Macromolecules 1993, 26, 2704-2710

Synthesis, Characterization, and Stability of Poly(3,4-dibutoxythiophenevinylene) Copolymers

Margaret L. Blohm,* James E. Pickett, and Paul C. Van Dort

Physical Chemistry Laboratory, GE Research and Development,
Schenectady, New York 12301

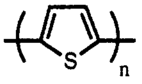
Received November 16, 1992; Revised Manuscript Received February 22, 1993

ABSTRACT: Poly(3,4-dibutoxythiophenevinylene) was prepared in two steps using nickel-catalyzed Grignard coupling reactions with 1,2-dichloroethylene to yield a high molecular weight polymer that could be cast into tough free-standing films. The visible spectrum showed an absorption maximum of 607 nm and a band gap of 1.62 eV. Doping with $FeCl_3$ turned the deep blue film to transparent light gray and resulted in a conductivity of 1 S cm^{-1} using the four-probe technique. DSC measurements revealed no T_g but showed a T_m at 168 °C. The unusual partial crystallinity was confirmed by wide-angle X-ray diffraction. The polymer exhibited good thermal stability but was susceptible to photooxidation and to reaction with ambient levels of ozone. Poly[bis(3,4-dibutoxythienylene)vinylene] was also prepared and characterized.

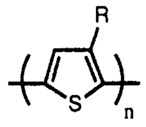
Introduction

Historically, the development of practical applications for conducting polymers has been limited by the poor processability and stability of the materials.[1,2] Recent advances, particularly in polythiophene chemistry, have shown the problems due to poor processability can be diminished or even solved. Substitution of thiophene in the 3-position with long-chain alkyl groups ($>C_4$) yields solution and melt-processable polymers without significantly sacrificing conductivity.[3-7]

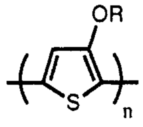
One research goal for conducting polymers has long been the reduction of the band gap so that the absorption of the undoped polymer shifts from the visible region to the near-infrared. A smaller band-gap conducting polymer would be easier to dope, have improved photoconductivity, and have larger nonlinear optical coefficients.[8] A common method of changing the polythiophene band gap is by substitution of the conjugated backbone; the energy of absorption decreases with alkyl substitution (**2**) and decreases still further with alkoxy substitution (**3**).[9] Electron donating substituents raise the energy of the highest occupied molecular orbital and consequently narrow the band gap.



(1)

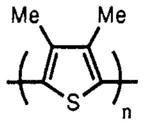


(2)

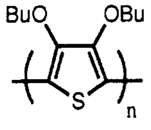


(3)

It is well-known that the polymerization of 3,4-disubstituted thiophenes yields polymers that have large band gaps and are difficult to dope.[10-12] Strong oxidants are required to produce polymers with reasonable conductivities. Increasing the degree of substitution or the length of the substituent changes the packing of the chains in the solid state. Both intrapolymer and interpolymer structures are dependent upon thiophene ring substitution, and both affect the electronic properties of the polymer. With disubstituted polythiophenes, the steric effect of the substituents on adjacent thiophene rings forces them out of coplanarity. These torsions introduced into the π-system of the polythiophene backbone increase the band gap, and the energy of the absorption maxima shifts to higher energy. For example, chemically polymerized poly(3,4-dimethylthiophene) (**4**)[13] is yellow and poly(3,4-dibutoxythiophene) (**5**) is green (λ_{max} = 460 nm),[14] absorbing at a much higher energy than their monofunctional analogs: poly(3-methylthiophene) is red and poly(3-methoxythiophene) is blue. Both **4** and **5** also require much stronger oxidants, such as $NOPF_6$, to become conductive. For these reasons, attempts to further reduce the polymer band gaps by increasing the substitution of the thiophene have not been effective.

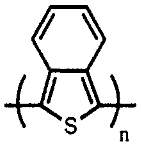


(4)

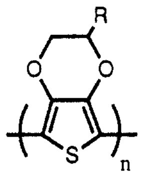


(5)

Evaluation of the electronic effects of disubstitution of thiophenes without the corresponding deleterious steric effects has only recently been attempted. In poly(isothianapthene) (**6**), Wudl successfully used aromatic stabilization to decrease the band gap to approximately 1.0 eV in the disubstituted thiophene.[15] Clearly, fusing the 3,4-disubstituents into a ring reduced the steric interactions, but the effects of disubstitution are difficult to separate from increased aromaticity. Although a very interesting polymer, **6** is difficult to synthesize and its characterization has been limited by its insolubility. The technique of reducing steric interactions by tying substituents back in a ring has also been used in poly(ethylenedioxythiophene) (**7**).[16,17] The dark blue polymer is easily oxidized by $FeCl_3$ to give an optically transparent conductive state (1.0 S cm^{-1}).



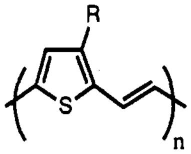
(6)



(7)

A successful approach to improvements in properties of polythiophenes has been to synthesize copolymers. Particularly interesting are the substituted poly(thiophenevinylenes). Poly(3-alkylthiophenevinylenes) (**8a**) and poly(3-alkoxythiophenevinylenes) (**8b** and **8c**) can be solution cast from common solvents to give tough, free-

0024-9297/93/2226-2704$04.00/0



(8)

8a, R = H
8b, R = methyl
8c, R = methoxy
8d, R = ethoxy

standing films. Because of the change in the electron density concurrent with alkoxy substitution, the absorption maxima of the doped films of poly(3-ethoxythiophenevinylene) indicated a band gap of 1.4 eV, while **8a** has a band gap of 1.6 eV. Doped polymer films are nearly optically transparent and have a light blue–gray color as indicated by slight tailing of the intense peak into the visible region.[18,19] Other thiophene copolymers have been studied, including poly(thienylenephenylene),[20] poly(dithienylenephenylene),[21] and poly(dithienylenevinylene),[22–24] but there have been no further reports of the effects of thiophene substitution on their properties.

The thiophenevinylene copolymers discussed above offer unique advantages for investigation of the effects of disubstitution on polythiophenes. The vinylene group would act as a physical "spacer" to reduce the steric interactions of disubstitution in the 3- and 4-positions of the thiophene ring. Disubstitution with the electron-donating alkoxy groups not only could improve the processability of the poly(thiophenevinylene) to include solution and perhaps even melt processability but also could decrease the band gap of the parent copolymer. Since the monoalkoxypoly(thiophenevinylene) is already a low-band-gap material, the possibility of a further decrease in the band gap upon disubstitution was even more intriguing. We report the synthesis and characterization of two new dialkoxythiophenevinylene copolymers.

Until recently, very few thorough studies have been published on the environmental stability of polythiophenes[25] required for various applications. The studies that have been done clearly demonstrate the importance of understanding the complex effects of changes in structure on stability. Recently, an investigation of polythiophenes at elevated temperatures showed that the degradation of thin films of poly(3-hexylthiophene) was rapid at 110 °C in air as measured by a decrease in conductivity of several orders of magnitude within 60 min.[26,27] The rate of loss of conductivity was reduced in a dry, argon atmosphere, and moisture was proposed as the primary agent. An excellent study by Rubner et al. reported the effects of the method of synthesis, alkyl chain length, dopant, temperature, and environment on the conductivity of poly(3-alkylthiophene) films.[28,29] They found films synthesized by ferric chloride oxidation were the most stable but that thermal stability decreased with increasing alkyl chain length. Since many improvements in polythiophene chemistry rely on alkyl substitution for property enhancement, the observations by both groups on the instability of these materials strongly suggest the need to understand the thermal dedoping process. Obviously, understanding the degradation is essential to using and potentially stabilizing polythiophene for a variety of applications.

The stability issues of greatest concern depend on the particular application. When considering polythiophenes in coatings applications, for example, stability to light becomes of primary importance. To our knowledge, there have been no systematic studies on the stability of polythiophene films to visible light. If the unique optical properties of poly(thiophenevinylenes) are to be exploited, their stability to all environmental conditions must be considered. We report here a study of the stability of undoped poly(dibutoxythiophenevinylene) thin films to both light and air.

Experimental Section

Tetrahydrofuran was freshly distilled from sodium–benzophenone ketyl. Diethyl ether was used from a freshly opened can as received. 1,2-Dibromoethane was freshly distilled. All other reagents were used as received. NMR spectra were obtained on a GE QE 300 spectrometer. UV–VIS–near-IR spectra were obtained on a Hitachi 3410 spectrophotometer. UV–visible spectra for the degradation experiments were obtained on a Shimadzu 240 spectrophotometer. Thermal analyses were performed on a Du Pont 951 thermogravimetric analyzer (TGA) and a Perkin-Elmer 2C differential scanning calorimeter (DSC). Elemental analysis was performed by Galbraith Laboratories. ESCA data were collected on a Surface Science Instruments X-Probe using monochromatic Al Kα X-rays. GPC analyses were obtained on a Waters gel permeation chromatograph with four banks of μstyragel columns (10^5, 10^4, 10^3, and 500 Å) and a 244 UV detector was used at a wavelength of 254 nm.

***trans*-1,2-Bis(3,4-dibutoxythiophene-2-yl)ethylene (10).** 3,4-Dibutoxythiophene (1.50 g, 6.57 mmol), prepared by adaptation of a method for dimethoxythiophene,[30] was dissolved in 16.5 mL of anhydrous diethyl ether in an oven-dried round-bottomed flask equipped with a nitrogen inlet. Butyllithium (3.00 mL of a 2.19 M solution in hexane) was added at room temperature using a syringe, and the resulting yellow solution was allowed to stir for 10 min. $MgBr_2{\cdot}Et_2O$, prepared by adding 0.597 g (6.9 mmol) of 1,2-dibromoethane to 0.64 g (26 mmol) of magnesium turnings in about 5 mL of anhydrous diethyl ether and stirring for 1 hour, was added using a cannula, and the suspension was stirred for 30 min. The reaction mixture was cooled with an ice bath, and a solution of 0.256 mL of *trans*-1,2-dichloroethylene (3.28 mmol) and ca. 7 mg (ca. 0.013 mmol) of $NiCl_2{\cdot}$[dppp][31] in 3 mL of anhydrous ether was added, using a cannula, to give a clear orange–yellow solution. The reaction mixture was stirred at room temperature for 21 h, after which it was diluted with 50 mL of ether and washed with 50 mL of water. The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated to give 1.47 g (93%) of an orange solid. The crude product was recrystallized from 12 mL of ethanol to give 0.85 g (54%) of product, mp 112–3 °C. NMR (300 MHz, $CDCl_3$): 1.98 (t, 6 H), 1.50 (m, 4 H), 1.75 (m, 4 H), 3.95 (t, 2 H), 4.10 (t, 3 H), 6.00 (s, 1 H), 6.97 (s, 1 H). Anal. Calcd for $C_{26}H_{40}O_4S_2$: C, 64.96; H, 8.39. Found: C, 64.41; H, 8.47.

Poly(3,4-dibutoxythiophenevinylene) (11). *Compound* **10** (0.5628 g, 1.171 mmol) was weighed into an oven-dried 100-mL round-bottomed flask. The flask was fitted with a stopper, septum, and reflux condenser equipped with a nitrogen inlet and was pump-purged four times with dry nitrogen. In a separate flask, $MgBr_2{\cdot}THF$ was prepared from 0.23 g of Mg turnings and 0.213 mL (2.459 mmol) of 1,2-dibromoethane in 10 mL of dry THF under strictly anhydrous and oxygen-free conditions and allowed to stand for 90 min to ensure complete reaction. To compound **10** was added at room temperature 15 mL of dry THF and 1.232 mL of a 1.940 M solution of *n*-butyllithium in cyclohexane. This clear amber solution was stirred for 10 min, and the $MgBr_2{\cdot}THF$ solution was added using a cannula, being careful to rinse all of the solution into the reaction with three small portions of THF. A white waxy solid formed immediately and then quickly redissolved. After 10 min the reaction mixture was cooled with an ice bath, and a solution of ca. 12 mg of $NiCl_2{\cdot}$[dppp] (1 mol % relative to BuLi) and 0.0912 mL (1.171 mmol) of *trans*-1,2-dichloroethane in 5 mL of THF (prepared under strictly dry and oxygen-free conditions at ice-bath temperature) was quantitatively transferred using a cannula and three THF rinses. The ice bath was replaced with a heating mantle, and the reaction mixture was heated to reflux overnight. The deep blue solution was transferred to an Erlenmeyer flask, and 300 mL of methanol was added. Filtration gave 0.5825 g of a fine black solid (98.6% crude yield) and a clear red filtrate. A mass of 0.5431 g of the solid was placed in a Soxhlet extractor and was treated with refluxing acetone for 3 h. The residue was dissolved

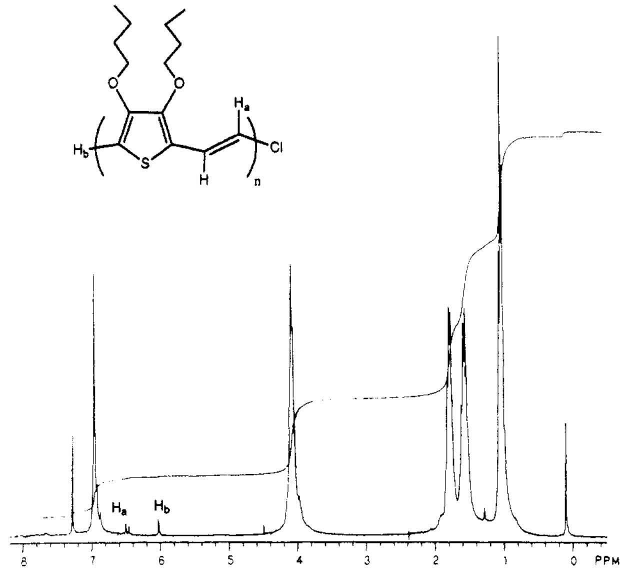


Figure 1. 300-MHz ^{1}H NMR of 11. End groups are seen at 6.5 and 6.0 ppm.

in chloroform and the solvent evaporated to yield 0.4931 g of blue-black solid. Anal. Calcd for $C_{14}H_{21}O_2S$: C, 66.36; H, 8.35. Found: C, 66.11; H, 8.17. ^{1}H NMR ($CDCl_3$): 1.0 (t, 6 H), 1.5 (m, 4 H), 1.8 (m, 4 H), 4.0–4.2 (m, 4 H), 6.95 (b s, 2 H). End groups are shown in Figure 1. End-group analysis from the NMR spectrum showed an average degree of polymerization of 49. A UV–visible spectrum of a film cast on quartz showed a λ_{max} at 607 nm with a shoulder at 670 nm. NMR analysis of solid recovered from the acetone extracts showed an average degree of polymerization of 11.

Poly[bis(3,4-dibutoxythienylene)vinylene] (15). To 12 mL of nitrogen-purged chloroform were added while stirring 0.40 g (2.48 mmol) of anhydrous $FeCl_3$ and 0.20 g (0.42 mmol) of compound 10. The reaction mixture immediately turned dark red and then gradually purple–blue. After 20 min, a green–gray film had deposited on the walls of the flask. The reaction mixture and the film were poured into 25 mL of methanol, and the resulting solid was filtered, washed 10 times with 2-mL portions of methanol, washed four times with 1:1 methanol/water, and finally washed four times with methanol. The solid turned blue–black during the washing, and the wash filtrate eventually became colorless. The yield of dried solid was 0.20 g (100%). Extraction of the solid with boiling chloroform yielded 0.060 g (32%) of soluble polymer. The insoluble portion was mainly the film residue from the reaction flask. The soluble polymer could be cast in tough, free-standing films with λ_{max} = 539 nm. Dipping the film into a nitromethane solution of $FeCl_3$ yielded a light gray color and a flat spectrum from 400 to 700 nm. Reprecipitation from $CHCl_3$/methanol and washing with acetone removed some red, low molecular weight material. ^{1}H NMR (CD_2Cl_2): 0.8–1.1 (b m, 6 H), 1.4–1.6 (b m, 4 H), 1.7–1.8 (b m, 2 H), 1.8–2.0 (b m, 2 H), 4.0–4.2 (b m, 4 H), 1.95 (b s, 0.7 H).

General Doping Procedure. A chloroform solution of polymer was spin cast onto a 5.0-cm glass disk. A 600-mL beaker was covered with a watch glass and purged with a continuous flow of nitrogen. About 0.5 cm of nitromethane and 100 mg of anhydrous $FeCl_3$ were added, and the beaker was swirled until a clear amber solution resulted. The polymer-coated disk was introduced. Generally, the color would change within 20 s, but the disks were allowed to remain in the solution with occasional swirling for 45 min to ensure complete doping.

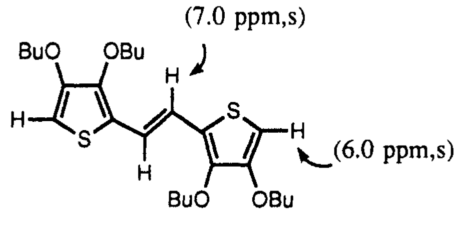
General Procedure for Degradation Experiments. Polymer was cast onto glass microscope slides, placed into quartz test tubes, and sealed with a serum cap. The appropriate gas was introduced into the tubes by a continuous purge through a needle for several hours, and then the tubes were sealed. UV–visible spectra were taken through the tubes without removing the samples. UV light was blocked where appropriate by wrapping the tube with Kodak yellow sheeting with a cutoff of about 440 nm.

Ozone Scavenging Experiment. A Pyrex U-tube was packed with about 12 in. of total length of high impact polystyrene pellets (HIPS, 10% butadiene rubber content) to within about $1^1/_2$ in. from each end. Cotton plugs held the polymer pellets in place. A piece of polymer film cast onto a glass slide was placed in the center of the $1^1/_2$-in. space, and serum caps pierced with a needle were placed on each end. The tube was placed flat on a benchtop, and air was drawn through the tube by means of a small vacuum pump. Periodically the samples were removed. UV–visible spectra were taken, and the rate of degradation upstream and downstream from the HIPS was determined. For the control experiment, the HIPS pellets were replaced with crystal polystyrene.

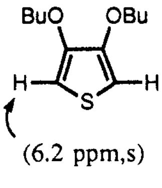
Results and Discussion

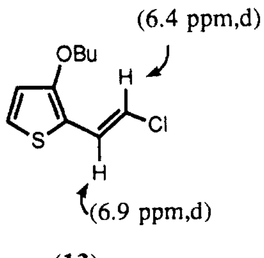
Synthesis and Characterization of Poly(3,4-dibutoxythiophenevinylene). The alternating copolymer, 11, was synthesized using a modification of Elsenbaumer's method for monoalkoxy-substituted poly(thiophenevinylenes).[18] The nickel-catalyzed Grignard coupling of 2 equiv of dibutoxythiophene with dichloroethylene yielded orange crystalline 10 in 90% yield (Scheme I). Reaction of 10 with a second 1 equiv of dichloroethylene gave a deep blue solution after overnight reflux. A black powder precipitated upon the addition of methanol. Low molecular weight oligomers with an average DP of 11 were removed from the product by Soxhlet extraction in acetone. The remaining dark blue powder was completely soluble in chloroform and isolated without further purification in 90% yield. Tough, flexible, free-standing gold films could be cast from chloroform solution.

The copolymer was characterized by ^{1}H NMR, and the spectrum taken in chloroform is shown in Figure 1. The butyl protons appear at 1.0, 1.6, and 1.8 ppm, with the α-methylene at 4.1 ppm. The vinylene protons in the copolymer average out to a singlet at 6.95 ppm. Interestingly, substitution of the thiophene ring in the 3- and 4-positions means there are no thiophene ring protons to interfere with the end groups, H_a and H_b; the two different end groups of the copolymer are clearly visible. The doublet at 6.5 ppm is assigned to the vinylic end group, while the singlet at 6.0 ppm is assigned to the thiophene end group. Compounds 10, 12, and 13 were used to verify the assignments and are shown below.



(10)

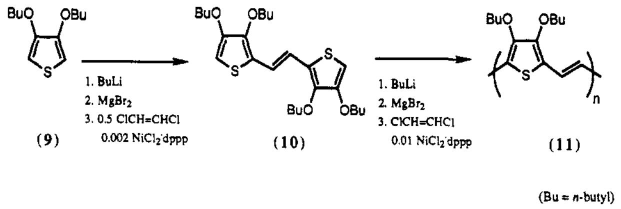




(12) (13)

GPC showed a very broad, bimodal molecular weight distribution, and when calibrated against a polystyrene standard, a value of M_n = 56 820 was obtained (DP = 232).

Scheme I



Because of the obvious problems in using polystyrene as a calibration standard for these materials, a more realistic measurement of molecular weight was made by end-group analysis. Due to the high solubility of the copolymer, we were able to make solutions concentrated enough to see the two different end groups by ^{1}H NMR. Integration of the peaks at 6.5 and 6.0 ppm against the internal vinylic peaks of the copolymer at 7.0 ppm gave a value for the polymer of $M_n = 12\,400$ (DP = 49). The relative amounts of the end groups varied slightly from sample to sample, but the calculated number-average molecular weights were consistently determined to be approximately 12 000. The toughness and flexibility of films of 11 confirm the formation of a good molecular weight polymer. This molecular weight is significantly lower than the molecular weights reported for polythiophenes synthesized by oxidation methods; however, the difference is most likely attributable to the Grignard method of synthesis which typically gives lower molecular weight polythiophenes.[8] The method of end-group analysis has also been applied to other very soluble polythiophenes, including electrochemically synthesized poly(3-dodecylthiophene).[32]

The thiophenevinylene copolymer was quite stable to weight loss by TGA under both air and nitrogen (Figure 2). The onset of weight loss was 200 °C with only 5% weight loss at 300 °C; above 300 °C, weight loss was rapid. Poly(3-alkylthiophenes) have been reported to have similar stabilities.[33,34] Analysis by DSC showed no detectable T_g, but the lack of an observable glass transition is not unusual for rigid backbone polymers since there is very little difference in the volume between the glassy and rubbery states. A T_m was observed at 168 °C by DSC (Figure 3). Reversible melting or softening was observed at 170 °C on a hot-stage microscope. The films were stable even in air to short periods at 220 °C before irreversible decomposition occurred. Partial crystallinity was verified by wide-angle X-ray diffraction (WAXD) measurements on unannealed films cast from chloroform. To our knowledge, crystallinity has not been observed for other nonaligned poly(thiophenevinylenes), but it has been observed in poly(3-alkylthiophenes). For comparison, poly(3-butylthiophene) softens at 275 °C and poly(3-octylthiophene) softens at 150 °C.[35]

The best method of doping films of 11 was by immersion in nitromethane solutions of anhydrous $FeCl_3$. After doping, conductivities of 1 S cm^{-1} were measured using the four-probe technique. The $FeCl_3$ doping process was reversible; doped films could be readily undoped by immersion in aqueous ammonium hydroxide and the undoped films retained their solubility in chloroform. After doping with $NOPF_6$, the films were not soluble after undoping. Pressed pellets of poly(3-alkoxythiophenevinylenes) have similar conductivities of 1.8 (**8d**) and 0.8 S cm^{-1} (**8c**) when doped with $FeCl_3$. Although the conductivity of 11 is not unusual for a poly(alkoxythiophenevinylene), it is unusual for polymers of a 3,4-disubstituted thiophene; after doping with $FeCl_3$ poly(3,4-dibutoxythiophene) (**5**) has a conductivity of 10^{-5} S cm^{-1}.[14] Clearly, the presence of the vinylene group has changed the electronic properties of the polythiophene.

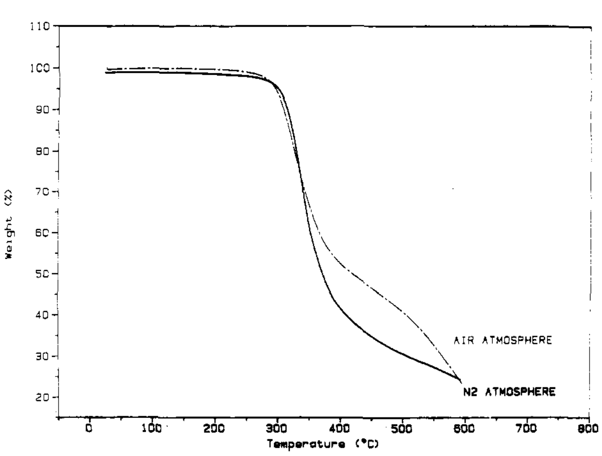


Figure 2. TGA of 11 powder in air and nitrogen atmospheres. Scan rate 10 °C/min.

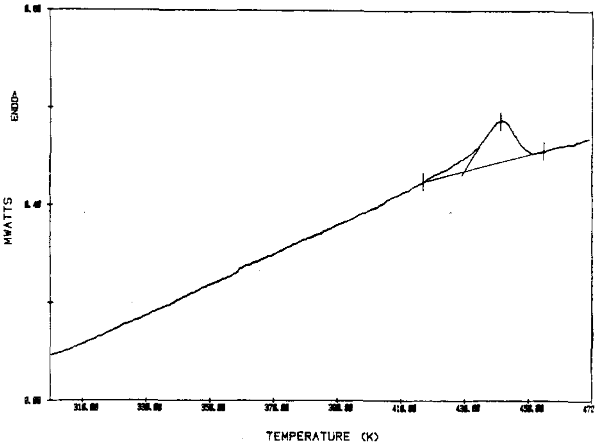


Figure 3. DSC of 11 powder in a nitrogen atmosphere. Scan rate 20 °C/min.

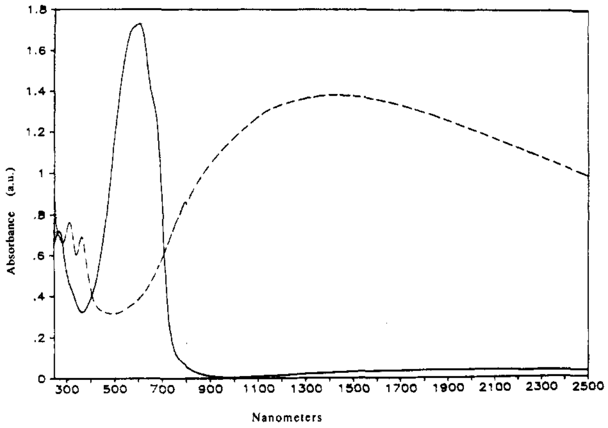


Figure 4. UV–visible–near-infrared spectra of a 0.22-μm cast film of 11 on a quartz substrate: (—) undoped, (- - -) same film after doping with $FeCl_3$.

The optical absorption spectrum of a thin film (0.22 μm) of 11 cast on quartz is shown in Figure 4. The undoped films are deep blue in transmittance and have a λ_{max} = 607 nm. Using the literature method of approximating band gaps by extrapolation of the low-energy absorption edge,[19] we calculate an E_g = 1.62 eV. The absorption maximum of the doped film has shifted out of the visible region into a broad, relatively intense absorption in the near-infrared (λ_{max} approximately 1600 nm). The shift in absorption makes the films nearly transparent in the visible region, having a light gray–blue color. The characteristics of the films of 11 allow the opportunity to select between contrasting transparency or absorbance in the visible and

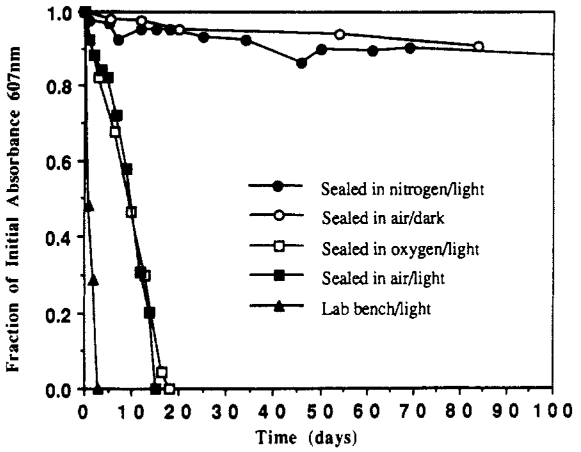


Figure 5. Degradation of polymer 11 under various exposure conditions.

near-infrared regions that suggests interesting applications for these materials in smart windows, displays, and switching devices.

Poly(3-alkoxythiophenevinylenes) have optical properties similar to those of 11; undoped **8d** has an absorption maximum at 600 nm, but the absorption maximum for the doped film is reported to be less than 1000 nm.[18,19] The estimated band gap for 11 is very similar to those obtained for 8c and **8d**, indicating no reduction in the band gap upon disubstitution of butoxy groups on the thiophene ring. However, comparison of 11 and poly(3,4-dibutoxythiophene) shows a very large reduction in band gap has occurred upon insertion of the vinylene spacer into the copolymer backbone; the absorption maximum has decreased by 150 nm. When compared to their polythiophene analogs, the decrease in the band gap upon insertion of the vinylene spacer is greater for 11 than for 8. Current research in polythiophenes is resulting in an ability to separate the effects of substituents on interchain packing from their effects on local electronic changes,[9] but that level of understanding has not yet been achieved for poly(thiophenevinylenes). Reduction of intrapolymer torsions may not be the only factor involved in the reduction of the band gap, but the comparison clearly demonstrates the positive effect of the vinylene spacer group on the electronic properties of the conducting polymer.

Stability Studies of Poly(3,4-dibutoxythiophenevinylene). Considering the interesting possibilities for the optical properties, an environmental stability study of films of 3 was conducted. The stability studies were completed on the undoped polymer since the changes in the strong, sharp absorptions in the visible region could be easily and quickly observed and we were primarily interested in optical properties, not conductivities. The stability of 11 in conditions most likely to be found in the environment was investigated: light, oxygen, and moisture. Very thin films (0.05 μm) of 11 were cast onto glass, and the absorbance of the undoped polymer at 607 nm was monitored after exposure to light, air, and moisture individually and in combination.

The films were stable when stored under nitrogen either in sunlight or in the dark and had a projected half-life of more than 500 days (Figure 5). Surprisingly, the films were equally stable when sealed under oxygen but kept in the dark. When exposed to both sunlight and oxygen, a much faster rate of degradation was observed. Films bleached within $t_{1/2}$ = 8–10 days when exposed to light and oxygen, and the rate of degradation was the same for samples sealed in either air or pure oxygen. Stability to light in the absence of oxygen and to oxygen in the absence of light suggests photooxidation as a mechanism of degradation for the copolymer under these conditions. The rates of photooxidation were reduced by the insertion of a UV cutoff filter between the film of 11 and the light source (Figure 6). Sealing samples in air but protecting them with a film of commercial UV screen (cutoff of 460 nm) resulted in a 3-fold increase in $t_{1/2}$ to 30 days.

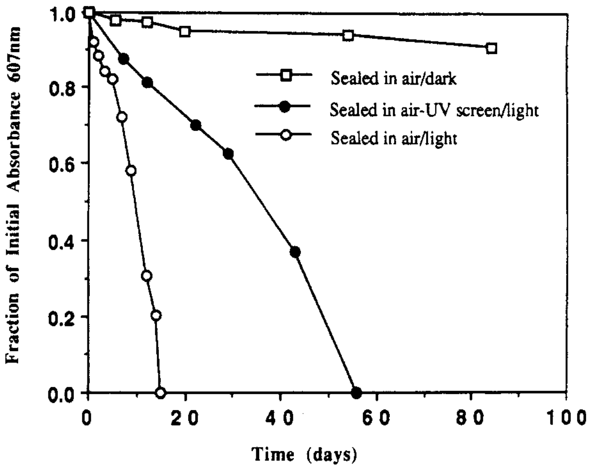


Figure 6. Effect of UV screen on the rate of bleaching of 11.

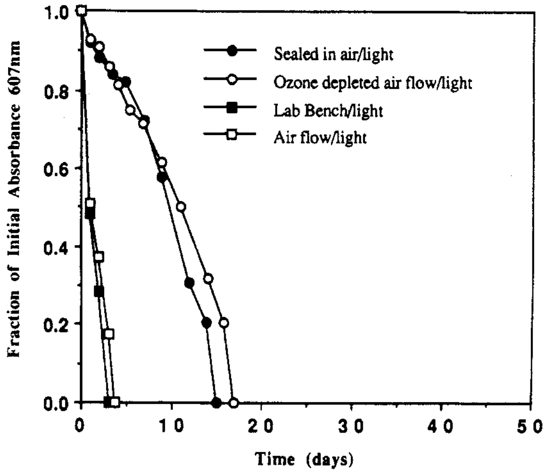


Figure 7. Effect of ambient ozone on the photodegradation of 11.

Different behavior was observed when the samples were exposed to unrestricted laboratory air, rather than sealed in quartz tubes. When samples were placed on the open lab bench, in either the presence or absence of light, the rate of degradation was extremely rapid (Figure 7; $t_{1/2}$ = 1–2 days). Three potentially active agents present in unrestricted air are oxygen, water, and ozone. Oxygen can be eliminated as the sole cause since these rates are 4–5 times greater than those observed in the sealed oxygen environments as discussed above. Adding sources of water vapor to the closed systems did not change the rate of degradation in sealed environments of air or nitrogen, indicating that the copolymer is relatively stable to moisture in the undoped state. To study the possible effects of ozone, a simple scrubbing system was designed. It is well-known that unsaturated rubbers react rapidly with ozone. To scavenge ozone from air, the air was passed through a 12-in. column packed with beads of high impact polystyrene (HIPS), which contained polybutadiene impact modifier; air can flow rapidly through the polymer beads, and the well-dispersed polybutadiene reacts rapidly with ozone, removing it from the air. Samples treated with this purified air degraded at the slower rate of samples

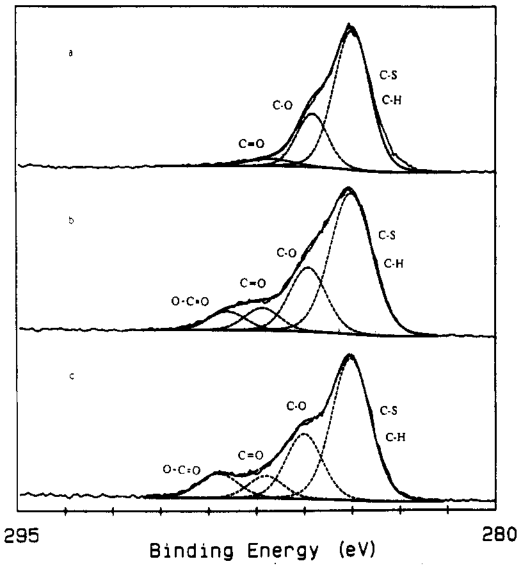


Figure 8. ESCA C 1s of an undoped film of 11 (a), after exposure to ozone (b), and after photooxidation (c).

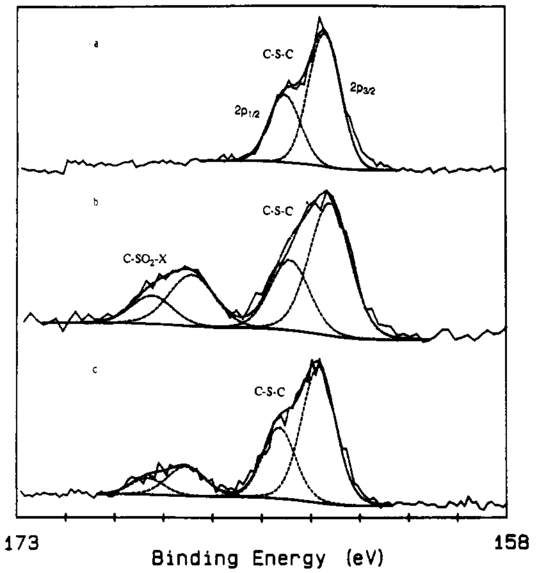


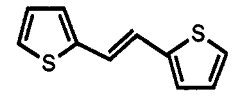
Figure 9. ESCA S 2p of an undoped film of 11 (a), after exposure to ozone (b), and after photooxidation (c).

kept in sealed environments under similar lighting conditions. A control experiment passing air through a column packed with crystal polystyrene beads, which lack polybutadiene, showed no reduction in the degradation rate. These results suggest ozone is the reactive species causing the fastest rate of degradation of 11. Samples kept in the open laboratory air are exposed to a continuous, low concentration of the highly reactive species, but when samples are kept in sealed tubes of air, the ozone is rapidly depleted and the films remain stable (Figure 5). Ozone would be expected to react rapidly with the electron-rich double bonds of the poly(thiophenevinylene) copolymer.

X-ray photoelectron spectroscopy (XPS) data obtained on thin films are consistent with the two degradation mechanisms of photooxidation and reaction with ozone. Films which had been exposed to ozone (Figures 8b and 9b) and films which had been exposed to sunlight and oxygen (Figures 8c and 9c) both show an increase in the surface oxygen content relative to the freshly synthesized film (Figures 8a and 9a). No distinction can be made between the two degraded samples from XPS data, since the observed spectra for the two films are within experimental error (10%). The C 1s line shows the presence of new high binding energy components at 287.7 and 288.9 eV from carbonyl and carboxyl groups, respectively. The S 2p line shows a new component at 167.9 eV, indicative of oxidation of the thiophene RSR to RSO_2R and accounting for approximately 20% of the total sulfur.

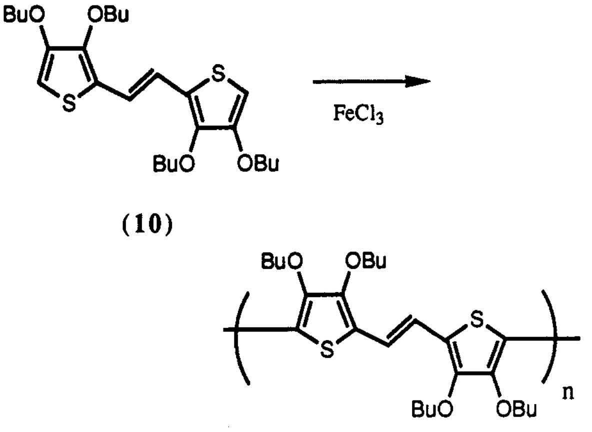
In summary, three separate rates of polymer degradation were observed. The films bleached only very slowly in sealed inert atmospheres in both light and dark and when sealed under air or oxygen but not exposed to UV light. Sensitivity to photooxidation led to films bleaching with a $t_{1/2}$ = 8–10 days when exposed to light and air, but reaction with atmospheric ozone levels caused films to bleach with a $t_{1/2}$ = 1–2 days. It should be noted that the films tested were very thin. Thicker films would appear to be more stable, as only the exposed surface would be degraded.

Synthesis and Characterization of Poly[bis(3,4-dibutoxythienylene)vinylene]. Unsubstituted poly(dithienylenevinylene) has been synthesized by the electropolymerization of 14,[22,23] by a cuprate coupling reaction of 14,[23] and by reaction of 14 with the harsh oxidant arsenic pentafluoride.[24] The resulting polymers were black, insoluble, infusable powders and therefore difficult to characterize. A ^1H NMR spectrum of a low molecular weight (DP = 7) material was obtained at 130 °C in DMSO but showed significant thiophene degradation.[36]



(14)

The substitution of the thiophene ring in the 3- and 4-positions should improve the processability of the poly(dithienylenevinylene), and, in addition, alkoxy substitution should lower the oxidation potential of the monomer, allowing the use of milder oxidative conditions. We found 10 could be easily polymerized by simple oxidative coupling using Fe(III) salts to yield a high molecular weight material (eq 1).



(10)

(15)

(1)

Tough, flexible, gold-colored films of 15 were cast from chloroform solution. The optical absorption spectrum of the undoped polymer film has an absorption maximum at 539 nm (Figure 10). Interestingly, this is about 80 nm higher in energy than the poly(3,4-dibutoxythiophenevinylene) (11). Attributing the difference in absorbance exclusively to steric interactions inherent in the dithienylene structure may not be valid, but the steric interactions could be an important factor. The copolymer can be doped into the conductive state with common oxidants such as $FeCl_3$. After doping, the absorption of films of 15

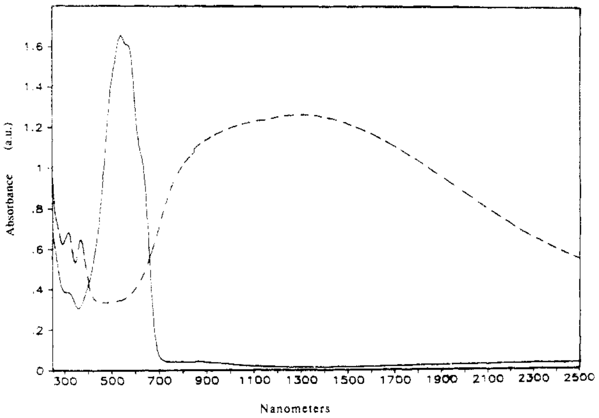


Figure 10. UV–visible–near-infrared spectra of a 0.30-μm cast film of **15** on a quartz substrate: (—) undoped, (- - -) same film after doping with $FeCl_3$.

shifts to the near-infrared with a broad maximum at 1290 nm. The conductivity measured using the four-probe technique on solution-cast films on quartz substrates averaged 0.03 S cm^{-1}.

Determination of copolymer molecular weight by GPC (against polystyrene standards) gave M_n = 121 430 which calculates to a degree of polymerization of 253 monomer units. Attempts to obtain more accurate molecular weights by NMR end-group analysis were unsuccessful because of the difficulty in removing the trace amounts of residual iron remaining from polymer synthesis.

Conclusions

New poly(thiophenevinylene) copolymers have been reported. Poly(3,4-dibutoxythiophenevinylene) (**11**) has been synthesized by a nickel-catalyzed Grignard coupling reaction. The alternating copolymer is very soluble in organic solvents, and tough, flexible, free-standing films can be cast from chloroform. The solubility is sufficient to determine an average molecular weight of 12 000 by ^1H NMR end-group analysis. The copolymer is easily doped and conductivities of 1.0 S cm^{-1} were obtained on unaligned films. Interestingly, partial crystallinity was observed by WAXD and DSC on unannealed films of **11**; films can be reversibly heated above the melting/softening point (168 °C) without noticeable decomposition, suggesting this copolymer is melt processible. Upon doping, the dark blue copolymer (λ_{max} = 607 nm) becomes a very light gray as the absorption maximum is shifted to lower energy ($\lambda_{max} \approx$ 1600 nm). The insertion of the vinylene spacer into the polymer backbone has decreased the absorption maximum of poly(3,4-dibutoxythiophene) by 150 nm. The most likely explanation for this decrease in the band gap is the increased planarity and reduced torsions in the polymer backbone. The effect of the vinylene spacer should be even more dramatic in the more sterically crowded poly(3,4-dialkylthiophenes). The dialkoxy substitution of **11** has not significantly altered the absorption spectrum of undoped **11** when compared to **8c** or **8d**. Undoped films were found to be unstable to photooxidation and reaction with ozone but were quite stable if kept protected. Understanding the methods of degradation of conducting polymers, such as **11**, is key to their successful development and use.

Poly[bis(3,4-dibutoxythienylene)vinylene] has been synthesized by the oxidation of **10** with $FeCl_3$. The dark blue, very soluble copolymer has an absorption maximum approximately 80 nm higher than **11**, and the conductivity when doped with $FeCl_3$ is only 0.03 S cm^{-1}. The steric interactions of the adjacent disubstituted thiophenes in the copolymer structure of **15** could account for these differences.

Acknowledgment. The authors thank Linda McCracken for thermal analyses, Dr. Mike Burrell for XPS, Dr. Mary Garbauskas for X-ray analysis, and Dr. Al Shultz for helpful discussions.

References and Notes

(1) Billingham, N. C.; Calvert, P. D. *Adv. Polym. Sci.* **1987**, *90*, 1.
(2) Tourillon, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker, Inc.: New York, 1986; Vol. 1.
(3) Yoshino, S.; Nakajuma, H. B.; Sugimoto, R. *Jpn. J. Appl. Phys.* **1987**, *26*, L1038.
(4) Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346.
(5) Gustaffson, G.; Inganas, O.; Salaneck, W. R.; Laakso, J.; Loponen, M.; Taka, T.; Österholm, J.-E.; Stubb, H.; Hjertberg, T. In *Conjugated Polymers*; Bredas, J. L., Silbey, R., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.
(6) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873.
(7) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212.
(8) Gorman, C. B.; Grubbs, R. H. In *Conjugated Polymers*; Bredas, J. L., Silbey, R., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.
(9) Aime, J.-P. In *Conjugated Polymers*; Bredas, J. L., Silbey, R., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.
(10) Elsenbaumer, R. L.; Jen, K.-Y.; Oboodi, R. *Synth. Met.* **1986**, *15*, 169.
(11) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1984**, *161*, 51.
(12) Roncali, J.; Garnier, F.; Garreau, R.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1500.
(13) Elsenbaumer, R. L.; Jen, K.-Y.; Miller, G. G.; Eckardt, H.; Shacklette, L. W.; Jow, R. In *Springer Series in Solid State Sciences. 76: Electronic Properties of Conjugated Polymers*; Kuzmany, H., Mehring, M., Roth, S., Eds.; Springer, New York, 1987.
(14) (a) Leclerc, M.; Daoust, D. *J. Chem. Soc., Chem. Commun.* **1990**, 273. (b) Leclerc, M.; Daoust, D. *Synth. Met.* **1991**, *41*, 529.
(15) Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717.
(16) (a) Blohm, M. L.; Pickett, J. E.; Van Dort, P. C. U.S. Patent 5,111,327, 1992. (b) Blohm, M. L.; Pickett, J. E.; Van Dort, P. C., manuscript in preparation.
(17) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.
(18) Jen, K.-Y.; Eckardt, H.; Jow, T. R.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1988**, 215.
(19) Eckardt, H.; Shacklette, L. W.; Jen, K.-Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91*, 1303.
(20) Danieli, R.; Ostoja, P.; Tiecco, M.; Zamboni, R.; Taliani, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1473.
(21) Reynolds, J. R.; Ruiz, J. P.; Child, A. D.; Nayak, K.; Marynick, D. *Macromolecules* **1991**, *24*, 678.
(22) (a) Tanaka, S.; Sato, M.; Kaeriyama, K. *Makromol. Chem.* **1985**, *186*, 1685. (b) Martinez, M.; Reynolds, J. R.; Basak, S.; Black, D. A.; Marynick, D. S.; Pomerantz, M. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 911.
(23) Bragadin, M.; Cescon, P.; Berlin, A.; Sannicolo, F. *Makromol. Chem.* **1987**, *188*, 1425.
(24) Kossmehl, G. *Makromol. Chem., Macromol. Symp.* **1986**, *4*, 45.
(25) Munstedt, H. *Polymer* **1988**, *29*, 296.
(26) Gustaffson, G.; Inganas, O.; Nilsson, J. O.; Liedberg, B. *Synth. Met.* **1988**, *26*, 297.
(27) Gustaffson, G.; Inganas, O.; Nilsson, J. O. *Synth. Met.* **1989**, *28*, C427.
(28) Wang, Y.; Rubner, M. F.; Buckley, L. J. *Synth. Met.* **1991**, *41*, 1103.
(29) Wang, Y.; Rubner, M. F. *Synth. Met.* **1990**, *39*, 153.
(30) Overberger, G. C.; Lai, J. *J. Am. Chem. Soc.* **1951**, *73*, 2956.
(31) Van Hecke, G. R.; Horrocks, W. D. *Inorg. Chem.* **1966**, *5*, 1968.
(32) Sato, M.; Morii, H. *Macromolecules* **1991**, *24*, 1196.
(33) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J. *Synth. Met.* **1987**, *22*, 79.
(34) Inganas, O.; Salaneck, W. R.; Österholm, J.-E.; Laakso, J. *Synth. Met.* **1988**, *22*, 395.
(35) Yoshino, K.; Nakajima, S.; Fujii, M.; Sugimoto, R.-I. *Polym. Commun.* **1987**, *28*, 309.
(36) Bragadin, M.; Cescon, P.; Berlin, A.; Sannicolo, F. *Synth. Met.* **1987**, *18*, 241.