Thermal Stability of High Molecular Weight Self-Doped Poly(anilineboronic acid)

Insun Yu, Bhavana A. Deore, Carmen L. Recksiedler, T. Christopher Corkery,† Alaa S. Abd-El-Aziz,† and Michael S. Freund*

Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada, and Department of Chemistry, University of Winnipeg, Winnipeg, Manitoba R3B 2E9, Canada

Received June 21, 2005; Revised Manuscript Received September 21, 2005

ABSTRACT: The molecular weight, thermal stability, and conductivity of chemically synthesized, self-doped poly(anilineboronic acid) have been determined. Gel permeation chromatography results indicate a number-average molecular weight of 1 676 000 g mol^{-1}, a weight-average molecular weight of 1 760 000 g mol^{-1}, and a polydispersity of ∼1.05. The high molecular weight is maintained following removal of boronic acid groups via *ipso*-substitution reactions, suggesting that boronic ester cross-links do not contribute significantly to the high molecular weight observed. According to thermogravimetric analysis results, the thermal stability of self-doped poly(anilineboronic acid) is greater than that of HCl-doped polyaniline and other self-doped forms of polyaniline. Unlike polyaniline, which experiences complete decomposition of the backbone above 400 °C, self-doped poly(anilineboronic acid) remains largely intact and possesses conductivity near 0.01 S cm^{-1}.

Introduction

Polyaniline (PANi) has been investigated extensively due to its high conductivity and environmental stability combined with its inexpensive and facile polymerization. These properties have resulted in its use in electronic devices,[1] energy storage,[2] and sensors.[3] The characteristics of chemically prepared PANi have been of great interest because bulk polymer is required for many industrial applications. The physical, chemical, and mechanical properties of a polymeric material are known to depend strongly on its molecular weight and molecular weight distribution. Unfortunately, chemically synthesized PANi in general suffers from low molecular weight and in turn poor mechanical properties. The typical range of molecular weights for chemically synthesized PANi reported in the literature varies between approximately 30 000 and 350 000 g mol^{-1} with polydispersity between 1 and 6.[4] Previous work has shown that higher molecular weights can be achieved by significantly lowering the reaction temperature[4b−e,5] or by introducing cross-links during polymerization.[6] However, these approaches are often time-consuming and in turn have not become widely accepted.

Additional shortcomings of PANi are its limited thermal stability and loss of conductivity at high temperature. The lack of stability is a result of several processes that take place in PANi upon heating: loss of dopant, oxidation of chains by oxygen, and cross-linking. Since the protonated polymer undergoes irreversible chemical modifications upon heating in air, its conductivity cannot be recovered by redoping.[7−9] The thermal stability together with conductivity at high temperature are important properties of a conducting polymer for most commercial applications such as high temperature: conducting coatings, electronic circuits, and polymer electrolyte membranes for fuel cell. Attempts to improve thermal stability have focused on stabilizing the dopant, which is typically volatile. Approaches include use of ring-substituted self-doped polyaniline,[10] N-substituted self-doped polyaniline,[11] high molecular weight dopants,[12] and blends and cross-linking.[13] To date, improvements have been limited due to the thermal reactivity of the dopants used. In addition, these strategies have had relatively little impact on thermal decomposition of the PANi backbone, which typically occurs above 400 °C.

Recently, we reported the synthesis of water-soluble poly(anilineboronic acid) (PABA) that can be switched between self-doped and non-self-doped states.[14] Initial results suggest that the solubility of the polymer produced under the polymerization conditions could lead to a high molecular weight polymer. In addition, we have shown that the polymer can be self-cross-linked to form a self-doped polymer exhibiting unprecedented hardness.[15] In this work, we explore the nature of the increased molecular weight, the thermal properties, and high-temperature conductivity stability of the polymer produced.

Experimental Section

Materials and Reagents. 3-Aminophenylboronic acid hydrochloride salt, D-fructose, ammonium persulfate, 1-methy-2-pyrrolidinone (NMP), and PANi emeraldine base (average M_w 100 000) were purchased from Aldrich and were used as received. Sodium fluoride and hydrogen peroxide (30%) were purchased from Fisher Scientific. Bulk distilled water was filtered and then ion-exchanged to yield 18.2 MΩ·cm quality water using Milli-Q-Academic A10 (Millipore Corp.).

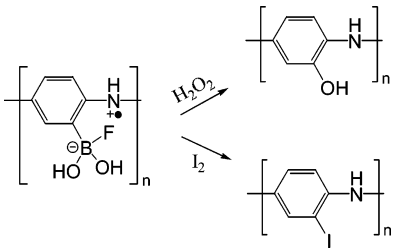
Preparation of PABA. Water-soluble PABA in the presence of D-fructose and fluoride was synthesized by reaction of an aqueous solution of 40 mM 3-aminophenylboronic acid and 40 mM sodium fluoride in 10 M D-fructose (19.5 mL) with 40 mM ammonium persulfate (0.5 mL, oxidizing agent) added over 10 min.[14] The mixture was stirred overnight at room temperature. The self-doped polymer obtained was precipitated in deionized water. Following centrifuging, the precipitate was washed with water and methanol until the filtrate becomes colorless. Further, the precipitate was washed with 0.5 M HCl to remove D-fructose.

Preparation of Substituted Polyaniline. *Poly(hydroxyaniline).* The precipitated PABA was reacted with 30% hydrogen peroxide for 10 min at room temperature.

* Corresponding author. E-mail: michael_freund@umanitoba.ca.
† Department of Chemistry, University of Winnipeg.

10.1021/ma0513158 CCC: $30.25
Published on Web 11/02/2005

Scheme 1. *Ipso*-Substitution Reaction of PABA with Hydrogen Peroxide and Iodine



Poly(iodoaniline). The precipitated PABA was reacted with aqueous solution containing iodine (4 mM), sodium acetate (0.24 M), acetic acid (0.361 M), and 5% methanol for 50 min at room temperature.

For both substitution reactions, the change in redox activity of the polymer was monitored frequently throughout the course of transformation using cyclic voltammetry. After the reaction, the obtained polymer was washed with distilled water and centrifuged until the upper solution was colorless. This procedure was repeated more than 20 times to fully remove the reactants.

Instrumentation and Measurement Conditions. Cyclic voltammetric measurements were performed using a CH Instrument CHI-660 workstation controlled by a PC. A three-electrode cell was used, which consisted of a glassy carbon disk working electrode (Bioanalytical Systems, 3.0 mm diameter), a platinum coil auxiliary electrode, and an Ag/AgCl reference electrode. Cyclic voltammograms were conducted in a 0.5 M HCl aqueous solution with a scan rate of 100 mV s^{-1}. The molecular weight of PABA was determined using a gel permeation chromatography (GPC) system. A PLgel 5 μm MIXED-C column (Polymer Laboratories Inc.) was used and calibrated with polystyrene standards in NMP. The column temperature was maintained at 70 °C. A MiniDAWN Tristar detector (Wyatt Technology) used to detect absorbance at 690 nm. The polymer samples were dissolved in NMP for 48 h and filtered through a 0.02 μm Anatop filter prior to injection. The concentration of the polymer samples were 0.033 mg mL^{-1}. The UV−vis spectra were obtained using an Agilent 8453 spectrophotometer. Polarization-modulated infrared reflection−absorption spectra (PM-IRRAS) of polymer thin films on indium-doped tin oxide (ITO, Rs = 6 ± 2 Ω/square, Delta Technologies, Ltd.) coated glass slides were recorded at a resolution of 8 cm^{-1} using a Nexus 870 spectrometer (Thermo Nicolet Corp.). A grazing angle of 67° was used to collect 300 interferograms for each spectrum. Thermogravimetric analysis (TGA) was performed on a Mettler TGA/SDTA851^e (Mettler Toledo) with a heating rate of 20 °C min^{-1} under nitrogen from 100 to 800 °C. Conductivity measurements were carried out using a four-probe device on pellets pressed at 10 000 psi for 5 min, under conditions were the distance between probes was significantly smaller than the thickness of the pellet.

Results and Discussion

Molecular Weight. In previous work, we demonstrated that chemically polymerized PABA in the presence of sodium fluoride and excess D-fructose is soluble under polymerization condition and results in a high molecular weight polymer.[14] At that time it was not clear whether interchain anhydride formation (i.e., cross-linking) between boronic acid groups on the polymer backbone contributed to the high molecular weight observed. To investigate this possibility, the boronic acid groups on the polymer were removed via an *ipso*-substitution reaction involving hydrogen peroxide and iodine (Scheme 1).[16] The reaction occurs rapidly in aqueous hydrogen peroxide solution and was monitored with cyclic voltammetry, ex situ, as a function of reaction time. A reaction time of 10 min was sufficient to completely convert the polymer as indicated by the evolution of the two sets of redox peaks characteristic of PANi to a single set of redox peaks corresponding to poly(hydroxyaniline).[16b] Similarly, the reaction of PABA with iodine resulted in a single set of redox peak corresponding to poly(iodoaniline). [16b]

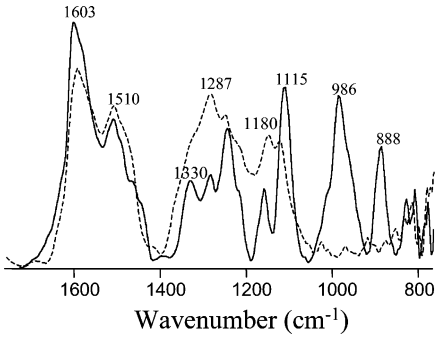


Figure 1. PM-IRRAS spectra of PABA before (—) and after (- - -) exposure to 30% H_2O_2 for 10 min.

Additional confirmation that the *ipso*-substitution reaction had reached completion was obtained with PM-IRRAS of a reacted thin film. The results are shown in Figure 1 before and after the reaction. IR bands characteristic of PANi are observed at 1603, 1510, and 1180 cm^{-1}, corresponding to quinoid, benzinoid, and the aromatic C−N stretching ring modes.[17] The data obtained for the unreacted PABA film also exhibited bands characteristic of the boronic acid functional group at 1115 cm^{-1} as well as 986 and 888 cm^{-1}, assigned to aromatic B−OH bending and the B−F stretching modes, respectively.[18] The asymmetric B−O stretching mode is observed at 1330 cm^{-1}. The ratio of the relative intensities of quinoid to benzenoid ring modes (I_{1603}/I_{1510}) is ∼1.6, which suggests that the percentage of imine units is higher than that of amine units. These results and the presence of B−F stretching vibration indicate that PABA is in its oxidized self-doped form. Following the reaction with hydrogen peroxide for 10 min, a change in the spectrum consistent with the replacement of boronic acid with hydroxyl groups is observed. All the characteristic bands of boronic acid at 888, 986, 1115, and 1330 cm^{-1} were not observed, and a new peak at 1287 cm^{-1} is observed, corresponding to O−H deformation and C−O stretching modes in phenol.[18] These results indicate that the boronic acid groups are replaced with hydroxyl groups during the 10 min reaction time.

In the literature, the molecular weight determination studies of PANi using GPC have used the reduced leucoemeraldine base form of polymer dissolved in 0.5% LiCl−NMP mobile phase.[19] The reduced leucoemeraldine form was prepared by reduction of emeraldine base form of PANi, either by dissolving in NMP containing various amounts of LiCl[19a,b] or by reduction with aqueous hydrazine.[19c−e] The reduced form was investigated at relatively high concentrations (above 0.5 mg mL^{-1}), and in turn the addition of lithium salt was reportedly required to prevent aggregation.[19b,20] In the present study, the concentration of the PABA solution was significantly lower (0.033 mg mL^{-1}) than the value where PANi is reported to aggregate (above 1 mg mL^{-1}); therefore, the lithium salt was not used in this study. Under these conditions, the weight-average molecular weight determined for in-house chemically synthesized PANi[21] and a commercially obtained PANi (M_w 100 000)

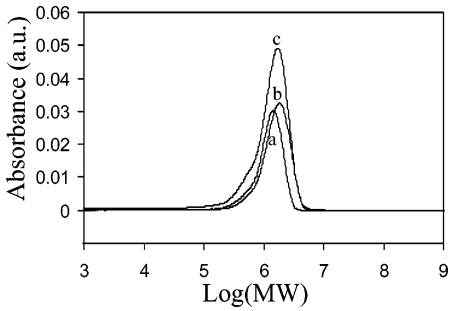


Figure 2. GPC chromatograms of PABA dissolved in NMP (a) before and after (b) iodination reaction and (c) exposure to 30% H_2O_2 for 10 min (increase in the absorbance is related to the spectral change after substitution reaction).

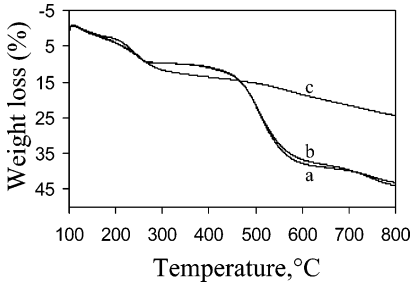


Figure 3. Thermograms of (a) PANi (M_w 30 000), (b) PANi (M_w 100 000), and (c) PABA (M_w 1 760 000) dried in air.

agreed with previous reports and showed no indication of aggregation.

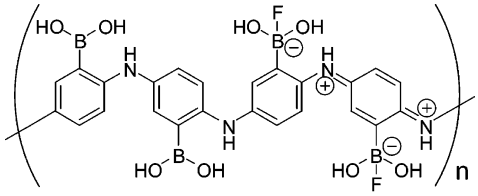
The molecular weight and molecular weight distribution of PABA and substituted PANi, determined using GPC, are shown in Figure 2. Figure 2a exhibits the unimodal molecular weight distribution with number- and weight-average molecular weights of 1 676 000 and 1 760 000 g mol^{-1}, respectively, and a polydispersity of 1.05. The molecular weight of the iodine- and hydroxyl-substituted polymer was determined under identical conditions exhibiting a single peak (see Figure 2b,c), corresponding to a weight-average molecular weight of 1 851 000 and 1 702 000 g mol^{-1}, respectively. The fact that the majority of the polymer retains its high molecular weight following the removal of the boronic acid group suggests that the high molecular weight observed for PABA is not due to significant boronic acid anhydride cross-linking. In general, for polyaniline, a bimodal GPC curve with high molecular weight fraction in leucoemeraldine[19] and emeraldine base[20b] form was observed using NMP elution. The addition of 0.5% LiCl to the NMP solution of the polymer resulted in a unimodal molecular weight distribution, which indicated that the high molecular weight fraction was caused by polymer aggregation.[20] However, in the case of PABA, the high molecular weight is likely resulted due to its solubility under polymerization condition where termination of polymer via precipitation[4] was prevented.

A broad molecular weight distribution is observed for poly(hydroxyaniline) and poly(iodoaniline) as a result of the *ipso*-substitution reaction. The decrease in molecular weight of poly(hydroxyaniline) is due to some decomposition of the polymer in the presence of peroxide over time. For PANi treated under the identical reaction conditions used for the *ipso*-substitution reaction with PABA, an increase polymer molecular weight of 50% was observed relative to the unreacted PANi. The increase in molecular weight is likely due to the cross-linking and branching by interchain reactions.[19d] These results indicate that any decomposition process in the presence of peroxide is associated with hydroxyl-substituted PANi. Indeed, if PABA is left in contact with the peroxide reaction mixture for prolonged periods of time, the polymer is completely dissolved, suggesting that decomposition is occurring rather than simple breaking of cross-links between lower molecular weight components. The mechanism of decomposition is likely similar to that of aminophenol in the presence of peroxide, which is reported to result in the formation of 1,4-hydroquinone and a series of dimeric species, eventually decomposing to organic acids such as muconic, maleic, fumaric, DL-malic, oxalic, and formic acid.[22] Regardless, this decomposition reaction occurs on a much longer time scale than the *ipso*-substitution reaction and does not interfere with observing the high molecular weight poly(hydroxyaniline).

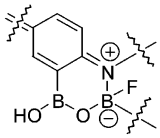
Thermal Stability. The high molecular weight and self-doping nature of PABA are expected to increase the thermal stability of polymer. In general, the thermal stability of PANi emeraldine salt is dominated by the characteristics of the dopant and the nature of dopant bonding to the polymer backbone. Following the loss of dopant, the structure of the backbone itself comes into play. Self-doped forms of PANi, such as sulfonated PANi, have been reported to be much more thermally stable than unsubstituted PANi doped with HCl.[23] Han et al. have reported that the mercaptopropanesulfonic acid-substituted self-doped PANi has better thermal stability than that of HCl-doped PANi and sulfonated PANi.[10] The covalently bonded electron-donating mercaptopropanesulfonic acid constituent group at the polymer backbone reportedly stabilizes the aromatic benzenoid ring, thereby reducing the decomposition of the backbone.[10] On the basis of our previous work, we postulated that PABA could have better thermal stability due to the cross-linked, self-doped nature of the polymer produced upon heating or drying under vacuum. Specifically, the anionic tetrahedral boronic acid acts as the dopant, is covalently linked to the polyaniline backbone, is electron donating, and serves to cross-link the polymer.

TGA of HCl-doped PANi shows three major weight losses under nitrogen.[23] The first loss is associated with the evaporation of water below 100 °C. The second loss occurs near 200 °C and is associated with the removal of HCl, resulting in the concomitant loss of conductivity. The third loss occurs above 400 °C and is associated with the decomposition of the PANi backbone. HCl-doped PANi with a molecular weight of 30 000 g mol^{-1} produced by a standard method[21] and a molecular weight of 100 000 g mol^{-1} (commercially obtained) both exhibit these transitions, as shown in Figure 3. While PABA exhibits a step near 200 °C, the weight loss above 500 °C is small relative to PANi. Interestingly, a slow rate of weight loss is observed throughout the thermogram, likely due to the gradual cross-linking process and the associated loss of water. Above 500 °C, the decomposition of the polymer occurs slowly, resulting in only 8% weight loss. The total weight loss for PABA was about 24% of the initial weight, which is significantly less than the nearly 50% weight loss exhibited by HCl-doped PANi. These results indicate that the self-doped PABA has greater thermal stability than that of HCl-doped PANi as well as self-doped sulfonated and mercaptopropanesulfonic acid-substituted PANi.[10,11,23]

Scheme 2. Emeraldine Salt Form of PABA A, Self-Doped in the Presence of Fluoride; Proposed Cross-Link Structure B, Resulting from an Interchain Dehydration Reaction between a Boronic Acid−Imine and a Boronic Acid Moiety, Hence Maintaining a Self-Doped State



A



B

The enhanced thermal stability is likely imparted by anhydride formation as a result of cross-linking. A proposed structure of the cross-link is shown in Scheme 2. There is significant precedence for the intermolecular reaction between boronic acid groups and imines in PABA in the presence of fluoride. For example, aryl boronic acid chemistry is rich with examples of the formation of boron chelates.[24] There are reports in the literature on the formation of six-member heterocyclic complexes containing a boron−imine dative bond such as fluorine containing-boron complexes[25] and the dimer of 2-aminophenylboronic acid formed in aprotic solvents and in the solid state.[26] The formation of proposed structure of cross-linked PABA shown in Scheme 2 is supported by infrared attenuated reflectance spectroscopy (IR-ATR) and magic-angle spinning (MAS) ^{11}B NMR spectroscopy.[15] The IR-ATR spectrum of heat-treated PABA (100 °C) pellet shows changes consisting of the cross-linking of PABA involving the formation of boronic acid anhydride and boron−nitrogen dative bonds while maintaining the basic polyaniline structure. The MAS ^{11}B NMR spectrum of heat-treated PABA shows the presence of three-coordinate and four-coordinate boron signals.[15] A two-dimensional multiple-quantum MAS experiment reveals that 21 ± 2% of the boron in the sample is four-coordinate.

Conductivity. The above results indicate that the cross-linked PABA should be self-doped and in turn conducting at high temperature since a negatively charged cross-link site (see Scheme 2) can simultaneously act as a dopant.[15] To determine the stability of conductivity for the various forms of PANi, polymer samples (HCl-doped PANi with a molecular weight of 30 000 and 100 000 g mol^{-1} and PABA with a molecular weight of 1 760 000 g mol^{-1}) were heated at 100 and 500 °C under vacuum for 24 h. The conductivities of the heat-treated polymers are shown in Table 1. The conductivity of HCl-doped PANi with M_w 30 000 and 100 000 g mol^{-1} pellets treated at 100 °C decreased from 7.95 to 0.19 and from 4.68 to 0.13 S cm^{-1}, respectively. The decrease in conductivity is attributed to the loss of the volatile dopant (HCl) at 100 °C as observed by TGA. These results are consistent with the previous literature, where the HCl-doped PANi loses its conductivity above 100 °C due to evaporation of dopant, and reports that the polymer is insulating above 400 °C where the backbone is completely decomposed.[7−9,22] As was the case with the TGA results, the role of molecular weight on thermal stability of the conductivity of PANi is not significant.

Table 1. Conductivities of PABA and PANi Pellets Heat-Treated at Different Temperatures

	conductivity (S cm^{-1})		
dry condition	PANi (M_w 30 000)	PANi (M_w 100 000)	PABA (M_w 1 760 000)
air	7.95	4.68	0.96
vacuum, 100 °C	0.19	0.13	0.10
vacuum, 500 °C	3.9×10^{-4}	3.3×10^{-4}	9.5×10^{-3}

The conductivity of self-doped PABA in the form of a compressed pellet of air-dried powder was 0.96 S cm^{-1}, which is similar to other self-doped PANi shown in the literature;[10] however, it is lower than HCl-doped PANi. This is likely due to distortion of the polymer backbone by the presence of the boronic acid substituent.[9] A decrease in conductivity from 0.96 to 0.10 S cm^{-1} is observed when PABA was treated at 100 °C. However, the relative decrease in conductivity of heat-treated PABA is less than that of HCl-doped PANi treated under identical conditions. This is likely due to the formation of a thermally stable boronic acid anhydride cross-link.

After heating to 500 °C under vacuum, the conductivities of the doped PANi declined significantly compared to that of the self-doped PABA. The conductivity of PANi and PABA is about 4×10^{-4} and 9.5×10^{-3} S cm^{-1}, respectively. In the case of PANi, the dramatic decrease in conductivity is a result of the decomposition of the backbone above 420 °C, as seen in the TGA data above. In contrast, the process of cross-linking in the PABA polymer above 100 °C may make a more thermally stable backbone when heated to high temperatures. These results suggest that while a conductivity of ∼0.01 S cm^{-1} is not as high as the native PANi under ambient conditions, it is sufficiently high for many applications and has the added benefit of functioning at extreme temperatures.

Conclusion

In summary, the high molecular weight observed for PABA is not due to cross-linking of boronic acid functional groups under the solution conditions used for GPC analysis. The thermal studies of PABA in comparison with different molecular weight HCl-doped PANi suggest that the self-doped PABA is thermally more stable due to anionic tetrahedral boronic acid groups covalently linked to the polyaniline backbone. The boronic acid anhydride formation as a result of cross-linking makes PABA stable above 500 °C. These results confirm that self-doped PABA is significantly more stable than other self-doped forms of PANi as well. The negatively charged boronic acid anhydride cross-link sites act simultaneously as the dopant, thereby enhancing thermal stability of PABA, without destroying conductivity.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canada Foundation for Innovation (CFI), the Manitoba Research and Innovation Fund, and the University of Manitoba is gratefully acknowledged. This research was undertaken, in part, thanks to funding from the Canada Research Chairs Program.

References and Notes

(1) (a) Quillard, S.; Corraze, B.; Poncet, M.; Mevellec, J. Y.; Buisson, J. P.; Evain, M.; Wang, W.; MacDiarmid, A. G. *Synth. Met.* **2003**, *137*, 921. (b) Ramamurthy, P. C.; Harrell, W. R.; Gregory, R. V.; Sadanadan, B.; Rao, A. M. *Synth. Met.* **2003**, *137*, 1497.

(2) Vivier, V.; Cachet-Vivier, C.; Cha, C. S.; Nedelec, J.-Y.; Yu, L. T. *Electrochem. Commun.* **2000**, *2*, 180. (b) Mu, S. *Synth. Met.* **2004**, *143*, 269.

(3) (a) Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 314. (b) Shoji, E.; Freund, M. S. *J. Am. Chem. Soc.* **2002**, *124*, 12486. (c) Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. *Nano Lett.* **2004**, *4*, 491. (d) Pringsherim, E.; Zimin, D.; Wolfbeis, O. S. *Adv. Mater.* **2001**, *13*, 819.

(4) (a) Abe, M.; Ohtani, A.; Umemoto, Y.; Akizuki, S.; Ezoe, M.; Higuchi, H.; Nakamoto, K.; Okuno, A.; Noda, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1736. (b) Mattoso, Luiz, H. C.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1994**, *68*, 1. (c) Adams, P. N.; Laughlin, P. J.; Monkman, A. P. *Synth. Met.* **1996**, *76*, 157. (d) Stejskal, J.; Riede, A.; Hlavata, D.; Prokes, J.; Helmstedt, M.; Holler, P. *Synth. Met.* **1998**, *96*, 55. (e) Beadle, P. M.; Nicolau, Y. F.; Banka, E.; Rannou, P.; Djurado, D. *Synth. Met.* **1998**, *95*, 29. (f) Yang, D.; Adams, P. N.; Mattes, B. R. *Synth. Met.* **2001**, *119*, 301.

(5) MacDiarmid, A. G.; Epstein, A. J. *Mater. Res. Soc. Symp. Proc.* **1992**, *247*, 565.

(6) Liu, G.; Freund, M. S. *Macromolecules* **1997**, *30*, 5660.

(7) Wei, Y.; Hsueh, K. F. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 4351.

(8) (a) Wang, Y.; Rubner, M. F. *Synth. Met.* **1992**, *47*, 255. (b) Kim, S.; Chung, I. J. *Synth. Met.* **1998**, *97*, 127.

(9) (a) Chen, S. A.; Hwang, G. W. *J. Am. Chem. Soc.* **1995**, *117*, 10055. (b) Gok, A.; Sari, B.; Talu, M. *Synth. Met.* **2004**, *142*, 41. (c) Zaidi, N. A.; Foreman, J. P.; Tzamalis, G.; Monkman, S. C.; Monkman, A. P. *Adv. Funct. Mater.* **2004**, *14*, 479.

(10) Han, C. C.; Lu, C. H.; Hong, S. P.; Yang, K. F. *Macromolecules* **2003**, *36*, 7908.

(11) Cataldo, F.; Maltese, P. *Eur. Polym. J.* **2002**, *38*, 1791.

(12) Lu, X.; Tan, C. Y.; Xu, J.; He, C. *Synth. Met.* **2003**, *138*, 429.

(13) Schmidt, V.; Domenech, S. C.; Soldi, M. S.; Pinheiro, E. A.; Soldi, V. *Polym. Degrad. Stab.* **2004**, *83*, 519.

(14) Deore, B. A.; Yu, I.; Freund, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 52.

(15) Deore, B. A.; Yu, I.; Aguiar, P. M.; Recksiedler, C.; Kroeker, S.; Freund, M. S. *Chem. Mater.* **2005**, *17*, 3803.

(16) (a) Simon, J.; Salzbrunn, S.; Prakash, G. K. Surya; Petasis, N. A.; Olah, G. A. *J. Org. Chem.* **2001**, *66*, 633. (b) Shoji, E.; Freund, M. S. *Langmuir* **2001**, *17*, 7183.

(17) Epstein, A. J.; McCall, R. P.; Ginder, J. M.; Macdiarmid, A. G. In *Spectroscopy of Advanced Materials*; John Wiley & Sons: New York, 1991.

(18) Socrates, G. *Infrared Characteristic Group Frequencies. Tables and Charts*, 2nd ed.; John Wiley & Sons: New York, 1994.

(19) (a) Angelopoulos, M.; Liao, Y. H.; Furman, B.; Graham, T. *Macromolecules* **1996**, *29*, 3046. (b) Yang, D.; Adams, P. N.; Goering, R.; Mattes, B. R. *Synth. Met.* **2003**, *135*, 293. (c) Zheng, W.; Angelopoulos, M.; Epstein, A. J.; MacDiarmid, A. G. *Macromolecules* **1997**, *30*, 2953. (d) Xeng, X. R.; KO, T. M. *Polymer* **1998**, *39*, 1187. (e) Wei, Y.; Hsueh, K. F.; Jang, G. W. *Macromolecules* **1994**, *27*, 518.

(20) (a) Zheng, W.; Angelopoulos, M.; Epstein, A. J.; MacDiarmid, A. G. *Macromolecules* **1997**, *30*, 7634. (b) Afzali, A.; Buchwalter, S. L.; Buchwalter, L. P.; Hougham, G. *Polymer*, **1997**, *17*, 4439.

(21) MacDiarmid, A. G.; Chiang, J.; Ritcher, A. F.; Somasiri, N. L. D.; Epstein, A. J. In *Conducting Polymers*; Alcacer, L., Ed.; D. Reidel: Dordrecht, The Netherlands, 1987; p 105.

(22) Vonga, D.; Marotta, R.; Napolitano, A.; d'Ischia, M. *J. Org. Chem.* **2002**, *67*, 6143.

(23) Yue, J.; Epstein, A. J.; Zhong, Z.; Gallagher, P. K.; Macdiarmid, A. G. *Synth. Met.* **1991**, *41*, 765.

(24) (a) Mohler, L. K.; Czarnik, A. W. *J. Am. Chem. Soc.* **1993**, *115*, 7037. (b) Kliegel, W.; Lubkowitz, G.; Pokriefke, J. O.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **2000**, *78*, 1325. (c) Hopfl, H.; Farfan, N. *Can. J. Chem.* **1998**, *76*, 1853.

(25) Vedejs, E.; Chapman, R. W.; Lin, S.; Muller, M.; Powell, D. R. *J. Am. Chem. Soc.* **2000**, *122*, 3047.

(26) Groziak, M. P.; Ganguly, A. D.; Robinson, P. D. *J. Am. Chem. Soc.* **1994**, *116*, 7597.

MA0513158