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A series of different benzaldehydes-4-tolyldiphenylamine polymers has been oxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetrachloro-1,4-benzoquinone (p-chloranil), and also doped by 10-camphorsulfonic acid in order to increase their conductivity. The doped polymers were characterized by ^1H NMR spectroscopy, cyclic voltammetry, UV, and IR spectroscopy. It was found by ^1H NMR spectroscopy that the oxidation yield increased with the increased amount of oxidation agent. It was shown that optical and electrochemical band-gaps of the polymers decreased after oxidation. Conductivity measurements revealed that the applied oxidation and doping procedure resulted in decreased electrical resistance of their initial polymers, down to the level of semiconducting materials. An increased thermal stability of the polymer after oxidation was confirmed by differential scanning calorimetry.

Keywords: hole transport polymer, 4-tolyldiphenylamine, aldehyde, doping, oxidation, DC conductivity

INTRODUCTION

Intensive efforts have been made to synthesize and characterize electronically conducting polymers. Unique properties of conjugated polymers were demonstrated by MacDiarmid, Shirakawa, Heeger, and

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colleagues in 1977 when they discovered that by chemical doping of such polymers it is possible to increase their electronic conductivity over several orders of magnitude [1]. Since then, electronically conducting materials based on conjugated polymers have been applied in diverse items such as sensors, biomaterials, light-emitting diodes, corrosion protection agents, and so on. Conjugated polymers can exhibit electron-hole conduction similar to conventional semiconductors. This effect is enhanced by chemical doping, which consists of treatment of the organic polymer by small quantity of dopant material, bringing about disproportionately large changes in its electronic, physical, and chemical properties.

Polymers having triphenylamine (TPA) units have been extensively used as excellent hole transport materials and photoconductors on the basis of their ability to form stable radical cations and high drift mobility [2–3]. There are two independent doping routes for polymers containing amine moiety [4]: chemical or electrochemical oxidation, and protonation through acid-base chemistry by the use of protonic acids. For example, the doping of emeraldine base form of polyaniline by aqueous protonic acids, caused an increase in conductivity of about 10 orders of magnitude, both for powders and free-standing films of the polymer [5]. Films cast from solution of polyaniline doped by *d,l*-camphorsulfonic acid are reported to have conductivities in the range of 100–400 Scm⁻¹ [4,6]. In contrast to polyaniline protonated with usual dopants, for example HCl, H₂SO₄, or HBF₄, which is insoluble in common organic solvents, the conductive form achieved by doping with *d,l*-camphorsulfonic acid can be readily dissolved in many conventional organic liquids such as: *m*-cresol, trifluoroethanol, xylene, and so on [7–9]. Such behavior considerably expands the potential application of these doped polymers due to direct solution processing.

The purpose of the present and the authors' related earlier studies was to prepare polymers containing triphenylamine (TPA) derivatives, which due to their hole transport ability can be used for electroluminescence and photorefractive devices, and for organic photoconduction [10–12]. The authors have reported previously [13] that by oxidation of triphenylamine-benzaldehyde polymers, their conductivity increased more than 100 times. It was also found that by the reaction of tolyldiphenylamine (TDPA) with other *para* substituted benzaldehydes it is possible to synthesize materials of the required electrochemical properties and good film-forming ability [10]. However, all prepared polymers showed low conductivities of magnitude 10⁻¹⁴ Scm⁻¹. This report investigates the oxidation, as well as doping, with camphorsulfonic acid to improve the conductivity of these polymer.

EXPERIMENTAL

Materials

Commercially available solvents were purified according to standard procedures. The other chemicals were of reagent grade and were used without further purification. The benzaldehyde-4-tolyldiphenylamine polymers were synthesized as in previous work [10].

Oxidation

Polymers were reacted with various amounts of DDQ or p-chloranil at room temperature using THF as a solvent. Typically, the oxidation reaction was performed as follows: to 100 mg of polymer in the powder form, 1 ml of THF solution of oxidant was added. The reaction mixture was allowed to stir vigorously over a period of several hours (see Table 1). The reacted polymer was recovered by pouring the reaction mixture into methanol. The precipitate was subsequently filtered off and washed with methanol until the filtrate was colorless. The polymer were dried in vacuum for 24 h.

Doping of Polymers with Camphorsulfonic Acid

Non-oxidized and oxidized polymers were doped by protonation with 10-camphorsulfonic acid (CSA). THF solutions with different concentration of CSA (see Table 3) was added to 50 mg of polymer powder and vigorously stirred for 48 h at room temperature. The doped polymers were cast on substrate glass and dried for several hours at room temperature.

TABLE 1 Oxidation of TDPA-BA Polymer

Oxidant	Polymer/Oxidant (mole ratio)	Yield of oxidation (%) ^a	
		24 h	48 h
p-Chloranil	1:0.5	30	55
	1:1.0	50	80
	1:1.5	80	80
DDQ	1:0.5	70	90
	1:1.0	95	98
	1:1.02	99	100

^aAccording to ¹H NMR signals intensity ratio of methine to methyl proton.

Measurement

^1H NMR measurements were performed on a JEOL α -500 spectrometer in deuterated chloroform using tetramethylsilane (TMS) as an internal standard. Gel permeation chromatograms (GPC) were obtained by using a column packed with styrene-divinylbenzene gel beads, and chloroform as eluent at 0.5 ml/min flow rate. A Jasco 880-PU pump and Jasco UV-970 detector were used. Standard polystyrenes were used as reference for molecular weight evaluation. UV spectra were recorded in chloroform solutions on a JASCO Ubsset-30 UV-VIS spectrometer. IR spectra were obtained by JASCO FT/IR 5300 spectrometer. A chloroform solution of the sample (0.25 mg/ml) was used to prepare a film on a NaCl disc. Glass transition temperatures (T_g) were determined from a differential scanning calorimetry (DSC) chart, which was recorded by Rigaku Thermoplus 2 DSC 8230 instrument under nitrogen atmosphere at heating rate of $10^\circ\text{C}/\text{min}$. Redox potential was measured by cyclic voltammetry in one-compartment cell with polarization unit (Toho PS-06). The measurement was conducted for the cast film on platinum working electrode and in dry acetonitrile containing tetra-*n*-butylammonium perchlorate (Bu_4NClO_4 , 0.1M) as an electrolyte under nitrogen atmosphere. Platinum spiral was used as the counter electrode, and Ag/AgCl as a reference electrode. Conductivity was measured by direct current method using the samples prepared as follows: A polymer solution in an appropriate solvent was filtered through a $5\ \mu\text{m}$ filter, followed by spreading on indium tin oxide (ITO) glass using a wire bar coater. The sample thickness was controlled to be approximately $50\ \mu\text{m}$ with the use of a Teflon spacer. The film was dried for several hours at room temperature. An aluminum electrode was prepared on the film surface by vacuum deposition at a pressure of 10^{-5} Torr, just before conductivity measurement to avoid oxidation of the aluminum surface. The film thickness was determined by a profilometer (Dektak II, Solan). An I-V characteristic was measured using an electrometer (ADVANTEST, R6451A).

RESULTS AND DISCUSSION

The studied polymers were prepared by condensation polymerization of 4-tolyldiphenylamine (TDPA) with benzaldehyde (BA), 4-cyanobenzaldehyde (CBA), 4-nitrobenzaldehyde (NBA) and methyl 4-formylbenzoate (MFBA) as reported earlier [10]. Two types of oxidizing agents were applied to oxidize these polymers: 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetrachloro-1,4-benzoquinone

(*p*-chloranil). The results of the oxidation of TDPA-BA polymer are given in Table 1. The oxidation yield, represented by the amount of remaining methine protons, was evaluated on the basis of the intensity ratio of the NMR signals of methine to methyl proton. It was found that the yield of reaction increased with increasing amounts of both oxidizing reagents. For DDQ oxidized polymer, almost equimolar amount of oxidant was necessary to remove completely the methine proton from the polymer chain, after 24 h. In the case of reaction with *p*-chloranil, the same or somewhat larger amount of oxidant resulted only in abstraction of 80% of methine protons, in twice as long reaction time (Figure 1). To complete the oxidation of this polymer, a large excess of *p*-chloranil (polymer:chloranil ratio 1:2) was applied. Such conditions, however, resulted in gelation of the polymer.

The authors described in earlier studies the proposed structure for oxidized benzaldehyde polymers and also the effect of the electron donor–acceptor nature of the substituent in the aromatic ring of the aldehyde monomer on the conductivity and Redox potential [10,13]. On the basis of an ESR measurement that indicated very low radical concentration, the authors suggested the presence of the quinoid structure as shown in Figure 2. To confirm these assumptions, a measurement of IR absorption of the oxidized polymer was carried out.

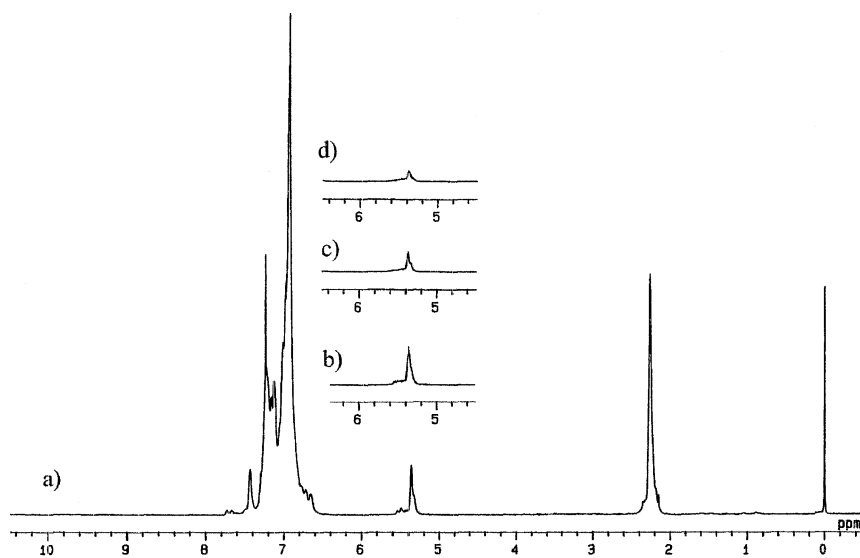


FIGURE 1 ^1H NMR spectra of TDPA-BA polymer: (a) unreacted; oxidized with the growing yield: (b) 30%, (c) 50%, (d) 80%.

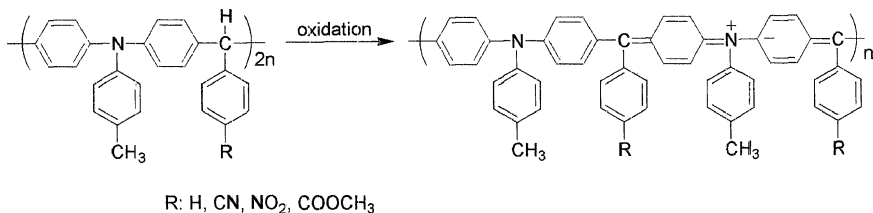


FIGURE 2 The scheme of the oxidation of polymers.

Infrared spectra of TDPA-BA polymer before and after oxidation by DDQ are presented in Figure 3. When comparing these spectra, they found a new, intense band at 1570 cm^{-1} . It is characteristic of the quinoid ring and it corresponds to a C = C stretching vibration. Other

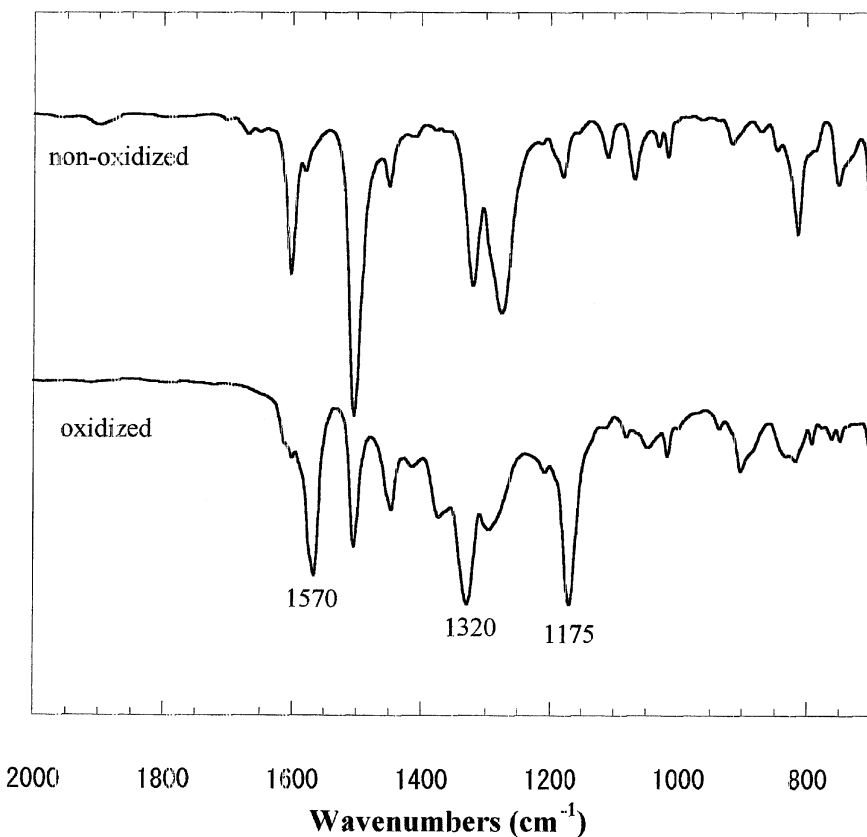


FIGURE 3 Infrared spectra of TDPA-BA polymer before and after oxidation by DDQ.

peaks coming from the quinoid ring were observed in oxidized polymer at around 1175 cm^{-1} and 1320 cm^{-1} . Quillard et al. proposed similar assignments for the vibrational peaks of polyaniline [14]. The postulated structure was also supported by the authors' observation on the NMR spectra of the oxidized polymers. The lack of observed characteristic peak broadening for all studied samples allows the exclusion of the presence of radical in the oxidized form of the polymer.

The results of UV absorption measurements are given in Table 2. All unreacted samples showed only one absorption around 313 nm. Oxidation led to a red shift of these peaks, attributed to charge transfer from the benzenoid to quinoid structure and indicated a larger and more defined conjugation [15]. Reacted samples had also an additional peak at about 721 nm. Optical bandgaps of polymers were determined from the onset at the high wavelength end of the absorption edge. Decreasing of the bandgap observed for all tested polymers indicated the changes in electronic structure of these materials after oxidation. Further evidence that such changes resulted in conductivity increase was provided by the results on the CV behavior (Table 2). In contrast to unreacted polymers [10], the authors observed for oxidized polymers only one pair of oxidation-reduction peaks. The value of electrochemical bandgap, not listed here, estimated from the difference between the onset of oxidation and reduction curves, was smaller than the optical bandgap; however, the decreasing trend after oxidation, was retained.

The electrical conductivities of the all tested polymers oxidized with DDQ, as well TDPA-BA sample doped with various amounts of CSA are presented in Table 3. The conductivity values of the non-oxidized polymers were in the range from $2.0 \times 10^{-15}\text{ S/cm}$ to $5.1 \times 10^{-14}\text{ S/cm}$. A 50% degree of oxidation was apparently sufficient to cause increase in conductivity of more than 2 orders or magnitude. Further oxidation

TABLE 2 Physical Properties of Polymers Completely Oxidized by DDQ

Polymer	Redox potential ^a (V)		λ_{max} (nm)	Optical bandgap ^b (eV)	T_{g}^b (°C)
	E_{pa}	E_{pc}			
TDPA-BA	1.08	0.89	329.5, 693.0	1.52 (3.54)	221 (199)
TDPA-MFBA	1.33	0.67	314.0, 722.5	1.56 (3.58)	259 (222)
TDPA-CBA	1.30	0.65	316.5, 721.5	1.57 (3.44)	276 (230)
TDPA-NBA	1.43	0.40	315.5, 721.5	1.57 (3.44)	252 (215)

^a E_{pa} and E_{pc} are oxidation and reduction potentials, respectively.

^bData in parentheses represent the values before oxidation.

TABLE 3 Electrical Conductivity of the Polymers

Polymers	DC conductivity (S/cm)	
	Non-oxidized polymer	Oxidized polymer ^a
TDPA-MFBA	5.1×10^{-14}	9.3×10^{-10}
TDPA-CBA	4.5×10^{-15}	3.6×10^{-9}
TDPA-NBA	2.0×10^{-15}	5.7×10^{-10}
TDPA-BA	4.0×10^{-15}	9.2×10^{-10}
TDPA-BA (10 mol-%CSA)	1.5×10^{-10}	1.2×10^{-9}
TDPA-BA (50 mol-%CSA)	7.1×10^{-8}	6.8×10^{-6}
TDPA-BA (100 mol-%CSA)	1.3×10^{-6}	5.2×10^{-10}

^a Completely oxidized polymers by DDQ.

and complete abstraction of methine protons, led to more than 5 orders of magnitude increase in conductivity. Oxidized TDPA-MFBA sample showed the highest conductivity among the studied polymers, of ca. 9.3×10^{-9} S/cm.

An Additional growth of conductivity up to level of 6.8×10^{-6} S/cm of oxidized TDPA-BA polymer was achieved after doping with camphorsulfonic acid, carried out in a THF solution of the polymer. The result of doping by CSA, given in Table 3, indicated that a medium degree of protonation was apparently sufficient to cause an increase in conductivity of more than 4 orders of magnitude. Interestingly, the conductivity initially increased with increasing of the dopant concentration, reached a maximum for 50 mol% of CSA, and then decreased when the highest concentration of CSA was achieved. It indicates that after a certain level of protonation was exceeded, the reduced conductivity arose from a reduction of the concentration of the charge carriers. Such phenomenon is consistent with the result of protonation of emeraldine base polyanilines, reported by Kang et al. [16]. Detailed investigations on the structure of the CSA-doped polymers are under way.

The thermal properties of the polymers were investigated by differential scanning calorimetry (DSC). The values of the glass transition temperature for non-oxidized and oxidized polymers, given in Table 2, indicate a distinct growth of thermostability after oxidation of all the examined polymers. It is worth noting, that in spite of the increased rigidity of the chain, due to the presence of the quinoid structure, oxidized polymers remained soluble and procesable in common organic solvents. The authors' found however, that consistent conductivity values are dependent on such factors as the type of solvent, concentration of the employed solution, time, and temperature of

the process of the solvent removal, as well as time and atmosphere of film storage.

CONCLUSIONS

The oxidation and chemical doping of 4-tolyldiphenylamine-benzaldehydes type polymers were aimed to increase the conductivity of these materials. It was found that a complete oxidation of such polymers and subsequent doping with camphorsulfonic acid resulted in an increased conductivity to the level of semiconducting materials. In order to synthesize soluble polymers with a doping level required for high conductivity, further studies and better characterization of their structure and explanation of the mechanism responsible for their increased conductivity are needed.

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