## Synthesis and Study of a Polymer Containing Di- and Triazenyl-*p*-phenylene Groups

A. A. Durgaryan, R. A. Arakelyan, N. A. Durgaryan, and E. E. Matinyan

Yerevan State University, ul. A. Manukyana 1, Yerevan, 375025 Armenia e-mail: durgaran@ysu.am

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**Abstract**—A polymer containing di- and triazenyl-*p*-phenylene groups in the main chain was synthesized for the first time. Doping of newly synthesized poly(triazene-1,3-diyl-*p*-phenylenes) and poly(triazene-1,3-diyl-*p*-diphenylenes) with perchloric acid is studied. The introduction of azophenylene groups in the chain of a polymer containing triazenylphenylene groups has almost no effect on electrical conductivity. The electrical conductivity of these polymers increases from  $10^{-9}$  to 0.8 S/m with increasing doping degree. The replacement of phenylene by diphenylene groups slightly reduces the electrical conductivity of the polymer doped with perchloric acid, while in the case of iodine doping, by contrast, the electrical conductivity slightly increases.

Keywords: azoarylene, triazene arylene, doping, electrical conductivity

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Electrically active polymers have found application in a number of industries [1–5]. This fact explains the interest in the synthesis of new polymers with properties optimal for specific applications [6–9].

We are the first to study the doping of polyarenes containing triazene-1,3-diyl groups. It was established that HCl doping raises their electrical conductivity to  $10^{-4}$  S/m [10, 11]. This phenomenon can be explained by the formation, like what is observed with polyaniline, of bipolarons which can exists as several mesomeric structures (Scheme 1).

Based on published data [12–14], we set ourselves the aim to study the dependence of the electrical conductivity of poly(triazene-1,3-diyl-1,4-arylenes) on their structure and the effect of introduction of 1,4phenylenediazene fragments in the main chain of polymers on the properties of the latter. We synthesized a polymer containing di- and triazenyl-*p*-phenylene groups and compared its electrical conductivity with those of triazynel-*p*-phenylene and triazenyl-4,4'-biphenylene copolymers.

The copolymers of 1-triazene-1,3-diyl-1,4-phenylene and 1-triazene-1,3-diyl-1,4-phenylene-2-tri-azene-1,3-diyl-1,4-phenylene (**Ia**) [11] and of 1-triazene-1,3diyl-4,4'-biphenylene and 1-triazene-1,3-diyl-4,4'biphenylene-2-triazene-1,3-diyl-4,4'-biphe-nylene (**Ib**) [10] were prepared by diazotization of 1 mol of benzidine or *p*-phenylenediamine with 1 mol of sodium nitrite followed by azo coupling in the corresponding conditions (Scheme 1).

Poly(1-triazene-1,3-diyl-1,4-phenylene-2-triazene-1,3-diyl-1,4-phenylene) (**IIa**) [11] and poly(1-triazene-1,3-diyl-4,4'-biphenylene-2-triazene-1,3-diyl-4,4'-biphenylene) (**IIb**) [10] were prepared by diazotization



## Scheme 2.

$$H_2N - Ar - NH_2 + NaNO_2 + 2HCl \longrightarrow H_2N - Ar - N_2^+Cl^- + NaCl + 2H_2O$$
$$H_2N - Ar - NH_2 + 2NaNO_2 + 4HCl \longrightarrow Cl^-N_2^+ - Ar - N_2^+Cl^- + 2NaCl + 4H_2O$$

$$nm \operatorname{H}_{2} \operatorname{N} - \operatorname{Ar} - \operatorname{N}_{2}^{+} \operatorname{Cl}^{-} + nl \operatorname{H}_{2} \operatorname{N} - \operatorname{Ar} - \operatorname{NH}_{2} + nl \operatorname{Cl}^{-} \operatorname{N}_{2}^{+} - \operatorname{Ar} - \operatorname{N}_{2}^{+} \operatorname{Cl}^{-}$$

$$\xrightarrow{\operatorname{CH}_{3} \operatorname{CO}_{2} \operatorname{Na}} [(-\operatorname{N}=\operatorname{N} - \operatorname{Ar} - \operatorname{HN} -)_{m} (-\operatorname{N}=\operatorname{N} - \operatorname{Ar} - \operatorname{N}=\operatorname{N} - \operatorname{HN} - \operatorname{Ar} - \operatorname{NH} -)_{1}]_{n}$$



Scheme 3.  $n \operatorname{Cl}^{-}\operatorname{N}_{2}^{+} - \operatorname{Ar} - \operatorname{N}_{2}^{+}\operatorname{Cl}^{-} + n \operatorname{H}_{2}\operatorname{N} - \operatorname{Ar} - \operatorname{NH}_{2} \xrightarrow{\operatorname{CH}_{3}\operatorname{CO}_{2}\operatorname{Na}} [-\operatorname{N}=\operatorname{N} - \operatorname{Ar} - \operatorname{N}=\operatorname{N} - \operatorname{HN} - \operatorname{Ar} - \operatorname{NH}_{-}]_{n}$ II



Scheme 4.



of the monomers with 2 mol of sodium nitrite followed by azo coupling with equivalent monomer amounts (Scheme 3).

According to <sup>1</sup>H NMR data, the synthesized polymers undergo tautomeric transformations.

Copolymer **III** which contains azophenylene and triazenylphenylene groups in the main chain was prepared by azo coupling of 1,4-bis(3-phenyltriazenyl)-

benzene with *p*-phenylenebis(diazonium chloride). 1,4-Bis(3-phenyltriazenyl)benzene was synthesized by reacting *p*-phenylenebis(diazonium chloride) with excess aniline (Scheme 4).

Like other triazene compounds [11, 12], at room temperature 1,4-bis(3-phenyltriazenyl)benzene is present as a mixture of tautomers.

The <sup>1</sup>H NMR spectrum of 1,4-bis(3-phenyltriazenyl)benzene in DMSO- $d_6$  contains signals of all

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tautomers. The signals of the protons ortho to the azo group are observed at 7.4–7.9 ppm (4H). The orthoprotons with respect to the amino group appear at 6.44–7.04 ppm. Other aromatic proton signals are observed at 7.04–7.4 ppm. The absence of the signal of the primary amino group provides evidence showing that azo coupling involves exclusively the amino group (Scheme 5).

The IR spectrum shows no absorption band of primary amino groups at 3400, 3450, and 1615 cm<sup>-1</sup> and contains stretching and deformation vibration bands of secondary amino groups at 3200, 3272, 3343, and 1600 cm<sup>-1</sup>. This finding can be considered as further evidence for the fact that azo coupling involves the amino group to form triazene groups.

The UV spectrum of 1,4-bis(3-phenyltriazenyl) benzene in DMSO (Fig. 1) displays absorption bands at  $\lambda_{max}$  264, 298 (shoulder), and 539 nm.

Polymer III is soluble in formic acid and partly soluble in methanol, DMSO, and DMF; it does not melt up to 603 K. Characteristical viscosity [ $\eta$ ] in formic acid at 298 K is 0.06 dL/g. The UV spectrum of polymer III contains absorption band at 366 nm due to azo groups.

We studied the dependence of the electrical conductivity of polymers **Ia**, **Ib**, and **III** on their structure upon perchloric acid doping. These three polymers have almost equal electrical conductivities, i.e. azophenyl groups have almost no effect on elec-



Fig. 1. UV spectra in DMSO of (1) polymer III and (2) 1,4-bis(3-phenylazenyl)benzene.  $c = 0.28 \times 10^{-3}$  M.



repeated structural units): (1) IIa, (2) III, and (3) Ia (insoluble fraction). Molecular weight of repeated structural units: 119 (Ia, IIa), 195 (Ib, IIb), and 111.5 (III).



**Fig. 3.** Dependence of electrical conductivity (log  $\sigma$ ) on perchloric acid doping degree (*Y*): (*1*) **IIa**, (*2*) **III**, (*3*) **IIb**, (*4*) **Ib**, and (*5*) **Ia** (insoluble fraction).

trical conductivity. A high doping degree the electrical conductivity of polymer Ia becomes slightly lower compared to the two other polymers (Fig. 2). As the doping degree increases, the electrical conductivities of polymers Ia, Ib, and III increases from  $10^{-9}$  to 0.8 S/m.

Benzidine polymers **Ib** and **IIb** have much lower electrical conductivities compared to polymers **Ia**, **IIa**, and **III** (Figs. 3 and 4). The lowest electrical conductivity is characteristic of polymer **IIb**, which is likely to be associated with the fact that in it phenylene groups are replaced by diphenylenes.

We also studied the dependence of the electrical conductivity of polymer III on the degree of iodine doping (Fig. 5). It was found that the electrical conductivity increases to  $10^{-2}$  S/m and becomes almost equal to those of polymers Ia and IIa [11]. Polymers Ib and IIb [10] have slightly higher electrical conductivities than polymers Ia, IIa, and III, which implies that in iodine-doped polymers replacement of phenylene by diphenylene groups increases electrical conductivity.

## **EXPERIMENTAL**

*p*-Phenylenediamine (pure grade) was additionally purified by vacuum sublimation (mp  $145-147^{\circ}$ C). Benzidine (pure grade) was recrystallized from water (mp  $122-125^{\circ}$ C). Sodium nitrite (analytical grade) was used as received. Polymers **Ia**, **Ib**, **IIa**, and **IIb** were prepared by the procedures in [10, 11].



**Fig. 4.** Dependence of electrical conductivity (log  $\sigma$ ) on perchloric acid doping degree (*Y*, mole dopant/weight doped polymer/100]: (*1*) **IIa**, (*2*) **III**, (*3*) **IIb**, (*4*) **Ib**, and (*5*) **Ia** (insoluble fraction).

The electrical conductivities of samples pressed in pellets were measured by the double-contact method on a Teraoommetr E6-137 instrument. The IR spectra (KBr) were taken on a Nicolet Nexus FTIR spectrometer. The <sup>1</sup>H NMR spectra were obtained on Varian Mercury-300 NMR Spectrometer. The UV spectra were measured on a Specord 50 instrument.

**1,4-Bis(3-phenyltriazen-1-yl)benzene.** A mixture of 1.00 g (9.25 mmol) of *p*-phenylenediamine and 8.0 mL of 38% HCl was heated on a water bath at 343 K for 2 h. The resulting solution was cooled down to 263 K and a solution of 1.28 g (18.5 mmol) of NaNO<sub>2</sub>



Fig. 5. Dependence of electrical conductivity (log  $\sigma$ ) on the doping degree of polymer III with iodine.

in 4.5 mL of water was added to it under stirring. After that a solutions of 8.4 g of sodium acetate in 42 mL of water (pH 5) was slowly added at 268 K to the reaction mixture, followed by a solution of 2.14 g (23 mmol) of aniline in 4 mL of alcohol. The reaction mixture was treated with NaHCO<sub>3</sub> until alkaline reaction. The precipitate was filtered off, washed on the filter with water until neutral washings, and recrystallized from alcohol. Yield 1.59 g (54.3%), mp 130°C. IR spectrum, v, cm<sup>-1</sup>: 3450, 3400, 3343, 3272, 3200, 3029, 1615, 1600, 1500, 1443, 1400, 1300, 1243, 1200, 1172, 1072, 1029, 833, 829, 757, 690.

**Poly(azo-***p***-phenylenazo-***p***-phenylene-2-triazene-1,3-diyl-***p***-phenylene-1-triazene-1,3-diyl-***p***-phenylene)** (III) was prepared in a similar way from 0.2813 g (2.6 mmol) of *p*-phenylenediamine, 0.3592 g (5.2 mmol) of NaNO<sub>2</sub>, and 0.8212 g (2.6 mmol) of 1,4-bis(3-phenyl-1-triazenyl)benzene in 19 mL of alcohol. The reaction mixture was treated with aqueous NaHCO<sub>3</sub>, and the precipitate was filtered off, washed with distilled water to neutral washings, and dried. Yield 0.93 g (80%). IR specrum (film), v, cm<sup>-1</sup>: 3343, 3057, 3025, 1600, 1500, 1450, 1400, 1300, 1240, 1140, 1040, 1029, 833, 757, 690.

**Doping with perchloric acid.** To an exact weight of finely ground polymer III we added (per 1 mol of triazene-1,3-diylarylene fragements) 0.2-1.5 mol of 1 N perchloric acid, and the mixture was allowed to stand for 2–3 days at room temperature. Water was then removed in a vacuum at 303 K, and the precipitate was dried to constant weight in a vacuum dessicator over  $P_2O_5$  (0.2 kPa). The dopant amount was calculated by the weight gain of the polymer.

**Doping with iodine.** To an exact weight of a finely ground polymer we added (per 1 mol of triazene-1,3-diylarylene fragements) 0.3, 0.5, 1, and 2 mol of a 0.19 N iodine solution in CCl<sub>4</sub>. The mixture was allowed to stand for 2–3 days at room temperature. The precipitate was filtered off and washed with two small portions of CCl<sub>4</sub>. The filtrate was titrated with a 0.1 N solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and the precipitate was dried to constant weight in a vacuum dessicator over  $P_2O_5$ 

(0.2 kPa). The dopant amount was calculated by the consumption of iodine and the polymer weight gain.

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