

SYNTHESIS OF ANILINE FRAGMENT CONTAINING POLIMERS
LINKED WITH DIFFERENT GROUPS

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Utilizing cost-effective and readily available monomers in conjunction with industrially employed methodologies, novel electroactive polymers have been successfully synthesized. These polymers incorporate aniline oligomers covalently linked through triazenarylene groups. The resulting polymers effectively combine the distinctive features of polyaniline (PANI) and linking group, thus expanding the range of polyaniline applications. To carry out the syntheses p-phenylenediamine, benzidine were used as monomers, the applied methods are oxidation-condensation and diazotization, azocombination. It has been shown that the electrical conductivities of iodine-doped polymers are approximately of the same order as the electrical conductivities of polyaniline, determined in the same way. Polymers containing 1,4-ditriazen-3-yl benzidine units have been shown to have higher electrical conductivity for the same length of oligoaniline chains. The resulting polymers exhibit fluorescent properties.

References 8, schemes 6, figures 1, tables 1

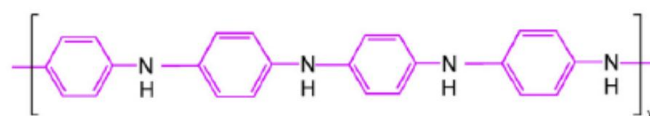
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Introduction: By the nature, the creation of intrinsically conducting polymers (ICP) and/or the improvement of the properties of these materials is in great scientific interest and is being studied by various scientific groups worldwide. It is known from the literature that polymers with conductivity

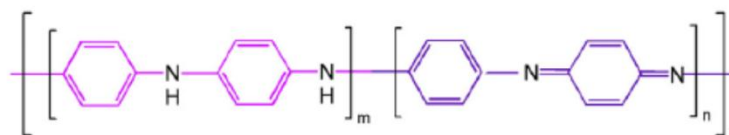
can be obtained only from a monomer with a certain structure. However, the problem of the synthesis of conductive polymers with well defined chemical structure and interesting properties can be solved by synthesizing oligomers of the conductive polymers and then modifying them by various methods with their subsequent incorporation in main polymer chain [1]. In case if the main chain remains conjugated, the polymers can show new properties characteristic of the linking groups.

In the presented work, it was aimed to realize the synthesis of new conductive polymers by connecting polyaniline oligomers with triazenaryl groups. Polymers containing such groups are of great interest in the field of optoelectronics.

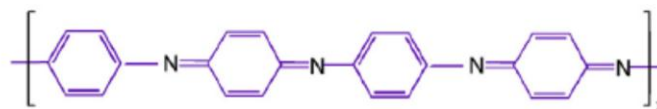
It is known from the literature that PANI has 3 main structural forms (oxidation levels): leucoemeraldine (fully reduced), emeraldine (half oxidized) and pernigranilin (fully oxidized). They differ from each other in the ratio of benzene and quinone rings in the repeated structural unit (Scheme 1).



Leucoemeraldine is a fully reduced form of PANI



Semi-oxidized form of emeraldine



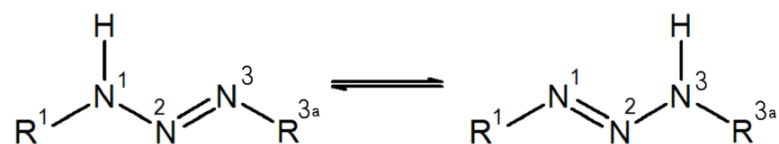
Pernigranilin is a fully oxidized form of PANI

Scheme 1. Chemical structure of PANI in different oxidation states [2].

The triazene, $\text{HN}=\text{NH}-\text{NH}_2$, is not stable under normal conditions, but was found as an intermediate product during the electrolytic treatment of hydrazine between high-voltage electrodes. In recent years, organic polymers have received considerable attention as materials used as various optical components in many modern technologies, such as holographic image recording devices, optical memory devices, optical waveguides, etc.,

because of their superior properties and reasonable prices to inorganic materials [3].

The triazene group has a unique structure, E-, Z-isomerism (Scheme 2), oxidation and complexing properties. Based on these properties, it is assumed that conjugated polymers containing the triazene group may be of some interest as electroactive polymers.



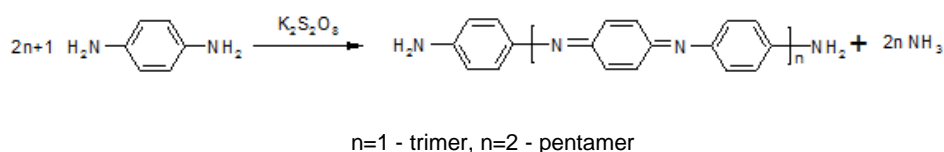
Scheme 2. Isomerism of triazene group

Based on previous works, conjugated polymers containing a triazene group in the main chain were obtained using the benzidine and p-phenyldiamine (p-FDA) monomers, as well as diazotization and azocoupling method for the synthesis of target polymers [4, 5].

Results and discussion. The synthesis of polymers with a new structure was carried out by connecting the corresponding oligomers of already used conductive polymers with different groups. The industrial method of synthesis were chosen: oxidation-condensation and diazotization, azocoupling. As a cheap and available monomers p-phenylenediamine, benzidine were used, aiming to obtain polymers in the structure of which the oligomers of the aniline are connected to each other by triazenylenes groups.

The triazene group has been chosen due to the fact that conjugated polymers containing such groups in the main structure are scarce studied and have received considerable attention as in various optical components in many modern technologies. The triazene group, with the ability to undergo cis-trans isomerism under the influence of a certain wavelength, belongs to the number of groups that can find application in these fields.

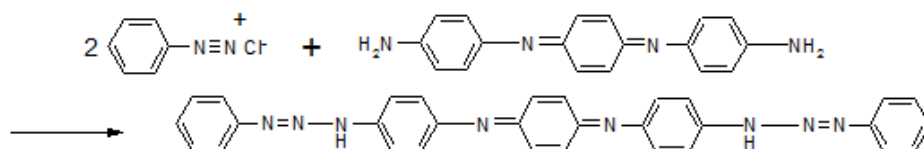
Trimers and pentamers with amino/amino end groups of aniline were chosen as oligomers. The presence of amine end groups makes it possible to use them as starting materials in further synthesis. The synthesis of the latter was also carried out by the method developed by us: the oxidation-condensation of p-phenylenediamine with potassium persulfate in a 1:4 molar ratio of acetic acid. This method is a one-step and convenient method for the synthesis of compounds with a pernigraniline-like structure (Scheme 3).



Scheme 3. Synthesis of pernigraniline-like structure

The resulting aniline oligomers were used as monomers to obtain polymers containing 1,3-triazendiyl group. In order to obtain a soluble polymer, the reaction was carried out using p-FDA:trimer: NaNO₂ in a molar ratio of 1:1:1.9. Such a reaction is carried out for the first time, and therefore diazotization and azocoupling of p-FDA with N,N'-di(4-aminophenyl)-1,4-benzoquinonediimine (trimer) was carried out according to the method developed for the preparation of polymer containing triazene groups based on p-FDA [6, 7] and the resulting mixture was kept at room temperature for 2 days. Assuming that the quinonediiminium groups present in the structure of the polymer have high reactivity, the reaction mixture was kept at -4 °C after carrying out the azocoupling in subsequent conversions.

In order to clarify the structural issues and to find out the accuracy of the chosen method, a model compound containing triazene groups was synthesized by carrying out the diazotization and azocoupling of aniline with the trimer in the molar ratio of aniline:NaNO₂ 1:1.12 and aniline:trimer in a 2:1 molar ratio (Scheme 4).

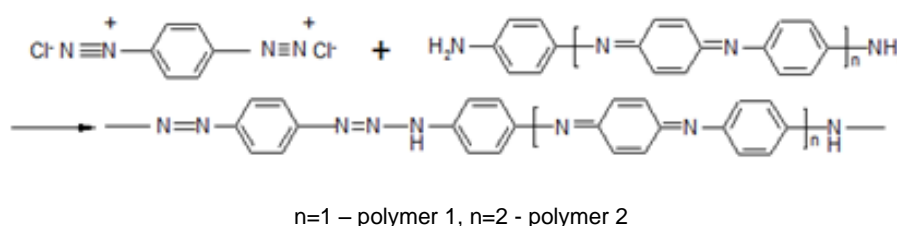


Scheme 4. Synthesis of model compound

During the azo coupling with the trimer, the temperature of the reaction mixture was maintained within -5 °C. After treatment with ether, the ether-insoluble fraction was extracted with methanol. The methanol-insoluble phase (86.4 % of initial mass) was also insoluble in chloroform, but soluble in DMSO. The latter does not melt up to 290 °C. The UV-Vis spectrum was compared with the UV spectra of the starting trimer and a polymer containing a triazene group obtained from diazotization of p-FDA and azocoupling with p-FDA [7]. The spectrum contains both absorptions of the original trimer, which underwent a "blue" hypsochromic shift, and absorptions due to newly formed triazene groups. The obtained results indicate that

under the mentioned conditions (at low temperature) the reaction really proceeds and side reactions can be avoided at the same time.

Under the same conditions, p-FDA diazotization with p-FDA:NaNO₂ 1:2 molar ratio and azocoupling with trimer and pentamer with p-FDA:trimer (pentamer) 1:1 molar ratio were studied and according to the spectral data, the expected polymers containing aniline oligomers connected by triazene groups were obtained (Scheme 5).



Scheme 5. p-FDA diazotization and azocoupling with trimer and pentamer and further linking aniline oligomers by triazene groups

The UV spectra of the obtained polymers were compared with the corresponding spectra of the starting trimer and the polymer obtained by p-FDA diazotization and azocoupling, which confirmed the structure of the obtained polymers. A comparison of the UV-Vis spectra shows the similarity of the spectrum of the obtained polymer 1 with the UV-Vis spectrum of the polymer obtained from p-FDA diazotization and azocoupling with p-FDA (Fig. 1).

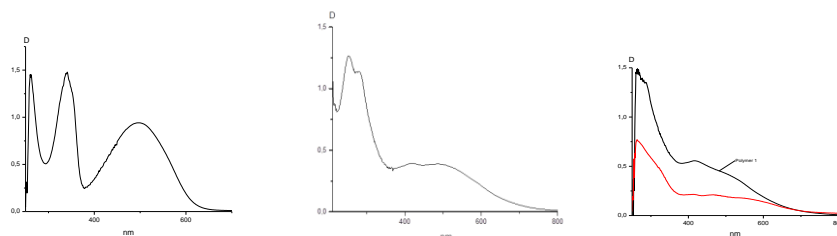
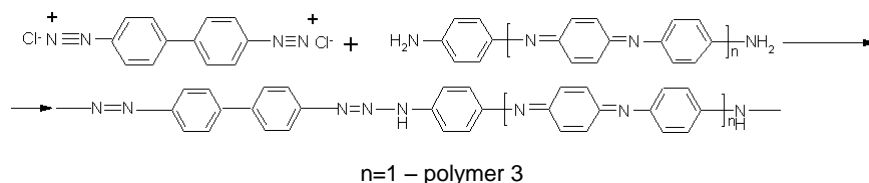


Fig. 1. Comparison of UV-Vis spectra. 1) Trimmer; 2) Model compound; 3) Polymer1 and p-FDA diazotized and p-FDA azocoupling.

Further studies of structure-properties of aniline oligomers connected with triazene groups continued with the introduction of a benzidine fragment into the polymer structure, obtaining polymer in the structure of which benzidine units are connected with triazene groups to aniline oligomers, particularly trimers (Scheme 6).



Scheme 6. Introduction of a benzidine fragment into the polymer structure

The dependence of the electrical conductivity of the resulting polymers on iodine doping was determined (Table 1). At a doping depth of 3.2, the specific electrical conductivity of polymer 1 was $9 \times 10^{-6} \text{ S/cm}$. It should be noted that at a doping depth of 1.0, the electrical conductivity of the polymer containing triazine groups obtained from the p-FDA and p-phenylenediazonium chloride is approximately 10^{-4} S/cm . When comparing doping depths, it should be kept in mind that the molar mass of the repeating structural unit of the polymer obtained from trimer is much larger than that obtained from p-FDA. Polymer 2 was doped with iodine, at a doping depth of 3.5 and the specific electrical conductivity was $6 \times 10^{-6} \text{ S/cm}$. Can be noticed that polymer 1 and 2 have approximately the same electrical conductivity. The specific electrical conductivity of polymer 3 at a doping depth of 4.5, was $1 \times 10^{-3} \text{ S/cm}$. From the results can be noticed that the polymer 3 exhibits the highest electrical conductivity.

The resulting polymers were also doped with hydrochloric acid, but it was found that their salt form is soluble in acids, thus the measurements of electroconductivity of dry polymers was impossible. A method is now in the stage of developed for determination of the electrical conductivity of polymers after doping with hydrochloric acid [8].

Table 1.

**Electrical conductivities of polymers doped with iodine
tetrachloromethane solution**

Polymer	Polymer : doping agent molar ratio	Polymer mole, <i>mmol</i>	$\text{I}_2 / \text{CCl}_4$ Solution volume, <i>ml</i>	Doping depth according to		Specific electrical conductivity, <i>S/cm</i>
				mass	Ti- tra- tion	
Polymer 1	1:7	0.0252	3.5	3.2	3.3	9×10^{-6}
Polymer 2	1:7	0.0299	4	3.8	3.2	6.1×10^{-6}
	1:8.6	0.0315	5	4	3.6	2.5×10^{-6}
Polymer 3	1:7	0.02705	4.3	4.2	4.5	9.3×10^{-5}
	1:8.6	0.02425	4.78	4.5	4.7	8.4×10^{-4}

Conclusion. It has been shown that aniline oligomers with amino/amino end groups can be used as monomers for the synthesis of further electroactive polymers at low temperatures. A new low molecular weight compound containing new bistriazenphenylene groups was synthesized. It has been shown that polymers containing a biphenylene group when doped with iodine have higher electrical conductivity than polymers containing a phenylene group with a similar structure. With such a structure, the electrical conductivity of polymers containing a longer oligomer chain is higher.

Experimental. Equipment: UV-Vis spectrometer - SPECORD 50, resistance meter - Applent AT512. For the synthesis the p-FDA is purified by sublimation ($T = 143\text{--}145\text{ }^{\circ}\text{C}$), the sulfuric salt of p-FDA is purified by recrystallization from the water, other materials is used as received.

Preparation of oligomers. 0.9 g (8.5 mmol) of p-FDA, 0.565 g (2.77 mmol) sulfuric salt of p-FDA, and 6.3 ml of acetic acid at $15\text{ }^{\circ}\text{C}$ are added to 0.997 g (3.67 mmol) of potassium persulfate and mixed for 25 hours. A solution of 7.8 g of Na_2CO_3 in 58 ml of ice water ($\text{pH}=9$) is added to the reaction mixture and left in the refrigerator. It is then filtered, washed with distilled water until $\text{pH}=7$ and free of sulfate ions. The separated material, by filtration, is extracted with diethyl ether and methanol. 0.25 g

is recrystallized from alcohol ($T_{\text{melt.}} = 227\text{--}230\text{ }^{\circ}\text{C}$).

Preparation of polymers. Diazotization of p-FDA with sodium nitrite and azocoupling with trimer in (1:2:1) molar ratio. To 0.0863 g (0.79 mmol) of p-FDA is added 0.48 ml of 35% hydrochloric acid solution over 45 minutes at room temperature. After the temperature is decreased to $-10\text{ }^{\circ}\text{C}$, 0.1109 g (1.6 mmol) of sodium nitrite is dissolved in 0.4 mL of water and very slowly is added dropwise. After the completion of the reaction, 0.215 g (0.75 mmol) of dry trimer is added to the diazotized p-FDA solution and the temperature is increased up to $-5\text{ }^{\circ}\text{C}$. After 15 minutes, a solution of 1.7 g of sodium acetate, dissolved in 1.8 ml of water, at a temperature of $-5\text{ }^{\circ}\text{C}$ is slowly added to the mixture until the $\text{pH}=5$, left for 30 minutes and moved to refrigerator (in the preliminary experiment, according to the developed method, it is kept at room temperature for 2 days). After 4 days, the reaction mixture is neutralized with sodium bicarbonate solution to $\text{pH} > 7$. The solution is filtered, and the precipitate is washed with water to $\text{pH}=7$, then with ether, methanol, successively. Obtained: 0.15 g (polymer I).

The materials are dried to constant weight in an oven at $50\text{--}70\text{ }^{\circ}\text{C}$ and a pressure of 2 kPa.

Diazotization and azocoupling of aniline with trimer at aniline:narium nitrite (1:1.12) molar ratio, aniline:trimer (2:1) molar ratio (model compound). The experiment is carried out analogously to the previous one using: 0.091 g (0.978 mmol) of aniline, 0.21 ml of 35% hydrochloric acid solution, 0.07 g (1.01 mmol) of sodium nitrite is dissolved in 0.15 ml of ice

water, 0.141 g (0.49 mmol) of trimer, \approx 0.49 g of sodium acetate is dissolved in 0.5 ml of water. 0.1 g is obtained.

Dianitrogenation of p-FDA with sodium nitrite and azocoupling with the pentamer in a (1:2:1) molar ratio. To 0.07375 g (0.683 mmol) of p-FDA, 0.44 mL of 35% hydrochloric acid solution is added over 45 minutes at room temperature. After lowering the temperature from -10 °C to -14 °C, 0.09425 g (1.366 mmol) of sodium nitrite, dissolved in 0.85 ml of water, and very slowly is added dropwise. 0.31965 g (0.68 mmol) of the dry pentamer is added to the resulting diazotized p-FDA solution and the temperature is increased up to -5 °C. After 15 minutes, solution of 1.553 g of sodium acetate is dissolved in 1.65 ml of water at a temperature of -5 °C and slowly added to the mixture until the pH=5, left for 1 hour and placed in a refrigerator. The next day, the reaction mixture is stirred for 3 h at 0 °C. The reaction mixture is filtered and the precipitate is washed with ice water until pH=7. The reaction mixture is neutralized with sodium bicarbonate solution to pH > 7. The solution is filtered and the precipitate washed with water until pH=7. It is then washed with methanol. Obtained: 0.39 g. (polymer 2).

Diazotization of benzidine with sodium nitrite and azo coupling with trimer in a (1:2:1) molar ratio. The experiment is carried out analogously to polymer 1 using 0.068 g (0.37 mmol) benzidine, 0.2 ml 35% hydrochloric acid solution, 0.051 g (0.74 mmol) sodium nitrite is dissolved in 0.45 ml water, 0.107 (0.37 mmol) trimer, 0.9 g of sodium acetate is dissolved in 1ml of water. 0.15 g is obtained (polymer 3). The materials are dried to constant weight in an oven at 50-70 °C and pressure of 2 kPa.

Doping of polymers with iodine. A certain volume of 0.178 N iodine tetrachloromethane solution is added to a certain weight of the polymer, left at room temperature, in a dark place for 3 days. It is then filtered, the filter with precipitate is washed once with a small amount of carbon tetrachloromethane, then placed in a desiccator containing phosphorus pentoxide and dried under a water vacuum to constant weight. The residue is titrated with sodium thiosulfate solution in the presence of starch. The procedure is repeated for all polymers.

Doping depth (Y) is calculated from both titration and polymer weight by equation 1;

$$Y = \frac{\text{Dopant mole}}{\text{Triazine structural unit mole}} \quad (1)$$

Moles of repeating structural units are calculated assuming that diazotization and azocoupling reactions proceeded quantitatively.

Conductivity measurement. 4- and 2-wire resistance measurement methods are applied to obtain the resistance of polymers. The specific electrical conductivity of the polymers are calculated by equation 2.

$$\sigma = \frac{l}{R \times A} \quad (2)$$

Where l is the thickness of polymer sample between copper electrodes, R is the resistance measured via equipment, A is the surface of the copper electrodes.

ՏԱՐԲԵՐ ԽՄԲԵՐՈՎ ՄԻԱՑՎԱԾ ԱՆԻԼԻՆԱՑԻՆ ՖՐԱԳՄԵՆՏ ՊԱՐՈՒՆԱԿՈՂ ՊՈԼԻՄԵՐՆԵՐԻ ՍՏԱՑՈՒՄԸ

Մ.Ս. ԹՈՐՈՍՅԱՆ, Ն.Շ. ՄԱՐՏԻԿՅԱՆ, Ն. Ա. ԴՈՒՐԳԱՐՅԱՆ

Էթան և մատչելի մոնոմերների և արդյունաբերության մեջ կիրառությունն գտած եղանակների հիման վրա սինթեզվել են նոր էլեկտրաակտիվ պոլիմերներ, որոնց կառուցվածքում անիլինի օլիգոմերները միացված են իրար տրիագենարիկենային խմբերով: Յուրյ է տրվել, որ ստացված պոլիմերները համատեղում են պոլիանիլինի և կապոլ խմբերի բնորոշ հատկությունները՝ ընդլայնելով պոլիանիլինի կիրառման բնագավառները: Սինթեզներն իրականացնելու համար որպես մոնոմեր օգտագործվել են մատչելի մոնոմերներ պ-ֆենիլենդիամինը, բենզիդինը, կիրառվող եղանակներն են օքսիդացմամբ կոնդենսումը և դիազոտացումը, ազոհամակցումը: Յուրյ է տրվել, որ յոդով դոպացված պոլիմերների էլեկտրահաղորդականությունները մոտավորապես նույն կարգի են, ինչ պոլիանիլինի՝ նույն եղանակով որոշված էլեկտրահաղորդականությունը: Յուրյ է տրվել, որ օլիգոանիլինային շղթաների նույն երկարության դեպքում ավելի բարձր էլեկտրահաղորդականություն ունեն 1,4-դիտրիագեն-3-իլ բենզիդինային միավորներ պարունակող պոլիմերները: Ստացված պոլիմերները ցուցաբերում են ֆլուորեսցենտ հատկություններ:

СИНТЕЗ ПОЛИМЕРОВ, СОДЕРЖАЩИХ АНИЛИНОВЫЕ ФРАГМЕНТЫ, СОЕДИНЁННЫЕ РАЗНЫМИ ГРУППАМИ

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На основе дешевых и доступных мономеров и методов, используемых в промышленности, синтезированы новые электроактивные полимеры, в структуре которых анилиновые олигомеры связаны между собой триазенариленовыми группами. Показано, что полученные полимеры сочетают в себе характерные свойства полианилина и связующих групп, расширяя области применения полианилина. Для проведения синтезов в качестве мономеров использовали доступные мономеры п-фенилендиамин, бензидин, применяемые методы – кон-

денсация с окислением и диазотированием, азосочетание. Показано, что электропроводность легированных йодом полимеров примерно того же порядка, что и электропроводность полианилина, определяемая таким же образом. Было показано, что полимеры, содержащие звенья 1,4-дитриазен-3-илбензида, обладают более высокой электропроводностью при той же длине олигоанилиновых цепей. Полученные полимеры проявляют флуоресцентные свойства.

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