Optimization of Polymerization Conditions of Furan with Aniline for Variable Conducting Polymers

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A high-throughput multiparameter optimization of chemical oxidative polymerization conditions has been developed for a facile synthesis of furan homopolymers and furan/aniline copolymers using a combinatorial method. The polymerization yield, molecular structure, and properties of the polymers would be optimized against typical polymerization parameters, including oxidant species, medium species, temperature, oxidant/ monomer ratio, monomer concentration, dopant concentration, and furan/aniline comonomer ratio. The electrical conductivity, lead ion adsorptivity, chemical resistance, and thermal behavior of the polymers were also elaborated. It is found that only a combination of $FeCl_3$ and nitromethane as oxidant and medium, respectively, is appropriate for the furan homopolymerization. The homopolymerization yield increases consistently with an increase in the monomer concentration from 0.05 to 0.2 M and the $FeCl_3$/furan molar ratio from 0.25 to 1.25. Although the as-prepared polyfuran exhibits very low conductivity, down to 10^{-11} S cm^{-1}, the HCl- and $HClO_4$-doped polyfurans possess much higher conductivities of 9.2×10^{-8} and 2.38×10^{-5} S cm^{-1}, respectively. In addition, the conductivity of the furan/aniline copolymer rises steadily with increasing aniline content, although the copolymerization yield shows a minimum at the furan/aniline molar ratio of 60/40, which is evidence of the occurrence of a real copolymerization between the furan and aniline monomers. The difficulty of synthesizing conducting polyfuran could be overcome to some extent by the polymerization in an appropriate condition optimized in this study. Particularly, the difficulty of synthesizing poly(furan-*co*-aniline) having much higher conductivity than the polyfuran would be largely conquered by chemical oxidative copolymerization of furan with aniline.

Introduction

The discovery of electrical conductivity of organic conjugated polymers has opened a novel and very important field of modern functional material science. In the past few years, a conducting polyaniline (PAN) has been the center of great interest because of its high electrical conductivity and chemical stability.[1-3] The heterocyclic polymers, such as polypyrrole and polythiophene, have also received a great deal of interest due to their high conductivity in the doped state accompanied by a much higher stability in air.[3-5] However, polyfuran has attracted relatively less attention because the polyfuran with a regular structure and high conductivity was synthesized with difficulty.

It is reported that polyfuran demonstrates some superior properties, such as electrochromic effect and good redox ability.[6] Moreover, the resource of furan is much greater, and thus, furan is much less expensive than pyrrole (PY) and thiophene, because the furan comes from an agricultural and sideline product that is a reproducible resource. These characteristics will attract the attention of more scientists in chemistry and materials science.

In the past decades, the electrochemical synthesis and properties of polyfuran,[5-9] copoly(furan/PY),[10] copoly(furan/ 2-methylfuran),[11] and polyfuran/polythiophene bipolymer films[12,13] have been studied. Nevertheless, it is observed that, due to the high oxidation potential of furan, a significant cleavage of the furan ring generally occurred during the electropolymerization, hence, strongly breaking the expected π-conjugated structure. The polymer obtained is dielectric or very low electrically conductive. Furthermore, the yield of the polyfuran formed thus is greatly restricted by the area of the electrode used. Therefore, a chemical oxidative polymerization of furan has been urgent. In fact, a few scientists have synthesized polyfuran[14] and polyfuran/poly-(2-chloroaniline) composites by chemical oxidative polymerization.[15] Although the conductivity of the polyfuran formed can reach $\sim 10^{-2}$ S cm^{-1}, the product is just an octamer. Such a low degree of polymerization is disadvantageous to practical processing and application. Unfortunately, a polyfuran with a higher degree of polymerization would exhibit lower conductivity, down to 10^{-13} S cm^{-1}.

Here, a combinatorial polymerization system for the synthesis of a soluble polyfuran and copoly(furan/aniline-(AN)) possessing much higher conductivity, widely variable conductivity, and much higher polymerization yield was optimized using a set of input variables that included reactant

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Scheme 1. An Ideal Chemical Oxidative Polymerization of Furan and Possible Structure of the Polyfuran Formed
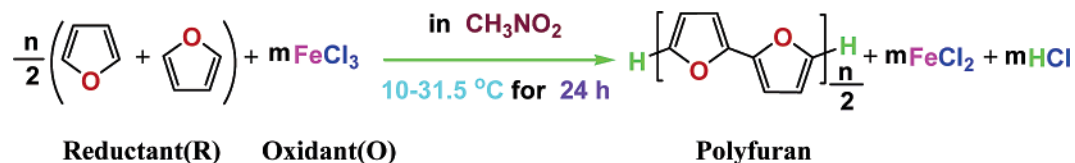
parameters (furan concentration, oxidant species, oxidant/monomer ratio, and furan/AN comonomer ratio) and processing variables (polymerization solvent species, temperature, and time). The structure and properties of the polymers obtained through the chemical oxidative polymerization were characterized in detail with infrared (IR), ultraviolet−visible (UV−vis), and solid-state high-resolution ^{13}C NMR spectra; wide-angle X-ray diffractometry; and differential scanning calorimetry. Several important properties, including the solubility, lead ion adsorbability, and electrical conductivity of the polyfuran and copoly(furan/AN) were elaborated.

Experimental Section

Furan, AN, $FeCl_3$, HCl, $HClO_4$, nitromethane(CH_3NO_2), and all other oxidants and solvents were chemically pure reagents and were used without further purification.

Chemical Oxidative Polymerization of Furan. The polyfuran was prepared with $FeCl_3$ as an oxidant in CH_3NO_2 through chemically oxidative polymerization (Scheme 1).[16−18] A representative procedure is as follows: Furan (0.01 mol) was dissolved in 25 mL of CH_3NO_2 at 15 °C in a water bath. $FeCl_3$ (0.01 mol) solution in 25 mL of CH_3NO_2 at 15 °C was then added dropwise to the furan solution with constant stirring for 0.5 h. The reactant solution was consistently stirred for 24 h in the water bath. The polyfuran precipitates formed thus were isolated from the reaction mixture by filtration and washed with an excess of ethanol and distilled water until the filtrate was colorless and dried under an IR lamp for 3 days. Finally, a crimson polyfuran powder with a faint gleam was obtained. The resultant polymer, that is, virgin sample, can be converted into its doped salt samples by dispersing the polymer particles in $HClO_4$ or HCl for 24 h. The $HClO_4$- and HCl-doped polyfurans are almost black.

Copolymerization of Furan with Aniline. The copolymers were also prepared in CH_3NO_2 through the chemically oxidative polymerization of furan and AN of various furan/AN ratios with $FeCl_3$ as an oxidant by a procedure similar to that described above. A blackish brown copolymer powder was obtained.

Characterization. The polymerization was followed by an open-circuit potential (OCP) technique using a saturated calomel electrode as a reference electrode and a Pt electrode as a working electrode. The chemical resistance of polyfuran was evaluated as follows: polyfuran powder, ~2 mg, was added to 1 mL of solvent and dispersed thoroughly after shaking intermittently for 2 h at ambient temperature. IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer on KBr pellets. The UV−vis spectra were measured on a Lambda 35 UV−vis spectrophotometer in the range of 190−900 nm in CH_3NO_2 or $HClO_4$. The solid-state ^{13}C NMR
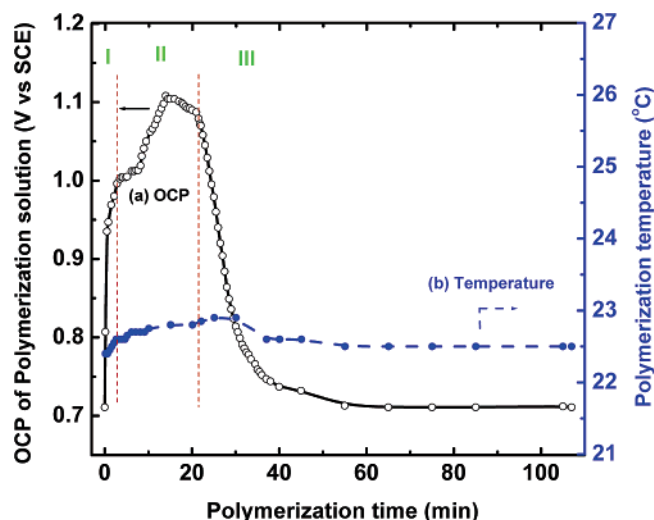

Figure 1. Dependence of (a) the open-circuit potential of the polymerization solution (15 °C and 0.15 M furan) and (b) the temperature of the polymerization solution (0.2 M furan) on the polymerization time at the same $FeCl_3$/furan molar ratio of 1/1 in the same polymerization medium of CH_3NO_2.

spectrum was acquired on an Infinityplus 300WB NMR spectroscope. The bulk electrical conductivity of the polymer powders was measured by a two-electrode method using the UT 70A multimeter at ambient temperature. Adsorption of Pb^{2+} from aqueous solution on polyfuran particles, which were prepared at a monomer concentration of 0.2 M and an oxidant/monomer molar ratio of 1/1 in CH_3NO_2 at 15 °C for 24 h, was evaluated in batch experiments. An aqueous solution of 25 mL at pH = 5.1 and a Pb^{2+} concentration of 200 mg/L was incubated with 50 mg of polyfuran particles at 20 °C. After a treatment period of 24 h, the polyfuran was filtered from the solution, and then the concentration of Pb^{2+} in the filtrate after adsorption was measured by an EDTA complex titration.[16,17] The wide-angle X-ray diffraction was obtained with a D/max 2550 X-ray diffraction instrument. The DSC curves were obtained in static air at a heating rate of 10 °C/min by using a CDR-4P differential scanning calorimeter made by Balance Equipment Factory of Shanghai, China.

Results and Discussion

Synthesis of the Polyfuran. The variation of the reaction solution OCP with the polymerization time at the furan concentration of 0.15 M is shown in Figure 1. Due to an intrinsically high oxidation potential of furan itself, the OCP of furan polymerization is very high, with an initial OCP of 0.71 V vs SCE that is much higher than those of AN[17−21] and PY.[19] When the oxidant solution was added to the furan solution, an immediate rise of OCP was observed. The variation of OCP with reactant concentration during the

polymerization (Scheme 1) is expressed by the Nernst equation,

$$OCP = E^0 + (RT/nF) \ln (c_O/c_R) \qquad (1)$$

where E^0 is the standard electrode potential of the polymerization, R *is* the gas constant, T is the absolute temperature, n is the number of electrons, F is the Faraday constant, and c_O and c_R are the concentrations of the oxidant and reductant. Obviously, the solution OCP during the polymerization will vary with the oxidant (FeCl$_3$)/reductant (furan monomer and oligomer) concentration ratio.

During the whole polymerization, there are three distinct stages in the OCP time plot, that is, an up stage, a plateau, and a down stage. A similar situation was observed during the chemical oxidative polymerizations of AN and PY;[16−21] however, only a small temperature rise of furan polymerization solution was revealed during the initial polymerization of 35 min, which is different from the AN and PY polymerizations, because the oxidative polymerizations of AN and PY are obviously exothermic.[16−21] This implies that the polymerization mechanism of furan differs from those of AN and PY.

In stage I of the furan polymerization, with dropwise addition of the oxidant solution into the furan solution, the OCP increased rapidly from 0.71 to 1.0 V vs SCE in 1 min. Since the oligomers formed can act as a reducer, the oligomers could also be oxidized and then propagate subsequent polymerization with residual monomers via an electrophilic aromatic substitution mechanism. However, the formation of the oligomers as a reductant would not increase the c_R value since the monomer concentration decreases significantly after they have oligomerized into oligomers. Therefore, the c_O/c_R ratio should not decrease when the oxidant solution is constantly dropped. Accompanying the OCP change, the color of the reaction solution consistently changes from colorless to straw yellow, pea green, green, blackish green, and eventually black.

As the polymerization proceeded, the potential reached a relatively steady plateau between 1.0 and 1.1 V vs SCE. In stage II, the polymer chains formed during stage I may be further oxidized by the oxidant. The chain propagation may continue on the oxidized chains to form a higher-molecular-weight polymer. These newly formed polymer chains may also be oxidized to participate in the chain propagation. This process is repeated again and again until most of the oxidant is consumed at the end of the plateau stage. After the plateau stage, the OCP declined stably and dramatically. Stage III should include further polymerization of oligomer chains with each other by a small amount of residual FeCl$_3$.

The variation of the OCP of the polymerization solution with the furan concentration and polymerization time was also studied using a fixed FeCl$_3$/furan molar ratio of 1/1 at 15 °C in CH$_3$NO$_2$ for 24 h. With an increasing furan concentration from 0.05, 0.1, 0.15, to 0.2 M, the time corresponding to the maximum potential shortens gradually from 22, 16.5, 14, to 9 min. This demonstrates a consistently accelerated polymerization with increasing furan concentration because at the higher furan concentration, the probability
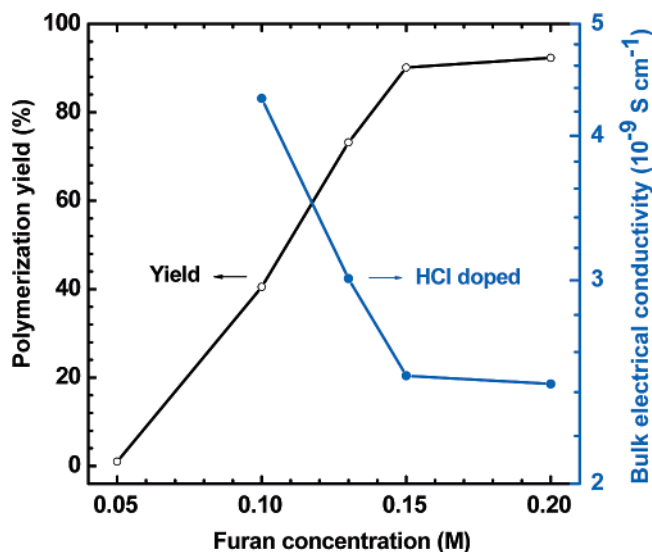

Figure 2. Effect of furan concentration on the polymerization yield and bulk electrical conductivity of polyfuran obtained at a fixed FeCl$_3$/furan molar ratio of 1/1 at 15 °C in CH$_3$NO$_2$ for 24 h.

of collision between monomer and oxidant or active chains must be great, thus resulting in rapid polymerization. It was also found that the initial equilibrium OCPs rise with an increase in the furan concentration, since the high initial oxidant concentration would lead to a high value of c_O/c_R (eq 1).

The strong effect of the furan concentration on the polymerization yield is shown in Figure 2. In this study, the yield is calculated on the basis of the number of furan monomers added. The yield increases monotonically from 39.5% to the highest value of 93.8% as the furan concentration is increased from 0.1 to 0.2 M. At a furan concentration of 0.05 M, only black solution could be obtained after 24 h. Even after a polymerization of 10 days, solid polymer precipitates were still insufficient to obtain a characterization. Therefore, the yield of 1% in Figure 2 is an estimated value. At a low concentration of furan, the probability of collision between monomer and oxidant/active end groups is low, and thus, the monomer does not have enough chance to link onto an active center to form a polymer, but some soluble black oligomers in polymerization medium indeed formed. It is concluded that the optimized furan concentration is 0.15−0.2 M due to their highest yield regardless of their relatively low conductivity.

Optimization of the Oxidant Species. Several representative inorganic oxidants, including CuCl$_2$, (NH$_4$)$_2$S$_2$O$_8$, K$_2$Cr$_2$O$_7$, KClO$_3$, KMnO$_4$, and FeCl$_3$ with different standard reduction potentials, were chosen as the oxidants for furan polymerization. It was found that no polymer could be obtained if CuCl$_2$ with the lowest standard reduction potential (0.58 V) was employed because the oxidation potential of furan is much higher (1.50−1.75 V).[10,12] Moreover, (NH$_4$)$_2$S$_2$O$_8$, K$_2$Cr$_2$O$_7$, KClO$_3$, and KMnO$_4$ could not be effective oxidants for furan polymerization because they could not dissolve in CH$_3$NO$_2$, and KMnO$_4$ tends to react with the solvent to form MnO$_2$. Fortunately, when FeCl$_3$ solution in CH$_3$NO$_2$ was added dropwise into the furan solution, the reaction solution color instantly and orderly became green; blackish green; blackish blue; and finally, black in 1 min. At the same time,

polymer precipitates appeared in the reaction solution in ~1 h. Apparently, FeCl$_3$ is only one appropriate oxidant for the chemical oxidative polymerization of furan among the six oxidants mentioned above. It is easily understood that FeCl$_3$ is also the best oxidant for chemical oxidative polymerization of PY.[19] It is more important that FeCl$_3$ can promote the oxidative coupling of furan rings by a redox process and also extract electrons from the polymer backbone to afford a polymer complex in which inorganic species, such as Cl$^-$ and FeCl$_4^-$ are present as counterions.[14] In particular, the redox equilibrium between Fe^{3-} and Fe^{2+} in the system can promote the reaction. Therefore, the FeCl$_3$ was carefully optimized as an ideal oxidant for the following investigation.

Optimization of the Medium Species. The furan polymerization can only be performed successfully in the neutral organic medium, rather than water or traditional acidic water, because (1) furan is almost water- or acidic water-insoluble, (2) the furan ring would be readily broken in an acidic medium, and (3) the oxidation potential (1.50–1.75 V) of furan is higher than the oxidative decomposition potential (1.5 V vs SCE) of an acidic aqueous solution.[10,12] It is well-established that an apolar solvent is not efficient in promoting the polymerization, probably due to the insolubility of FeCl$_3$ in the apolar medium.[14] Moreover, polar protic solvents could not be used because the hydrolysis of FeCl$_3$ in protic solvents may form acid, consequently favoring both cationic polymerization and cleavage of furan to give undesirable nonaromatic units.[14] In this study, we have examined furan polymerization in polar aprotic solvents with high nucleophilic character, such as CHCl$_3$, CH$_3$CN, DMF, DMSO, NMP, and CH$_3$NO$_2$, that are good solvents for furan.

Because CH$_3$CN was used in combination with FeCl$_3$, only a brown solution formed; and no polymer precipitation occurred. When DMF, DMSO, or NMP was utilized, a small amount of flocculent polymer precipitate was observed after 24 h, and the color of the final polymerization solutions was scarlet, yellow, and scarlet, respectively. CHCl$_3$ may be an unsuitable reaction solvent because FeCl$_3$ is insoluble in it. Auspiciously, when CH$_3$NO$_2$ was applied, the system color immediately became dark and completely black in 1 min with dropwise addition of FeCl$_3$ solution into the furan solution, as discussed earlier. Apparently, CH$_3$NO$_2$ is only one good solvent for chemical oxidative polymerization of furan among the six solvents mentioned above. Probably, CH$_3$NO$_2$ can increase the solvation of the FeCl$_3$ by coordination between the CH$_3$NO$_2$ and FeCl$_3$, thereby reducing the Lewis acidity and further the cationic polymerizability of furan. It should be noted that furan polymerization would be prohibited if a small amount of absolute ethanol were mixed into CH$_3$NO$_2$. Perhaps, the ethanol would break the solvation of the FeCl$_3$ by the CH$_3$NO$_2$. In conclusion, CH$_3$NO$_2$ was selected as an optimal medium for the following study.

Optimization of the Oxidant/Monomer Ratio. The effect of the oxidant (FeCl$_3$)/monomer (furan) ratio on the polymerization yield is shown in Figure 3. With an increasing FeCl$_3$/furan molar ratio from 0.25/1 to 1.25/1, the polymerization yield rises steadily from 35.8 to 112.1%. At the lower oxidant content, the oxidant is consumed very rapidly
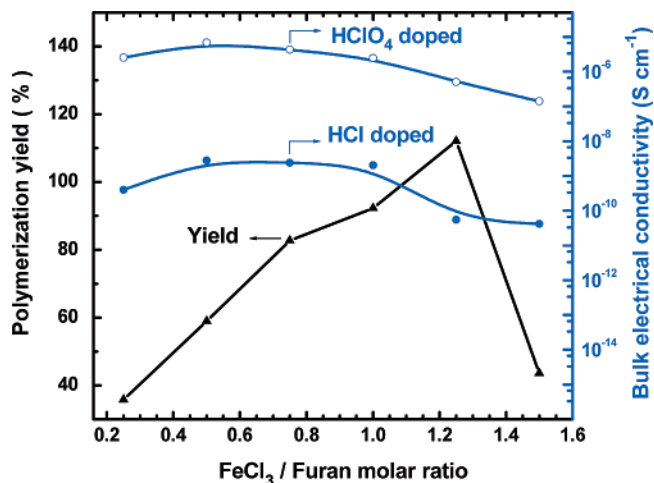

Figure 3. Effect of the FeCl$_3$/furan molar ratio on the polymerization yield and bulk electrical conductivity of polyfuran obtained at a furan concentration of 0.2 M at 15 °C in CH$_3$NO$_2$ for 24 h.

so that some monomers might not be oxidized to polymerize, ultimately resulting in a much lower yield. When more oxidant was added, obviously, more monomers could be oxidized to take part in the polymerization. Note that too high a polymerization yield of 112.1% appears at the FeCl$_3$/furan molar ratio of 1.25/1(Figure 3), possibly due to the embedment of some Fe^{3+} and Fe^{2+} salts in the as-prepared polymers during the polymerization. A similar phenomenon was also found in other works.[14,19] On the other hand, at a FeCl$_3$/furan molar ratio of 1.5/1, a much lower polymerization yield of only 43.6% was again perceived because some furan monomer and polymer were overoxidized. It seems that the optimal FeCl$_3$/furan molar ratio would be 1/1 for both high yield and high conductivity, that is, the stoichiometric coefficients, $n = m$ in Scheme 1. That is to say, equal molar numbers of FeCl$_3$ and furan monomer are optimal for the most efficient formation of polyfuran with a good π-conjugated structure. The optimum FeCl$_3$/furan molar ratio of 1/1 is lower than the theoretically optimized FeCl$_3$/pyrrole molar ratio of 2.33/1 because of much higher oxidation sensitivity or instability of furan, as compared to pyrrole.[19]

Optimization of the Polymerization Temperature. The dependence of the polyfuran yield on the polymerization temperature is shown in Figure 4. As the polymerization temperature rises from 10 to 31.5 °C for a constant polymerization time of 24 h, the yield tends to decrease because the stronger oxidizing ability of the oxidant and faster reaction at higher temperature could result in faster formation of more active centers in the system and then relatively more water-soluble oligomers. The enhanced volatility of furan monomer at an elevated temperature could be another reason for the reduced yield owing to the greater loss of the monomer at the higher temperature, especially at the temperature that is close to the boiling point (32 °C) of the furan monomer. Therefore, the optimal polymerization temperature could be around 15 °C, on the basis of a combination of the second-highest yield and the fourth-highest conductivity.

Structural Analysis of the Polyfurans. IR Spectra. The IR spectra of the polyfurans obtained with different FeCl$_3$/furan ratios and furan concentrations are shown in Figures
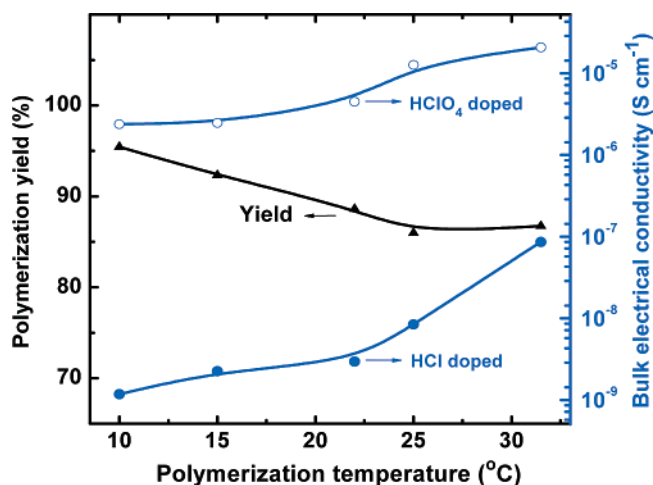
Figure 4. Effect of the polymerization temperature on the polymerization yield and bulk electrical conductivity of the polyfurans obtained at a furan concentration of 0.2 M and $FeCl_3$/furan molar ratio of 1/1 in CH_3NO_2 for 24 h.
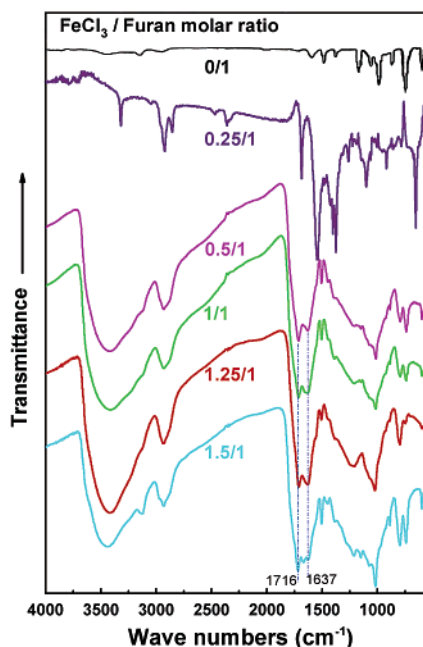

Figure 5. FTIR spectra of the polyfurans obtained with different $FeCl_3$/furan molar ratios at a furan concentration of 0.2 M in CH_3NO_2 at 15 °C for 24 h.

5−6. Four characteristic bands of 2,5-disubstituted furan units were observed, that is, the C−H out-of-plane vibration at 738 cm^{-1},[15] C−O−C stretching vibration at 1015 cm^{-1},[10] C=C stretching vibration in the furan ring at 1503[15] and 1625 cm^{-1},[12] and the aromatic C−H stretching at 3125 cm^{-1}.[9] The presence of these bands may indicate the formation of polyfuran. Furthermore, another noticeable IR feature is that the band around 787 cm^{-1} due to an α-substituted five-membered heterocyclic polymer appears in all the polymers, suggesting the α-position linkage between the furan rings.[10] It should be noted that the peaks at 1710, 2928, and 3424 cm^{-1} assigned to the stretching of carbonyl, aliphatic C−H structures, and hydroxyl groups, respectively, were seen. The occurrence of these three bands possibly implies the breakage of a few furan rings with the consequent generation of nonconjugated structures.[9] Maybe, the HCl formed in
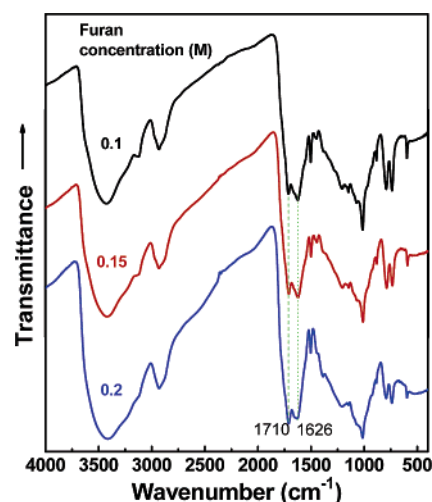

Figure 6. FTIR spectra of the polyfurans obtained at the different furan concentrations in CH_3NO_2 at the polymerization temperature of 15 °C with a $FeCl_3$/furan molar ratio of 1/1 for 24 h.

Scheme 1 could prompt the formation of nonconjugated structures to some extent.[11] There is no doubt that broken furan units will interrupt the conjugated structure along the molecular chain.

It is seen from Figure 5 that the polyfuran formed at the $FeCl_3$/furan molar ratio of 0.25/1 exhibits the weakest bands at 1686 and 3319 cm^{-1}, but the strongest band at 1540 cm^{-1}. On the contrary, the polyfuran formed at a $FeCl_3$/furan molar ratio of 1.5/1 exhibits the strongest bands at 1716 and 885 cm^{-1} that are attributed to C=O and olefinic alcohol groups, respectively.[14] Apparently, the polymer formed at a $FeCl_3$/furan ratio of 1.5/1 is overoxidized by the excessive oxidant, consequently leading to the cleavage of the furan rings. This behavior would badly shorten the conjugated length of the polyfuran, which is coincident with the results of the UV−vis analysis below. This could be one of the most important reasons that the polyfuran obtained thus has a much lower electrical conductivity (Figures 2−4) than polypyrrole and PAN, because the aromatic rings of PY and AN are very stable during the chemical oxidative polymerization. Note that all of the polymers prepared with a $FeCl_3$/furan molar ratio in a range of 0.5−1.25/1 display similar IR characteristics. That is to say, their macromolecular structures are almost identical, which is further confirmed by nearly the same conductivity, in Figure 3.

Figure 6 shows the IR spectra of the polyfurans obtained at different furan concentrations. The band at 1710 cm^{-1} tends to become stronger, but the bands at 1503 and 1626 cm^{-1} tend to decline with an increasing furan concentration from 0.1 to 0.2 M, signifying that the number of broken furan rings in the polyfuran seems to increase, but the number of aromatic furan units decreases, because the reaction rate is too fast to form a well π-conjugated polymer under a high furan concentration and also a high oxidant concentration. This also agrees with the results displayed in Figure 2.

Polymerization temperature has a slight influence on the structure of the polyfuran. The band at 1710 cm^{-1} becomes weaker and the band at 1625 cm^{-1} assigned to the stretching vibration of the C=C gets slightly stronger as the polymerization temperature is elevated from 10 to 31.5 °C. This
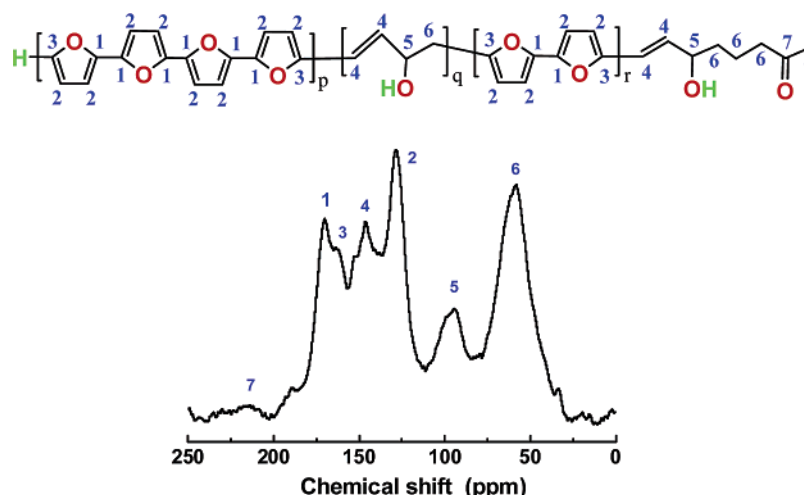
Figure 7. Solid-state high-resolution ^{13}C NMR spectrum of polyfuran obtained at the furan concentration of 0.2 M in CH_3NO_2 at a polymerization temperature of 31.5 °C and $FeCl_3$/furan molar ratio of 1/1 for 24 h.

implies that the polymer obtained at a higher temperature contains a longer π-conjugated structure. This phenomenon may be ascribed to the enhancement of the oxidative polymerizability of furan at elevated temperature because furan polymerization is scarcely exothermic (Figure 1). This has been confirmed by an increased conductivity in Figure 4. The slightly exothermic polymerization of furan is quite different from the significantly exothermic polymerization of PY, AN, and diaminonaphthalene,[16,17,19,21] implying their different polymerization characteristics.

UV–Vis Spectra. The UV–vis spectra of the furan monomer and polyfurans with different $FeCl_3$/furan ratios were studied in two solvents. Two absorption bands appear in the UV–vis spectra of the virgin polymer solution in CH_3NO_2. The strong absorption (band I) at 380 nm is assigned to the $\pi-\pi^*$ transition of the furan rings of polyfuran backbone, and a weak absorption (band II) around 650 nm to the $n-\pi^*$ transition of the quinoid rings.[15–18] This indicates that the polyfuran obtained should be a π-conjugated polymer, because the furan monomer in CH_3NO_2 does not display any UV–vis absorbance between 360 and 900 nm. Note that UV–vis absorbance in the wavelength range of 200–360 nm could not be recorded because of a strong interference from CH_3NO_2 solvent.

When $HClO_4$ was employed as the testing solvent, it was found that the band II around 650 nm dramatically becomes weak because of the chain flection and solubility decrease of the polyfurans with changing solvents from CH_3NO_2 to $HClO_4$. However, no significant difference of the UV–vis spectra was found with changing the $FeCl_3$/furan molar ratio from 0.25/1 to 1.5/1. It seems that the polyfuran structure does not vary significantly with the $FeCl_3$/furan ratio. This is basically consistent with the results of the IR spectra in Figure 5.

Solid-State ^{13}C NMR Spectrum. It appears that a high-resolution ^{13}C NMR spectrum of polyfurans has not been found until now because most of the polyfurans with a high molecular weight are not totally soluble in traditional deuterated solvents. Therefore, the structure characterization of the polyfurans has to be performed with the solid-state ^{13}C NMR technique. As shown in Figure 7, the solid-state

^{13}C NMR spectrum of the polyfuran exhibits a signal at 170 ppm that can be assigned to the carbon atoms in the α-position on furan units, whereas the signal at 163 ppm is related to the same α-carbons in the terminal furan rings, where the shielding effect is weaker. Moreover, the strongest signal around 128 ppm may be ascribed to the carbon atoms in the β-position in the polyfuran chains. A similar ^{13}C NMR spectrum of an ordered oligo(furan) has been reported.[14] These findings further confirm that the polyfuran obtained here consists essentially of a π-conjugated structure. Note that the resonance peaks of the carbon atoms on the alkyl, hydroxyl, alkene, and carbonyl groups around 58, 94, 146, and 213 ppm, respectively, are also observed in Figure 7. That is to say, the polyfuran is dominated by the repetitive furan units but contains a few cleaved furan rings. Therefore, the π-conjugated structure was interrupted by the opened furan units to some extent, which coincided with the UV–vis spectra and low conductivity discussed below.

Wide-Angle X-ray Diffractograms. There is only one broad peak at the Bragg angle of around 20° in the wide-angle X-ray diffractograms of the powders of pristine and HCl/*m*-cresol-doped polyfurans in a Bragg angle range from 5 to 90°, suggesting that both polymers are amorphous. This also implies that the product obtained is a real polymer rather than the liquid monomer or ordered oligomers. Furthermore, no significant difference between the diffractograms of both polyfurans is revealed, demonstrating that the supramolecular structure would not vary with the HCl and *m*-cresol doping process.[22–23]

Properties of the Polyfuran. Bulk Electrical Conductivity. The pristine polyfuran particles have a very low conductivity down to 10^{-11} S cm^{-1}, but their conductivity would increase to 6.9×10^{-6} S cm^{-1} upon acid doping, as shown in Figures 2–4. The low conductivity is basically verified by IR, UV–vis, and NMR spectra. It is seen from Figure 2 that there is a small enhancement of the conductivity with a decrease in the furan concentration from 0.2 to 0.1 M, since the π-conjugated structure of the polyfuran formed could be reserved successfully in a mild condition including lower furan and also oxidant concentrations. From Figure 3, the HCl-doped polyfuran exhibits the maximal conductiv-

Table 1. Effect of the Doping Acid Concentration on the Conductivity of the Polyfurans Obtained at $FeCl_3$/Furan Ratio of 1/1 in CH_3NO_2 at 31.5 °C for 24 h

concn of doping acid (M)	bulk electrical conductivity (S cm^{-1})	
	HCl	HClO$_4$
1.0	8.58×10^{-8}	2.38×10^{-5}
11.8	9.20×10^{-8}	2.07×10^{-5}

ity of 2.78×10^{-9} S cm^{-1} at a $FeCl_3$/furan molar ratio of 0.5/1, possibly due to the best conjugated structure of the polyfuran obtained at this $FeCl_3$/furan ratio. As shown in Figure 4, the conductivity of the HCl-doped polyfuran increases monotonically from 1.17×10^{-9} to 8.58×10^{-8} S cm^{-1} with an increase in the polymerization temperature from 10 to 31.5 °C. It could be attributed to the higher oxidative polymerizability, less cleavage of the furan rings, and longer conjugated structure at a higher polymerization temperature. This is substantially coincident with a decreased intensity of C=O absorbance in the IR spectra with an increase in the temperature.

It should be noted that the conductivity of the polyfuran will be enhanced significantly from 10^{-8} to 10^{-5} S cm^{-1} if HCl is replaced by $HClO_4$ as doping acid under the same conditions, as illustrated in Figures 3−4 and Table 1. In other words, $HClO_4$ possesses a stronger doping ability than HCl because $HClO_4$ is a stronger acid. A similar phenomenon was observed for the oxidative polydiaminoanthraquinone in our laboratory; however, the variation of HCl and $HClO_4$ concentrations hardly ever influences the conductivity of the polyfurans, as listed in Table 1.

It seems that the difficulty of synthesizing conducting polyfuran could be overcome to some extent by the chemical oxidative polymerization developed in this study, as compared to electropolymerization. It is of interest that the conductivity of polyfuran would be remarkably enhanced by a simple copolymerization of the furan with AN, as discussed below. In other words, the difficulty of synthesizing conducting polyfuran would be greatly overcome by copolymerizing furan with AN. In particular, the chemical oxidative copolymerization between the furan and AN would resolve the thorny problem that a real furan/AN copolymer would not be successfully obtained by electropolymerization because of the great difference between the oxidation potentials of the furan and AN.

Chemical Resistance and Pb^{2+} Adsorptivity. The polyfuran showed good chemical resistance. It could partially dissolve only in hot $HClO_4$ at around 70 °C to form a brown solution, but it would not dissolve in most common solvents, such as NMP, THF, DMF, $CHCl_3$, CH_3COOH, CCl_4, or $HClO_4$, at ambient temperature. The good insolubility of the polyfuran also indirectly indicates that the polyfuran has a high molecular weight, a strong interaction between the polymer chains, and an aromatic conjugated structure. In other words, there are only a few opened furan units in the polyfuran chains because the polyfuran containing many opened furan units should be soluble in the organic solvents mentioned above. As a result, the molecular weight of the polyfuran has not been investigated due to the absence of appropriate solvents.
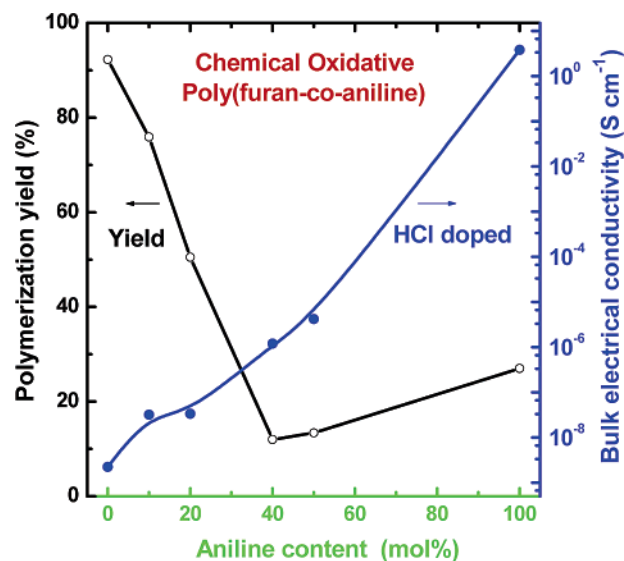
Figure 8. Effect of the aniline content on the copolymerization yield and bulk electrical conductivity of poly(furan-*co*-aniline)s obtained at a monomer concentration of 0.2 M in CH_3NO_2 at 15 °C for 24 h. The copolymer samples for the examination of the conductivity were doped in 1 M HCl.

The polyfuran has an adsorbability of heavy metal ion. The adsorption capacity and adsorptivity of Pb^{2+} onto 50 mg of polyfuran powders are found to be 33.3 mg/g and 33.3%, respectively. Just like the nitrogen atoms on aromatic amine polymers, the lone pair electrons on the O atom in the furan ring could attract the Pb^{2+} ions to a certain extent.

Furan/AN Copolymerization. The effect of the furan/AN ratio on the copolymerization yield and conductivity of furan/AN copolymer is shown in Figure 8. It is seen that the yield is nonmonotonically dependent on the comonomer ratio, presenting a minimum value of 12.0% at an AN content of 40 mol %. This discloses a lower copolymerizability between furan and AN monomers than their respective homopolymerizability. In other words, the chain propagation between an activated furan end group and an AN monomer (or between an activated AN end group and a furan monomer) is prohibited by each other to some extent. This retardant copolymerization finally results in a lower yield than the respective homopolymerization yields. The nonmonotonic variation of the copolymerization yield with comonomer ratio clearly suggests a copolymerization effect or a strong interaction between furan and AN monomers. Specifically, the furan/AN polymer prepared by the chemical oxidative polymerization is a real copolymer rather than a mixture of furan and AN homopolymers. This would be supported by the fact that the DSC curve of the furan/AN-(60/40) polymer is not a simple addition between the furan and AN homopolymers (Figure 9). Three scans show mainly exothermic peaks at 432, 525, and 342 °C for the polymers with furan/AN molar ratios of 100/0, 60/40, and 0/100, respectively, although their exothermic enthalpy decreases consistently with decreasing furan content.

The obtainment of a real furan/AN copolymer could be also further proved by the IR spectra in Figure 10. The bands around 2928 and 1700 cm^{-1} become weaker with increasing AN content from 0 to 100 mol %, but the peaks at 1160 cm^{-1} attributed to an in-plane C−H bending vibration in
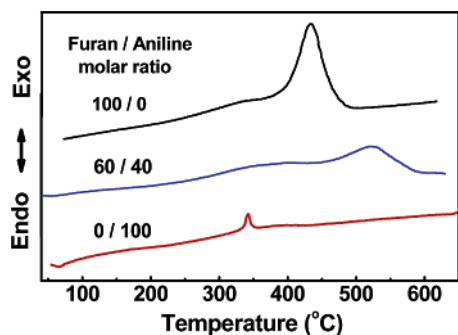
Figure 9. DSC thermograms of poly(furan-*co*-aniline)s synthesized in CH_3NO_2 at the polymerization temperature of 15 °C, monomer concentration 0.2 M, and $FeCl_3$/monomer molar ratio of 1/1 for 24 h.
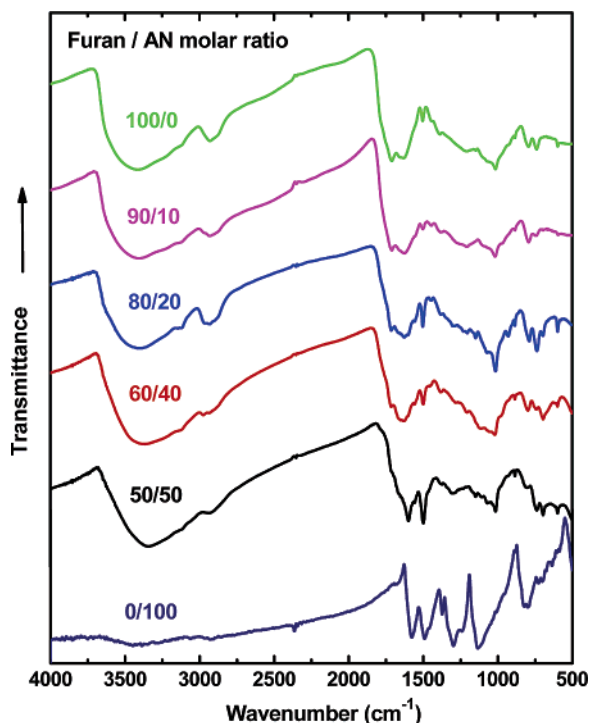

Figure 10. IR spectra of the poly(furan-*co*-aniline)s prepared with the different furan/AN molar ratios in CH_3NO_2 at a polymerization temperature of 15 °C and $FeCl_3$/monomer molar ratio of 1/1 for 24 h.

phenylene units[19] get stronger, suggesting an increased AN unit in the copolymer. At the same time, the absorption peak at 1633 cm^{-1} shifts to a higher wavenumber (1642 cm^{-1}) with increasing AN content from 0 to 50 mol %, then shifts to a lower wavenumber (1580 cm^{-1}) with increasing AN content from 50 to 100 mol %. The systematically structural variation with the furan/AN ratio might verify the formation of a real furan/AN copolymer.

Also from Figure 8, the conductivity of the copolymer powders doped by HCl increases monotonically and gradually from 2.24×10^{-9} to 3.82 S cm^{-1} with an increase in the AN content from 0 to 100 mol %, because higher AN-unit content would result in more quinoid units, a higher doping level, and a longer conjugated length. Furthermore, if doped by $HClO_4$ instead of HCl, the conductivity of the copolymer can be further improved, reaching up to 4.42×10^{-5} and 7.22×10^{-4} S cm^{-1} for $HClO_4$-doped copolymers with the AN contents of 50 and 40 mol %, respectively. The

corresponding conductivity of the HCl-doped copolymer is 4.20×10^{-6} and 1.20×10^{-6} S cm^{-1}, respectively. Moreover, $HClO_4$ is, indeed, certified to be a more efficient dopant for the preparation of furan-containing polymer with a higher conductivity than HCl. In summary, it is interesting that a widely variable electrical conductivity moving across 11 orders of magnitudes between 10^{-11} and 10^0 S cm^{-1} (Figures 3 and 8) could be simply realized for the furan/AN copolymer. In other words, the polymer conductivity could be adjusted facilely in a range of 11 orders of magnitude, as expected.

Conclusions

A facilely scaleable synthetic procedure affording polyfuran and furan/AN copolymer with a widely variable conductivity in good overall yields has been successfully developed with the help of a chemical oxidative polymerization with $FeCl_3$ as the oxidant in CH_3NO_2. The polymerization yield, structure, and properties of the polyfuran and furan/AN copolymers have been significantly optimized by regulating the oxidant species, oxidant/monomer ratio, monomer concentration, comonomer ratio, polymerization solvent, and temperature. The polyfuran has adsorbability on Pb^{2+} and a strong chemical resistance. The conductivity of the polyfuran tends to increase with aptly reducing the monomer concentration and oxidant/monomer ratio, elevating polymerization temperature, or using $HClO_4$ as the dopant instead of HCl. A retardant copolymerization occurs between the furan and AN monomers. An extensively variable conductivity between 10^{-11} and 10^0 S cm^{-1} could be simply realized for the furan/AN copolymer, as expected. The difficulty of synthesizing conducting polyfuran could be overcome to some extent by the chemical oxidative polymerization developed by this study, as compared with electrochemical synthesis. Particularly, a key problem in the synthesis of the highly conducting poly(furan-*co*-aniline)s would be resolved by the chemical oxidative copolymerization of furan with AN. This article makes it possible to optimize the chemical oxidative polymerizations of the derivatives of furan with aniline.

Supporting Information Available. FTIR spectra of the polyfuran obtained at different polymerization temperatures, UV−vis spectra, wide-angle X-ray diffractograms, and ^{13}C NMR spectrum simulated by the Chemoffice2004 of the polyfuran are available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) MacDiarmid, A. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2581.
(2) Huang, J.; Kaner, R. B. *J. Am. Chem. Soc.* **2004**, *126*, 851.

(3) Acevedo, D. F.; Miras, M. C.; Barbero, C. A. *J. Comb. Chem.* **2005**, *7*, 513.

(4) Liu, Y. C.; Chung, K. C. *Synth. Met.* **2003**, *139*, 277.

(5) Abou-Elenien, G. M.; El-Maghraby, A. A.; El-Abdallah, G. M. *Synth. Met.* **2004**, *146*, 109.

(6) Shilabin, A. G.; Entezami, A. A. *Eur. Polym. J.* **2000**, *36*, 2005.

(7) Salzner, U.; Lagowski, J. B.; Pickup, P. G.; Poirier, R. A. *Synth. Met.* **1998**, *96*, 177.

(8) Hernandez, V.; Lopez-Navarrete, J. T.; Zotti, G.; Veronelli, M.; Zerbi, G. *Synth. Met.* **1995**, *69*, 391.

(9) Carrillo, I.; Sanchez de la Bianca, E.; Gonzalez-Tejera, M. J.; Hernandez-Fuentes, I. *Chem. Phys. Lett.* **1994**, *229*, 633.

(10) Wan, X. B.; Zhang, W.; Jin, S.; Xue, G.; You, Q. D.; Che, B. *J. Electroanal. Chem.* **1999**, *470*, 23.

(11) Demirboga, B.; Onal, A. M. *Synth. Met.* **1999**, *99*, 237.

(12) Talu, M.; Kabasakaloglu, M.; Yildirim, F.; Sari, B. *Appl. Surf. Sci.* **2001**, *181*, 51.

(13) Kabaskaloglu, M.; Talu, M.; Yildirim, F.; Sar1, B. *Appl. Surf. Sci.* **2003**, *218*, 84.

(14) Benvenuti, F.; Galletti, A. M. R.; Carlini, C.; Sbrana, G.; Nannini, A.; Bruschi, P. *Polymer* **1997**, *38*, 4973.

(15) Gok, A.; Sari, B.; Talu, M. *J. Appl. Polym. Sci.* **2003**, *88*, 2924.

(16) Li, X. G.; Liu, R.; Huang, M. R. *Chem. Mater.* **2005**, *17*, 5411.

(17) Li, X. G.; Huang, M. R.; Li, S. X. *Acta Mater.* **2004**, *52*, 5363.

(18) Li, X. G.; Huang, M. R.; Hua, Y. M. *Macromolecules* **2005**, *38*, 4211.

(19) Li, X. G.; Chen, R. F.; Huang, M. R.; Zhu, M. F.; Chen, Q. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2073.

(20) Wei, Y.; Hsueh, K. F.; Jang, G. W. *Polymer* **1994**, *35*, 3572.

(21) Li, X. G.; Lü, Q. F.; Huang, M. R. *Chem.—Eur. J.* **2006**, *12*, 1349.

(22) MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1994**, *65*, 103.

(23) Dhanabalan, A.; Riul, A.; Goncalves, D.; Oliveira, O. N. *Thin Solid Films* **1998**, *327*, 60.

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