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ELECTRICALLY CONDUCTING THIOPHENE POLYMERS

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ABSTRACT

Electrically conducting 3-alkylthiophene polymers with pentyl, octyl, dodecyl, and hexadecyl alkyl groups were prepared. Iodine, trifluoroacetic acid, and dodecylbenzenesulfonic acid were used as dopants of the polymer backbone. The conductivities of the doped films were in the range 10^{-6} to 10^{-1} S/cm. Applications of the prepared materials in electronics and optoelectronics were examined.

INTRODUCTION

The increased electrical conductivity of dielectric polymers such as polyolefins or vinyl polymers has been studied for many years. Polymer composites with conductivity up to 1 S/cm can be obtained by incorporation of additives with high conductivity, e.g., carbon black, metal powders, or metal complexes [1].

A new field opened after the discovery that the electrical conductivity of some polymers with conjugated double bonds, e.g., polyacetylene, can be increased by the addition of electron donors or acceptors [2]. The intrinsic conductivity of these polymers is caused by similar defects in the structure of the material, as it is in the case of semiconductors [3]. Addition or subtraction of electrons from conjugated polymers causes the change from insulators into conductors. Solitons, polarons, and bi-

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polarons formed on the polymer backbone by the action of dopant are the carriers of electricity [4]. The nature of electrical conduction is dependent on both the structure at the electronic and molecular levels and the larger-scale morphology [5]. The conducting polymers are not only interesting from the scientific point of view, but they are also promising as industrial materials. It is probable that by the end of this century conducting polymers will become engineering materials [6].

THEORETICAL

In the last 20 years many types of conducting polymers have been prepared. Most of them are insoluble and nonprocessable, some are sensitive to oxygen and water. From a practical point of view, the conducting polymers must be sufficiently environmentally stable. Polypyrroles and polythiophenes have been the focus of the research for the last few years. Both these groups of polymers show excellent thermal and air stability, and they can be substituted to alkylated products that are melt and solution processable [7, 8]. Aromatic rings in the main chain are responsible for the stiffness and strong interchain interactions. Solubility is achieved by incorporation of appropriate side groups, e.g., flexible alkyl chains with at least four carbon atoms or oligoethers. The steric hindrance is forcing adjacent rings to twist out of coplanarity along the backbone by this substitution of thiophene rings. The conductivity of polymer is practically independent on the length of the side chain up to dodecyl [9]. By attaching a polar sulfo-group to the end of the alkyl chain, a water-soluble self-doped polymer can be prepared. [10, 11]. The result of covalent bonding of the doping group to the polymer backbone is that the conjugated main chain cannot be fully doped [12].

The delocalized π-system of conjugated double bonds in the main chain undergoes charge transfer reactions with an oxidizing or reducing agent during the doping. In their undoped state, conjugated polymers all behave like *p*-type semiconductors [13].

Iodine is the dopant most often used for intrinsically conducting polymers. It can easily transfer one electron into the conjugated system, but as a weak Lewis acid it is rather weakly bound to polymer and does not form a stable donor-acceptor complex. It is known that *p*-type polyacetylene (prepared by the action of dopants such as HF, BF_3, and I_2) slowly loses conductivity even under vacuum or argon [14]. A lower tendency to evaporation than iodine is exhibited by fluorosulfonic, trifluoromethyl sulfonic, and toluene sulfonic acid, which can form a more stable complex with the conjugated polymer chain [15, 16].

EXPERIMENTAL

A group of polythiophenes substituted in the 3-position by linear alkyl chains $-(CH_2)_x-CH_3$ for $x = 4, 7, 11$, and 15 was synthesized using two different chemical techniques. The starting 3-alkylthiopenes were prepared by coupling of alkylmagnesiumbromide with 3-bromothiophene in anhydrous diethylether in the presence of the phosphine complex of nickel chloride [17]. The purity of monomers was monitored by gas chromatography.

Poly(3-alkylthiophene) was synthesized in the first procedure by ferric chloride-catalyzed dehydrogeneration of the responsible 3-alkyl derivative of thiophene [18]. The reaction was carried out in a rigorously deoxidized and dehydrated chloroform [19]. The resulting polymer has molecular weight as large as 2.5×10^5.

The second procedure uses nickel-catalyzed condensation of the 3-alkyl-2,5-dibromothiophene with magnesium powder [20]. The dibromo derivative of 3-alkylthiophene was prepared by bromination in the benzene solution [21]. The resulting polymer has a molecular weight of approximately 4×10^3.

RESULTS AND DISCUSSION

In the last years a few types of conducting polymers with good stability and processability have been synthesized. A more serious problem was to find a dopant that could provide the environmentally stable conductivity of the conjugated polymer backbone. Toward this goal, the activity of iodine was examined first. The doping experiments on polymer films or powders were performed from the vapor phase in a desiccator in the dark. Figure 1 shows the time dependence of iodine uptake for unsubstituted polythiophene which was prepared by the nickel-catalyzed condensation of 2,5-dibromothiophene. The iodine content in polymer powder increases with the time of exposure to the dopant vapors, but the rate of absorption decreases slowly.

From the synthesized alkylated thiophene polymers, poly(3-dodecylthiophene) prepared by ferric chloride-catalyzed polymerization was

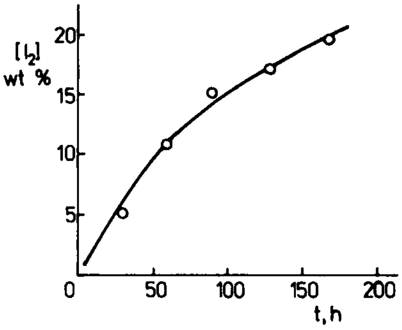

FIG. 1. Dependence of iodine content in polythiophene as a function of doping time.

taken for more detailed investigation of doping. Because of the long aliphatic side chain, the high-molecular polymer is very soluble in organic solvents and it has electrical conductivity comparable to unsubstituted polymer [9]. The films were cast from toluene and the electrical conductivity was measured by the standard four-probe method. The dependence of conductivity of poly(3-dodecylthiophene) as a function of dopant content (expressed as number of monomer units per one iodine molecule) is shown in Fig. 2.

It can be seen that the highest conductivity is achieved at the ratio one iodine molecule per two monomer units. Additional increasing of iodine

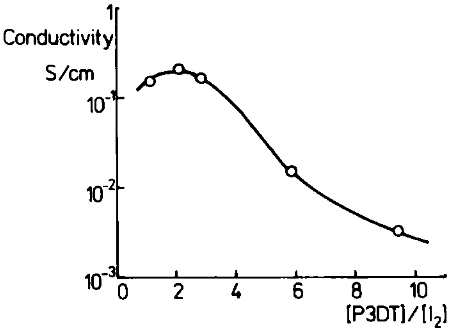

FIG. 2. Dependence of electrical conductivity of poly(3-dodecylthiophene) (P3DT) as a function of iodine content.

content does not improve the conductivity of polymer. The free dopant that does not take part in the charge transfer complex is probably added to the double bonds, and by this action the conjugated system can be disrupted. The greatest disadvantage of using iodine as a dopant is that it evaporates gradually from the polymer matrix.

It is known from the literature [15] that different protonic acids can be used as dopants for poly(phenylene vinylene). One of the strongest is trifluoroacetic acid. The doping experiments were performed on the poly(3-dodecylthiophene) films exposed to the acid vapors. The dependence of electrical conductivity as a function of trifluoroacetic acid content is shown in Fig. 3. The values obtained using the same concentration of dopant are about two orders of magnitude lower compared with the iodine. Trifluoroacetic acid is not very sensitive to water and has the ability to repel moisture. The decrease of conductivity compared with iodine can be explained by the protonation of the main chain by the acid. The presence of sp^3 carbon atoms during the bipolarons formation can lead to the disruption of conjugation [15].

Sulfonic acids are used for doping of conjugated polymers, too. The best way to prepare a homogeneous mixture of thiophene polymer with the dopant is to mix the solutions of both components in a common solvent. The doped film can be obtained after the evaporation of solvent. Poly(3-dodecylthiophene) is highly soluble in polar and nonpolar solvents such as toluene, chloroform, tetrahydrofurane, and others. Lower alkyl- and arylsulfonic acids are soluble only in very polar solvents, e.g., water. By the introduction of longer alkyl chains to the arylsulfonic acid,

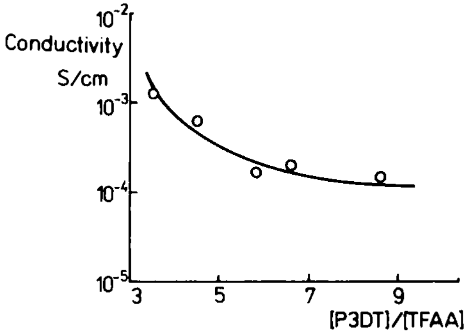

FIG. 3. Dependence of electrical conductivity of poly(3-dodecylthiophene) (P3DT) as a function of trifluoroacetic acid (TFAA) content.

solubility in solvents with lower polarity can be achieved. Dodecylbenzenesulfonic acid is highly soluble in toluene, and it was therefore used for doping of poly-(3-dodecylthiophene). The dependence of electrical conductivity as a function of dopant content is indicated in Fig. 4. In comparison with Fig. 2 it is clear that the conductivity is about four to five orders of magnitude lower than in the case of iodine. In spite of this, the electrical conductivity of the films is environmentally more stable—the acid has a boiling point above 200°C and is not water-sensitive. In addition, the doping dodecylbenzenesulfonic acid can function as a plasticizer for the polythiophene film.

During measurements of electrical conductivity it has been observed that the doped polymers exhibit some interesting properties. The contact point of the metal electrode with the thiophene polymer forms an electrochemical cell. This junction is sensitive to the presence of light. The thiophene polymer alone has the ability to store the electrical charge and can therefore be used in rechargeable batteries.

CONCLUSION

A group of alkyl-substituted polythiophenes was synthesized using two procedures. Polymers with better mechanical properties were prepared by the dehydrogenation polymerization of 3-alkylthiophenes. Iodine as a dopant allowed preparation of materials with conductivities up to 0.2 S/cm, but their environmental stability is low. Trifluoroacetic

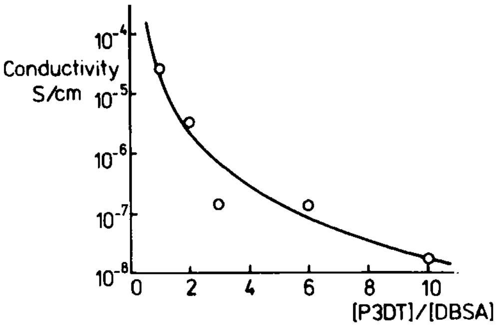

FIG. 4. Dependence of electrical conductivity of poly(3-dodecylthiophene) (P3DT) as a function of dodecylbenzenesulfonic acid (DBSA) content.

and dodecylbenzenesulfonic acids are less effective than iodine, but the stability of prepared materials is higher. Substituted thiophene polymers can be used after doping in rechargeable batteries, in photoeletrochemical cells, for electromagnetic shielding, and in other applications.

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