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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF LINEAR OLIGOANILINES

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Two types of linear oligomers, namely Ph/NH_2 and NH_2/NH_2 end-capped oligoanilines have been synthesized by S_NAr coupling/reduction sequence. The ^1H NMR spectra of obtained compounds are strongly influenced by electron withdrawing or electron donating effects of the terminal groups (NO_2 or NH_2, respectively). The UV-Vis spectra of nitroamines exhibit two peaks characteristic for two types of the phenylene substituents (-NH- or NO_2), whereas UV-Vis spectra of oligoanilines show only one peak attributed to the Π-Π* *transition in the phenylene rings. The oxidation of oligoanilines was also followed by UV-Vis spectroscopy.*

INTRODUCTION

Polyaniline has attracted considerable attention due to its good stability and processibility in the conducting state. However, the properties of polyaniline depend strongly on its structure. For this reason oligoanilines can be considered as good model compounds to elucidate the structure, isomerization and possible molecular interaction of polyaniline. Aniline oligomers can be divided into three classes depending on their terminal groups, i.e. oligomers capped with a phenylene ring at one end and an amine group on the other (Ph/NH_2)*, oligomers capped with two amines groups (NH_2-NH_2) and oligomers capped with two phenylene rings (Ph/Ph). Recently, Ph/NH_2 and Ph/Ph end-capped oligomers have been synthesized by the methods involving different types of condensation [1–5].

In this study we report a new method of preparing Ph/NH_2 and NH_2/NH_2 end-capped oligoanilines, namely S_NAr coupling of 4-fluoronitrobenzene to corresponding arylamines followed by the reduction of NO_2 groups. The

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structure of obtained compounds (trimers and tetramers of both types) was characterized by ^{1}H NMR spectroscopy. The oxidation of oligoanilines was followed by UV-Vis spectroscopy.

EXPERIMENTAL

N-phenyl-1,4-phenylenediamine, 4,4'-diaminodiphenylamine sulfate, triethylamine, dimethyl sulfoxide (DMSO), 4-fluoronitrobenzene, $FeCl_3$, ammonium persulfate, Sn powder, hydrazine monohydrate were purchased from Aldrich Chemical Co. Acetone, dichloromethane, ethyl acetate, sodium pyrosulfite, HCl, KOH, NaOH were purchased from POCh (Poland). N-phenyl-1,4-phenylenediamine was crystallized from water and dried over KOH in vacuum desiccator. Triethyl amine was dried over KOH. DMSO was stored over thermally activated molecular sieves 4 Å. 4-fluoronitrobenzene, Sn powder, the oxidants and the solvents were used as supplied.

All nitroamines were prepared on the same way. Arylamines (10 mmol), 4-fluoronitrobenzene (10 mmol in the case of NH_2/NH_2 arylamine or 5 mmol in the case of Ph/NH_2 arylamine) and triethylamine (10 mmol) were dissolved in 15 ml of DMSO under argon atmosphere. The solution was stirred and heated at 90°C for 3 days. Then it was allowed to cool to room temperature, purred onto 200 ml of distilled water and filtered. The brown-orange solid was precipitated and washed several times with distilled water. The crude product was purified by liquid chromatography using silica gel. In the case of NO_2/NO_2 nitroamines the mixture of acetone/CH_2Cl_2, 1:4 was used as an eluent. In the case of Ph/NO_2 nitroamines the mixture of ethyl acetate/CH_2Cl_2, 1:4 was used. The powder was recrystallized from methanol.

Nitroamines were reduced to aryloamines using Sn powder and HCl. Nitroamine (2.5 mmol) was stirred with 5 ml of 37% HCl under argon atmosphere for 15 min. Tin powder (40 mmol in the case of NO_2/NO_2 nitroamines or 20 mmol in the case of the reduction of Ph/NO_2 nitroamines) and 37% HCl (25 ml) were added in portions and the mixture was refluxed for 3 h until white-yellow precipitate was formed. After cooling to room temperature NaOH granules were slowly added with constant stirring to adjust the pH to 12. The white precipitate was filtered, washed with 20% $_{wt}$ NaOH solution then with distilled water. The powder was dried over KOH in vacuum desiccator.

SPECTROSCOPIC MEASUREMENTS

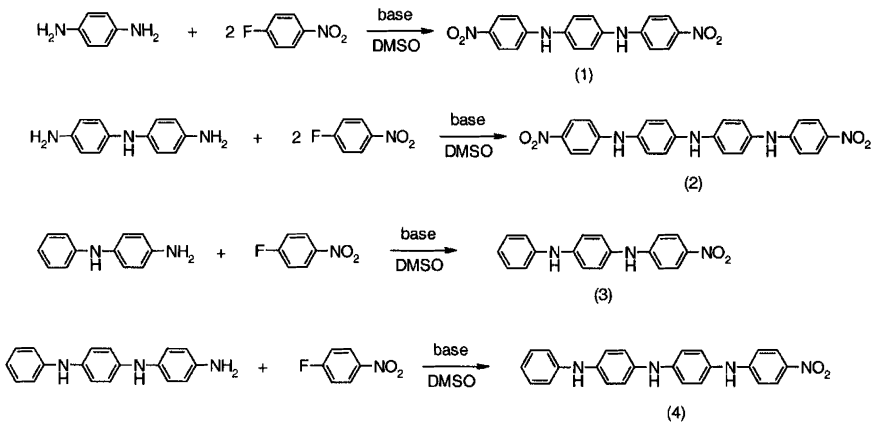
^{1}H NMR spectra were recorded in DMSO-d_6 solution on Varian Mercury 400 MHz.

UV-Vis-NIR spectra were registered on Lambda 2 (Parkin-Elmer) spectrophotometer in the spectral range of 250–1100 nm.

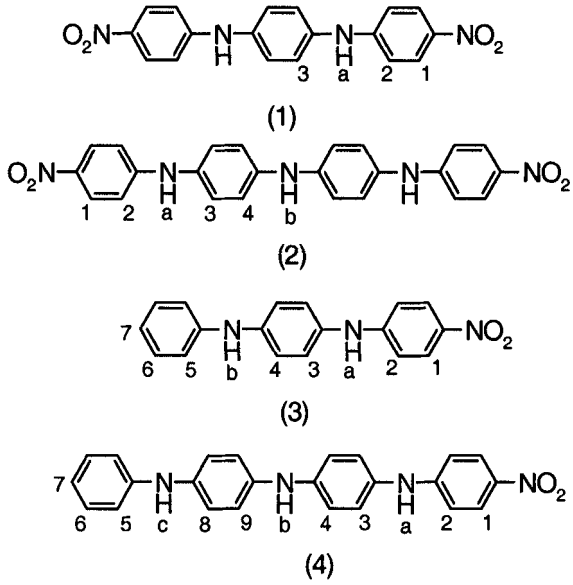
RESULTS AND DISCUSSION

This synthetic approach is based on the fact that activated fluoroarens can react with arylamines in dipolar aprotic solvents according to S_NAr mechanism. As activating groups the electron withdrawing groups like for example NO_2 or CN are frequently used. In our method we use 4-fluoronitrobenzene, arylamines and triethylamine as a base to obtain linear arylnitroamines. S_NAr coupling is followed by the reduction of nitro groups to corresponding amine which can serve as a reagent for next step of the elongation of the molecule (Scheme 1).

The ^{1}H NMR spectra of synthesized nitroamines in DMSO-d_6 are presented in Figures 1 and 2. The signals in the 9.3–7.8 ppm region are related to the −NH− protons. The location of these signals is strongly influenced by the electron withdrawing effect of the terminal nitro groups. Among our 4 studied oligomers, this effect is the biggest in the case of NO_2/NO_2 trimer (the −NH− proton signal appear at 9.29 ppm) whereas it is the lowest in the case of Ph/NO_2 tetramer. The signals corresponding to aromatic protons in orto-positions to nitro groups appear ca. 8.05 ppm independently of the molecule length. For symmetry reasons the spectra of NO_2/NO_2 oligomers are very simple. The spectra of unsymmetric Ph/NO_2 oligomers are richer and show. Two triplets located at ca. 7.2 ppm and 6.7 ppm, which confirm the presence of terminal phenylene ring. The observed ^{1}H NMR spectra agree with the postulated formulas of synthesized oligomers.

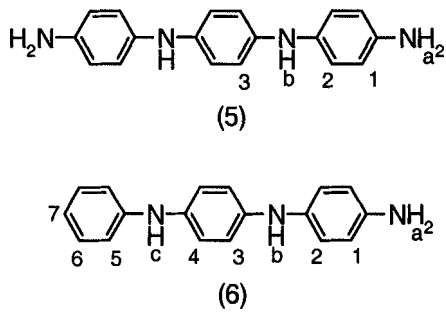


SCHEME 1 The synthesis of NO_2/NO_2 and Ph/NO_2 trimers and tetramers. Corresponding oligomers are prepared by the reduction of nitro groups.



SCHEME 2 Two types of oligomers: Ph/NO_2 and NO_2/NO_2 end-capped oligomers.

The UV-Vis spectra in DMSO of nitroamines (Figs. 3 and 4) exhibit two peaks located at 264–303 nm and at 430 nm. The high energy peak can be attributed to the Π-Π^* transition in the benzoid ring with two amine (−NH−) substituents, whereas the peak at 430 nm can be ascribed to the same transition but in the benzoid rings with one amine (−NH−) and one nitro groups in p-position. The relative intensities ratio of both peaks depends on the type of the molecule. The spectrum of Ph/NO_2 trimer shows the peaks of comparable intensities. In the case of NO_2/NO_2



SCHEME 3 Two types of trimers: Ph/NH_2 and NH_2/NH_2 end-capped triamnines.

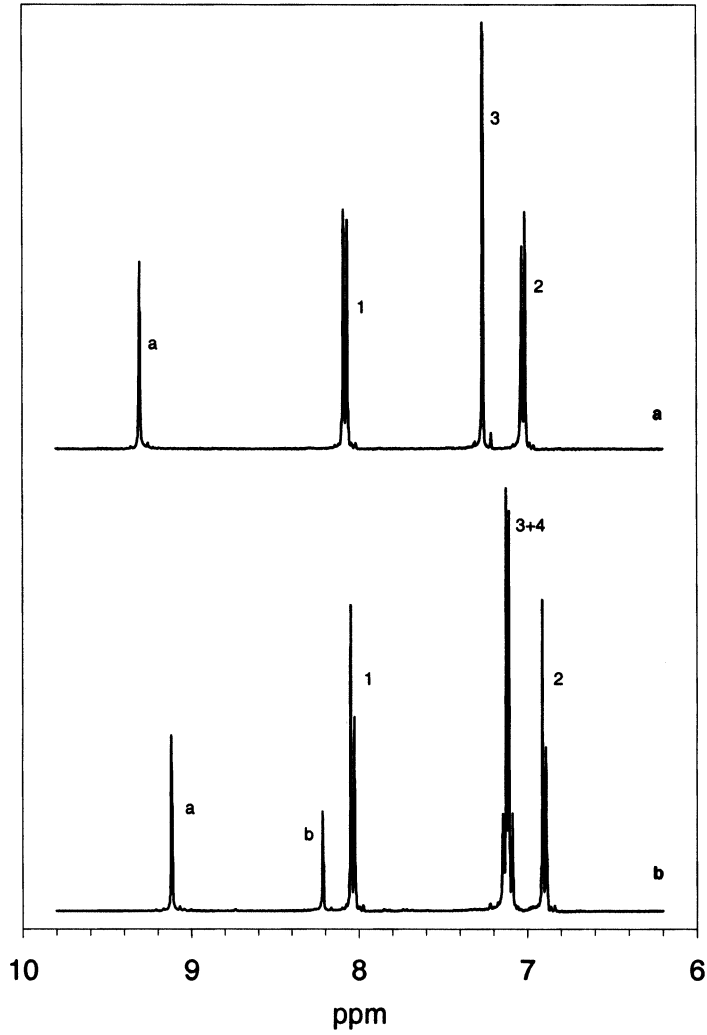


FIGURE 1 The ^{1}H NMR spectra in DMSO-d_6 solution of NO_2/NO_2 end-capped oligomers (a) trimer, (b) tetramer.

trimer spectrum the peak related to NH-Ph-NH excitation is small as compared with that corresponding to NH-Ph-NO_2 excitation.

The reduction of nitroamines changes the spectroscopic properties of the compounds. The ^{1}H NMR spectra of oligomers are influenced by the electro-donating character of amine groups (Fig. 5). The signals of terminal NH_2 group protons appear in the 4.72–4.57 ppm region. The positions of

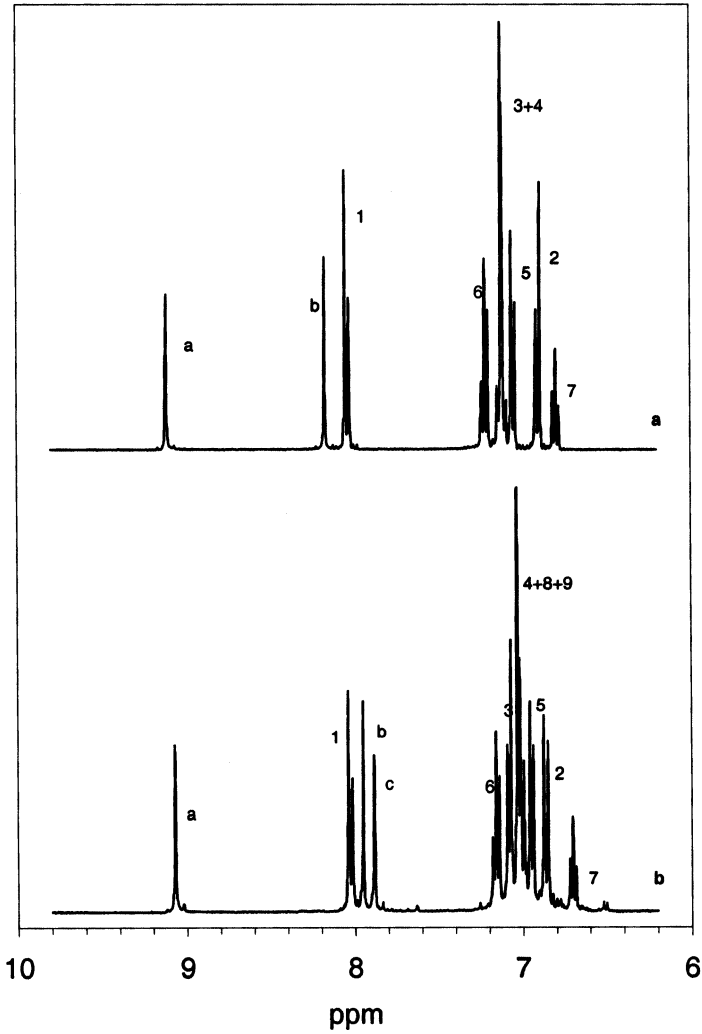


FIGURE 2 The ^{1}H NMR spectra in DMSO-d_6 solution of Ph/NO_2 end-capped oligomers (a) trimer, (b) tetramer.

other —NH— signals are also deplaced to the lower δ values as compared to the signals observed in nitroamines spectra.

Oligoanilines can be easily oxidized and this process can be followed by UV-Vis spectroscopy measurements. The UV-Vis spectra in DMSO of oligoanilines exhibit only one peak located at ca. 320 nm (Fig. 6). The oxidation process gives rise to new absorptions. The peak in the vicinity of 1000 nm

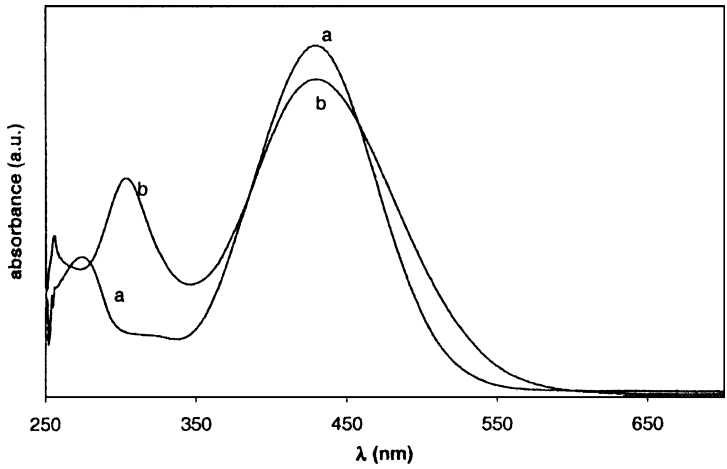


FIGURE 3 The UV-Vis spectra in DMSO of NO_2/NO_2 end-capped oligomers (a) trimer, (b) tetramer.

appears in the initial stages of the oxidation and vanishes when the oxidation proceeds in the spectra of aniline tetramers whereas it is always present in the case of trimers spectra. It should be also noted that the character of the spectra depends on the length of the molecules (trimer or tetramer) and is not influenced by the nature of the terminal groups (NH_2/NH_2 or Ph/NH_2).

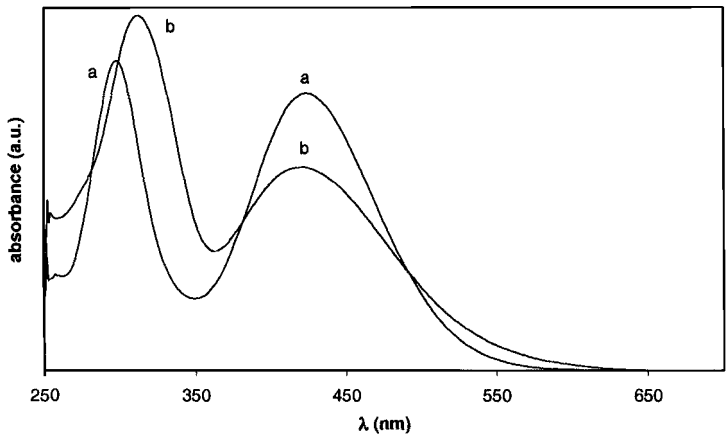


FIGURE 4 The UV-Vis spectra in DMSO of Ph/NO_2 end-capped oligomers (a) trimer, (b) tetramer.

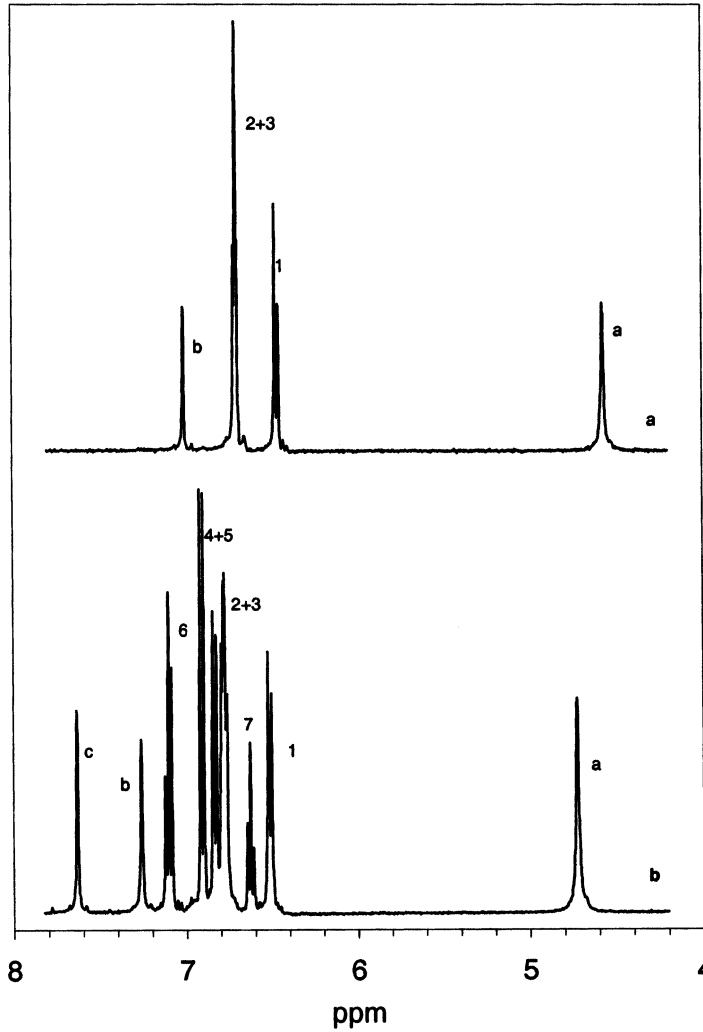


FIGURE 5 The ^{1}H NMR spectra in DMSO-d_6 solution of trimers (a) NH_2/NH_2, (b) Ph/NH_2 end-capped.

CONCLUSIONS

Two types of aniline oligomers were synthesized by S_NAr coupling/reduction sequence. The spectroscopic properties of oligonitroamines as well as oligoanilines depend on the length of the molecule and the chemical nature of the terminal groups. The oxidation of oligoanilines was followed by

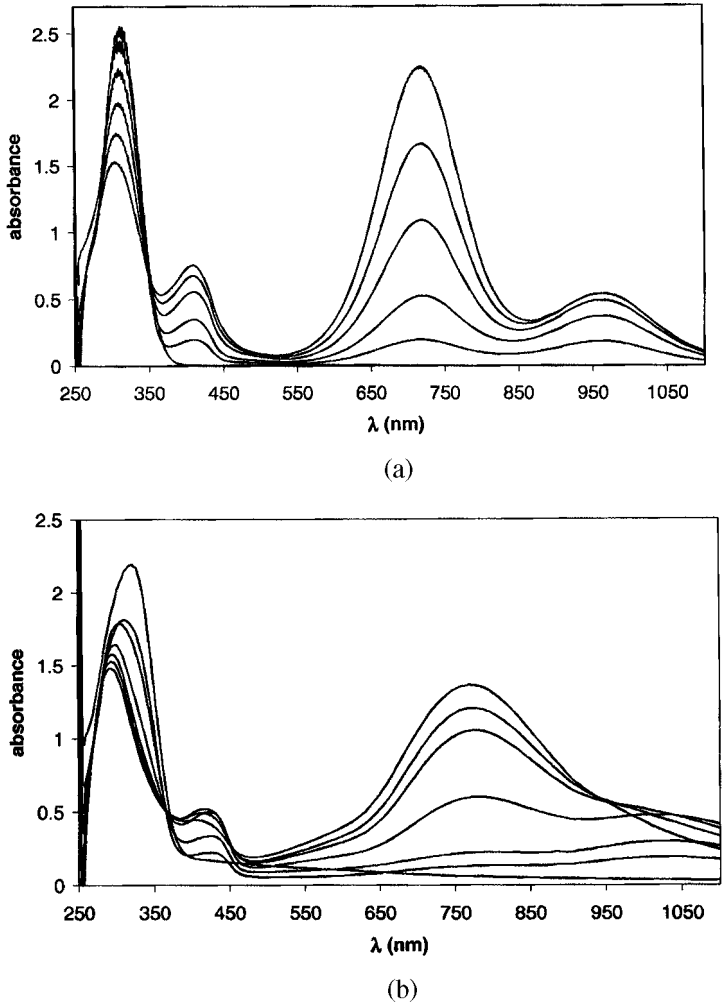


FIGURE 6 The UV-Vis spectra in DMSO of Ph/NH_2 trimer (a), Ph/NH_2 tetramers (b) oxidized with ammonium persulfate in 0.1 M HCI solutions.

UV-Vis spectroscopy. The spectra of oxidized tetramers exhibit the spectroscopic features similar to the observed in polianiline.

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