Synthesis and Characterization of Poly(aniline-*co*-*o*-anisidine): A Processable Conducting Copolymer

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ABSTRACT: An attempt has been made toward the chemical synthesis of poly(aniline-*co*-*o*-anisidine). It has been found that this conducting polymer is soluble in common organic solvents such as acetone, dimethylformamide (DMF), tetrahydrofuran (THF), and *N*-methylpyrrolidinone (NMP) at room temperature. The characterization of poly(aniline-*co*-*o*-anisidine) has been carried out using FTIR, UV–visible, DSC, and electrical conductivity measurements.

Introduction

Conducting polymers have recently attracted much attention.[1–12] Among the various conducting polymers, studies on polyaniline have led to phenomenal growth of literature.[6,9,11–17] One of the principal reasons for such an increased interest in polyaniline is its many technological applications such as in electronic displays,[2] electrochemical batteries,[18] biosensors,[19] and molecular electronics,[20] etc. However, the commercial exploitation of most of these applications based on polyaniline is closely linked with the ease of processibility[21] of this interesting conducting polymer. Accordingly, the processibility of polyaniline has been the subject of several investigations in the past few years. A large number of experimental techniques such as preparation of molecular composites,[13,14,16] preparation of soluble precursors of conducting polymers, vacuum evaporation, plasma polymerization, photochemical synthesis, and preparation by chemical means[11,12] in solution or in a gaseous state, etc., have been utilized to improve upon the processibility of conducting polymers.[21] It may be remarked that the chemical method of improving processibility has the added advantage of producing a conducting polymer in bulk.[9] We have therefore followed the chemical technique to improve upon the poor processibility of polyaniline by copolymerizing it with *o*-anisidine that has been known to be soluble in conventional organic solvents.

Another reason that has prompted us to undertake the present research is the reported observation that when aniline is electropolymerized with *o*-anisidine, the resulting material exhibits interesting electrochromic behavior. A switching time of 25 ms is obtained, while that of electropolymerized polyaniline was found to be 125 ms as reported earlier.[15] In view of these interesting results, we have conducted detailed investigations on chemically polymerized poly(aniline-*co*-*o*-anisidine). In this paper, we report the results of these studies carried out on poly(aniline-*co*-*o*-anisidine) using FTIR, UV–visible, differential scanning calorimetry, and electrical conductivity.

Experimental Section

(i) Synthesis. A mixture consisting of 6.6 mL of aniline (0.1 M) and 8.3 mL of *o*-anisidine (0.1 M) was dissolved in 150 mL of 1 M HCl. This solution was maintained at 0–5 °C and constantly stirred for about 1 h. To this solution was added drop by drop another solution prepared by dissolving 15 g of ammonium persulfate in distilled water. The reaction was continued for 4 h, after which a green precipitate was filtered and was first washed with 1 M HCl until the disappearance of the color of the filtrate. Subsequently, it was washed with methanol and with diethyl ether. The precipitate was dried over P_2O_5 for about 72 h. To get an undoped conducting polymer, the precipitate was treated with aqueous ammonia having a pH of 12. A similar procedure was followed to get both undoped polyaniline and poly(*o*-anisidine).

(ii) Characterization. The FTIR studies on each of the samples of poly(aniline-*co*-*o*-anisidine), polyaniline, and poly(*o*-anisidine) in their respective undoped states using KBr-pressed pellets have been conducted on a Nicolet FTIR (Model 510P) spectrometer. The spectroscopic measurements on each of such samples in the UV–visible region have been recorded on a Shimadzu Model UV 160A spectrophotometer. Thermal studies of undoped poly(aniline-*co*-*o*-anisidine) and also of both polyaniline and poly(*o*-anisidine) in their respective undoped states have been carried out on a Perkin-Elmer differential scanning calorimeter DSC-7. The differential scanning calorimeter has been calibrated using a number of samples such as indium, tin, and zinc, etc. The heating rate in each case has been maintained at 20 °C/min. The electrical conductivity measurements on both undoped and doped samples of poly(aniline-*co*-*o*-anisidine), polyaniline, and poly(*o*-anisidine) have been done using a two-probe technique.

Results and Discussion

Figure 1 shows the structures of aniline and *o*-anisidine and a schematic of various conducting polymers such as polyaniline, poly(*o*-anisidine), and poly(aniline-*co*-*o*-anisidine) synthesized in the present work.

FTIR spectroscopic measurements on various samples mentioned in the preceding section are shown in Figure 2. Curve a in Figure 2 exhibits the infrared spectrum of undoped poly(aniline-*co*-*o*-anisidine). This curve shows peaks at 3400, 2940, 1570, 1498, 1300, 1267, 1260, 1157, 1020, 950, and 840 cm^{-1}, respectively. This FTIR spectrum is similar to the one observed in the case of undoped polyaniline[22] (curve b). The absorption peaks observed at 1267 and 1020 cm^{-1} (curve a) have been associated with the presence of an *o*-methoxy group in this conducting copolymer. These vibration bands are also present in the FTIR spectrum of poly(*o*-anisidine) (curve c). However, the shift observed in the case of the *o*-methoxy group in the FTIR spectrum of poly(aniline-*co*-*o*-anisidine) indicates the presence of *o*-anisidine moieties in the polyaniline chains. To further confirm this result, an FTIR spectrum of a composite of polyaniline and poly(*o*-anisidine) prepared by physical mixing of the powders of these respective conducting polymers obtained by ball milling has been taken. The results are shown by curve d in Figure 2, wherein no significant shift in either of the vibration bands described in curve a of poly(aniline-*co*-*o*-anisidine) is seen. These observations suggest that the resulting structure of a conducting polymer perhaps contains chains having both units of aniline and *o*-anisidine.

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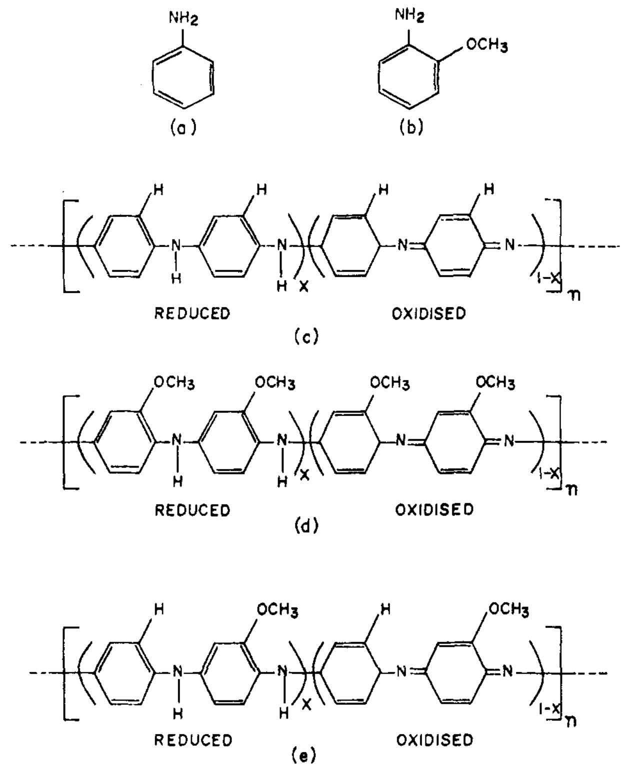

Figure 1. Structure of (a) aniline, (b) *o*-anisidine, (c) polyaniline, (d) poly(*o*-anisidine), and (e) a random copolymer poly(aniline-*co*-*o*-anisidine) for different oxidation states ($x = 1$, leucoemeraldine; $x = 0.75$, protoemeraldine; $x = 0.25$, nigraniline; $x = 0$, pernigraniline).

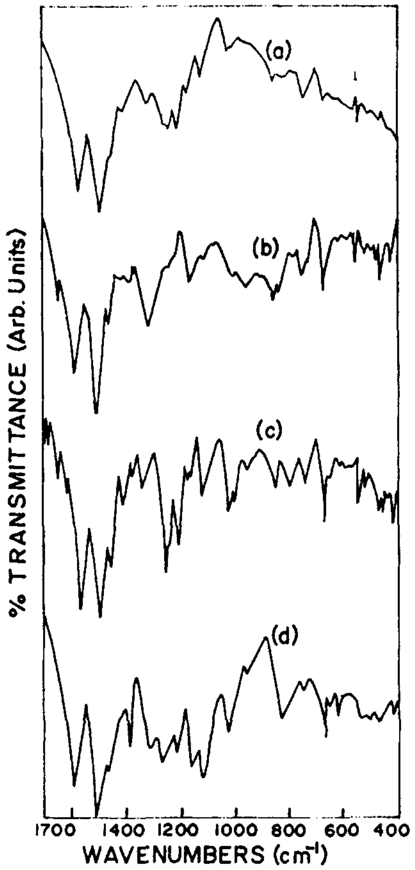

Figure 2. FTIR spectra of (a) poly(aniline-*co*-*o*-anisidine), (b) polyaniline, (c) poly(o-anisidine), and (d) a 1:1 composite of b and c in their respective undoped states.

Optical absorption measurements of poly(aniline-*co*-*o*-anisidine), polyaniline, poly(*o*-anisidine), and a 50/50 composite of polyaniline and poly(*o*-anisidine) in their respective undoped states have been conducted at room temperature in the UV-visible region. The results of these measurements are shown in Figure 3. The absorption spectrum (curve a) in Figure 3 obtained in the case of poly(aniline-*co*-*o*-anisidine) is similar to the one observed for undoped polyaniline (curve b). However, we find that there is a notable shift observed in the case of absorption peaks such as 329 and 625 nm attributed to π–π^* transition and n–π^* transition, respectively.[23,24] In order to further verify this important result, we have carried out optical absorption measurements in a 50/50 composite of undoped polyaniline and undoped poly(*o*-anisidine). Curve d obtained in the case of such a composite shows two absorption peaks at 323 and 624 nm, indicating a small shift of these peaks toward those observed in the case of undoped polyaniline (curve b). These results point out that *o*-anisidine moieties perhaps play a significant role toward the determination of the chain length of this conducting copolymer.

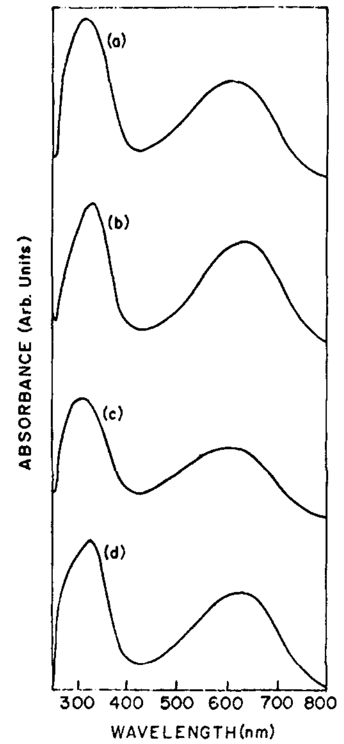

Figure 3. UV-visible spectra of (a) poly(aniline-*co*-*o*-anisidine), (b) polyaniline, (c) poly(*o*-anisidine), and (d) a 1:1 composite of b and c in their respective undoped states in NMP solution.

The results of differential scanning calorimetric experiments conducted at the rate of 20 °C/min on undoped samples of poly(aniline-*co*-*o*-anisidine), polyaniline, poly(*o*-anisidine), and a composite of undoped polyaniline and poly(*o*-anisidine) have been given in Figure 4. Curve a in Figure 4 shows the thermogram obtained in the case of poly(aniline-*co*-*o*-anisidine). We notice that an endothermic peak appears at 100 °C followed by a strong exothermic peak at 450 °C that indicates the degradation of this conducting polymer. The transition observed at 190 °C has been designated as the glass transition temperature of this conducting copolymer. Curve b in Figure 4 exhibits the thermogram obtained in the case of undoped polyaniline. The endothermic peak seen at 100 °C in this curve has been attributed to the evaporation of any residual water. The onset of glass transition in undoped polyaniline begins at 170 °C, and the degradation of the conducting polymer begins at 360 °C. Curve c (Figure 4) is the thermogram observed in the case of a sample of

Table I. Electrical Conductivity (in Undoped and Doped States), Glass Transition Temperature (T_g), Decomposition Temperature (T_D), and Solubility in Various Solvents Experimentally Determined for Poly(aniline-*co*-*o*-anisidine), Polyaniline, and Poly(*o*-anisidine)

material	room-temp conductivity (ohm^{-1} cm^{-1}) undoped	doped	T_g (°C)	T_D (°C)	solubility
poly(aniline-co-o-anisidine)	2.5×10^{-11}	1.2×10^{-2}	190	470	acetone, chloroform THF, DMF, DMSO, and NMP
polyaniline	5.8×10^{-11}	10	170	360	NMP, DMF, DMSO, and THF
poly(o-anisidine)	1.3×10^{-12}	7.0×10^{-4}	240	460	acetone, chloroform THF, DMF, DMSO, and NMP

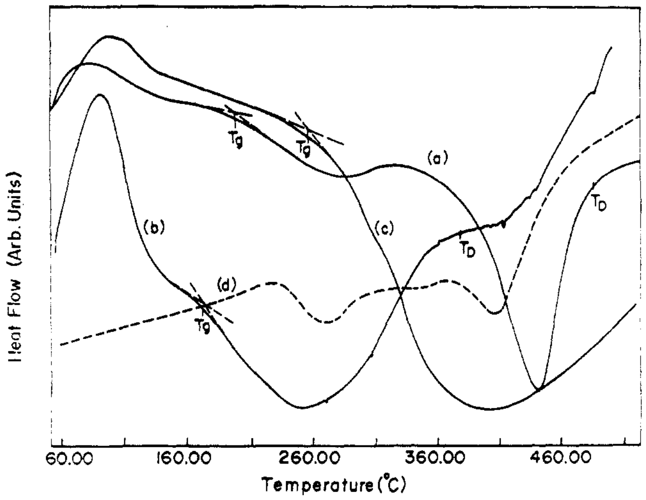

Figure 4. DSC thermograms obtained at a heating rate of 20 °C/min for (a) poly(aniline-*co*-*o*-anisidine), (b) polyaniline, (c) poly(*o*-anisidine), and (d) a 1:1 composite of b and c in their undoped states. T_g and T_D indicate the onset of glass transition and thermal degradation, respectively, of different conducting polymers.

undoped poly(*o*-anisidine). The glass transition temperature for this conducting polymer in its undoped state is 240 °C. Curve d in Figure 4 shows the thermogram obtained in case of the 50/50 composite of undoped polyaniline and undoped poly(*o*-anisidine). This thermogram exhibits two exothermic peaks at 260 and 390 °C that are characteristic of the presence of undoped polyaniline and undoped poly(*o*-anisidine), respectively. It is interesting to see that the thermogram (curve a) obtained in the case of poly(aniline-*co*-*o*-anisidine) is quite different from the one observed for that of a composite of polyaniline and poly(*o*-anisidine) in their respective undoped states. The absence of any apparent base-line drift in this thermogram (curve d) attributed to the glass transition phenomenon indicates that the compositional fluctuations play a key role toward the determination of the thermal behavior of this interesting composite.[25] These observations, however, further confirm that the chemical synthesis of a copolymer of undoped poly(aniline-*co*-*o*-anisidine) has occurred.

Room-temperature conductivity measurements on doped and undoped forms of poly(aniline-*co*-*o*-anisidine), polyaniline, and poly(*o*-anisidine) have been carried out, and the results are given in Table I along with other characteristics. It has been found that the electrical conductivity of poly(aniline-*co*-*o*-anisidine) is lower than that of polyaniline but is higher by 2 orders of magnitude than that of poly(*o*-anisidine). This result is due to the incorporation of the less conductive *o*-anisidine moieties into the polyaniline chain during the chemical synthesis of this conducting polymer. Furthermore, since the reactivity of *o*-anisidine is higher than that of aniline, this is likely to result in shorter chains in the poly(aniline-*co*-*o*-anisidine) copolymer probably due to formation of more reactive anisidinium ions compared to those of anilinium ions. This chemical reaction is likely to lead to a reduced conjugation length, resulting in the lower value of the electrical conductivity of poly(aniline-*co*-*o*-anisidine). Incidently, this observed behavior of the electrical conductivity of poly(aniline-*co*-*o*-anisidine) is in agreement with the reported value of the electrical conductivity measured for a random copolymer of methylaniline and aniline.[16] From these experimental results, it can be tentatively concluded that a random copolymer of aniline and *o*-anisidine has been synthesized (Figure 1c).

The solubility of poly(aniline-*co*-*o*-anisidine), polyaniline, and poly(*o*-anisidine) has also been determined at room temperature, and the results have been given in Table I. As this table indicates, poly(aniline-*co*-*o*-anisidine) is soluble in DMF, THF, chloroform, acetone, NMP, etc., at room temperature. However, among the various solvents, the solubility of undoped poly(aniline-*co*-*o*-anisidine) has been found to be best in NMP. In view of this interesting result, it has been possible to cast films of the desired size of poly(aniline-*co*-*o*-anisidine).

Conclusions

The synthesis of poly(aniline-*co*-*o*-anisidine) has been accomplished using a chemical method. FTIR, UV–visible, DSC, and electrical conductivity measurements have revealed that poly(aniline-*co*-*o*-anisidine) is a random copolymer.

The observed lower value of the electrical conductivity of poly(aniline-*co*-*o*-anisidine) has been explained in terms of the incorporation of *o*-anisidine moieties in polyaniline chains. The excellent solubility of undoped poly(aniline-*co*-*o*-anisidine) is an indication that this processable conducting polymer has enough scope for technological applications.

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Registry No. (Aniline)(anisidine) (copolymer), 126415-16-5.