



Syntheses and investigation of polymers containing 1-triazene-1,3-diyl and 1,4-phenylene group

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ABSTRACT

Triazene-group-containing polymers have been synthesized from *p*-phenylenediamine precursors by diazotization and azo-coupling methods. For this purpose, two pathways have been used. The effect of monomer/sodium nitrite ratio on the solubility of the polymers, as well as the dependence of properties such as electrical conductivity and ESR upon the main chain structure, have been investigated. Solubility tests showed that the lower the sodium nitrite/*p*-phenylenediamine molar ratio (<1), the higher the solubility of the resulting polytriazene. ¹H NMR, IR, and UV/vis absorption spectroscopies have been used to elucidate the chemical structures of the polymers obtained. Electrical conductivity studies and ESR measurements have been conducted on both as-synthesized and doped polymer samples. The room temperature electrical conductivity of the obtained polymers was found to increase from 10⁻¹¹–10⁻⁹ to 7 × 10⁻³–2 × 10⁻² S/m upon doping with iodine. According to ESR spectroscopy data, this increase in conductivity may be attributed to improved charge carrier (polaron) mobility. An important feature of these polymers is that their conductivity may be increased up to 10⁻⁴ S/m by doping with hydrochloric and sulfuric acids.

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1. Introduction

Conducting polymers constitute an important class of materials, due to their novel physical properties and prospects of their application in various areas of technological importance. The conductive polymers belonging to polyenes or polyaromatics such as polyacetylene, polyaniline, polypyrrole, polythiophene, poly(*p*-phenylene), poly(*p*-phenylenevinylene) classes have been studied extensively [1–4]. Among these polymers polyaniline is one of the most studied, because of its excellent electrical, magnetic and optical properties, and environmental stability.

In particular, among nitrogen containing polymers polyazarylenes attract considerable attention because of their use in commercial applications related to data recording, wave length conversion, light amplification, optical computing, and so on [5–7].

A range of polymer-supported triazenes and their metal-bound analogues were screened for use in catalysis and organic synthesis [8,9]. UV laser ablation of triazene polymers is the objective of intense experimental and theoretical research due to the potential applications in electronics [10–12].

Hence, the conjugated triazene-group-containing polymers may be of a big interest because of their applications possibility.

Syntheses of poly(triazene-1,3-diyl-di-1,4-phenylene) from 4,4'-diaminodiphenyl were reported by Berlin et al. [13] and recently the polymer with identical structure was synthesized and doped with iodine and hydrochloric acid in paper [14].

In this paper we describe preparation of triazene- and 1,4-phenylene group containing conjugated polymers by diazotization and azo-coupling of *p*-phenylenediamine (PPD) precursors and present the results of electric conductivity and ESR properties of doping of the obtained polymers with iodine, sulfuric and hydrochloric acids.

2. Experimental

2.1. Measurements

The inherent viscosity of DMSO solution was determined at 25 °C, using Ubbelohde viscometer.

The UV/vis spectra of the polymer samples were recorded in 1 cm quartz cuvettes with Specord 65 spectrometer. FT IR Nicolet Nexus spectrometer was served for obtaining FT-IR spectra in the range of 5000–600 cm⁻¹ (KBr pellets). ¹H NMR spectra were obtained in deuterated dimethylsulfoxide using Mercury 300 Varian NMR spectrometer.

Electrical conductivity was measured on the preliminarily prepared pellets by two-probe method using Teraohmmeter E6-137. The solid samples were used for recording ESR spectra by Radiopan,

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Table 1
Data for diazotization and azo-coupling of PPD.

Parent materials					Obtained polymers		
PPD		NaNO ₂ in H ₂ O			Insoluble in DMF	Soluble in DMF	Yields
g	mmol	g	mmol	ml	g; %	g; %	%
3.007	28.0	1.940	28.0	7	2.37; 71.6	0.94; 28.4	100
1.5155	14.0	0.9520	13.8	3.3	0.78; 49.0	0.81; 51.0	95.4
3.0000	27.8	1.7996	26.1	6.24	1.21; 39.0	1.89; 61.0	93.6
1.4939 ^a	13.8	2.0362	29.5	7.375	2.26; 82	0.49; 18	84.2

^a See Section 2.3.1.2.

SE/X-2543 spectrometer. For ordering to remove the moisture the samples were evacuated before recording the spectra. Determination error for line width was ± 0.01 mT, and for *g*-factor was within ± 0.001 .

Potentiometric titration with NaOH aqueous solution was used for the determination of HCl after doping filtrate solution. NaOH aqueous solution prior to use was standardized by primary titration with standard 0.1N HCl aqueous solution.

2.2. Materials

PPD was purified by sublimation (mp 416–418 K). Water was used after distillation. All other chemicals were of analytical grade and were used as received without any further purification.

2.3. Polycondensation and doping procedures

2.3.1. Diazotization and azo-coupling reaction of PPD (Table 1)

2.3.1.1. Poly(1-triazene-1,3-diyl-1,4-phenylene-co-1-triazene-1,3-diyl-1,4-phenylene-2-triazene-1,3-diyl-1,4-phenylene) P(I-co-II). PPD was mixed with 36% hydrochloric acid (1 mol PPD–585.7 ml hydrochloric acid) in a three-necked flask (250 ml) equipped with a mechanical stirrer and thermometer. The reaction mixture was mixed at room temperature to dissolve PPD. A pink solution was obtained, cooled down to about 263 K and treated with a small portions of sodium nitrite solution with continuous stirring for about 40 min accompanied with gradual change of color to brown as the diazotization was going on. When the reaction was completed, the temperature was raised to 268 K, buffered at pH = 5 through addition of sodium acetate solution (1 mol PPD–428.6 g sodium acetate dissolved in 2.1 l water) and maintained at room temperature for 2 days. The precipitated polymeric powder was collected by filtration, washed with distilled water, treated with 5% sodium hydrocarbonate aqueous solution, kept overnight, washed thoroughly with water till neutral reaction and dried in air. Then, soluble part of polymer was extracted by DMF and precipitated by water. The polymers obtained were dried in vacuo (323 K/2 kPa) and were stored in a desiccator over phosphorus pentoxide.

2.3.1.2. Poly(1-triazene-1,3-diyl-1,4-phenylene-2-triazene-1,3-diyl-1,4-phenylene) P(II). The diazotization was carried out by the above-mentioned procedure using PPD–sodium nitrite molar ratio equal to 1:2. Then in order to carry out the azo-coupling reaction, the equivalent amount of PPD was added into the reaction mixture under stirring while the temperature was raised to 268 K. Sodium acetate was then added and the mixture was kept overnight at room temperature. Then the solution was poured into water and the precipitate was collected and dried. Subsequent procedure was similar to the mentioned above.

2.3.2. Doping by iodine

Different amounts of 0.18N iodine solution in CCl₄ were added on the polymer powder with determined weight and kept at room temperature. After 3 days, polymer was filtered, washed with small

amount of CCl₄ and dried under vacuum (0.2 kPa) in a desiccator with P₂O₅. Iodine content in polymers was determined via filtrate titration with Na₂S₂O₃ 0.1N solution and by polymers' weight increase.

2.3.3. Doping by hydrochloric and sulfuric acids

Doping procedure is different for soluble and insoluble in DMF fractions of polymers.

2.3.3.1. Procedure for soluble in DMF fractions of polymers.

Hydrochloric acid of 0.1N (0.5N, 1N or 2N) was added to polymer powder in proportion 100 ml to 1 g. The mixture was kept at room temperature for 5–6 days and water was removed under vacuum by water pump at 313 K, and then dried in the vacuum desiccator on P₂O₅ till constant weight. Dopant content in polymers was determined via polymers' weight increase and the determination of hydrochloride in polymer.

2.3.3.1.1. Determination of hydrochloric acid in doped polymer.

Higher than requisite quantity of NaOH solution with defined value of concentration was added to the doped polymer sample and kept at room temperature for 6 days. Then 2 ml of solution was taken and titrated with 0.1N HCl.

2.3.3.2. Procedure for insoluble polymers.

Hydrochloric and sulfuric acids of 0.1N, (0.5N, 1N or 2N) was added to polymer powder in proportion 100 ml to 1 g. The mixture was kept at room temperature for 5–6 days. Then precipitate was filtered and washed with ethyl alcohol till neutral reaction and dried under vacuum (0.2 kPa) in a desiccator with P₂O₅. Dopant content in polymers was determined via filtrate titration with 0.2N NaOH aqueous solution.

The doping level was calculated by the formula

$$Y = \frac{\text{mol of dopant}}{\text{mol of triazene-1,3-diylphenylene moieties}}$$

3. Results and discussion

3.1. Synthesis

The new conjugated polymers incorporating triazene groups were synthesized through a classical reaction scheme of diazotization of PPD with subsequent azo-coupling. For the synthesis of the studied polymers, two approaches were used:

- Firstly, PPD was reacted with sodium nitrite in a 1:1 molar ratio. The resulting diazonium compound coupled in situ with the unreacted amino groups, leading directly to the final polymer, which contained two types of repeat units in its main chain: i.e. poly(1-triazene-1,3-diyl-1,4-phenylene-co-1-triazene-1,3-diyl-1,4-phenylene-2-triazene-1,3-diyl-1,4-phenylene) P(I-co-II)-1 (Scheme 1).

The obtained polymer, P(I-co-II)-1, was found to be only partially soluble in DMF (29%).

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