room temperature conductivity was about three orders of magnitude, whereas for R = $C_{15}H_{31}$ and $C_{18}H_{37}$ the decrease was five to six orders of magnitude [131]. The poly(3-alkylpyrroles) (79) could also be obtained by $FeCl_3$ polymerization, and the conductivity of films was around 0.01 S cm^{-1}, and they were soluble in $CHCl_3$ and *o*-dichlorobenzene in the oxidized state [131].

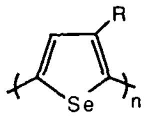
Poly(3-octylpyrrole) (79, R = C_8H_{17}) has also been independently prepared by both electrochemical polymerization and oxidative coupling using $Cu(ClO_4)_2$ and $Fe(ClO_4)_3$ [132]. The ClO_4^--doped film showed UV-Vis-near-IR absorptions at 344, 496, and 1240 nm similar to poly(3-methylpyrrole) but different from polypyrrole, while in pyridine solution, the material prepared by oxidative coupling and doped with $Fe(ClO_4)_3$ exhibited a spectrum which consisted of two peaks at 388 and 620 nm. A solution of the electrochemically prepared material as well as solutions of the polymer in $CHCl_3$ gave spectra which resembled those from the pyridine solution. This behavior is in marked contrast to that of poly(3-octylthiophene) (64) [132].

A large number of *N*-substituted polypyrroles have been prepared and studied, many for modifying electrode surfaces [133]. An *N*-substitution in polypyrrole usually lowers the electronic conductivity of the doped material, presumably by sterically twisting adjacent rings out of planarity. Unfortunately the properties such as solubility and melting point, which would make these polymers processable have not been reported, most likely due to the fact that their processability is limited. This is true, for example, for the *N*-alkyl substituents (up to butyl) [134] and for long-chain substituents on the nitrogen containing other functional groups [135]. On the other hand, a benefit of *N*-substitution is the ability to vary the conductivity of the fully oxidized, and stable, form of the pyrrole copolymer. We have obtained free-standing films of poly(pyrrole-co-*N*-phenylpyrrole) which have conductivities that range from 10^{+2} S cm^{-1} to 10^{-3} S cm^{-1} as a function of copolymer composition [135a].

In addition, a chiral polypyrrole, 79, R = 2-methylbutyl, as a co-polymer with pyrrole, has been reported but was not well characterized [120b]. The lack of processability of these pyrrole-based polymers precludes further discussion here.

G. Poly(3-Alkylselenophene)

Very recently the preparation and properties of poly(3-alkylselenophenes) (80,81) has been reported [136]. They were prepared by

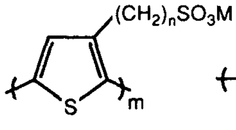


80: R = C_6H_{13}
81: R = $C_{12}H_{25}$

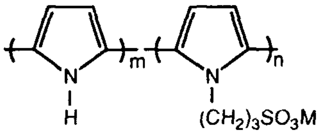
$FeCl_3$ or electrochemical polymerization of the monomers and were soluble in solvents such as $CHCl_3$, CCl_4, and CH_2Cl_2. The dodecyl polymer 81 melted around 250°C, substantially higher than the corresponding thiophene polymer 66. The hexyl derivative 80 did not melt up to 300°C. The I_2-doped polymer films showed conductivities of about 10^{-3} S cm^{-1}, as did electrochemically prepared films doped with BF_4^- ions, similar to poly(selenophene) itself [136]. Thermochromism was not observed, presumably because of the decreased coplanarity of the selenophene rings resulting from the steric hindrance between the alkyl groups and the large selenium atom of the adjacent ring. This increased torsion of the rings also explains the relatively high band gap of 2.4 eV [136].

H. Self-Doped Polyheterocycles

Since the conducting state of a polyheterocycle contains positive charges, there must be compensating anions present. The preparation of charge compensating conducting (self-doped) polyheterocycles, where anionic sites are incorporated into the polymer, was first reported in 1987 by the Wudl and Heeger group (82 and 83) [137], by ourselves (84) [138], and by Pickup (85) [139]. Subsequent reports have involved preparation and study of 86 and 87 [140a] and 88 [141]. Polymers 82, 83, and 88 could not be prepared electrochemically from the sulfonic acids or sulfonates directly. The methyl esters were used for 82 and 83, and the ester groups in the polymers were then converted to the free sulfonate [137]. The copolymer 84, containing about 75% of pyrrole rings could be prepared directly via electrochemical copolymerization [138]. Polymer 88 was prepared



82: n = 2
83: n = 4



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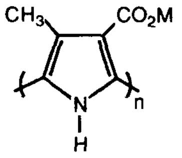

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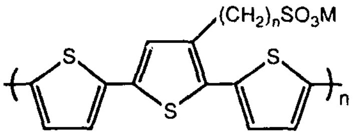

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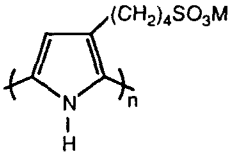

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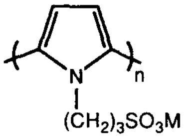

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by $FeCl_3$ polymerization of the monomer [141]. Polymers 85-87 could be prepared directly by electrochemical polymerization [139,140a]. Polymers 82,83, and 86-88 are reported to be water-soluble in both the undoped and doped states [137,138,140a]. The conductivity of undoped films of 82, M = Na^+, was between 10^{-7} and 10^{-2} S cm^{-1} depending on the relative humidity, while it was ~10 S cm^{-1} after bromine doping. The band gap of this polymer was about 0.5 eV higher than that of polythiophene itself. Unlike the poly(3-alkylthiophenes) the UV-Vis spectra of cast films and aqueous solutions are virtually identical. Upon electrochemical doping, 82, M = Na^+, showed two new UV-Vis bands characteristic of bipolaron formation. Spontaneous doping was also observed at low pH [137]. A series of polymers similar to 84 containing a four-carbon spacer between the pyrrole and the sulfonate has been reported by Bidan et al. [140b].

There have been both electrochemical and microgravimetric studies of films of these self-doped polymers verifying the concept that redox switching of these systems involves cations and/or protons moving in and out [141,142]. Polymer 85, which showed fairly low conductivity when doped (ca. 10^{-5} S cm^{-1}), has been demonstrated to be a cation exchange polymer which can bind large cations reversibly [139]. The high charging and discharging rates indicate that it is also a facile ion conductor. Polymer 84 has also been shown to be capable of binding and transporting cations such as $Ru(NH_3)_6{}^{3+}$ and $Ru(bpy)_3{}^{2+}$ (bpy = 2,2'-bipyridyl) [143].

Polymers 86 and 87 showed electrochemically doped conductivities of pressed pellets of 0.01 and 0.1 S cm^{-1}, respectively, but films obtained from aqueous solution by evaporation at 70°C showed conductivities of 10^{-8} S cm^{-1} [140a].

VI. CONDUCTING POLYMER SOLUTIONS

The polyacetylenes, poly(arylene vinylenes), and soluble polyheterocycles are most conveniently processed in their insulating states and subsequently doped to become conductors. An interesting advancement has been made in the preparation of solutions of polymers in the conducting form [144]. Thus processing, for example spin coating, leads directly to conducting polymer films.

This work was catalyzed by the discovery that AsF_3, a nonoxidizing inorganic solvent, could swell films of poly(phenylene sulfide) (PPS) and accelerate its rate of doping with the strong oxidant AsF_5 [145]. The interest in PPS was originally generated because it is a commercially available dopable thermoplastic (Phillips Petroleum, Ryton) which was dopable [146-149]. Typically, treatment of PPS films with 400 torr of AsF_5 leads to an initial increase in conductivity to 10^{-5} S cm^{-1} which, over a period of days, ultimately reaches 10^{-2} S cm^{-1}. Analysis of arsenic distributions in these films showed that most of the dopant was concentrated at the film surface. Diffusion into the bulk of the film, and homogeneous doping, was prevented by an impenetrable skin. If the PPS is exposed to 180 torr of AsF_3, the vapor pressure of AsF_3 at room temperature, and subsequently, AsF_5 is added to a total pressure of 300 torr, much faster conductivity increases are observed. Within 10 min the polymer attains a conductivity of 10^{-2} S cm^{-1} and approaches 1 S cm^{-1} in 2 h. Dopant ion distribution studies indicated the arsenic atoms to be distributed throughout the entire polymer with little concentration gradient, thus showing diffusive processes were not impaired. This is likely due to a solvating effect of the doped sites on the polymer chain by AsF_3.

This phenomenon has been exploited in the preparation of solutions of PPS in the conducting form [149a,b]. These solutions are formed by first dispersing PPS powder in AsF_3 and subsequently exposing this dispersion to an oxidizing agent (e.g., AsF_5). An immediate color change occurs as the polymer dopes and dissolves to yield a deep blue solution. Slow vacuum removal of solvent from the solution leads to coherent films of conducting PPS with better electrical properties than films doped using gas-phase techniques.

Ac measurements (400 Hz) of the conducting PPS solutions yield a conductivity of 2×10^{-2} S cm^{-1}. Applications of dc techniques, on the other hand, show the solution to have ionic character since polarization is observed. Cast films exhibit dc conductivities which range from 25 to 200 S cm^{-1}, and the conductivity becomes predominantly electronic in the solid state.

In addition to being electrically conductive, 0.2 *M* conducting PPS solutions are paramagnetic exhibiting a Dysonian line shape

[150] at room temperature. This is indicative of a highly electrically conductive system and is also observed for metal ammonia solutions.

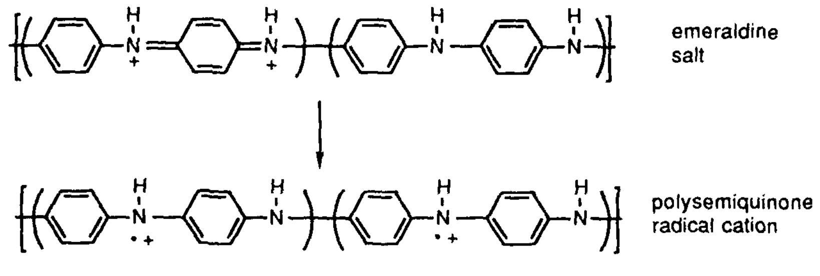
This concept for forming conducting polymer solutions has not been limited to PPS. For example, poly(*p*-phenylene oxide) (PPO) can be handled in a similar manner, and films of PPO have a conductivity of 100 S cm^{-1} when solution cast.

The AsF_5/AsF_3 system has also been found to be useful for the polymerization of aromatic molecules to form conducting polymer solutions [144,151]. For example, polythiophene has been prepared from bithiophene, poly(3-methylthiophene) from 3-methylthiophene, polypyrrole from pyrrole and polyphenylene from bi-, ter- and sexiphenyl. This has been studied in detail for the case of poly(3-methylthiophene) (60) [151]. Addition of excess AsF_5 (2 moles/monomer) to an AsF_3 solution of 3-methylthiophene leads to a deep blue solution. When the AsF_3 was removed from this solution, films having conductivities as high as 28 S cm^{-1} were obtained.

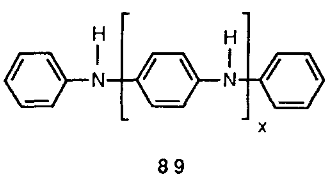
VII. POLYANILINE

Although one of the oldest known conducting polymers [152,153], a resurgence of interest has occurred in polyaniline. Its proton dopability has been viewed as a new concept [154] in conducting polymers and techniques have been developed to obtain it as a highly soluble and processable polymer. Polyaniline stands out from the previously mentioned redox dopable polymers in that it can be rendered conductive by partial oxidation of the fully reduced (leucoemeraldine base) form or by partial protonation of the half-oxidized (emeraldine base) form. The resulting emeraldine salt exists as a polysemiquinone radical cation, as shown in Scheme 7, with conductivity attributable to the formation of a polaron band. The proton addition and redox doping are reversible and follow a cyclic pattern as initially suggested by Hjertberg et al. [155]. Thus, the conductivity of the polymer is a function of the pH at which the

Scheme 7



polymer is prepared. Initial preparations of polyaniline led to insoluble materials whose structures were difficult to definitively characterize. This was circumvented by both model compound studies [156,157] and a separate synthesis of poly(*p*-phenylene amineimine) [158]. The specific model included *N,N'*-diphenyl-*p*-phenylenediamine (89, x = 1), *N,N'*-bis[4-(phenylamino)phenyl]-1,4-benzenediamine (89, x = 3) and a phenyl-capped octaaniline (89, x = 7). A series of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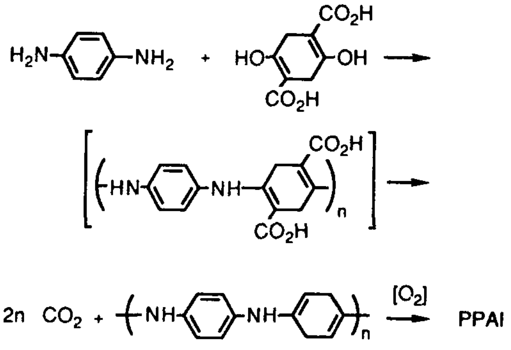
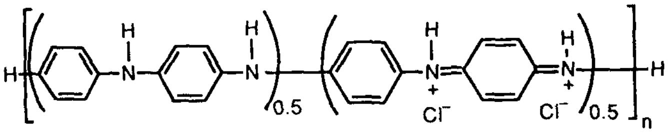
structural, electrochemical, spectroscopic, Brønsted acid-doping, and electrical conductivity measurements on these model compounds showed them to be fully representative of the polymer prepared via the oxidation of aniline itself. To elucidate whether or not polyaniline (PANI) is a purely para-linked poly(phenylene amineimine) (PPAI) Wudl et al. [158] synthesized a model polymer via Scheme 8 through which they could "honor the oldest organic polymer with the oldest method of structure proof: synthesis." Their synthetic route was developed to allow linkage through nitrogen atoms only at the para position, would produce high-molecular-weight polymer under mild conditions and would have a known mechanism of polymerization. Comparison of the properties of PPAI with polyaniline showed the PPAI to be an excellent model both structurally and electronically. Of special note here is the fact that polyaniline "is devoid of incorporation of *o*-phenylenediamine moieties in the backbone" and that the PPAI was DMF soluble.

Scheme 8



More commonly, polyaniline is prepared by the polymerization of aniline using $(NH_4)_2S_2O_8$ in HCl [159]. It is prepared as the "emeraldine hydrochloride" which can be represented by structure 90 or, a possibly more correct presentation, as 91 in the polaronic form. This form of polyaniline is highly conducting but completely insoluble.



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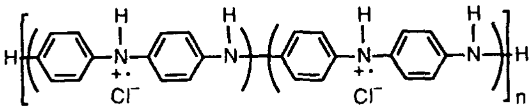

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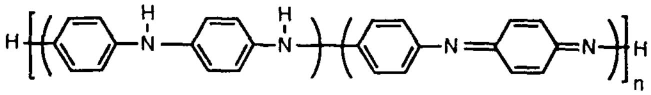
A highly soluble and processable form of polyaniline, termed "emeraldine base," (92) can be prepared by the NH_4OH deprotonation



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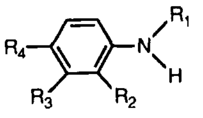
of emeraldine hydrochloride [159]. A variety of solvent systems are available for the polymer in this form, including 80% aqueous acetic acid, 60-80% aqueous formic acid, DMSO, and *N*-methylpyrrolidone (NMP). Freestanding films of the base form can be obtained by casting from the organic solvents while films of the doped material can be obtained by casting from acid [160]. Treatment of the neutral insulating base film with HCl subsequently leads to the conducting form as detailed in Scheme 7.

A wide spectrum of molecular weights have been reported for polyaniline. GPC elution times for polyaniline synthesized in DMF/1% acetic acid were compared to a series of structurally similar compounds and a molecular weight of 80,000 was deduced for the polymer [161]. A GPC comparison of polyaniline extracted with a 20% NaOH/THF solution, which had been prepared by electropolymerization of 0.1 *M* aniline in 0.1 *M* H_2SO_4, to polystyrene standards led to a molecular weight of 9000 [162]. Wei and co-workers [163] separated the THF soluble fraction from the THF insoluble/DMF soluble fraction of polyaniline hydrochloride deprotonated with NH_4OH. Due to the inaccuracies inherent in the GPC technique they utilized a tetrameric model compound of polyaniline to correct their molecular weights derived from polystyrene standards. A bimodal molecular weight distribution was observed with the low molecular weight fraction (only THF soluble) having a range of 2200-4800 while the high-molecular-weight fraction had a range of 170,000-200,000.

The above descriptions of soluble polyaniline are limited to the neutral insulating forms. Heeger and co-workers [164,165] have found that the emeraldine hydrochloride form of polyaniline is soluble in 97% sulfuric acid with polymer concentrations up to 20 wt%. Homogeneous viscous, purple black, polymer solutions are obtained. A viscosity molecular weight study of this polyaniline in the base form showed it to have a viscosity molecular weight average between 12,000 and 40,000 dependent upon whether the rigid-chain or flexible-chain limit was used. Semicrystalline films with spherulitic morphologies were reported for materials cast from H_2SO_4. A major benefit of solubility in the doped form is the ability to spin fibers of the polymer as a conductor. Dry-jet wet spinning into cold water from 96% H_2SO_4 led to fibers that dried with a smooth, shiny and metal-like appearance. Although only weak orientation was observed for these fibers, conductivities of 20-60 S cm^{-1} were measured.

As was described earlier for the poly(3-substituted thiophenes), substitution along the polyaniline backbone has been utilized as a means of improving the processability [166-172]. In this case a broad family of polymer derivatives are possible since substitution can be accomplished on the monomers at either the main-chain nitrogen or the aromatic rings as shown in 93. For example, Wei and co-workers [168-171] have investigated polyanilines substituted with alkyl, aryl, sulfonyl, and amino groups on the ring (R_2,R_3) along with alkyl, aryl, benzyl, and $-CH_2CN$ substituents on the nitrogen (R_1). Since aniline preferentially oxidatively polymerizes at the position para to the amine, only aryl substituents (R_4) can be used there. Ring substitution with small methyl and ethyl groups led to a marked decrease in the yield and molecular weights of the polymers when compared to the unsubstituted parent polymer. Increasing the size of the substituent to propyl or larger essentially prohibits polymerization altogether. The position of the substituent on the ring is also important as indicated by an overall yield of



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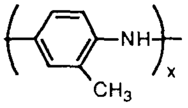
80% for the preparation of poly(2-methylaniline) (94) and only 29% for poly(3-methylaniline) (95) shown in the base form for simplicity. Interestingly, the substituents have little influence on the conductivity



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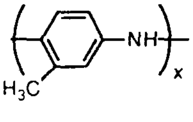
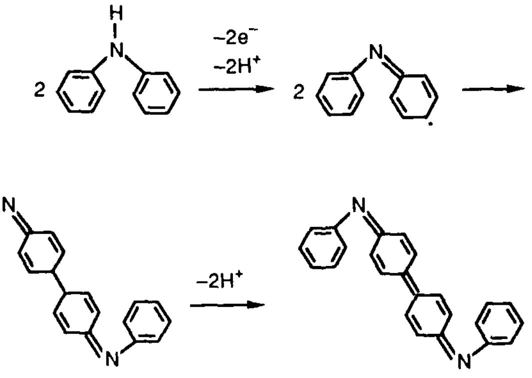


95

of the polymer obtained with both methyl derivatives exhibiting conductivities of 0.3 S cm^{-1} and the 2-ethyl derivative 1 S cm^{-1}, while the polyaniline itself, prepared under these conditions, has a conductivity of 5 S cm^{-1}. Although these polyaniline derivatives are insoluble in the as-prepared, conducting forms, treatment with base yields polymers that are highly soluble in $CHCl_3$ and THF.

The preparation of *N*-substituted polyanilines also results in electroactive polymers. In general the polymerization mechanism is believed to proceed through the typical head-to-tail coupling, but, in the case of *N*-aryl substituted anilines, an alternative mechanism has been proposed [171], which is outlined in Scheme 9. Both poly(*N*-phenylaniline) and poly(*N*-naphthylaniline) have been prepared in this manner and exhibit low conductivities of 2 × 10^{-3} S cm^{-1}.

Scheme 9



VIII. BLENDS, COMPOSITES, AND LATEXES OF CONDUCTING POLYMERS

Multicomponent materials, including polymer blends and composites, are prepared to obtain specific properties which are contributed by the various components. Blending and composite techniques are used extensively in polymer science to improve material strength, thermal stability, gas diffusivity, etc. In the development of electronically conducting polymers, blend and composite formation allows a conducting polymer to be dispersed in an insulating matrix as either a continuous, phase-separated, or possibly miscible component. At sufficiently high compositions of the conductor, electron transport and electroactivity is possible.

A. Polyacetylene Composites

Again turning to a polyacetylene system as a prototype to illustrate conducting polymer blend formation, Wnek and Galvin [173,174] developed methods of in situ polymerization to form polyacetylene within a polymeric matrix. In their method, low-density polyethylene (LDPE) was used as a matrix due to its availability as a film, its mechanical strength and expected inertness to Ziegler-Natta-type initiator systems. The composite is formed by initially swelling the LDPE in the initiator solution, impregnating the film throughout. This swollen matrix is then washed to remove surface catalyst residues and exposed to acetylene gas. Polymerization occurs as the monomer diffuses into the membrane with the polymerization rate being maximized at high temperatures (110°C) where the matrix polymer is soft. Using this method, $(CH)_x$-LDPE composites with up to 15 wt% $(CH)_x$ could be obtained. Subsequent doping with I_2 yields strong, flexible films with conductivities as high as 10 S cm^{-1}. Analysis of the electrical properties of the doped films as a function of composition shows an interesting percolation-like transition at 3-4 wt % of $(CH)_x$. Even at such low contents of conducting components, conductivities as high as 1 S cm^{-1} could be obtained. It has been proposed [175] that this percolation threshold can be correlated with the surface tension differences between the two phases.

In extending this idea of in situ polymerization, Rubner et al. [176] polymerized acetylene in polybutadiene (PB), and this composite exhibited rubbery elastic properties at low $(CH)_x$ loadings and behaved more plasticlike at high $(CH)_x$ loadings. As made, these composites could be chemically doped with I_2 and $FeCl_3$ or electrochemically doped to conductivities of 10-100 S cm^{-1}. These elevated conductivities were found down to $(CH)_x$/PB compositions as low as 15/85. Working with these materials in the 40-60% $(CH)_x$ composition, stretch elongation led to composites with significantly enhanced conductivities. The most dramatic example of this is illustrated by a conductivity increase of 15 to 575 S cm^{-1} for a 40/60 $(CH)_x$/PB composite that was stretched by a factor of 6 prior to I_2 doping.

In addition to in situ polymerization methods, $(CH)_x$ composite materials have been prepared by polymerizing acetylene onto material surfaces. For example, Schoch [177] has developed methods for preparing $(CH)_x$ on both Kevlar and glass fabrics. Polymerization was accomplished by soaking the fabrics with the typical $Ti(OBu)_4/AlEt_3$ initiator system. SEM analyses indicate the $(CH)_x$ forms as a coating on the fabric fibers and does not penetrate into the fibers themselves.

B. Poly(Arylene Vinylene) Composites

The development of the water soluble precursor prepared poly(arylene vinylenes) has led Karasz et al. [178-180] to investigate blending of the precursor polymers with other water-soluble polymers. The observation that polyacrylamide (PAcr) blend films with the PPV-soluble precursor displayed optical clarity and mechanical integrity was suggestive of a compatible polymer blend [178]. With heating, elimination to form the fully conjugated PPV could be accomplished within the PAcr matrix and the films retained their optical transparency. DSC analysis of these blends showed the T_g of PAcr to be unaffected, and thus the blend is actually completely phase separated. This concept was extended to a variety of water-soluble matrix polymers including poly(ethylene oxide) (PEO), poly(vinyl pyrrolidone) (PVP), poly(vinyl methyl ether) (PVME), methyl cellulose (MC), and hydroxypropyl cellulose (HPC) [179]. All of these blends are dopable, after heating to form the PPV, by AsF_5 vapor to conductivities of 1-100 S cm^{-1}. Whereas the in situ polymerization of $(CH)_x$ in LDPE was found to improve the ambient atmospheric stability of conductivity, this is not the case for the PPV/PAcr blends. This is most likely due to the ability of PAcr to absorb atmospheric water which subsequently reacts with, and degrades, the doped complex.

Soluble precursor routes to conjugated polymers typically yield space-filling films. Since both gas-phase and electrochemical doping require diffusion of dopant species through the films, doping rates can be quite slow. The blending of polar matrix polymers, having low glass transitions (i.e., PEO, PVME, and HPC) with PPV was found to greatly enhance the rate of gas-phase AsF_5 doping. On the other hand, use of glassy polymers in these blends (i.e., MC and PVP) depressed the doping rate and ultimate conductivity [179]. For example, a 50:50 wt% unoriented blend of PEO and PPV attained a conductivity of 200 S cm^{-1}, about an order of magnitude higher than that for unoriented PPV films alone.

Electrochemical doping rates are also seen to increase dramatically in certain PPV blends [179,180]. For the case of a PPV/PEO with a

50:50 wt% composition, the elimination process was optimized to yield the most fully conjugated PPV while limiting thermal degradation of the matrix polymer. When the PEO is present at $\geq$ 40% in the solid state, it is obviously phase separated with the formation of 100-500 μm diameter spherulites. During electrochemical doping this PEO phase can complex Li^+ ion from electrolyte and assist in rapid ion transport through the membrane. Electrochemical doping studies showed that, in addition to accelerated doping rates with increased PEO content, doping homogeneity improved also.

C. Poly(3-Alkylthiophene) Blends

The advent of truly thermoplastic poly(3-alkylthiophenes) has opened up significant opportunities for blend and composite formation using compounding methods commonly used in the plastics industry. As pointed out earlier, Heeger et al. [129] prepared poly(3-hexylthiophene-*co*-3-benzylthiophene) (P3HBzT), by electropolymerization of monomer mixtures, which was highly soluble in chloroform, toluene, dichloromethane, and tetrahydrofuran. Although bulk yields via electrochemical polymerization are typically quite low, the copolymer could be prepared in significantly higher yields than either homopolymer. In these initial studies, miscible solutions of P3HBzT and polystyrene (PS) were prepared in $CHCl_3$ and films cast from these solutions. Spectroscopic results suggest that, upon film formation, the P3HBzT and PS phase separate. This has been observed in our labs with optical microscopy for blends of PS with electrochemically prepared poly(3-hexylthiophene) (63) [181]. At low 63 concentrations, spheres of poly(3-hexylthiophene) are dispersed in the PS matrix while at high 63 volume fractions the polythiophene is observed as a continuous phase. This is consistent with the observation [129] that P3HBzT/PS blends with >30% volume fraction of P3HBzT could be doped with $NOPF_6$ to conductivities greater than 1 S cm^{-1} while the conductivity drops precipitously to ca. 10^{-8} S cm^{-1} at 15% volume fraction P3HBzT, indicating a conductor-to-insulator transition due to percolation.

In addition to solution processing, the fusibility of poly(3-alkylthiophenes) at relatively low temperatures allows melt processing and blending with a wide variety of thermoplastics. This has been exploited by researchers at Neste Oy (Kulloo, Finland) and collaborators in the preparation of blends with poly(ethylene-*co*-vinyl acetate) (EVA), poly(ethylene-*co*-butyl acrylate), PS, and polyethylene [77,182-184]. Most of this work has centered on poly(3-octylthiophene) (64) since it exhibits good melt flow properties at processing temperatures below 200°C with little or no degradation. Films and sheets of 64/EVA blends were made by compression molding at various compositions, along with film blowing extrusion which allowed preparation of 10-cm-wide films over 100 m long. As was observed with the P3HBzT/PS blends, these 64/EVA blends undergo a percolation transition and can be $FeCl_3$ doped to conductivities > 1 S cm^{-1}. In these blends the reported transition is between 5-10% weight fraction although conductivities of 10^{-4} S cm^{-1} have been observed at compositions as low as 3% of 64. This latter point suggests low percolation thresholds may be obtainable, ultimately yielding low-cost conducting polymer blends with very high mechanical integrity. As discussed earlier, the optical absorption behavior of these polymers undergo significant changes with temperature which are related to the chain conformation. This is also the case in blends of poly(3-alkylthiophenes) as demonstrated by Yoshino et al. [95] in polystyrene, poly(methyl methacrylate), and ethylenepropylene copolymer (EPR) matrices. Interestingly, this conformational change can also be induced mechanically. Stretching of poly(3-docosylthiophene) (69)/EPR blends up to draw ratios of 12 led to a significant blue shift in the absorption maximum [104]. It is suggested that increased torsion about the bonds between thiophene rings takes place in elongated samples making the effective conjugation length shorter.

D. Electrochemical Composite Formation

In addition to the formation of multicomponent materials containing conducting polymers by chemical and physical methods, electrochemical techniques have also proven to be useful. The anodic electropolymerization of a variety of heterocycles has been used to produce freestanding films. In the case of pyrrole, electropolymerized in the presence of aromatic sulfonates (e.g., tosylate, benzene sulfonate), flexible films with tensile strengths approximately equal to polystyrene were obtained [185]. By combining the electrical properties of electropolymerized polyheterocycles with the physical properties of a variety of matrix polymers, a new family of multicomponent conducting and electroactive polymers have been obtained.

The electropolymerization of heterocycles within swollen polymers previously deposited on electrode surfaces were the first systems investigated [186-191]. Poly(vinyl alcohol) (PVA) films were cast on Pt electrodes, lightly cross-linked, and subsequently swollen with an aqueous solution of 0.1 *M* $CuSO_4$ and 0.1 *M* pyrrole [186]. Non-cross-linked PVA was also used by changing the solvent system to 50:50 $CH_3CN{:}H_2O$. Application of an anodic potential to the electrode causes pyrrole electropolymerization to begin at the electrode surface and polymer grows through the swollen membrane. The growth of the polypyrrole can be stopped at any point, yielding a film conducting on one side and insulating on the other. On the other hand, growth of the polypyrrole through the entire PVA matrix yields films having conductivities of 0.1-10 S cm^{-1} on both sides. These films were found to exhibit superior mechanical properties to poly(pyrrole sulfate) with a doubling of the ultimate tensile strength and an order of magnitude increase in the elongation to break. The generality of this concept was shown by the preparation of both polypyrrole [187-189] and polyazulene [189] composites with poly(vinyl chloride) prepared in acetonitrile electrolytes which exhibited conductivities of 50 S cm^{-1} and 10^{-2} S cm^{-1}, respectively.

The ability to control the physical properties of these composites has been demonstrated. Utilizing a vinylidene fluoride/trifluoroethylene copolymer as a matrix, Niwa et al. [190] prepared polypyrrole composites with an elongation to break of greater than 120%. Changing the matrix to a more flexible polyurethane and utilizing a tosylate electrolyte, Bi et al. [192] obtained polypyrrole composites with elongation to break of up to 640%.

Another benefit of electrochemical composite film formation is the ability to control the optical density of the films by the amount of conducting polymer incorporated [191]. The changes in optical absorption during electrosynthesis of films of poly(pyrrole tosylate) and poly(pyrrole tosylate)/poly(vinyl chloride) composites have been compared. Homopolymer and composite films prepared with a charge density of 0.032 C cm^{-2} both exhibit a transmittance to visible light in the range of 40-70%, indicating approximately the same amount of pyrrole was polymerized. The mechanical properties, though, are completely different. The composite was obtained as a 12-μm-thick freestanding film, while the homopolymer formed a nonuniform film of 0.05-0.07 μm which could not be removed intact from the electrode surface. Since the conducting polymer forms initially at the electrode/matrix polymer interface, a highly conducting surface can be obtained quickly. Conductivities of up to 5 S cm^{-1} with an optical transmittance of 60% were measured.

A method for overcoming the inhomogeneities across the film thickness caused by in situ electropolymerization was developed by Wang et al. [193]. They recognized that the amount of electrolyte that could diffuse into a membrane was quite low and found that, by blending electrolyte with host polymer (in this case PVC) prior to coating, conducting film uniformity was greatly improved. Examination of the conductivity across the film thickness, after electropolymerization of pyrrole through an electrolyte blended and unblended PVC for 20 min, showed over a 10 order of magnitude difference.

The use of ionomers as ion-containing matrix polymers on electrode surfaces has allowed the formation of conducting polymer composites where the matrix contributes the dopant anion and acts as an effective medium for ion transport. Due to its well-known stability during electrochemical processes, the perfluorosulfonated ionomer, Nafion, has been used in a number of studies [194-198]. Although free electrolyte is used during synthesis, it is most likely unable to penetrate into the membrane and thus charge balance is retained during electrosynthesis by the expulsion of counter cations. The electrochemical charge transport properties of polypyrrole/Nafion membranes during switching is highly dependent on the nature of the cation [197]. Polypyrrole itself, on the other hand, often has electrochemical charge transport properties which are a strong function of the electrolyte anion employed.

In experiments directed to open up the morphology of these conducting polymer composites and obtain higher current densities during electrochemical switching, Martin and co-workers [195,198] developed a composite electrode based on a fibrous form of polytetrafluoroethylene known as Gore-tex (GT). Although GT is mechanically strong, chemically stable and has an open structure its fluorinated surface causes it to be extremely hydrophobic and not easily wetted. To circumvent this, the GT membrane was impregnated with a coating of Nafion. In fact, this Nafion-impregnated Gore-tex (NIGT) was found to be a better ionic conductor than Nafion itself. Pyrrole was found to polymerize easily in the NIGT membranes to form conducting composites. In addition, polymerization currents were actually found to be higher at Pt coated with NIGT than at Pt alone due to a negative shift in the oxidation potential of the monomer.

Conducting polymer/matrix polymer composites have also been formed by initially solubilizing the matrix polymer in the monomer/electrolyte solution and allowing the matrix to deposit during electropolymerization. This has been investigated for both neutral thermoplastics [199], such as PVC, and a variety of polyelectrolytes [200-211]. A benefit here is that, since the matrix is depositing directly with the conducting polymer, a more homogeneous film is obtained. In the case of polyelectrolytes, where the matrix polymer is serving as the dopant species also, there is necessarily an intimate mixing of polymer chains and the system can be viewed as a molecular composite.

The one-step deposition of poly(3-methylthiophene) (60)/PVC composites described by Roncali and Garnier [199] shows how the morphology of the film obtained is dependent on the mode of growth of the conducting polymer when the polymer is grown within a preexisting matrix. This is not the case in these composites, as the morphology of the matrix affects the electropolymerization process. The composition and electrical properties of these polymers can be controlled by varying either the deposition charge or reagent concentration. For example, by changing the deposition charge from 0 to 456 mC cm^{-2} at a current density of 5 mA cm^{-2} films

Table 1. Electrical Conductivities of Various Polypyrrole/Polyelectrolyte Composites

Polyelectrolyte	Solvent	Conductivity ($S\ cm^{-1}$)	Ref.
Poly(2-acrylamido-2-methyl propanesulfonic acid)	CH_3CN/H_2O H_2O	4×10^{-2} 2.9	200 202
Poly(methacrylic acid)	CH_3OH/H_2O	1.7	200
Chlorosulfonate polyethylene (hydrolyzed)	THF/H_2O	1×10^{-3}	200
Poly(acrylamide-*co*-2-acrylamido-2-methyl propanesulfonic acid)	CH_3OH	1×10^{-1}	200
Sulfonated poly(vinyl alcohol)	DMF/H_2O	2.6	200
Sulfonated styrene/(hydrogenated) butadiene triblock copolymer	$THF/C_6H_5NO_2$	9×10^{-3}	200
Poly(4-styrenesulfonic acid)	H_2O	9.4	202
Sodium poly(4-styrenesulfonate)	H_2O/dioxane H_2O	3×10^{-2}-5.0 2×10^{-1}	203 204
Sodium poly(vinylsulfonate)	H_2O	7.4	202
Potassium poly(vinylsulfate)	H_2O	10.0	204
Poly(styrene-*co*-maleic acid) (VERSA-TL4, National Starch)	H_2O	6.2	202
Sodium sulfonate of naphthalene/formaldehyde copolymer (Stepantan-A, Stepan Co.)	H_2O	6.2	202
Sodium poly(phenyleneterephthalamide propanesulfonate) (sulfonated Kevlar)	H_2O	1.0	211

of 1.5-3.0 μm were obtained that contained 0-42% of poly(3-methylthiophene) (60).

The electropolymerization of heterocycles in solutions of polyelectrolytes leads directly to doped conducting composites films and is an extremely versatile technique. For the case of polypyrrole composites, Table 1 lists a number of the polyelectrolytes that have been used as the ionic matrix. Two major benefits stand out from using these polyelectrolytes. The first is the ability to use aqueous electrolytes making disposal of waste electrolyte significantly less costly. Second, the polyelectrolyte imports its mechanical and physical properties to the overall composites properties. These films are flexible and may be heat-processable. For example, a film of polypyrrole/poly(styrene sulfonate) (PSS) is slightly flexible, but when heated to above the glass transition (T_g) of the PSS it becomes highly flexible and can be easily fit to a nonplanar surface. In some cases where the T_g of the polyelectrolyte is lower than room temperature [200] the conducting composites are actually melt-processable and elastic.

The controllable physical, mechanical, electrical, and ion transport properties of these polyheterocycle/polyelectrolyte molecular composites have also allowed them to be used for some specific applications, including electrochemical deionization [201,208] and electrodes in polymer/metal and all polymeric batteries [205,209].

E. Conducting Polymer Latexes

Colloidally dispersed latexes of polypyrrole [212-217] and polyaniline [218] have been used to prepare processable conducting organic polymers. Initial polypyrrole latexes were prepared by the electropolymerization of pyrrole in the presence of latex particles having a high concentration of bound sulfonate or sulfate groups on their surface [212]. Using a number of commercially available latexes encompassing acrylates, methacrylates, vinylidene chlorides, EVAs and styrenics, thick (up to 1/4 inch) films were obtained having conductivities from 10^{-3} to 5 S cm^{-1}. These materials could be ground, solvent swollen and sheared to yield dispersions from which air-stable electrically conducting films could be cast or spin coated.

The chemical ($FeCl_3$) polymerization of pyrrole in aqueous solutions of methylcellulose was investigated by Bjorklund et al. [213] in the preparation of colloidal polypyrrole which could be cast to form films having conductivities up to 2×10^{-1} S cm^{-1}. This method, originally employed by Edwards et al. [214] with other conducting polymers, was extended by Armes et al. [215], who carefully examined the conditions necessary to reproducibly prepare colloidal polypyrrole with a high degree of control of particle morphology.

Highly monodisperse particles were prepared having mean diameters on the order of 75-150 nm which, when pressed into pellets, yielded electrical conductivities up to 5 S cm^{-1}. These authors conclude that "steric stabilization is required to produce aqueous latex dispersions" and that "charge stabilization is ruled out under the high ionic strength conditions present" in discussing the properties of these colloids. When using poly(4-vinylpyridine) steric stabilizer, it has been found that the polypyrrole latex exhibits reversible acid/base-induced flocculation-stabilization behavior [217]. In strongly acid solution the vinyl pyridine units of the stabilizer are believed to be protonated and thus provides an electrostatic contribution to stabilization which helps disperse the colloid. Addition of base to give a pH of $>3.6 \pm 0.1$ leads to flocculation as the vinyl pyridine units are deprotonated.

IX. SUMMARY

It is evident now that processability and high mechanical integrity can be attained for essentially any conducting polymer system. The full range of techniques available to the polymer chemist-copolymerization, processable precursors, substituent effects, blend formation, composite formation, latex formation, and even electrochemical film formation—can be applied to the development of useful materials. These principles and techniques, coupled with the atmospheric stability of a number of conducting polymer systems (especially the polyheterocycles and polyaniline), indicate these materials are prime candidates for use in specific applications.

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