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SYNTHESIS AND PROPERTIES OF A SOLUBLE POLYTHIOPHENE DERIVATIVE WITH A URETHANE SIDE CHAIN

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ABSTRACT

A solution processible thiophene polymer with a hydrogen-bond-forming urethane group in the side chain, viz., poly[2-(3-thienyl)ethanol *n*-butoxycarbonylmethylurethane] (PURET), has been synthesized. The polymer is soluble in a wide variety of solvents such as chloroform, dimethylsulfoxide, *N*-methylpyrrolidone, and trifluoroacetic acid among others. Optical quality thick films are obtained by solution casting. The presence of extensive hydrogen bonding is established with the help of temperature-dependent infrared spectroscopy. NMR spectroscopic study indicates the presence of about 33% regio-isomeric defects in the polymer. The polymer forms yellow-colored solutions (λ_{max} = 430 nm) in most of the organic solvents, while in trifluoroacetic acid the polymer is oxidized and exhibits an additional band with an absorption maximum at around 780 nm. The conductivity of the polymer is in the order of 1 S/cm.

INTRODUCTION

Polythiophenes and other π-conjugated polymers continue to attract great scientific interest due to their expanded melt and solution processibility. Applications of these types of materials in electronics [1], light-emitting diodes [2], sensors [3], and nonlinear optics [4], for example, have been reported. The heterocyclic polymers such as polythiophenes and polypyrroles, as a class of materials, present special opportunities [5] because of the possibilities in structural modification and the ease of formation by either chemical [6] or electrochemical [7] polymerization techniques. Polythiophene is a conjugated conducting polymer with superior electronic and mechanical properties and is stable toward oxygen and humidity at ambient temperatures [8, 9]. The delocalized electronic structures due to extended π-conjugation along the backbone, unfortunately, make the polymer rigid and intractable. The intractability, with possible crosslinking at the 3-position of thiophene during polymerization, makes the polymer insoluble and infusible, causing nonprocessibility of this type of materials. The processibility of polythiophene can be achieved by introducing a flexible side chain of four or more carbons at the 3-position of thiophene. Long-chain substitution at the 3-position of the thiophene ring reduces chain intractability and also β-coupling during polymerization [10].

Modifications in the chemical and physical properties of the heterocyclic conjugated polymers are readily achieved by attaching an appropriate functional group in the side chain. The derivitization at the 3-position is easy with the thiophene compared to pyrrole, where the ring nitrogen must be protected in the latter [11]. This makes the thiophene monomer a suitable material for structural modification [12] to achieve such desired bulk properties in the polymer as water solubility [13], second order nonlinear optical activity [14], optical rotation [15], ionic conductivity [16], or liquid crystalline properties [17].

Recently, we reported the synthesis and second-order nonlinear optical properties of a thiophene-based copolymer with flexible alkyl groups and second-order nonlinear optical (NLO) active chromophores in the side chains [14]. The highly hydrophobic nature of the octyl groups (about 67 mol% as side chains) used in the copolymer reduced the solubility of the polymer in highly polar solvents in which the NLO chromophoric groups are soluble. The solubility of the polymer in highly polar solvents can be achieved by replacing the hydrophobic alkyl groups with flexible polar groups in the side chain. The polar hydrogen bond formable, butoxycarbonylmethyl urethane side group was reported to solubilize rigid polymers such as polydiacetylenes in common organic solvents [18].

In this work we report the synthesis of a urethane side-chain-containing polymer, poly[2-(3-thienyl)ethanol *n*-butoxycarbonylmethylurethane], to realize solubility in a wide variety of solvents. The resulting polymer is found to be highly soluble in chloroform, tetrahydrofuran, *N*-methylpyrrolidone, dimethylsulfoxide, dimethylformamide, and trifluoroacetic acid among others. The detailed results of the syntheses, polymer characterizations including spectroscopic studies, molecular weight determinations, and thermal characteristics of the polymer are discussed in this paper.

EXPERIMENTAL

Materials

The 2-(3-thienyl)ethanol, dibutyltin dilaurate, ferric chloride, and organic solvents used in this study were obtained from Aldrich Chemical Co. and used without further purification. The butyl isocyanatoacetate was purchased from Eastman Kodak Co. and used as received.

Synthesis of 2-(3-Thienyl)ethanol *n*-Butoxycarbonylmethylurethane (URET)

The 2-(3-thienyl)ethanol (3.42 g, 30 mmol) was loaded with 15 mL dry tetrahydrofuran (THF) to a 100-mL round-bottomed flask under argon atmosphere. A drop of dibutyltin dilaurate was added to the reaction flask as catalyst. After purging the flask for 5 minutes, a solution of butyl isocyanato acetate (4.9 g, 32 mmol) in 10 mL dry THF was added over a period of 5 minutes with stirring. The contents of the flask were poured into 100 mL of cold water after stirring the reaction mixture for 5 hours, and extracted with ether (3 × 20 mL). The organic extracts were combined, washed with cold 0.5 N hydrochloric acid (20 mL), followed by distilled water (3 × 30 mL). The crude extract was dried over anhydrous $MgSO_4$, ether was rotary evaporated, and the product was purified by column chromatography (silica gel, using 1:3 ethyl acetate:hexane as eluent). The product, a clear liquid, was obtained in 80% yield. IR (neat, in cm^{-1}): 3362 (s, ν_{N-H}), 3104 (w, aromatic ν_{C-H}), 2962 and 2937 (w, ν_{C-H}), 1727 (s, $\nu_{C=O}$, ester carbonyl), 1708 (s, $\nu_{C=O}$, urethane carbonyl). ^1H NMR ($CDCl_3$, δ in ppm): 7.39 (d, J_{C-H} = 4.9 Hz, 1H, aromatic, 7.21 (s, 1H, aromatic, 7.06 (d, J_{C-H} = 4.9 Hz, 1H, aromatic), 5.46 (broad, s, 1H, $-NH-$), 4.26 (t, J_{C-H} = 6.7 Hz, 2H, $-CH_2-$), 4.14 (t, J_{C-H} = 6.5 Hz, 2H, $-CH_2-$), 3.88 (d, J_{C-H} = 6.2 Hz, 2H, $-CH_2-$), 2.97 (t, J_{C-H} = 6.7 Hz, 2H, $-CH_2-$), 1.65 (m, J_{C-H} = 6.5 Hz, 2H, $-CH_2-$), 1.42 (m, J_{C-H} = 7.2 Hz, 2H, $-CH_2-$), 0.94 (t, J_{C-H} = 7.2 Hz, 3H, $-CH_3$).

Polymerization of URET

The 2-(3-thienyl)ethanol *n*-butoxycarbonylmethylurethane (URET) was polymerized by the chemical dehydrogenation method [19] using anhydrous ferric chloride. A 10-mmol (2.75 g) solution of monomer in 30 mL chloroform was polymerized using 40 mmol (6.48 g) ferric chloride at room temperature under a nitrogen atmosphere. After stirring for 12 hours, the polymer, poly[2-(3-thienyl)ethanol *n*-butoxycarbonylmethylurethane] (PURET), was precipitated in 400 mL methanol. The precipitate was washed with methanol using the Soxhlet extraction method for 3 days to remove oligomeric and iron impurities. The PURET polymer was finally washed with aqueous ammonia solution followed by methanol to remove the trace amounts of iron impurities. The purified polymer was then dried overnight under vacuum at room temperature. Yield 95%. FT-IR (cast from chloroform solution on NaCl window , in cm^{-1}): 3343 (m, ν_{N-H}), 2960 and 2874 (s, ν_{C-H}), 1749 (s, $\nu_{C=O}$, ester carbonyl), and 1724 and 1705 (s, $\nu_{C=O}$, urethane carbonyl), 1526 (w, $\nu_{C=C}$), 837 (γ_{C-H} out-of-plane, thiophene ring). ^1H NMR ($CDCl_3$, δ in ppm): 7.18 and 7.15 (1H, aromatic), 5.54 (broad, s, 1H, $-NH-$), 4.44 and 4.36 (2H, $-CH_2-$, respective head-to-tail coupled, and head-to-head and tail-to-tail coupled defects), 4.15 (t, 2H, $-CH_2-$), 3.96 (d, 2H, $-CH_2-$), 3.19 (1.3 H, $-CH_2-$, head-to-tail coupling), 2.99 (0.7 H, $-CH_2-$, head-to-head and tail-to-tail coupling defects), 1.63 (m, 2H, $-CH_2-$), 1.40 (m, 2H, $-CH_2-$), 0.95 (t, 3H, $-CH_3$). GPC ($CHCl_3$, in g/mol): M_n = 53,000; M_w = 345,000. UV (λ_{max}, in nm): 430 (DMSO); 426 (NMP); 425 ($CHCl_3$); 422 (acetone), 480 (cast film).

Characterization

The ^{1}H-NMR spectral data were obtained on a Bruker ARX-250 NMR spectrometer equipped with a 5-mm broadband probe. A two-dimensional homonuclear proton COSY-45 experiment was used to elucidate the proton–proton connectivity in the monomer and in the polymer. The infrared (IR) spectra were recorded on a Perkin-Elmer 1760X FT-IR spectrometer. The FT-IR spectrometer was equipped with a variable temperature apparatus to collect the data at elevated temperatures. The UV-Vis spectra were recorded using a Perkin-Elmer Lambda-9 UV/VIS/NIR spectrophotometer. The emission (fluorescence) characteristics of the polymer were studied using a 10-mW argon ion laser. The laser beam was collimated with a cylindrical lens, and the illuminated area of the sample was imaged on to the entrance slit of the monochromator. A 500-μm slit width of the monochromator provided a 6-Å spectral resolution. Emission was scanned from 520 to 665 nm for the solution sample (excited at 465 nm) and from 590 to 730 nm (excited at 584 nm) for the spin-cast film. The signal was detected with a cooled photomultiplier tube at −20°C and subsequently sent to a photon counter with an integration time of 1 second. Both the photon counter and the monochromator were interfaced to a personal computer.

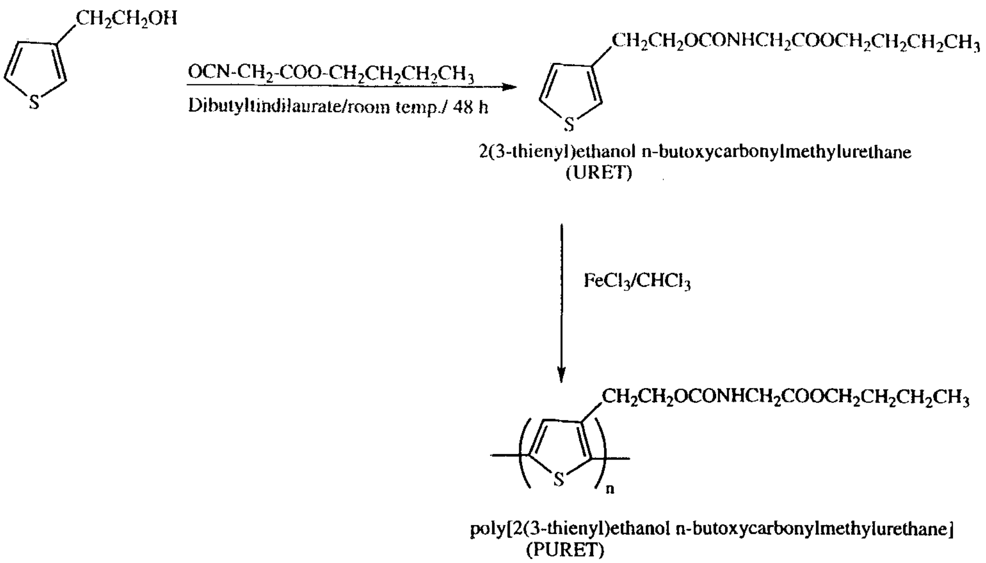
The number- and weight-average molecular weights were determined using a gel permeation chromatography instrument (GPC-Waters Model 510 pump, Model 410 refractive index detector, and model 730 module with 500-10^5 Å Ultrastyragel columns in series) relative to polystyrene standards. The column was injected with 100 μL of the polymer solution in chloroform (1 mg/mL) and was eluted with chloroform.

A differential scanning calorimeter (DSC 2910, TA Instruments) was used at a heating rate of 10°C/min to record the thermograms of the polymer. The thermal degradation temperatures (T_d) of the polymers were determined using a thermogravimetric analyzer (TGA 2950, TA Instruments, Inc.) at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Syntheses and Solution Properties

The urethane functionalized thiophene monomer, 2-(3-thienyl)ethanol *n*-butoxycarbonylmethylurethane (URET), and the polymer, poly[2-(3-thienyl)ethanol *n*-butoxycarbonylmethylurethane] (PURET), were synthesized as shown in Scheme 1. The PURET polymer was purified by Soxhlet extraction with methanol for 3 days to remove the iron impurities. The purified polymer was found to be highly soluble in tetrahydrofuran (THF), chlorinated solvents, dioxane, toluene, and also in such polar solvents as dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), and dimethylsulfoxide (DMSO), forming a reddish brown solution which becomes yellow upon dilution. The polymer was also found to be soluble in trifluoroacetic acid (TFA), furnishing a greenish yellow colored solution. Thick polymer films were obtained with good optical quality from these solutions. Since the polymer is soluble in polar solvents such as DMF, DMSO, and NMP, it can be solution blended with other optical polymers, viz., second-order nonlinear optical polymers or highly polar commodity plastics, to achieve desired electrical, optical, and mechanical



SCHEME 1. Syntheses of urethane functionalized thiophene monomer (URET) and polymer (PURET).

properties. The hydrogen-bond-forming polar groups in the PURET polymer are expected to suppress the phase segregation of the individual polymers in such a blend. The polymer is also feebly soluble in acetone and acetonitrile. The polymer is completely insoluble in methanol and hydrocarbons, hence any of these solvents can be used to fractionate the polymer.

The number- and weight-average molecular weights of the resulting polymer are strongly dependent on the reaction time of the polymerization. The number- and weight-average molecular weights of the polymer were calculated as 53,500 and 345,000 g/mol, respectively, when the polymerization time was 12 hours. The respective number- and weight-average molecular weights were calculated as 29,000 and 68,500 g/mol when the reaction time for the polymerization was 1 hour. The polymer is very sparingly soluble in solvents such as chloroform and THF when the reaction time is more than 24 hours. The latter is soluble only in highly polar solvents such as DMF, NMP and TFA, suggesting that the polymer formed is of very high molar mass.

1D and 2D ^{1}H-^{1}H COSY NMR Spectroscopic Study

Figure 1 shows the one-dimensional proton NMR spectrum of the PURET polymer in $CDCl_3$ (the NMR spectrum of the monomer is not shown, but the chemical shifts of all the protons are reported in the Experimental Section). The chemical shifts of the protons were assigned based on the splitting patterns as well as the coupling constants (J_{C-H}) of each of the protons. In order to elucidate the proton-proton connectivity, two-dimensional ^{1}H-^{1}H COSY-45 NMR experiments were performed for both the monomer and the polymer. The contour plots of the 2D ^{1}H-^{1}H COSY-45 NMR experiment of the monomer in DMSO-d_6 are shown in

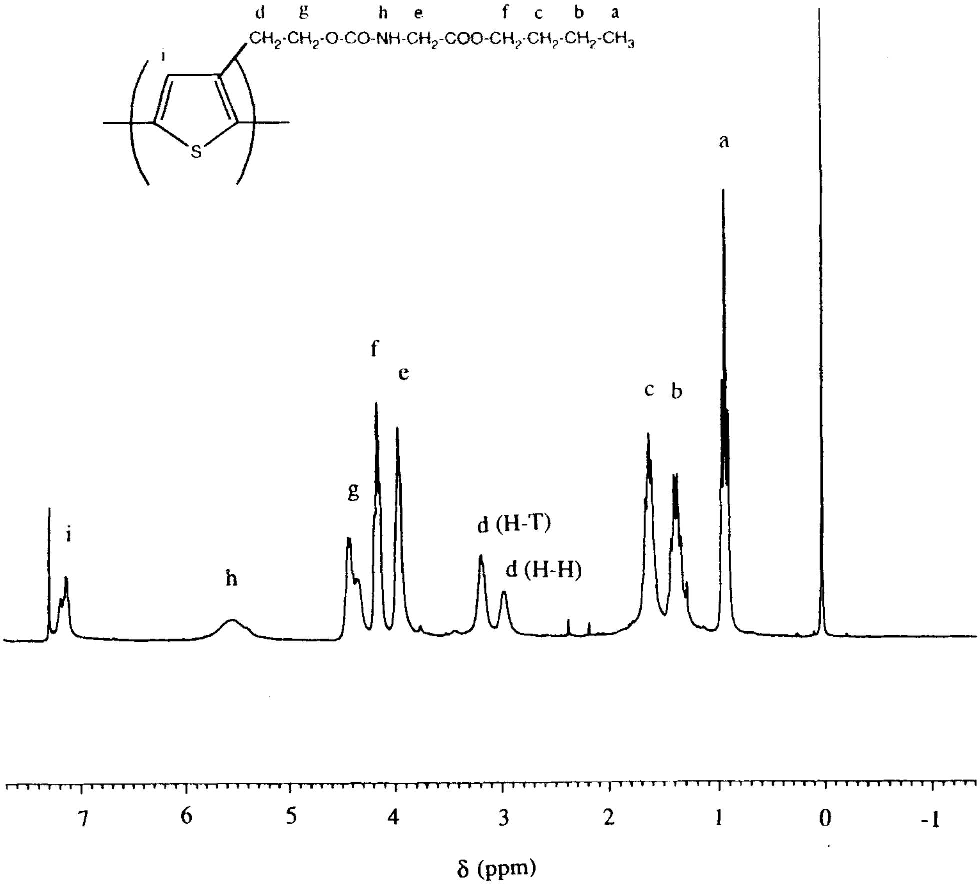


FIG. 1. ^{1}H-NMR spectrum of PURET polymer.

Fig. 2. The resonance peaks for six methylene protons appear in the 3.7–4.5 ppm region of the ^{1}H-NMR spectra. The methylene protons (e) which appear at 3.88 ppm have a cross peak with the NH proton (h) at 5.46 ppm. Their connectivity was also confirmed from the doublet splitting nature of this methylene protons. The methylene protons (f) at 4.14 ppm form a cross peak with the protons (c) at 1.65; hence these methylene protons correspond to the carbomethoxy group. The methylene protons (g) at 4.26 ppm generate a cross peak with the methylene protons (d) at 2.97 ppm. The peaks at 2.97 and 4.26 are, therefore, assigned to the respective α- and β-methylene groups adjacent to the thienyl group.

All the peaks that were present in the monomer are also present in the polymer, except two of the aromatic protons with resonances at 7.21 and 7.39 ppm (Fig. 1). The presence of the proton at the β-position of the thiophene in the polymer essentially indicates the linear structure of the polymer. The peaks at 4.26 and 2.97 ppm, which correspond to the respective β- and α-methylene groups, are split into two resonances each. At the field strength of 250 MHz, the peaks due to the α-methylene group are sufficiently resolved from each other to allow accurate inte-

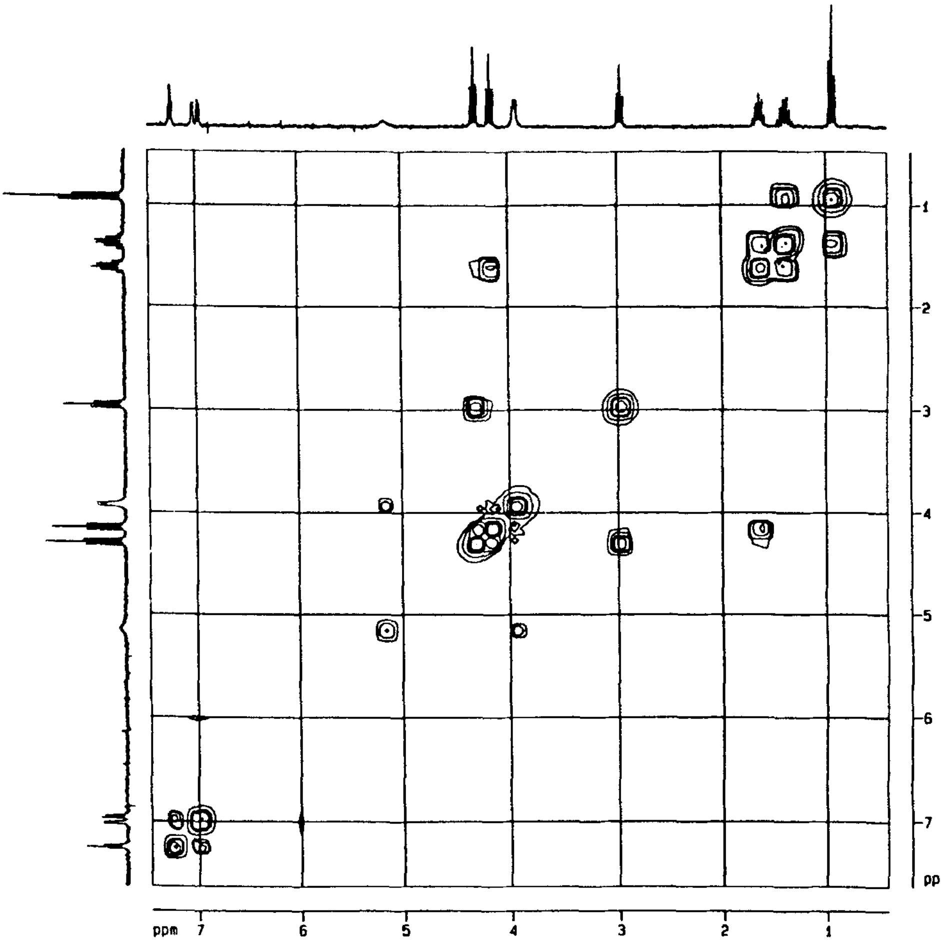


FIG. 2. ^1H-^1H 2D COSY NMR spectrum of URET monomer.

gration, while the splitting for the β-protons is not very well resolved. The peaks due to the α-methylene protons occur at 2.99 and 3.19 ppm. The former corresponds to the methylene units of head-to-head and tail-to-tail coupling defects (regio-defects) while the latter corresponds to that of head-to-tail coupled (regio-regular) thiophene units. The relative areas of the integration of these resonance peaks suggest the presence of about 33% coupling defects. This type of miscoupled units was also reported to be present in the polyalkylthiophenes [20]. The presence of 30–50% head-to-head and tail-to-tail coupled thiophene units was reported in the synthesis of poly(3-alkyl thiophenes) using the ferric chloride oxidation method [21]. Similarly, the peaks at 4.44 and 4.36 ppm correspond to the respective head-to-tail coupled and defect (head-to-head and tail-to-tail) coupled β-methylene groups. The deconvoluted areas of these peaks suggest the presence of about 30% of the coupling defects in the polymer. The peaks in the 7.0–7.2 ppm region are not well resolved and have a multiplet splitting. These peaks arise from the β-proton of the thiophene ring for various regio-isomeric units in the polymer chain. The contour plot of the 2D ^{1}H-^{1}H COSY-45 NMR experiment of the polymer in DMSO-d_6 is shown (0.4–4.8 ppm) in Fig. 3.

The peaks due to α- (2.96 ppm) and β-methylene (4.26 ppm) groups in the polymer are split into two peaks each, as shown in Fig. 3. Interestingly, the α-protons at 3.19 ppm show a cross peak only with the β-protons at 4.44 ppm. Similarly, the α-protons at 2.99 ppm shows a cross peak only with the β-protons at 4.36 ppm. This results strongly supports the view that the peaks at 2.99 and 4.36 ppm arise from the defect coupled thiophene units and the peaks at 3.19 and 4.44 ppm arise from the head-to-tail coupled thiophene units.

Infrared Spectroscopic Studies

The FT-IR spectrum (Fig. 4) was recorded by casting the polymer film on a KBr plate. The presence of the NH groups in the polymer was confirmed from the broad band between 3200 and 3500 cm^{-1}. The presence of the ester carbonyl group

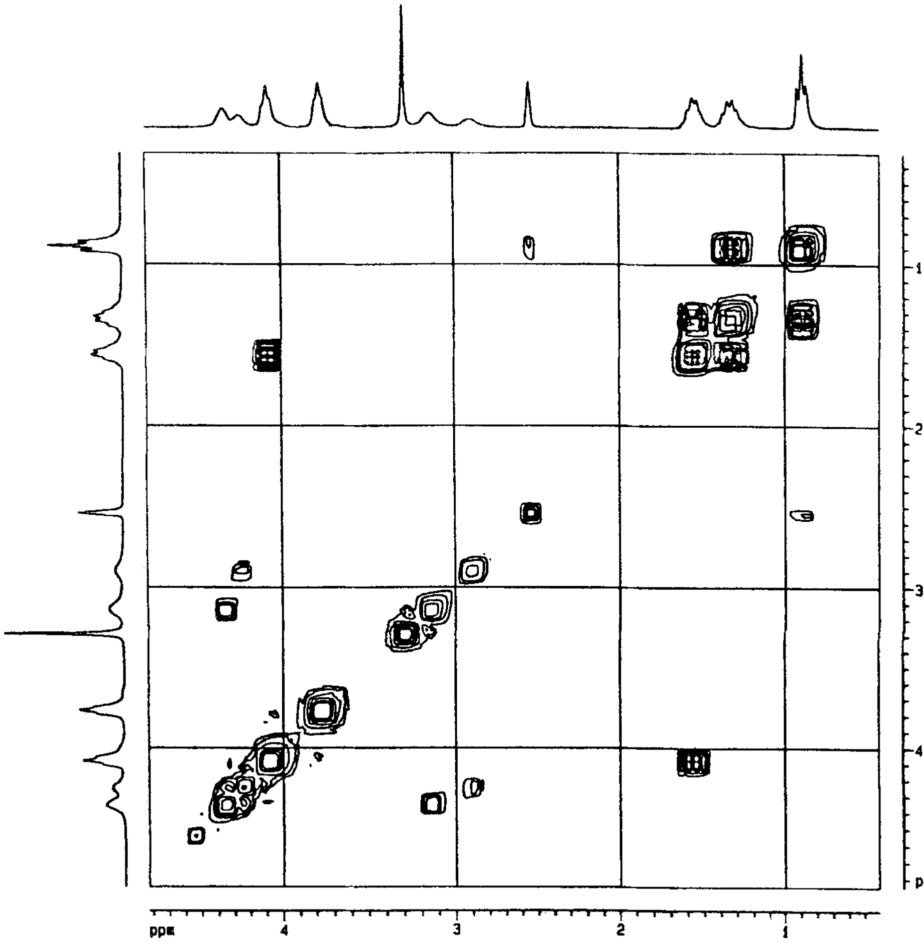


FIG. 3. ^{1}H-^{1}H 2D COSY NMR spectrum of PURET polymer.

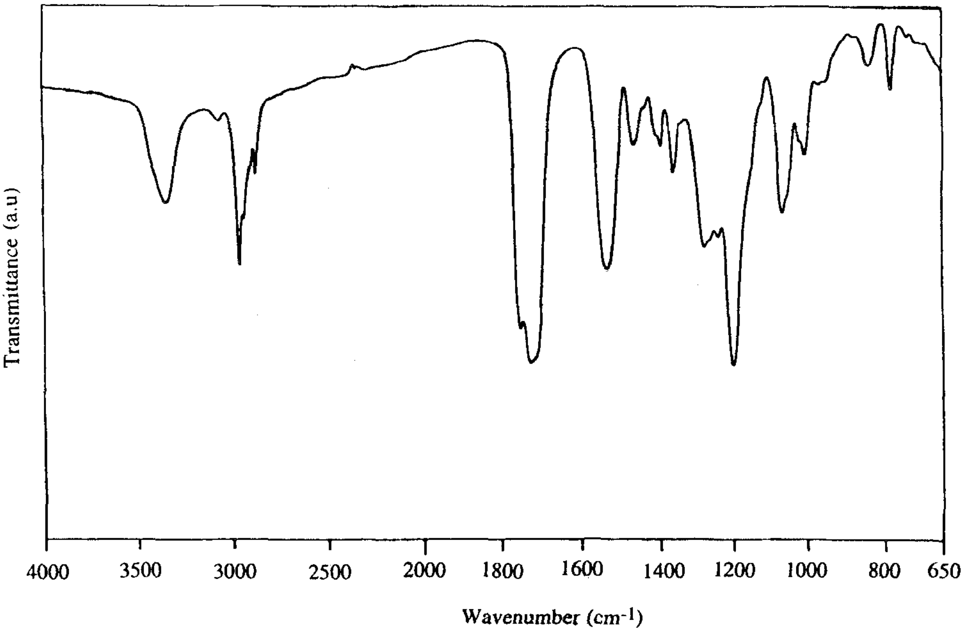


FIG. 4. FT-IR spectrum of PURET polymer.

was confirmed from the peak at 1749 cm^{-1}. The urethane carbonyl group exhibits two carbonyl peaks at 1724 and 1704 cm^{-1}, and these are attributed to the respective free and hydrogen bonded units [24]. The peak at 837 cm^{-1} is due to the bending vibration of the β-proton of the backbone, which is characteristic of the 2,3,5-trisubstituted thiophene ring [22], indicating the existence of a linear polymer chain.

Figure 5 (A and B) shows the spectral changes in the 3550–3150 cm^{-1} region upon heating and reheating after subsequent cooling to room temperature. The NH stretching band between 3200 and 3500 cm^{-1} shows a broad peak centered around 3340 cm^{-1} with a shoulder at ca. 3430 cm^{-1}. The bands at 3430 and 3340 cm^{-1} are assigned to the NH stretching modes of the free and hydrogen-bonded NH units of the urethane groups, respectively, at room temperature. This is consistent with the reported values for simple polyurethanes [23] and also for urethane-substituted polydiacetylenes [24]. The intensity of the peak at ca. 3340 cm^{-1} dramatically decreases with temperature, and the intensity of the shoulder at a higher wavenumber increases with the emergence of a new peak at ca. 3430 cm^{-1} at higher temperatures. The area under this peak decreases with temperature. The recovery of the area under this peak upon cooling, however, eliminates the possibility of degradation of the sample at higher temperatures. The stability of the polymer up to 220°C was also confirmed from TGA analysis of the sample. This type of decrease in the area of the peak with temperature was also observed in simple polyurethanes [23]. The change in the area of the peak with temperature is attributed to the difference in the absorption coefficient values between free and hydrogen-bonded NH groups, whose relative contributions are dependent on temperature. This observation clearly demonstrates the intermolecular nature of the hydrogen bonding between the urethane

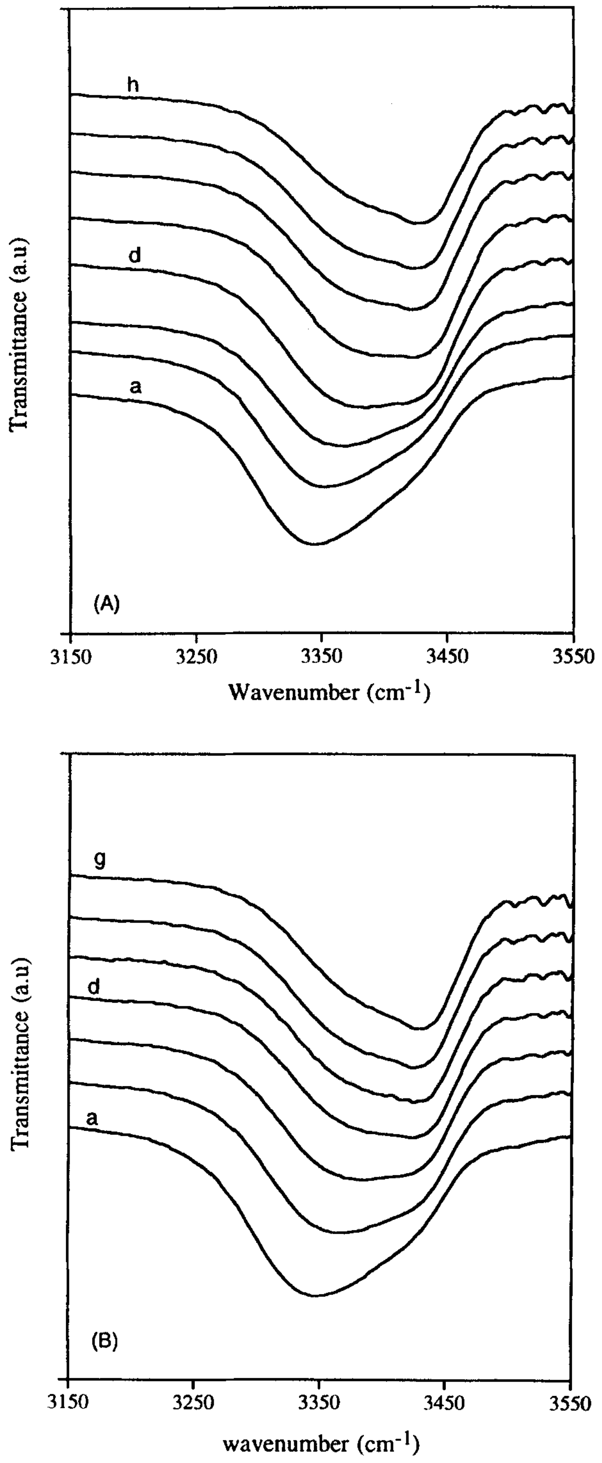


FIG. 5. FT-IR spectra from a cast film of PURET polymer in the 3150-3550 cm^{-1} region. (A) Recorded at various temperatures (from a to h): 30, 60, 90, 120, 136, 154, 163, and 180°C. (B) Recorded (after subsequent cooling to room temperature) at various temperatures (from a to g): 30, 80, 110, 136, 154, 163, and 182°C.

groups. However, the polymer showed two bands at ca. 3340 and 3430 cm^{-1} in chloroform, and their relative contribution did not change with the concentration of the polymer. This strongly suggests the formation of intramolecular hydrogen bonding in addition to intermolecular hydrogen bonding.

Spectral changes are also observed in the 1620 to 1820 cm^{-1} region of the spectra from the urethanyl-substituted polythiophene derivative due to the sensitivity of the urethane carbonyl groups on hydrogen bonds. Figure 6 (A and B) shows the spectral changes in this region upon heating and upon reheating after subsequent cooling to room temperature. The spectrum recorded at 30°C is equally dominated by the peak contributions at 1705 and 1724 cm^{-1}. The peaks at 1705, and 1724 cm^{-1} are assigned to the stretching vibrations of the hydrogen-bonded and free carbonyl groups of the urethane moiety, respectively. The peak at 1749 is assigned to the stretching vibration of the ester carbonyl. There is no change in this peak upon an increase in temperature. As the temperature increases, the urethane carbonyl peak narrows, centering around 1725 cm^{-1} at higher temperatures, with a reduction of the peak intensity at lower wavenumbers. This suggests that the hydrogen bonds are broken and the carbonyl groups are "free" at higher temperatures. Similar changes have been observed in other polyurethane macromolecules and are attributed to the large changes in the force constants between the free and hydrogen-bonded moieties [24]. All the spectra were recorded from the same sample. The spectral identities are recoverable upon cooling the sample back to room temperature (Fig. 5B), proving the re-formation of the hydrogen bonds on cooling.

Thermal Characterization

TGA studies at a heating rate of 20°C/min (Fig. 7) of the polymer PURET showed that this polymer is stable up to about 220°C under a nitrogen atmosphere. Most of the simple polyurethanes are also reported [24] to degrade at ca. 220°C, suggesting the degradation of the side chain at this temperature.

The DSC thermogram of the polymer at a heating rate of 10°C/min is shown in Fig. 8. While the poly(3-octylthiophene) shows a weak single melting endotherm [25] in the 130–150°C temperature range, with a very weak glass transition at ca. −10°C, the urethane functionalized polythiophene derivative PURET is amorphous with a well-defined glass transition temperature at 18°C. The polymer does not show any crystalline melting endotherms up to 220°C. The amorphous nature of the polymer was also confirmed from x-ray diffraction studies of the polymer. The polymer shows a broad amorphous halo in the region $2\theta = 20$ to 30°, with no crystalline peak at low angles. Poly(3-alkylthiophenes) are reported to exhibit crystalline structures with identification of alkyl chains. Thick sheets of polymer films with excellent optical quality were obtained by solution casting (with no scattering in the visible region). This type of solution processible, amorphous films is highly valuable in optical applications. The free standing films obtained are very flexible with excellent mechanical properties. This suggests that the rigid thiophene backbone is embedded in the highly disordered urethane side groups.

Electronic Absorption and Emission Spectroscopic Studies

The UV-Vis spectra of the PURET polymer in chloroform (spectrum 1) and in trifluoroacetic acid (spectrum 2) are presented in Fig. 9. The polymer showed an absorption maximum at ca. 430 nm in most of the organic solvents with a tail

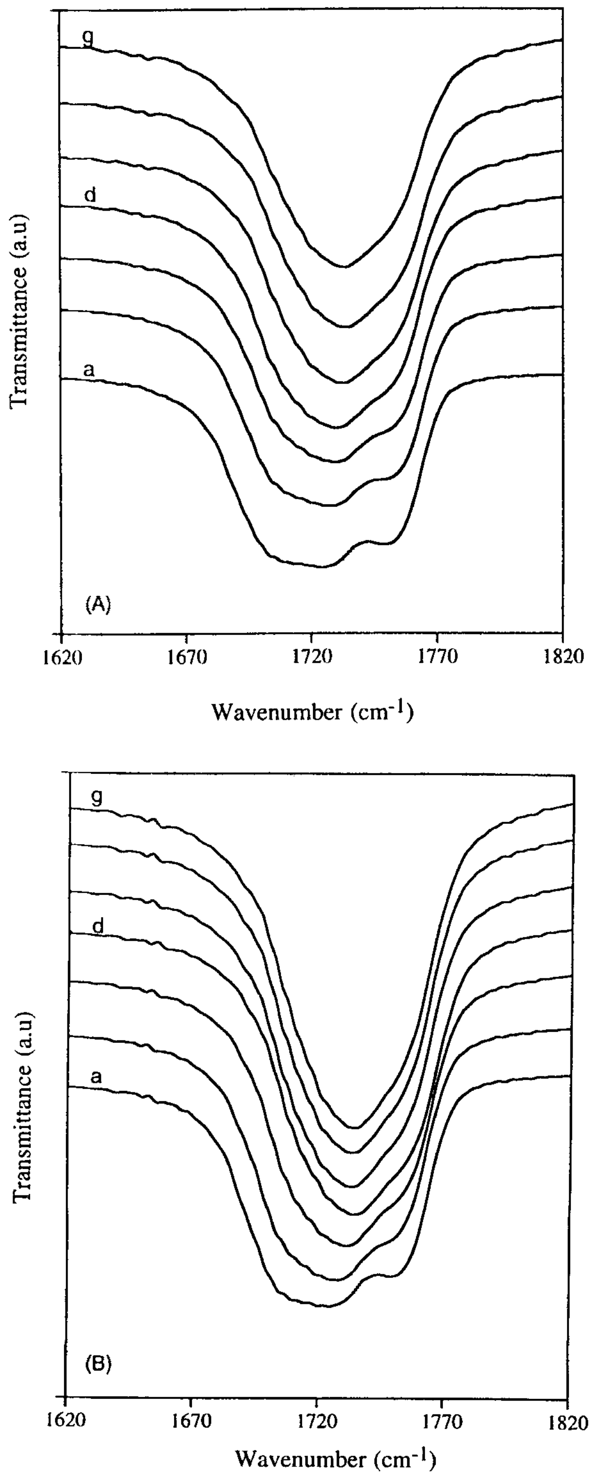


FIG. 6. FT-IR spectra from cast film of PURET polymer in the 1620–1820 cm^{-1} region. (A) Recorded at various temperatures (from a to g): 30, 60, 90, 120, 154, 163, and 180°C. (B) Recorded (after subsequent cooling to room temperature) at various temperatures (from a to g): 30, 80, 110, 136, 154, 163, and 182°C.

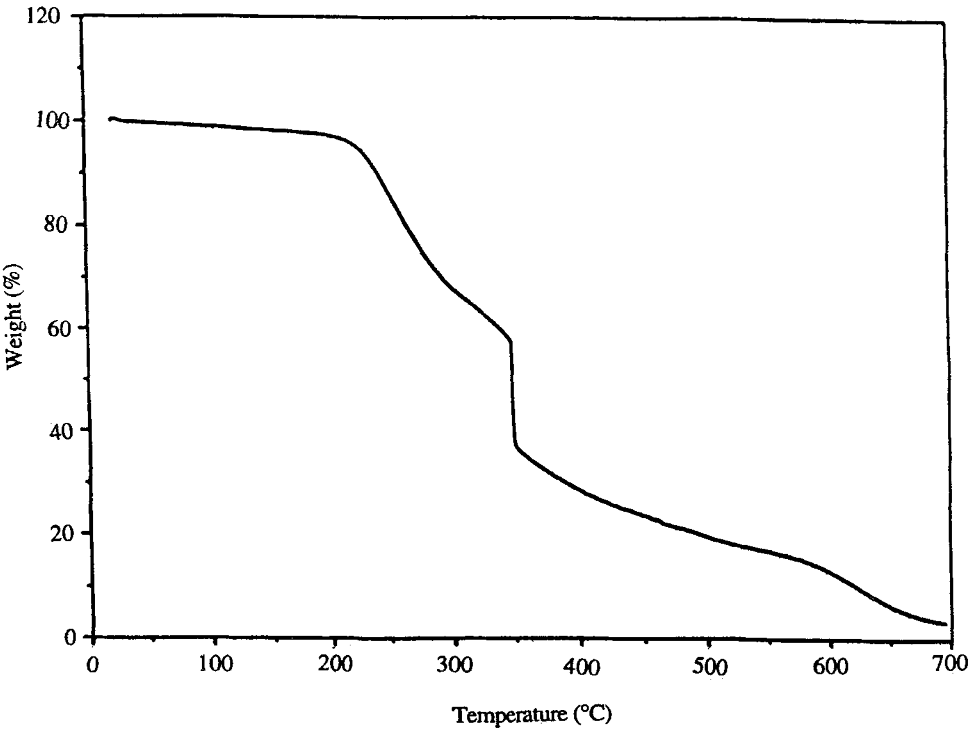


FIG. 7. TGA diagram of PURET polymer at a heating rate of 20°C/min.

extending up to 570 nm, indicating the presence of extended π-conjugation and multiple conjugation lengths along the main chain of the polymer. The polymer showed two broad absorption bands with peaks at 410 and 780 nm in trifluoroacetic acid. The broad band with a peak at 780 nm is suggested to be due to the oxidation band of the polymer. The oxidation of the oligothiophenes by TFA has been reported in the literature [26]. The methoxy derivatives of the terthiophene ($\lambda_{max} = 386$ nm) and quatrathiophene ($\lambda_{max} = 414$ nm) have been reported to exhibit additional broad bands with absorption maxima at 590 and 630 nm, respectively, when these polymers are treated with TFA.

To the best of our knowledge, this is the first report where a polythiophene derivative has been oxidized by the protonation of the backbone by TFA. The urethane side chains help in solubilizing the polymer in TFA. The oxidation peak disappears when the polymer is cast from TFA solution, with the formation of a broad band with an absorption maximum at 490 nm. This indicates that the polymer is reduced back to the neutral state upon elimination of the TFA. The polymer showed a absorption maximum at 480 nm when cast from other organic solvents.

The polymer was also characterized by the fluorescence spectroscopic technique. Figure 10 shows the emission spectra of the polymer in DMSO solution (spectrum A) and in the solid state (spectrum B). The solution spectrum was recorded by exciting at 465 nm and the solid spectrum was recorded by exciting at 484 nm. The DMSO solution of the PURET polymer gives a bright yellow fluorescence

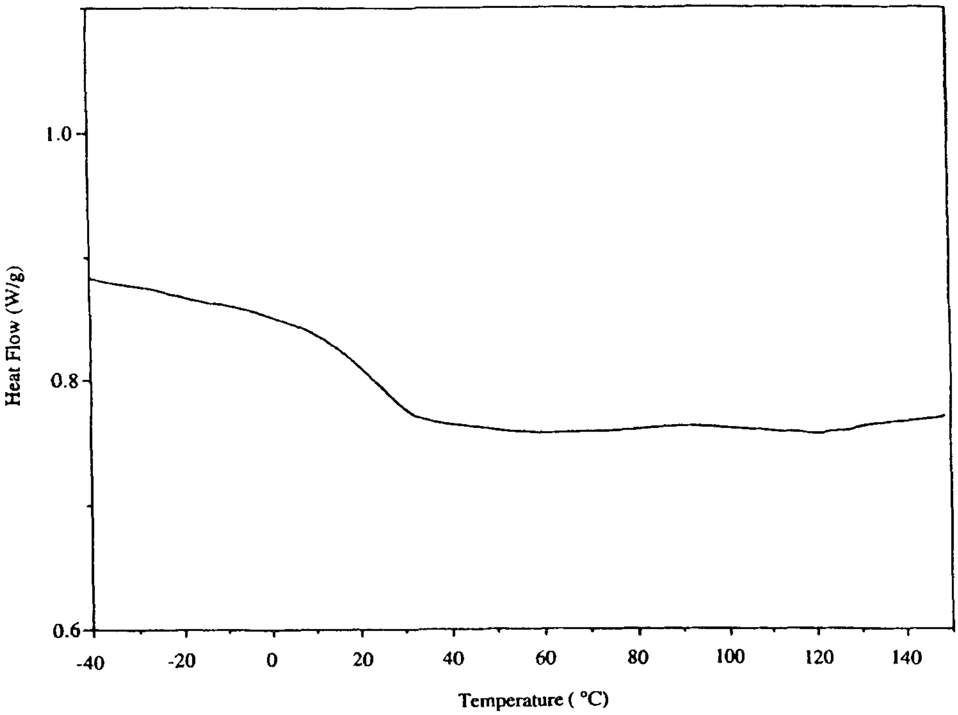


FIG. 8. DSC thermogram of PURET polymer at a heating rate of 10°C/min.

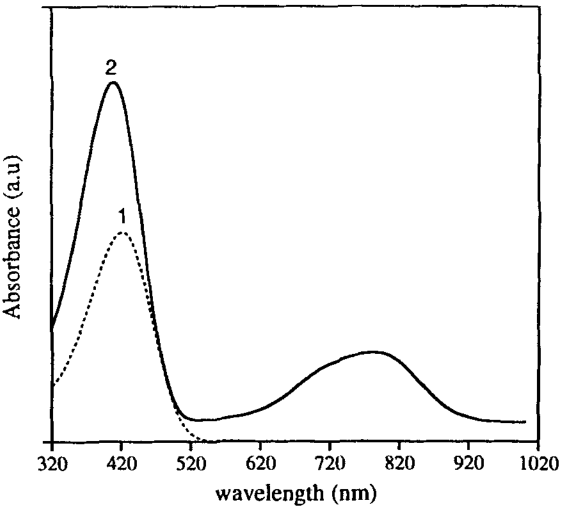


FIG. 9. UV-Vis spectra of PURET in (1) chloroform and (2) TFA.

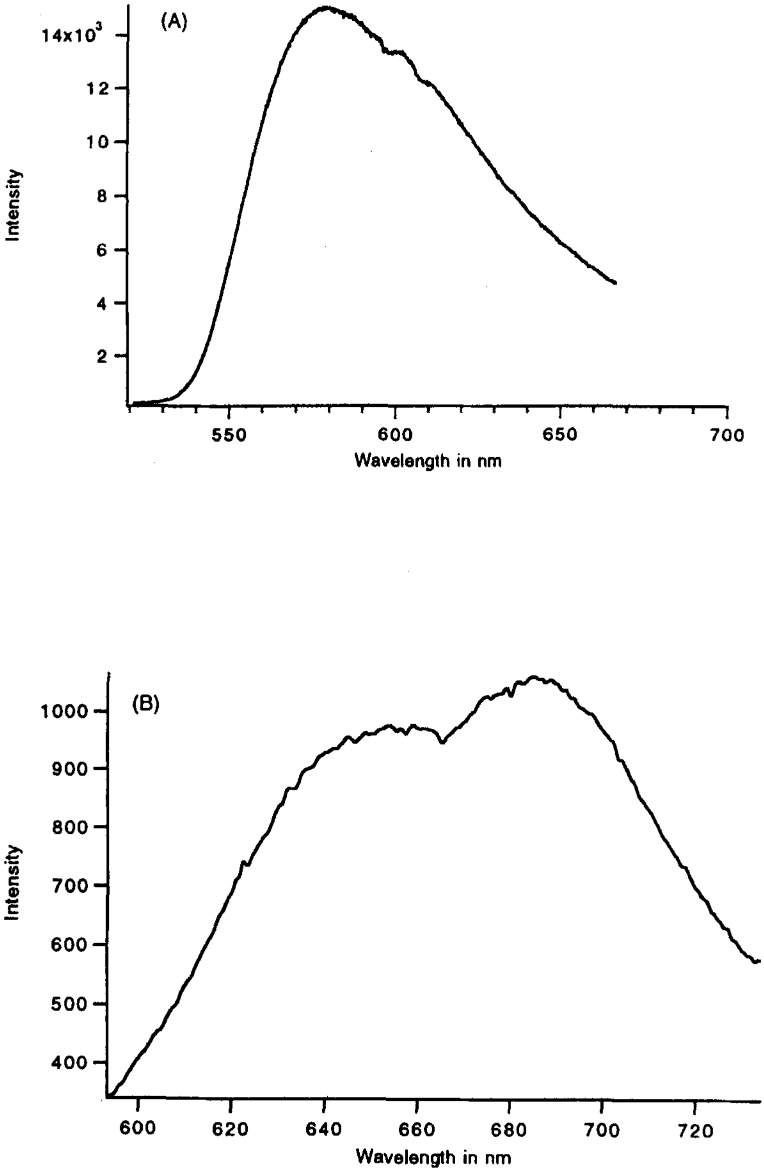


FIG. 10. Emission spectra of the PURET polymer in (A) DMSO (λ_{ex} = 465 nm) and (B) spin cast film (λ_{ex} = 484 nm).

with a maximum emission wavelength of 570 nm. This corresponds to the onset of the $\pi \rightarrow \pi^*$ transition of the electronic absorption spectrum. This is comparable with the regio-random polyalkylthiophenes made by the ferric chloride oxidation method [27]. The fluorescence yield, as expected, is lower for the solid sample compared to the solution. The emission peaks in the solid state are blue shifted compared to the regio-regular poly(3-alkylthiophenes), but are comparable to the poly(3-alkylthiophenes) with about 30% coupling defects. The 0.15 eV (approximate) spacing between the two peaks in the solid-state emission spectrum corresponds to the phonon modes of the vibronic stretching of the C=C bond [28].

The conductivities of iodine- or ferric chloride-doped PURET polymer films were measured in the order of 1 S/cm.

CONCLUSIONS

We have synthesized a new, solution processible polythiophene derivative (PURET) with a polar, hydrogen-bond-forming urethane group in the side chain. The polymer was highly soluble in a wide variety of solvents such as chloroform, tetrahydrofuran, dimethylsulfoxide, *N*-methylpyrrolidone, and trifluoroacetic acid among others. Polymer films with a good optical quality can be prepared by solution casting. The molecular weight of the polymer was strongly dependent on the polymerization time. The presence of extensive hydrogen bonding between the urethane moieties was demonstrated with variable temperature infrared spectroscopy. The ^{1}H-NMR spectrum suggests the presence of about 33% head-to-head coupling defects in the polymer. The DSC thermogram showed a glass transition at around 18°C, unlike poly(3-alkylthiophenes). The amorphous nature of the polymer was also confirmed by the x-ray diffraction technique. The PURET polymer is stable up to 220°C, which is comparable to simple polyurethanes. We are presently investigating the synthesis and nonlinear optical properties of the copolymer of this polar, hydrogen-bond-forming thiophene monomer with a NLO chromophore functionalized thiophene monomer. Results from these studies will be reported.

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