

NEW SYNTHESIS OF NH<sub>2</sub>/NH<sub>2</sub> CAPPED POLYANILINE  
TETRAMERS 4,4'-DI(p-AMINOANILINO)-DIPHENYLAMINE

E. E. MATINYAN\*

*Chair of Organic Chemistry YSU, Armenia*

New method of synthesizing NH<sub>2</sub>/NH<sub>2</sub> capped polyaniline tetramer – 4,4'-di(p-aminoanilino)-diphenylene, by oxidative condensation of 4-aminoacetanilide with N-acetyldiphenylamine and subsequent hydrolysis of the obtained 4,4'-di(p-acetylamino)-N-acetyldiphenylamine is discussed.

**Keywords:** polyaniline, emeraldine, tetraaniline, oxidative condensation, oligoaniline.

**Introduction.** Polyaniline occupies a special place among the electroactive polyconjugated polymers due to its stability to the action of the environmental conditions, and because of its easy and cheap method of synthesis as well as its unique properties [1–3]. It has a broad spectrum of probable use as anticorrosion covering [4, 5], in accumulator batteries [6], as bio- and chemosensor [7–9], etc. [10]. The most important oxidation state of polyaniline is the emeraldine base form, since it can be doped by strong acids to create the conducting form, which can be readily and reversibly dedoped back to the insulating emeraldine base form. The emeraldine oxidation state of polyaniline possesses three benzene rings for every quinoid ring. Amine/phenyl-capped tetraaniline, hereafter referred to as tetraaniline, therefore represents an important model compound for polyaniline, because it is the shortest oligomer that can represent the emeraldine oxidation state.

More recently, other methods for the synthesis of oligoanilines have been reported. A titanium alkoxide-mediated coupling of anilines with phenols has been used to prepare phenyl-capped tetraaniline and pentaaniline [11]. The palladium-catalyzed amination of aryl halides and triflates has emerged as a powerful method for the synthesis of a wide variety of arylamines [12–15]. Pernigraniline and its oligomers were obtained by condensation of quinones with aromatic amines to form poly(quinoneimine)s [16–18] and the reaction of N,N'-dichloro-1,4-benzoquinonodiimin with organometallic compounds [19]. Zang W.J. et al. have oxidized N-phenyl-1,4-phenylenediamine to tetraaniline; they report that oxidation of the latter compound affords 16-mer. Phenyl/NH<sub>2</sub> capped polyaniline tetramer was obtained by the method of oxidative condensation of N-phenyl-p-phenylenediamine

---

\* E-mail: [emmamatinyan@mail.ru](mailto:emmamatinyan@mail.ru)

under the influence of ferric chloride [20]. It is also noted that the p-phenylenediamine and 4,4'-diaminodiphenylamin with diphenylamine under the influence of ammonium peroxodisulfate form correspondingly trimers and tetramers, and the reaction of phenyl capped oligomers with phenylenediamine the degree of polymerization of ammonium peroxodisulfate is increased by one [21]. Having in mind that aniline oligomer has a similar structure with a unit cell is a tetramer of aniline, the oxidized form of which is called emeraldin, as it was shown, may also exhibit the same properties as polyaniline, also the fact that aniline oligomers joining other groups can produce polymers with interesting properties [22, 23], we have begun research into the synthesis of aniline tetramer with  $\text{NH}_2/\text{NH}_2$  capped groups.

**Experimental Part.** N-Acetyldiphenylamine, p-nitro- and p-aminoacetanilid were obtained by known methods [24–26]. All other chemicals were of analytical grade and were used without any further purification. Water was used after distillation. The vacuum (0.2 kPa) desiccator with  $\text{P}_2\text{O}_5$  was used for drying the obtained compounds. The UV-vis spectra of the polymer samples were recorded in 1 cm quartz cuvettes with Specord-65 spectrometer. FT-IR Nicolet Nexus spectrometer served for obtaining FT-IR spectra in the range of 5000–600  $\text{cm}^{-1}$  (ATR attachment with ZnSe crystal and KBr pills).  $^1\text{H}$  NMR spectra were obtained in deuterated dimethylsulfoxide using Mercury-300 Varian NMR spectrometer.

*Oxidative Condensation of p-Aminoacetanilide with N-Acetyldiphenylamine, under the  $\text{K}_2\text{S}_2\text{O}_8$ .* 5 g (33.3 mmol) of p-aminoacetanilide was mixed with 3.52 g (17 mmol) N-acetyldiphenylamin and 56.6 ml acetic acid in a flask equipped with a magnetic stirrer. The reaction mixture was stirred at room temperature to dissolve. During continuous stirring 2.64 ml of 5N hydrochloric acid and the solution of 11.48 g (42.5 mmol)  $\text{K}_2\text{S}_2\text{O}_8$  in 67.5 ml of water were added. The reaction was carried out at 291–293 K about 36 h. The precipitated powder was collected by filtration, washed with distilled water, treated with 1% sodium hydrocarbonate aqueous solution up to pH 9 and stirred for 10 h. Afterwards, obtained compound was washed with water till neutral reaction and then with hot water for N-acetyldiphenylamine extraction. 4,4'-Di(p-acetylaminoanilino)-N-acetyldiphenylamine was purified by reprecipitation from alcohol/water, and dried in vacuum (323 K/2 kPa) desiccator with phosphorus pentoxide. Yield – 3.31 g (40%), m.p. 623 K.

*Alkaline Hydrolysis of 4,4'-Di(p-Acetaminoanilino)-N-Acetyldiphenylamine.* 1.53 g (3 mmol) 4,4'-di(p-aminoanilino)-diphenylamine was stirred with 12.7 ml (23 mmol) 1.8 N methanolic solution of sodium hydroxide at 343–353 K for 33 h. The powder was collected by filtration, washed with distilled water till neutral reaction. The product was purified by precipitation from DMF/alcohol, and dried in vacuum (323 K /2 kPa) desiccator with phosphorus pentoxide. Yield – 0.82 g (71%).

**Results and Discussion.** The  $\text{NH}_2/\text{NH}_2$  capped aniline tetramer has been obtained by the interaction of 4,4'-diamino-diphenylamine sulfate (10 g worth \$ 25) with 4-fluoronitrobenzene (100 g worth \$ 28.5), followed by the reduction of obtained N,N'-di(p-nitrophenyl)-phenylenediamine [15].

We develop a new cheaper method for  $\text{NH}_2/\text{NH}_2$  capped aniline tetramer synthesis by oxidative condensation of p-aminoacetanilid (25 g – \$ 10.5) with N-acetyldiphenylamine (100 g – \$ 15) with potassium peroxodisulfate. According to  $^1\text{H}$  NMR, IR and UV spectroscopic data 4,4'-di(p-acetylaminoanilino)-N-acetyldiphenylamine was formed (Fig. 1, Scheme 1).

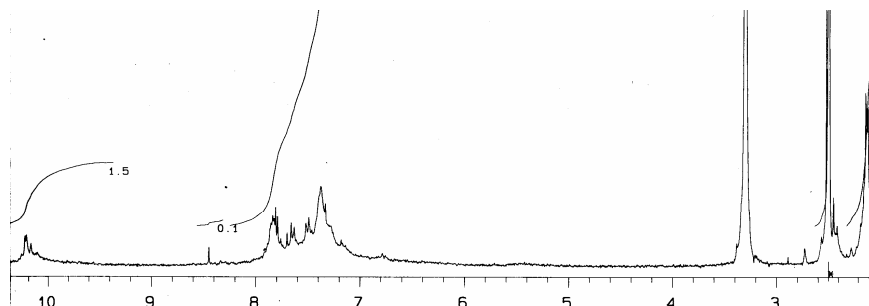
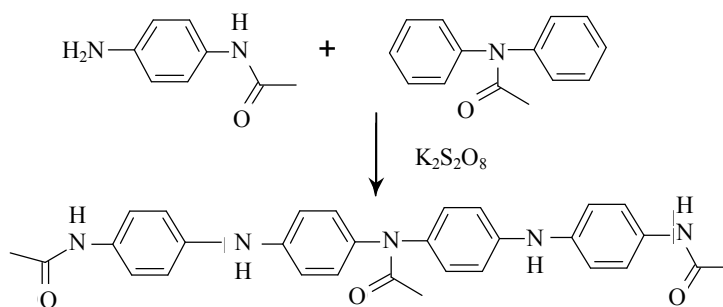


Fig. 1. <sup>1</sup>H NMR spectrum of 4,4'-di(p-acetylaminoanilino)-N-acetyldiphenylamine.

<sup>1</sup>H NMR spectrum of the compound ((CD<sub>3</sub>)<sub>2</sub>SO, δ, ppm (Fig. 1)) features the accordance of integral intensities of aliphatic protons (chemical shifts at 2.13 ppm) (9 H) with integral intensities of aromatic protons signals: (chem. shifts at 6.70–8.30 ppm) (18 H) and NH protons (chem. shifts at 10.10–10.50 ppm) (2 H) are kept. Chemical shifts in the range of 7.10 to 7.65 ppm can be attributed to the protons *ortho* to the amino groups, and in the range of 7.70 to 8.00 ppm, to the chemical shifts of the protons *ortho* to the acetylamino groups.



Scheme 1.

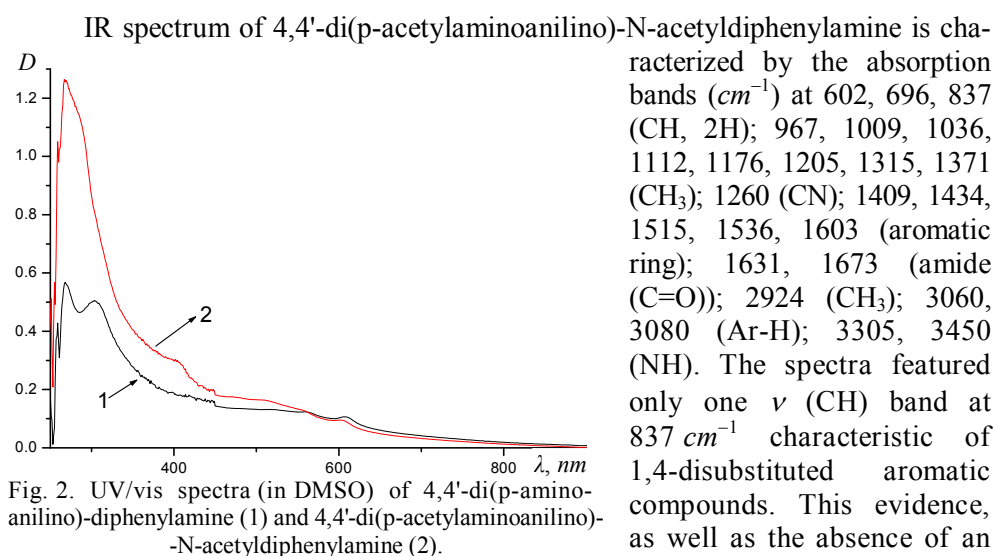


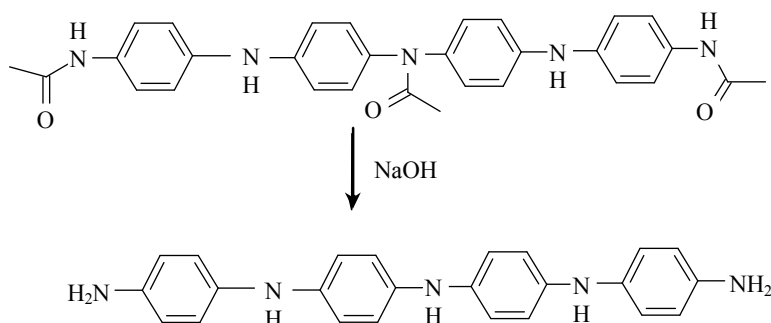
Fig. 2. UV/vis spectra (in DMSO) of 4,4'-di(p-aminoanilino)-diphenylamine (1) and 4,4'-di(p-acetylaminoanilino)-N-acetyldiphenylamine (2).

IR spectrum of 4,4'-di(p-acetylaminoanilino)-N-acetyldiphenylamine is characterized by the absorption bands ( $cm^{-1}$ ) at 602, 696, 837 (CH, 2H); 967, 1009, 1036, 1112, 1176, 1205, 1315, 1371 (CH<sub>3</sub>); 1260 (CN); 1409, 1434, 1515, 1536, 1603 (aromatic ring); 1631, 1673 (amide (C=O)); 2924 (CH<sub>3</sub>); 3060, 3080 (Ar-H); 3305, 3450 (NH). The spectra featured only one  $\nu$  (CH) band at  $837\text{ cm}^{-1}$  characteristic of 1,4-disubstituted aromatic compounds. This evidence, as well as the absence of an

absorption at  $880\text{ cm}^{-1}$ , confirmed that the reaction had occurred with the amino group.

UV/vis spectra of the 4,4'-di(p-aminoanilino)-diphenylamine and 4,4'-di-(p-acetylaminoanilino)-N-acetyldiphenylamin are shown in Fig. 2. They are characterized by the transition absorption band at  $\lambda_{\text{max}}=275\text{ nm}$ , attributed to  $\pi-\pi^*$ -transitions of amino and acetylamino groups connected benzenoid moieties.

The next step to obtain  $\text{NH}_2/\text{NH}_2$  capped aniline tetramer consists in the hydrolysis of the obtained 4,4'-di(p-acetylamino)-N-acetyldiphenylamine (Scheme 2).

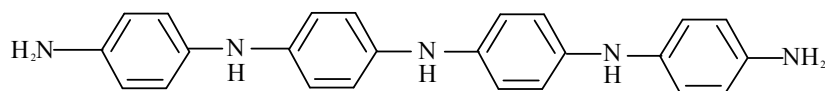


Scheme 2.

$^1\text{H}$  NMR, IR and UV spectroscopic data of the obtained 4,4'-di(p-aminoanilino)-diphenylamine was compared with the corresponding spectra of the compound obtained in different ways [15]. The  $^1\text{H}$  NMR spectrum (deuterated DMSO,  $\delta$ , ppm) characterized by the absence of chemical shifts of aliphatic protons and appearance of chemical shifts at 5.1–5.8 (4 H) of  $\text{NH}_2$  protons, at 6.00–8.30 (19 H) of aromatic (16 H) and NH (3 H) protons.

In UV spectrum absorption bands at 268 nm and 304 nm could be assigned to  $\pi-\pi^*$ -transitions of the aromatic ring connected to aminophenyl groups. The comparison of the obtained data with corresponding UV spectra data of the same compound described in [15] and leucoemeraldine (polymer having the same structure as tetramer) [27] shows appearance of the same absorbance at 308 nm (in DMSO) and 320 nm (in NMP).

IR spectrum of the obtained compound, absorption spectra of the carbonyl group was absent and fully correspond to those described in the literature spectral data of the same compound and are typical of the reduced form of polyaniline, i.e. leucoemeraldine:



Scheme 3.

Absorption of N–H or  $\text{NH}_2$  stretching vibrations are viewed at  $3342, 3403\text{ cm}^{-1}$ , C–H, C–C stretching at  $1609, 1515\text{ cm}^{-1}$ , C–N stretching at  $1264\text{ cm}^{-1}$ , plane deformation C–H at  $1170\text{ cm}^{-1}$ ; no plane deformation 1,4-disubstituted aromatic C–H at  $828\text{ cm}^{-1}$  in  $1170; 1384; 1515; 1605; 2922; 3022\text{ cm}^{-1}$ .

IR spectrum of the compound described in the literature [16] is the absorbance at ( $cm^{-1}$ ) 3387; 3345; 3022; 1609; 1511; 1303; 1263; 1223; 817.

*Received 29.08.2012*

#### REFERENCES

1. Handbook of Conducting Polymers (2nd Ed., T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds, eds.). New York, Basel, Hong Kong: Mercel-Dekker, 1998.
2. **Pron A., Rannou P.** Procesible Conjugated Polymers: from Organic Metals and Superconductors. // *Prog. Polym. Sci.*, 2002, v. 27, p. 135.
3. **Kumar D., Sharma R.C.** Advances in Conductive Polymers. // *Eur. Polym. J.*, 1998, v. 34, № 8, p. 1053.
4. **MacDiarmid A.G.** Short Cours on Conductive Polymers. NY, New Paltz: SUNY, 1985.
5. **Tallman D.E., Spinks G.M., Dominis A. J., Wallace G.G.** Electroactive Conducting Polymers for Corrosion Control. // *J. Solid State Electrochem.*, 2002, v. 6, p. 73.
6. **Rahmanifar M.S., Mousavi M.F., Shamsipur M., Heli H.** A Study on Open Circuit Voltage Reduction as a Main Drawback of Zn-polyaniline Rechargeable Batteries. // *Synth. Meth.*, 2005, v. 155, № 3, p. 480.
7. **Gerard M., Chaubey A., Malhotra B.D.** Aplication of Conducting Polymers to Biosensors. // *Biosens. Bioelectron.*, 2002, v. 17, p. 345.
8. **Karyakin A.A., Lukachova L.V., Karyakina E.E., Orlov A.V., Karpachova G.P.** The Improved Potencometric pH Response Modified with Procesible Polyaniline. Aplication to Glucose Biosensor. // *Analytical Commun.*, 1999, v. 36, p. 153.
9. **Kaempgen M., Roth S.** Transparent and Flexible Carbon Nanotube/Polyaniline pH Sensors. // *J. Electroanal. Chem.*, 2006, v. 586, № 1, p. 72.
10. **Mirmohseni A., Solhjo R.** Preparation and Characterization of Aqueous Polyaniline Battery Using a Modified Polyaniline Electrode. // *Eur. Polym. J.*, 2003, v. 39, № 2, p. 219.
11. **Wang W., MacDiarmid A.G.** New Synthesis of Phenyl/Phenyl End-Capped Tetraaniline in the Leucoemeraldine and Emeraldine Oxidation States. // *Synth. Meth.*, 2002, v. 129, p. 199–205.
12. **Rebourt E., Joule J.A., Monkman P.** Polyaniline Oligomers; Synthesis and Characterisation. // *Synth. Meth.*, 1997, v. 84, p. 65–66.
13. **Sadighi J.P., Singer R.A., Buchwald S.L.** Palladium-Catalyzed Synthesis of Monodisperse Controlled Lenght and Functionalized Oligoanilines. // *J. Am. Chem. Soc.*, 1998, v. 120, p. 4960–4976.
14. **Kulszewicz-Bajer I., Rózyńska I., Kuryek M.** Synthesis and Spectroscopic Properties of Aniline Tetramers. Comparative studies. // *New J. Chem.*, 2004, v. 28, p. 669–675.
15. **Dirattista J., Schmidt B.M., Padias A.B., Hall H.K.** Substituent Effect on the Polycondensation of Quinones with Aromatic Amines to Form Polyquinoneimines. // *J. Polym. Scie., Part A, Pol. Chem.*, 2002, v. 40, p. 43.
16. **Hall H.K., Padias A.B., Williams P.A., Gosau J., Boone H.W., Park D.K.** Novel Polyaromatic Quinone Imines. // *Macromolecules*, 1995, v. 28, № 1, p. 1–8.
17. **Williams P.A., Ellzey K.A., Padias A.B., Hall H.K.** New Polyaromatic Quinone Imines form Antraquinone. // *Macromolecules*, 1993, v. 26, p. 5820.
18. **Yamamoto T., Nurulla I., Ushiro A.** Organometallic C-N Coupling between N,N'-Dichloro-p-benzoquinone Diimine and Grignard Reagents and Its Application to Synthesis of Polyanilines. // *Tetrahedron Letters*, 2001, v. 42, p. 8653.
19. **Zhang W.J., Feng J., MacDiarmid A.G., Epstein A.J.** Synthesys of Oligomeric Anilines. // *Synth. Meth.*, 1997, v. 84, p. 119–120.
20. **Wei Y., Yang C., Wei G., Feng G.** A New Synthesis of Aniline Oligomers with Tree to Eight Amine Units. // *Synth. Meth.*, 1997, v. 84, p. 289–290.
21. **Zhu K., Wang L., Jing X., and Wang F.** Poly(phenylene Sulfide-Tetraniline): The Soluble Conducting Polyaniline Analogue with Well-defined Structures. // *Macromolecules*, 2001, v. 34, p. 8453.

22. **Buga K., Pokrop R., Majkowska A., Zagorska M., Planes J., Genoud F., Pron A.** Alternate Copolymers of Head to Head Coupled Dialkylbithiophenes and Oligoaniline Substituted Thiophenes: Preparation, Electrochemical and Spectroelectrochemical Properties. // *J. Mater. Chem.*, 2006, v. 16, p. 2150.
23. **Wang Y., Tran H.D., Liao L., Duan X., Kaner R.B.** Nanoscale Morphology, Dimensional Control and Electrical Properties of Oligoanilines. // *J. Am. Chem. Soc.*, 2010, v. 132, p. 10365.
24. **Berlin A.A.** Poluchenie N-Acetyldiphenylamina. // *Russ. Gen. J. Chem.*, 1944, v. 14, № 6, p. 445.35–37 (in Russian).
25. *Preparativnaya Org. Khim. M.: Goschimizdat*, 1959, p. 288 (in Russian).
26. **Gitis S.S., Glaz A.I., Ivanov A.V.** Praktikum po Organicheskoy Khimii. M.: Vysshaya Shkola, 1991, p. 210–211 (in Russian).
27. **Albuquerque J.E., Mattoso L.H.C., Balogh D.T., Faria R.M., Masters J.G., MacDiarmid A.G.** A Simple Method to Estimate the Oxidation State of Polyanilines. // *Synth. Meth.*, 2000, v. 113, p. 19–22.