

Iodine Doping of Poly(3-undecylbithiophene) and Its Composites with Polystyrene Using Supercritical Carbon Dioxide

Kimberly F. Abbett,¹ Aryn S. Teja,¹ Janusz Kowalik,² Laren Tolbert²

¹School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

²School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received 10 April 2003; accepted 4 May 2003

ABSTRACT: Partially doped conductive poly(3-undecylbithiophene) and its composites with porous, crosslinked polystyrene were chemically doped with iodine using supercritical carbon dioxide to transport iodine to the conductive regions of the composite. The amount of iodine incorporated into the composite increased from 9.3 wt % at ambient conditions without carbon dioxide to 21.4 wt % in the presence of supercritical carbon dioxide. The conductivity of

the composite increased by up to two orders of magnitude with iodine doping using supercritical carbon dioxide. The highest conductivity was obtained in samples treated at moderate temperatures and pressures (313 K and 20.7 MPa). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3876–3881, 2003

Key words: composites; conducting polymers; chemical doping; morphology; supercritical carbon dioxide

INTRODUCTION

The semiconductor band structure of conductive polymers such as polypyrrole or polybithiophene permits electron removal by oxidation, leading to a positively charged polymer and an associated anion. These charges are generally strongly delocalized and result in the conductive properties of the resultant polymer.¹ Oxidation of the polymer requires the incorporation of oxidants (dopants) such as Cl^- , I_3^- , ClO_4^- , and CF_3SO_3^- into the structure during synthesis. However, undoped or partially doped polymers may also be doped after synthesis by chemical, electrochemical, or other means.¹ In chemical doping of partially doped polymers, a solution containing the dopant is contacted with the conductive polymer, leading to partitioning of the dopant between the solvent and the polymer phases. However, the solvent must be removed from the polymer after doping. Moreover, the doping rate and partitioning of the dopant are difficult to control when there is a liquid solvent present.² Doping without a solvent, or using a solvent that can easily be removed, is therefore of considerable interest in the development of practical applications of conductive polymers.

To create practical devices, the mechanical properties of conductive polymers must generally be improved by forming blends or composites with an insulating polymer or with an insulating matrix.³ This is done either by dispersing the conductive polymer into the host polymer matrix or by *in situ* polymerization of the conductive polymer within the insulating matrix. As an example of the latter, conducting polymers have been grown in the pores of templates such as zeolites,^{4,5} controlled pore size membranes,^{6,7} and synthetic opals.⁸ The template structure of the host allows interconnected networks of conducting polymer to be assembled and facilitates improved order at the molecular level that leads to enhanced electrical conductivity.^{9,10} However, a drawback of *in situ* polymerization inside a host matrix is that organic solvents are generally used to transport the oxidant and/or the monomer into the pores of the host, resulting in generation of volatile organic compounds and environmental problems.

In the present work, the chemical doping of partially doped poly(3-undecylbithiophene) (P3UBT) and its composites with porous, crosslinked polystyrene (PS) was studied using supercritical carbon dioxide to transport the dopant (iodine) to the pores of the host polymer. The porous host (PS) was synthesized by a method that leads to a structure with uniform pores.¹⁰ Furthermore, we previously showed¹¹ that a P3UBT/PS composite can be prepared by *in situ* polymerization of 3-undecylbithiophene (3UBT) using supercritical carbon dioxide as the solvent and ferric triflate as the oxidant. Conductive composites of P3UBT/PS with a conductivity of 10^{-4} S/cm were

Correspondence to: A. Teja.

Contract grant sponsor: Office of Naval Research; contract grant number: N00014-95-1-1116.

Contract grant sponsor: U.S. Department of Energy.

obtained in these studies. In the present work, the additional doping of these composites by iodine was studied as a function of carbon dioxide pressure and temperature. Supercritical CO₂ has received considerable attention in the literature¹² as a solvent/carrier for deposition and impregnation because it offers high mass transport rates, is easily removed by depressurization, and allows *in situ* removal of unreacted monomer and other impurities. Its solvent power can be tuned continuously by changing the pressure and temperature. Supercritical CO₂ is also known to swell many polymers, which facilitates mass transport and deposition.^{13,14} Moreover, iodine has appreciable solubility in supercritical CO₂,¹⁵ so that significant quantities can be transported to the host matrix. The effect of CO₂ pressure and temperature to "tune" the amount of iodine and hence the conductivity was also examined.

EXPERIMENTAL

Materials

The monomer 3-undecylbithiophene (3UBT) and the oxidant ferric triflate were synthesized according to procedures described in the literature.^{10,11} Coleman grade CO₂ (99.9% purity) was purchased from Air Products (Bethlehem, PA) and used as received. Iodine was obtained from Aldrich (Milwaukee, WI) with a stated purity of 99.8% and also used as received. Porous, crosslinked polystyrene (PS) was prepared according to the procedure described by Park and Ruckenstein.¹⁰ These authors have shown that their procedure yields a polymer with uniform pores of about 10 μm. Furthermore, we previously showed¹⁶ that the porous structure of PS prepared in this manner allows supercritical CO₂ to diffuse rapidly through the polymer without appreciable swelling at 313 K and 10.5 MPa.

Composite preparation

A simple two-step batch process was used for the *in situ* polymerization of 3UBT in PS at 313 K and 10.5 MPa. In the first step, the host polymer and ferric triflate were placed in separate vials in a high-pressure Paar reactor, and the reactor was pressurized with carbon dioxide until a pressure of 10.5 MPa was attained at 313 K. These conditions were maintained for a length of time necessary for maximum uptake of CO₂ (determined in separate experiments according to procedures described elsewhere¹⁶). In the second step, the oxidant-containing host polymer was placed in contact with a mixture of CO₂ and monomer (3UBT) until a maximum was reached in the uptake of CO₂ into the host polymer matrix. The polymerization of 3UBT occurred inside the

oxidant-containing pores of the polymer host. The vessel was then quickly depressurized, and the host substrate weighed to obtain the mass gain attributed to the synthesized P3UBT. The actual amount of P3UBT was subsequently determined by elemental analysis. The composite was characterized using an optical microscope, by elemental analysis, and by UV-vis spectroscopy. Finally, the electrical conductivity of the sample was measured with a probe consisting of four parallel copper wires pressed onto the composite sample. A constant current was supplied through the outer wires of the probe and the voltage drop across the inner wires was measured to obtain the resistivity of the material. The measurements were repeated at various positions of the probe and values of the resistivity were averaged.

Doping experiments

Doping of P3UBT

A 1-cm² film of the polymer was cast from its THF solution and placed in a glass container, and the film was connected to a four-point probe for electrical conductivity measurements. A known mass (3 g) of iodine was then placed in the container, and the container was sealed to allow iodine to diffuse into the polymer under its own vapor pressure at 313 K. The voltage and current through the probes were measured until the resistivity attained a steady value.

Ambient doping of the composite

A 1-cm² film of the P3UBT/PS composite and 3 g of iodine, separated by glass beads, were placed in a glass container maintained at 313 K and 0.1 MPa. The glass beads ensured that transfer of iodine to the film was solely by diffusion. Diffusion time was measured with a stopwatch, starting at the instant when the polymer film was placed in the container. The sample was removed from the container at various times, and any surface deposits of iodine were quickly dusted off. The sample was then transferred to a Mettler (Greifensee, Switzerland) AE163 balance where its mass gain (attributed to iodine) was measured to ±0.0001 g. Mass gain and time data were recorded until no changes in mass could be observed. The electrical conductivity of the film was then measured with a four-point probe and recorded. The conductivity measurements were repeated at several positions of the probes on the film, and averaged.

Supercritical doping

The amount of iodine transferred from a supercritical phase to a 1-cm² film of the conductive composite was obtained by a series of absorption experiments. The

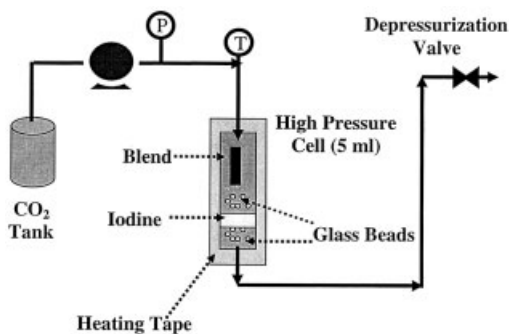


Figure 1 Apparatus for supercritical doping experiments.

apparatus used in the experiments is shown in Figure 1. The polymer film and 3 g of iodine, again separated by glass beads, were loaded into a 5-mL pressure vessel (Thar Designs, Pittsburgh, PA) and the vessel was pressurized by the addition of CO₂. After the pressure reached its specified value, steady-state conditions (temperature and pressure) were maintained for a specified time interval. At the end of this time interval, the vessel was depressurized quickly, any surface deposits of iodine quickly dusted off, and the host polymer transferred to a Mettler AE163 balance. Here, the initial mass gain and subsequent loss were monitored to ± 0.0001 g. Several experiments (conducted over different time periods) were performed to obtain an iodine uptake curve at the specified conditions of temperature and pressure. Finally, the experiments were repeated at several temperatures and pressures.

RESULTS AND DISCUSSION

Iodine doping of P3UBT

The conductivity of pure P3UBT attributed to iodine doping is plotted in Figure 2 as a function of time. The intrinsic conductivity of the polymer (at $t = 0$) was found to be 10^{-8} S/cm, which is also the conductivity of P3UBT reported by Kowalik et al.¹⁷ The conductiv-

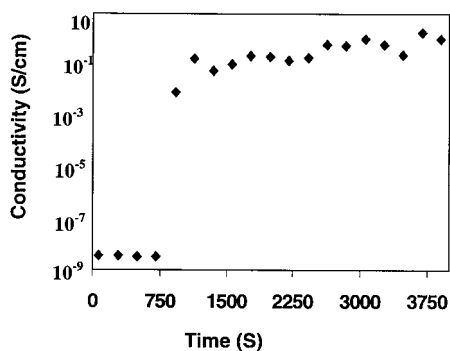


Figure 2 Conductivity as a function of time during iodine doping of P3UBT at ambient conditions.

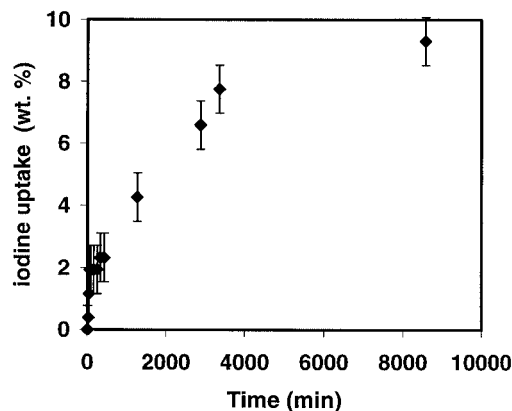


Figure 3 Iodine uptake as a function of time for a P3UBT/PS composite exposed to iodine vapors at 313 K and 0.1 MPa.

ity increased to about 1 S/cm after iodine doping for about 10 min. Similar results were also reported by Kowalik et al.¹⁷ for P3UBT synthesized in nitrobenzene. The P3UBT samples synthesized in nitrobenzene and those synthesized in supercritical CO₂ used in this work have been shown¹¹ to have similar molecular weights, structures, and effective conjugations.

Ambient doping of P3UBT/PS composites

Conducting composites of P3UBT/PS were prepared at 10.5 MPa and 313 K and their conductivity was measured. The value obtained, 2.4×10^{-6} S/cm, is higher than that of pure P3UBT synthesized at the same conditions, lending support to the hypothesis that synthesis of conducting polymers in a template leads to improved order at the molecular level and hence higher conductivity.^{9,10} (It should be added, however, that our pure P3UBT sample did not contain any excess ferric triflate, whereas the composite con-

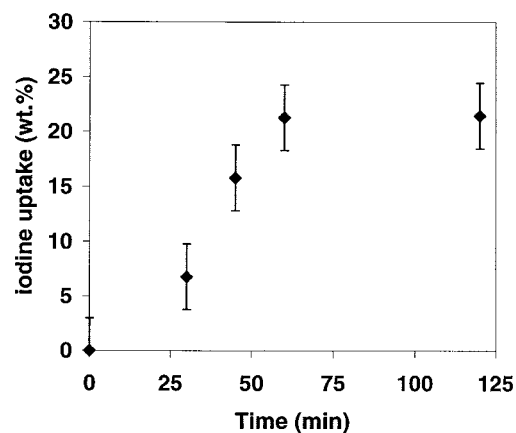


Figure 4 Iodine uptake of a P3UBT/PS composite at 10.5 MPa and 313 K.

TABLE I
Properties of Iodine-Doped P3UBT/PS Composites

| Doping conditions | Time (min) | Iodine content of composite (wt %) | Initial conductivity (S/cm) | Final conductivity (S/cm) |
|----------------------------------|------------|------------------------------------|-----------------------------|---------------------------|
| 298 K, 0.1 MPa | 8500 | 9.3 | 2.4×10^{-6} | 1.1×10^{-5} |
| 313 K, 10.5 MPa, CO ₂ | 60 | 21.4 | 2.4×10^{-6} | 1.2×10^{-4} |

tained appreciable amounts of ferric triflate.¹¹) The results of ambient doping of P3UBT/PS composite films are shown in Figure 3. The uptake of iodine after about 8500 min was about 9.3 wt %, and the conductivity of the film increased from its initial value of 2.4×10^{-6} S/cm to 1.1×10^{-5} S/cm after iodine treatment. The time taken to reach a steady-state value in iodine uptake by the composite, however, was several orders of magnitude higher than the time taken for iodine uptake by P3UBT, because iodine had to reach regions of P3UBT the composite. Furthermore, the partial pressure of iodine is quite low (0.00014 MPa at 313 K²⁰), resulting in the partitioning of only a modest amount of iodine.

Supercritical doping

The results of supercritical doping at 10.5 MPa and 313 K are shown in Figure 4 where the amount of iodine uptake is plotted as a function of time. The maximum amount of iodine uptake was 21.3 wt % after 60 min. The higher pressure leads to an increase in iodine fugacity and therefore iodine uptake by the composite. In addition, the time needed for maximum mass gain is much shorter because of the increase in diffusion coefficient of supercritical CO₂.¹⁶ Both these effects lead to two orders of magnitude increase in conductivity from an initial value of 2.4×10^{-6} S/cm to a final value of 1.2×10^{-4} S/cm (Table I).

Effect of temperature and pressure

Supercritical doping was also investigated at several temperatures and pressures. Doping experiments

were performed for 60 min at 313 K and pressures of 10.5, 20.7, and 34.5 MPa; and at 10.5 MPa and temperatures of 363 and 413 K. Conductivities of the samples were measured at the end of each experiment with a four-point probe. The results are summarized in Table II. Initial conductivity of the film was 2.4×10^{-6} S/cm in all cases. Final conductivities of the samples doped at 313 K and 10.5 MPa, and at 363 K and 10.5 MPa, were 1.2×10^{-4} S/cm in each case. The conductivities were also uniform throughout the samples, with the standard deviation being on the order of 10^{-5} S/cm. The conductivity of the film doped at 413 K and 10.5 MPa did not increase from its initial value, probably because of a loss in conjugation resulting from the high temperature. This can lead to lower electrical conductivity, as discussed by Pei et al.¹⁸ In addition, the experimental temperature (413 K) was higher than the melting temperature of iodine (387 K), thus allowing iodine to condense as a liquid on the surface of the film. Therefore, the iodine uptake measured at this temperature is not reliable and is not reported in Table II. A sample doped at 313 K and 34.5 MPa also exhibited a negligible increase in conductivity (4.9×10^{-6} S/cm), probably as a result of the limited iodine uptake in this experiment.

The iodine uptake by each sample was measured by weighing the sample before and after each doping experiment. Results are shown in Table II. The samples doped at 313 K and 10.5 MPa, and at 363 K and 10.5 MPa, exhibited the same increase in conductivity and also the same mass gain of iodine (about 21%). On the other hand, the sample doped at 313 K and 20.7 MPa showed the highest increase in conductivity (2.4×10^{-3} S/cm) and a 16 wt % uptake of iodine. More-

TABLE II
Properties of Iodine-Doped P3UBT/PS Composites Using CO₂

| Pressure (MPa) | Temperature (K) | Iodine solubility ^a (mol fraction $\times 10^4$) | Iodine content (wt %) | Average conductivity (S/cm) | Standard deviation (S/cm) |
|----------------|-----------------|--|-----------------------|-----------------------------|---------------------------|
| 10.5 | 313 | 1.96 | 21.4 | 1.2×10^{-4} | 7.4×10^{-5} |
| 10.5 | 363 | 4.48 | 21.3 | 1.1×10^{-4} | 3.6×10^{-5} |
| 10.5 | 413 | 38.6 | — | 5.4×10^{-6} | 4.6×10^{-7} |
| 20.7 | 313 | 2.66 | 16.0 | 2.4×10^{-3} | 4.5×10^{-4} |
| 34.5 | 313 | 2.53 | 3.7 | 4.9×10^{-6} | 4.1×10^{-6} |

^a Interpolated from the data of Fang et al.¹⁷

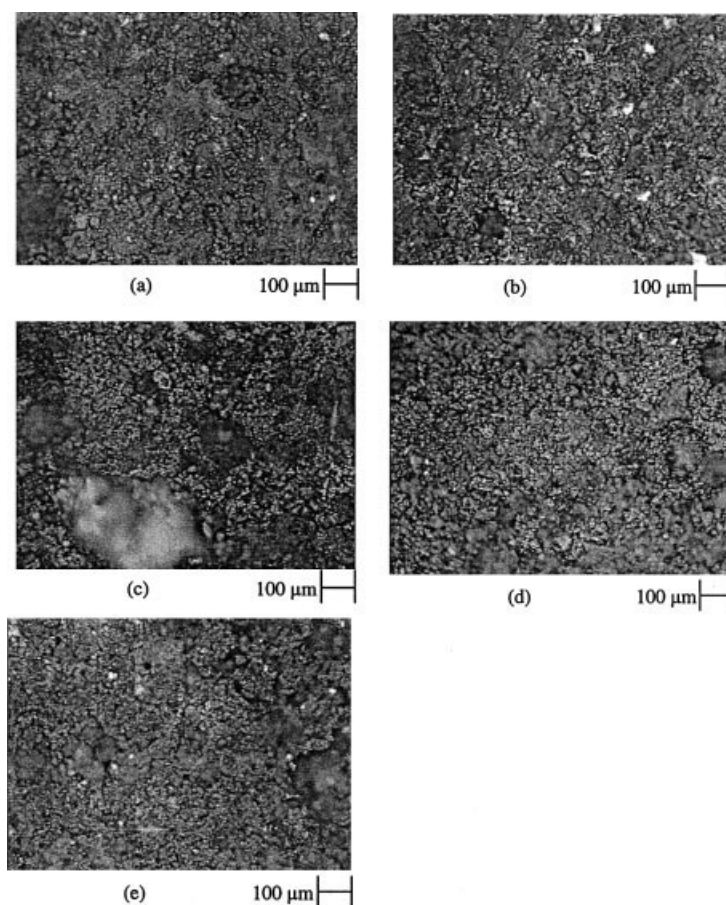


Figure 5 Micrographs of composites after doping at (a) 313 K, 10.5 MPa; (b) 363 K, 10.5 MPa; (c) 413 K, 10.5 MPa; (d) 313 K, 20.7 MPa; and (e) 313 K, 34.5 MPa.

over, the conductivity was uniform (standard deviation 4.5×10^{-4} S/cm) across the sample. Finally, the sample doped at 313 K and 34.5 MPa did not exhibit uniform conductivity, and was able to take up only 3.7 wt % of iodine. As pressure increases, the amount of CO_2 absorbed in a host polymer is likely to increase. However, pneumatic stress can lead to lower mobility at high pressures¹⁹ and could have resulted in the small amount of iodine uptake at 34.5 MPa.

The morphologies of the doped samples are shown in Figure 5. All samples exhibited similar morphologies with interconnected domains of conducting polymer throughout the host substrate. The only exception is the sample doped at 413 K and 10.5 MPa. Under an optical microscope, this sample was found to contain segregated domains of conductive polymer leading to lower conductivity.

CONCLUSIONS

Partially doped conductive polymer composites can be additionally doped by iodine using supercritical CO_2 to transport the dopant to conductive regions of the composite. Supercritical doping of P3UBT/PS

composites with iodine resulted in an increase in iodine uptake from 9.3 wt % at ambient conditions to 21.3 wt % under supercritical conditions, and up to two orders of magnitude increases in the conductivity.

The highest increases in conductivity were obtained in samples treated at moderate temperatures and pressures (313 K and 20.7 MPa). Higher temperatures led to lower effective conjugation of the conductive polymer, and higher pressures to pneumatic stresses that resulted in a lower uptake of iodine. Changes in temperature and pressure also affect iodine solubility in supercritical CO_2 , and the partitioning of iodine between the supercritical phase and the composite. All these effects must be considered in processes to “tune” electrical conductivity of polymer composites by supercritical iodine doping.

The authors gratefully acknowledge partial support for this project by the Georgia Institute of Technology Molecular Design Institute, under prime contract N00014-95-1-1116 from the Office of Naval Research, and from the U.S. Department of Energy.

References

1. Chandrasekhar, P. *Conducting Polymers: Fundamentals and Applications*; Kluwer: Boston, 1999.
2. Schopf, G.; Koßmehl, G. *Polythiophenes: Electrically Conductive Polymers*; Springer-Verlag: Berlin, 1997.
3. De Jesus, M. C.; Fu, Y.; Weiss, R. A. *Polym Eng Sci* 1997, 37, 1936.
4. Martin, C. R. *Science* 1994, 266, 1961.
5. Martin, C. R. *Acc Chem Res* 1995, 28, 61.
6. Demoustier-Champagne, S.; Duchet, J.; Legras, R. *Synth Met* 1999, 101, 20.
7. Delvaux, M.; Duchet, J.; Stauvax, P.-Y.; Legras, R.; Demoustier-Champagne, S. *Synth Met* 2000, 113, 275.
8. Cassagneau, T.; Caruso, F. *Adv Mater* 2002, 14, 34.
9. Son, S.-H.; Lee, H.-J.; Park, Y.-J.; Kim, J.-H. *Polym Int* 1998, 46, 308.
10. Park, J. S.; Ruckenstein, E. J. *Electron Mater* 1992, 21, 205.
11. Abbett, K. F.; Teja, A. S.; Kowalik, J.; Tolbert, L. *Macromolecules* 2003, 36, 3015.
12. Berens, A. R.; Huvard, G. S.; Korsmeyer, R. W.; Kunig, F. W. *J Appl Polym Sci* 1992, 46, 231.
13. Perman, C. A.; Bartkus, J. M.; Choi, H. H.; Reichert, M. E.; Witcher, K. J.; Kao, R. C.; Stefely, J. S.; Gozum, J. U.S. Pat. 5,508,060, 1995.
14. Watkins, J. J.; McCarthy, T. J. *Macromolecules* 1994, 27, 4845.
15. Fang, R. B.; Zheng, S. H.; Zhang, W. H. *Chem J Chin Univ* 1997, 18, 869.
16. Webb, K. F.; Teja, A. S. *Fluid Phase Equil* 2000, 160, 1029.
17. Kowalik, J.; Tolbert, L.; Narayan, S.; Abhiraman, A. S. *Macromolecules* 2001, 34, 5471.
18. Pei, Q.; Inganaes, O.; Gustafsson, G.; Granstrom, M.; Andersson, M. *Synth Met* 1993, 55, 1221.
19. Briscoe, B. J.; Kelly, C. T. *Polymer* 1995, 36, 3099.
20. DIPPR Data Bank, American Institute of Chemical Engineers; AIChE: New York, 1998.