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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Ertugrul Sahmetlioglu^{ab}; Ufuk Arikan^a; Levent Toppare^b; Huseyin Yuruk^a; Hasan Mart^a

^a Department of Chemistry, Nigde University, Nigde, Turkey ^b Department of Chemistry, Middle East Technical University, Ankara, Turkey

To cite this Article Sahmetlioglu, Ertugrul , Arikan, Ufuk , Toppare, Levent , Yuruk, Huseyin and Mart, Hasan(2006) 'Synthesis and Characterization of Conducting Graft Copolymers Based on Oligophenols', Journal of Macromolecular Science, Part A, 43: 10, 1523 – 1530

To link to this Article: DOI: 10.1080/10601320600896751

URL: <http://dx.doi.org/10.1080/10601320600896751>

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Synthesis and Characterization of Conducting Graft Copolymers Based on Oligophenols

ERTUGRUL SAHMETLIOGLU,^{1,2} UFUK ARIKAN,¹
LEVENT TOPPARE,² HUSEYIN YURUK,¹
AND HASAN MART¹

¹Department of Chemistry, Nigde University, Nigde, Turkey

²Department of Chemistry, Middle East Technical University, Ankara, Turkey

Oligo-2-aminophenol (OAF) was synthesized with oxidative polycondensation of 2-aminophenol and hydrogen peroxide in an aqueous alkaline medium at 80°C. Oligo-2-aminophenol with thiophene side groups (TOAF) was obtained by the reaction of OAF and thiophene-3-acetic acid. Graft copolymers of TOAF and pyrrole were synthesized by electrochemical polymerization in p-toluene sulfonic acid (PTSA)/water medium. Characterization of the graft copolymer (TOAF-g-Py), was carried out by combination of techniques including thermal gravimetry (TGA), cyclic voltametry, size-exclusion chromatography, ¹H-NMR and FTIR. The conductivities were measured by the four-probe technique.

Keywords graft copolymers, conducting polymers, electrochemical polymerization, oxidative polycondensation

Introduction

Polypyrrole is one of the most studied polymers, and it was first synthesized by electrochemical polymerization in 1968 (1). Polypyrrole has been considered as one of the most promising conducting polymers due to its high conductivity, thermal and environmental stabilities and the low oxidative potential of its monomer (2, 3). Electropolymerization has various favorable advantages, such as; the reactions occur at room temperature with controllable film thickness, and homogenous films can be obtained on the electrode surface (4). Poor mechanical specifications were improved by synthesizing graft copolymers with side groups such as pyrrole or thiophene (5, 6). Conducting polymers have received great interest due to their several applications in rechargeable batteries, electrochromic devices, and chemical sensors (7).

Oligomer synthesis via the oxidative polycondensation method has several advantages such as availability of the oxidant and protection of the functional groups (OH, CHO, etc). Oligophenol derivatives can be used for the synthesis of epoxy resins and block graft copolymers (8, 9).

Received April 2006; Accepted May 2006.

Address correspondence to Levent Toppare, Department of Chemistry, Middle East Technical University, 06531, Ankara, Turkey. Tel.: 00 90 312 2103251; Fax: 00 90 312 2101280; E-mail: toppare@metu.edu.tr

In the present work TOAF was synthesized by condensation of OAF with 3-thiophene acetic acid. The copolymer TOAF-g-PPy was synthesized via electrochemical polymerization in PTSA-water medium. The copolymers were characterized via Cyclic Voltammogram (CV), FTIR, TGA, and conductivity measurements.

Experimental

Materials

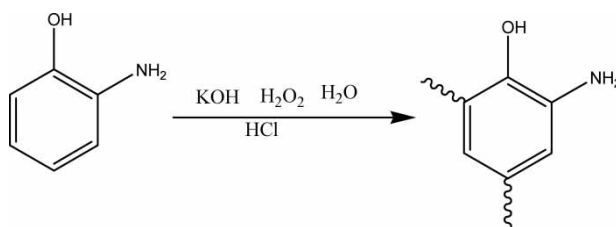
All chemicals used were analytical grade. Thiophene-3-acetic acid, 2-aminophenol, H_2O_2 , tetrahydrofuran, tetrabutylammonium tetrafluoroborate, sodiumdodecyl sulfate, p-toluene sulfonic acid were obtained from Aldrich. Chloroform, acetonitrile, KOH and HCl, were supplied by Merck Co. Pyrrole was purchased from Aldrich and distilled before use and stored at 4°C.

Instruments

The infrared spectra were obtained by using a Jasco FT/IR-300E. 1H -NMR spectra were recorded in DMSO- d_6 on a Bruker 250 MHz 1H -NMR. Thermal behavior of the materials were investigated with a DuPont 2000 Thermal Analyzer under nitrogen atmosphere with a scan rate of 10°C/min. Cyclic voltammetry experiments were performed under N_2 atmosphere and room temperature by using a Wenking POS 73 potentiostat. Molecular weights of oligomers were measured by gel permeation chromatography using Agilent 1100 R1. The solvent was tetrahydrofuran, and the flow rate at 30°C was 0.3 mL/min. Conductivity measurements were carried out with a four-probe technique.

Oxidative Polycondensation of 2-aminophenol with H_2O_2

Oligoaminophenol was synthesized via the oxidative polycondensation reaction of aminophenol (Scheme 1). Aminophenol (0.75 M) and KOH (0.75 M) were mixed in 10 mL of water and the mixture was placed in a 100 mL three-necked round-bottomed flask. The reaction temperature was 70°C. 31 mL of aqueous solution of H_2O_2 (30%) was slowly added to the reaction mixture. The reaction mixture was stirred at 85°C for 5 h, then cooled to room temperature, and then 0.75 M of HCl (37%) were added to the reaction mixture. The product was washed with hot water several times and dried at 95°C (8).



Scheme 1. Oligomer formation.

Synthesis of Oligo-2-aminophenols Containing Thiophene Side Groups

0.01 moles of oligo-2-aminophenol (OAF) and 0.015 moles of thiophene acetic acid were dissolved in tetrahydrofuran (THF) and stirred for 5 h at 80°C. The product was washed several times with water and dried under low pressure (Scheme 2).

Synthesis of Copolymer TOAF and Pyrrole (TOAF-g-Py)

Synthesis of copolymers was performed in a typical three electrode cell containing platinum foil working and counter electrodes and Ag/Ag⁺ (0.01 M) reference electrode by constant potential electrolysis at room temperature. The synthesis of copolymers was carried out by the electrochemical polymerization on TOAF coated electrodes. Polymerization reactions were carried out by applying +1.1 V for 80 min. Two types of electrolyses were used. In the first route, the solution contains 0.02 M pyrrole, 0.05 M PTSA, supporting electrolyte, and 10 mL water. The second one contains 0.02 M pyrrole, 0.05 M TBAFB, supporting electrolyte, and 10 mL acetonitrile.

As previously described, the anode was removed from the cell and kept in chloroform for 6 h to remove the ungrafted precursor polymer (Scheme 3).

Results and Discussion

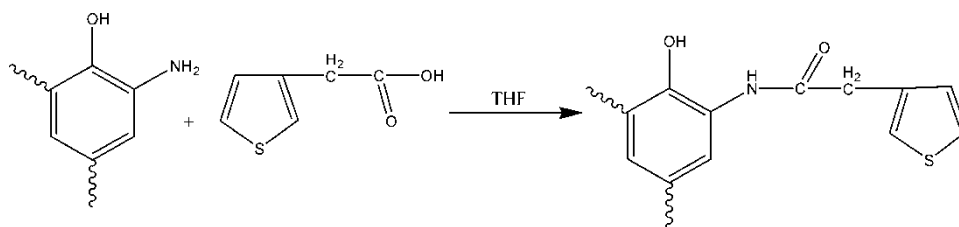
¹H-NMR Spectrometry

Aromatic protons of OAF in ¹H-NMR were observed between 6.80 and 7.30 ppm. The peaks at 4.90 and 4.20 ppm indicated NH₂ and OH protons. The peaks at 7.50–7.00 ppm belong to aromatic protons (Scheme 4) and the peak at 3.50 shows the methylene protons which are next to thiophene. Hydroxyl protons and N-H of Schiff base gave peaks at 4.20 and 8.00 ppm respectively (Figure 1).

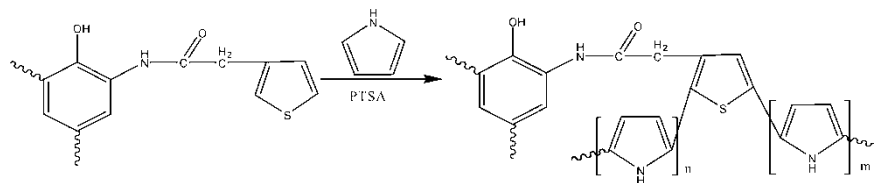
FTIR Spectrometry

The FTIR spectrum of OAF (Figure 2) shows the peaks for the –NH₂ stretching at 3400–3200 cm⁻¹, –OH stretching at 3400 cm⁻¹, C-H bending at 3050 cm⁻¹ and C=C stretching at 1550 cm⁻¹.

In the FTIR spectrum of TOAF (Figure 3), the peak observed at 3400 cm⁻¹ belongs to the NH₂ group. The peaks at 3062 and 1290 cm⁻¹ belong to aromatic C-H bending and C-N, respectively. The peaks at 1500 cm⁻¹ and 1350 cm⁻¹ occur from C=C bending, the broad absorption centered at 1722 cm⁻¹ is attributed to carbonyl groups of both remaining acetyl moieties and newly formed acetyl thienyl ones.



Scheme 2. Synthesis of Oligo-2-aminophenols containing thiophene side groups.



Scheme 3. Synthesis of copolymers of oligo-2-aminophenol with thiophene side groups and pyrrole (TOAF-g-Py).

The FTIR spectrum of p-toluene sulfonic acid (PTSA) doped TOAF/PPy (Figure 4) reveals peaks at 1480, 3400, 3050 and 1550 cm^{-1} due to N-H, C-H, and C=C stretchings, respectively which are characteristics to pyrrole. The characteristic peak for carbonyl in TOAF is observed at 1722 cm^{-1} . These results prove that the polymerization of pyrrole through TOAF chain has occurred.

Thermal Analyses

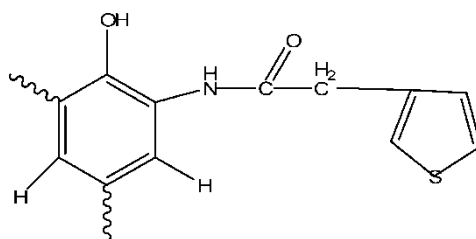
TGA of TOAF-g-Py (PTSA doped) contains several endothermic transitions at 111°C, 330°C, and 493°C (Figure 5). The first one is due to the removal of the solvent from the polymer matrix, the second transition is attributed to the removal of the dopant anions and the third one represents the decomposition of the sample.

Cyclic Voltammetry

Cyclic voltammetry experiments were performed in a acetonitrile-TBAFB, solvent-electrolyte couple. The cyclic voltammogram at Figures 6(a) and 6(b) represent PPy and TOAF-g-Py, respectively. In the cyclic voltammogram of pyrrole, a redox peak, which revealed increasing height with increasing scan number, was observed at 0.53 V (Figure 6a). However, the redox peak of the copolymer shifted to 0.57 V. The increment of current increase for PPy and the copolymer were different when the voltammograms of pure PPy and TOAF-g-PPy are compared. These results indicate that synthesis of graft copolymer of oligo-2-aminophenol with thiophene side groups and pyrrole was achieved.

SEC Measurements

The number average molecular weight, weight average molecular weight and polydispersity index values of oligoaminophenol were found to be 307 g/mol, 308 g/mol and 1.005,



Scheme 4. Oligo-2-aminophenol with thiophene side groups.

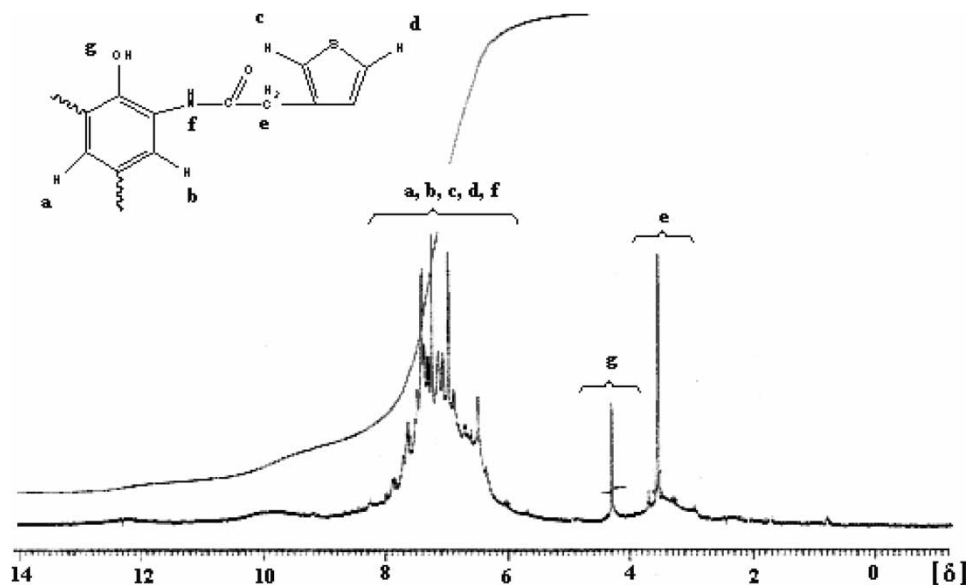


Figure 1. ¹H NMR spectrum of OAF.

respectively. The number average molecular weight, weight average molecular weight and polydispersity index values of TOAF were 539 g/mol, 630 g/mol and 1.17, respectively. Therefore, as it is seen, the different index values of oligoaminophenol prove that the reaction of oligoaminophenol with thiophene acetic acid took place.

Conductivity Measurements

Conductivity measurements were carried out by using the standard four-probe technique. The conductivity of the electrode side of TOAF/PPy doped with PTSA was 4.1 S/cm.

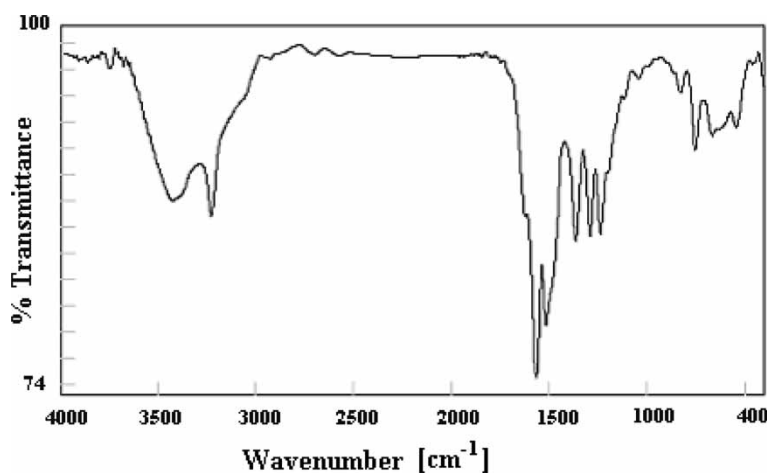


Figure 2. FTIR spectrum of OAF.

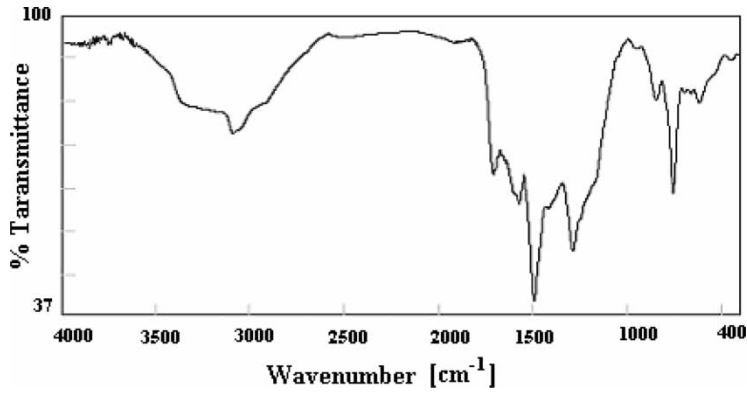


Figure 3. The FTIR spectra of TOAF.

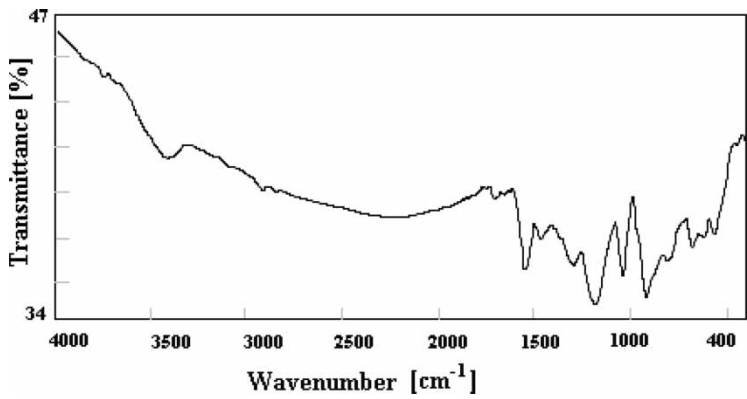


Figure 4. The FTIR spectra of TOAF/PPy (PTSA doped).

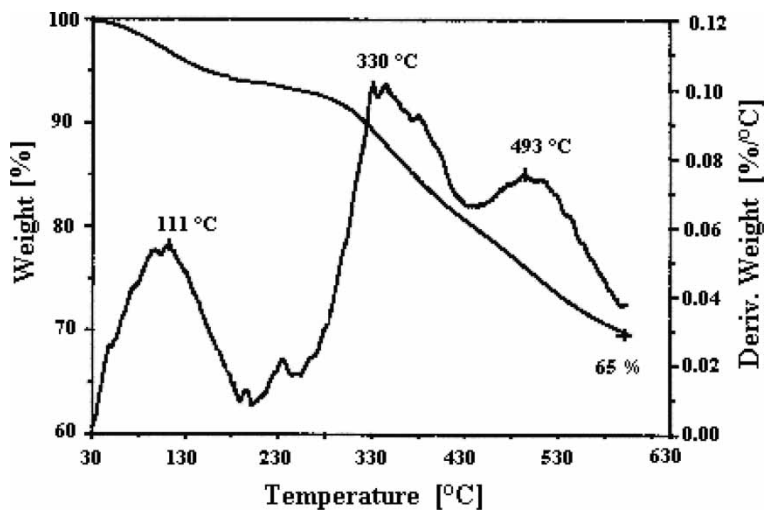


Figure 5. The TGA for TOAF/PPy (PTSA doped).

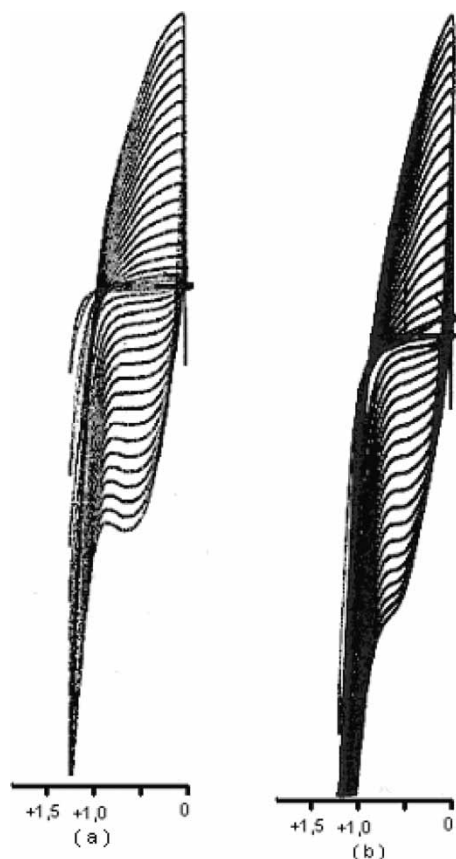


Figure 6. Cyclic voltammograms for PPy (a) and TOAF/PPy (b).

The conductivity of the solution side of the TOAF/PPy doped with PTSA was 4.5 S/cm. The conductivities of both the electrode and solution sides were also in the same order of magnitude, which reveals the homogeneity of the films.

Conclusions

The syntheses and characterization of TOAF, as well as its copolymers with Py via $^1\text{H-NMR}$, CV, size-exclusion chromatography, FTIR, DSC and conductivity measurements were achieved. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index values of TOAF-g-Py were found to be 539 g/mol, 630 g/mol and 1.17, respectively. PTSA doped graft copolymer of TOAF-g-Py was also synthesized and characterized with similar methods. The conductivity measurements of the electrode side and solution side of TOAF/PPy doped with PTSA were 4.1 and 4.5 S/cm, respectively.

Acknowledgements

Authors are grateful for the TUBITAK-104M406 grant.

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