SYNTHESIS, OXIDATION AND PHOTOPHYSICAL PROPERTIES OF NOVEL DERIVATIVES OF ACYCLIC AROMATIC AMINES

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Conjugated acyclic arylamine derivatives, *N*-(4-methylphenyl)-*N*-(2-methyl-1-phenylpropyl)amine and *N*-(4-methoxyphenyl)-*N*-(2-methyl-1-phenylpropyl)amine, have been synthesized and characterized. Their photophysical properties have been investigated in polar methanol and non-polar cyclohexane solutions, and in PS and PMMA polymer matrices. The influence of the environment polarity as well as of the substituent in *para*-position of the aryl on the absorption, emission spectra and the fluorescence quantum yield has been studied. In the absorption and emission spectra, the observed absorption and emission band maxima were red shifted and the observed quantum yield was higher in the polar solution in comparison with the non-polar solution or polymer matrices. The distance of short- and long-wavelength absorption maxima in the methoxy derivative was larger and the emission band was red shifted in comparison with the methyl derivative. Chemical and photochemical oxidation of the prepared amines gives unstable nitroxides. High intramolecular quenching was observed in polymer matrix after photochemical oxidation of the amines.

Keywords: Amines; Nitroxides; Oxidations; Photochemistry; Fluorescence spectroscopy.

Free nitroxyl radicals are of great importance for several reasons. They play an important role in the mechanism of light and partially heat stabilization of polyolefins. In this case, stable free nitroxyl radicals are formed from their precursors – sterically hindered amines (HAS) – during stabilization[1]. The free nitroxyl radical can influence photochemical and photophysical processes due to its paramagnetic effect. Intermolecular quenching of excited singlet and triplet states of probes was observed in the presence of free nitroxyl radicals[2]. In the nineties, a specific group of probes with nitroxyl radical bounded in the molecule has been synthesized and investigated[3–6]. The formation or decay of the free radical, followed by ESR measurements,

is associated with on/off switching of the chromophore emission as a result of intramolecular quenching. Generally, the efficiency of intramolecular quenching in these probes depends on the size of the linker, which connects the chromophore with radical center, and on the medium[3–6].

In recent years, an intensive study of free nitroxyl radicals was prompted by the new polymerization method, living free radical polymerization (LFRP). This technique offers the control of molecular weight and molecular weight distribution (polydispersity) in the radical polymerization as well as a possibility of preparation of polymers with required design[7,8]. In most cases, 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO) is used in combination with peroxide as a polymerization initiator[9–12]. Its >N–O–R form can be used as unimolecular initiator without using peroxides. However, some problems are still to be overcome. For example, applicable monomers are limited mainly to styrene derivatives. High polymerization temperatures (above 110 °C) are required for polymerization. To overcome these problems, different structures of nitroxyl radicals and/or its >N–O–R form were studied[13–15]. Common method of preparation of these initiators is from appropriate hindered amines.

In our approach, we intend to study photophysical properties of two new aromatic amines. At the same time, a study of chemical and/or photochemical oxidation to nitroxides was planned. Due to direct conjugation of the aromatic ring with the free electron pair of nitrogen, a marked intramolecular quenching of fluorescence could be achieved.

EXPERIMENTAL

Measurements

Films were prepared by casting from chloroform solutions (1 ml containing 1 mg of amine and 20 mg of polymer) on 2.5 × 4 cm glass plates. The plates were covered with a Petri dish to slow solvent evaporation. This procedure resulted in films with good optical quality. After separation of films from glass plates by dipping into distilled water, the films were dried under vacuum to remove residual solvent.

For irradiation, a medium pressure mercury arc in a Spectramat apparatus (Ivoclar A.G., Schaan, Liechtenstein) with the whole spectrum was used.

NMR spectra (δ, ppm; *J*, Hz) were recorded on a Varian 300 MHz spectrometer (Varian, Germany). UV spectra were recorded on a Shimadzu UV1650PC spectrophotometer (Shimadzu, Japan). Steady-state emission spectra were recorded on a Perkin–Elmer MPF4 spectrofluorimeter (Perkin–Elmer, Norfolk (CT), U.S.A.), which was connected through interface and A/D converter to a microcomputer for data collection[19]. Emission of solutions was measured at the right angle in a 1 × 1 cm cell. Solutions were deaerated by bubbling with argon for 10 min immediately before measuring. The emission spectra of doped polymer films

were measured in the presence of air using a front-face arrangement in special sample holder at 45°.

The quantum yield of methanol and cyclohexane solutions was determined using anthracene as standard and assuming its low sensitivity to the medium. Anthracene was used as standard owing to its solubility and compatibility with different matrices used. For our purpose, this kind of comparison was sufficient. The quantum yields were determined according to Eq. (*1*)

$$\Phi_F = \Phi_F^S \frac{\int_0^\infty I_F(v)\,dv}{\int_0^\infty I_F^S(v)\,dv} \left(\frac{1 - 10^{A^S}}{1 - 10^A} \right) \tag{1}$$

where Φ_F^S is the quantum yield of anthracene as a standard, which was assumed to be 0.25 for all environments[20]. For relative quantum yield, the value of Φ_F^S for anthracene was set at 1. Integrals $\int_0^\infty I_F(v)\,dv$ and $\int_0^\infty I_F^S(v)\,dv$ are the areas under emission curves of the probe and standard, respectively, A and A^S are absorptions of the probe and standard at the excitation wavelength. Anthracene was excited at 356 nm.

Chemicals

Benzaldehyde, 4-methylaniline, 4-methoxyaniline, isopropylmagnesium chloride (2 M ether solution, Aldrich), $Sc(OTf)_3$ (Fluka), ethyl acetate (Chemapol), 70% *meta*-chloroperoxybenzoic acid (mCPBA, Aldrich), Na_2CO_3 (Slavus, Bratislava), Na_2SO_4 (Mikrochem, Bratislava), CaH_2 (Lachema, Praha) and isohexane (Hexol, Slovnaft) were used as received. Ethanol (Centralchem, Bratislava) was redistilled for the synthesis of imines and used as received for crystallizations. Toluene (Centralchem, Bratislava) for reactions under anhydrous conditions was distilled from sodium, but for extraction it was used as received. Dichloromethane (Slavus, Bratislava) was dried over CaH_2.

Synthesis

The studied compounds were synthesized using multistep reactions according to Scheme 1.
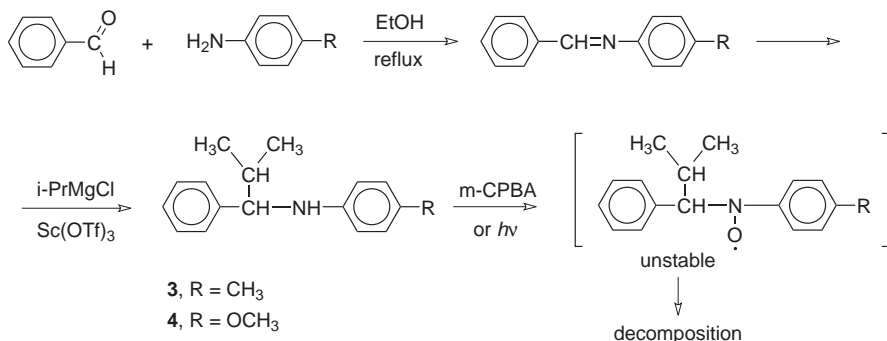
SCHEME 1
Synthesis of amines **3** and **4** and the respective nitroxides

N-(4-Methylphenyl)-N-(1-phenylmethylidene)amine (1)

Compound **1** was synthesized according to the published procedure[16]. Benzaldehyde (10.6 g, 0.1 mol) was added to the solution of *p*-toluidine (10.7 g, 0.1 mol) in ethanol (50 ml). The reaction mixture was refluxed for 30 min and the solvent was evaporated. The residue was purified by distilling off the unreacted benzaldehyde and crystallization from ethanol. The product was obtained in 61% yield as yellow crystals, m.p. 27–29 °C (ref.[16] 30–32 °C). ^{1}H NMR (300 MHz, CDCl$_3$): 8.38 (s, 1 H, CH); 7.84 (m, 2 H, H$_{Ar}$); 7.39 (m, 3 H, H$_{Ar}$); 7.13 (m, 4 H, H$_{Ar}$); 2.31 (s, 3 H, -CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): 159.3 (CH=N); 149.3 (C$_{Ar}$-N); 136.2 (C$_{Ar}$); 135.6 (C$_{Ar}$); 131.1 (C$_{Ar}$H); 129.6 (2 × C$_{Ar}$H);128.6 (4 × C$_{Ar}$H); 120.7 (2 × C$_{Ar}$H); 20.9 (-CH$_3$).

N-(4-Methoxyphenyl)-N-(1-phenylmethylidene)amine (2)

Compound **2** was synthesized similarly to compound **1** [16]. The crude product was filtered off and recrystallized from ethanol. The gray plates of pure product were obtained in 74% yield, m.p. 69.5–71 °C (ref.[16] 69–70 °C). ^{1}H NMR (300 MHz, CDCl$_3$): 8.47 (s, 1 H, CH); 7.88 (m, 1 H, H$_{Ar}$); 7.87 (m, 1 H, H$_{Ar}$); 7.45 (m, 3 H, H$_{Ar}$); 7.23 (ddd, 2 H, J = 8.7, 6.6, 2.4, H$_{Ar}$); 6.92 (ddd, 2 H, J = 8.7, 6.6, 2.4, H$_{Ar}$); 3.01 (s, 3 H, -OCH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): 158.4 (CH=N); 158.2 (C$_{Ar}$-N); 144.8 (C$_{Ar}$); 136.3 (C$_{Ar}$); 131.0 (C$_{Ar}$H); 128.7 (2 × C$_{Ar}$H); 128.5 (2 × C$_{Ar}$H); 122.1 (2 × C$_{Ar}$H); 114.3 (2 × C$_{Ar}$H); 55.4 (-OCH$_3$).

N-(4-Methylphenyl)-N-(2-methyl-1-phenylpropyl)amine (3)

Compound **3** was synthesized according to the published procedure[17,18]. To a solution of compound **1** (0.2 g, 1 mmol) in dry toluene (1 ml) was added Sc(OTf)$_3$ (0.49 g, 0.1 mmol) and then isopropylmagnesium chloride (0.2 g, 2 mmol) dropwise at –5 °C. The reaction mixture was stirred at room temperature for 5 h in Ar atmosphere and then the reaction was stopped with aqueous solution of ammonium chloride. The mixture was extracted with toluene, dried over anhydrous sodium sulfate and the solvent was evaporated under vacuum. After purification by silica column chromatography using toluene as an eluent, a highly viscous yellow liquid was obtained in 84% yield. ^{1}H NMR (300 MHz, CDCl$_3$): 7.27 (d, 4 H, J = 4.2, H$_{Ar}$); 7.19 (m, 1 H, J = 4.2, H$_{Ar}$); 6.86 (d, 2 H, J = 8.0, H$_{Ar}$); 6.41 (d, 2 H, J = 8.0, H$_{Ar}$); 4.08 (d, 1 H, J = 6.0, CH-N); 3.97 (bs, 1 H, NH); 2.15 (s, 3 H, -CH$_3$); 2.01 (m, 1 H, J = 6.0, 6.6, CH); 0.96 (d, 3 H, J = 6.6, -CH$_3$); 0.90 (d, 3 H, J = 6.6, -CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): 145.3 (C$_{Ar}$); 142.6 (C$_{Ar}$); 129.5 (2 × C$_{Ar}$H); 128.1 (2 × C$_{Ar}$H); 127.2 (2 × C$_{Ar}$H); 126.7 (2 × C$_{Ar}$H); 126.2 (C$_{Ar}$); 113.4 (C$_{Ar}$H); 64.1 (CH-N); 34.8 (CH); 20.3 (-CH$_3$); 19.7 (-CH$_3$); 18.6 (-CH$_3$). For C$_{17}$H$_{21}$N (239.4) calculated: 85.31% C, 8.84% H, 5.85% N; found: 85.31% C, 8.85% H, 5.87% N. MS, *m/z* (rel.%): 239 (50), 196 (100), 180 (15), 118 (35), 91 (40), 77 (15).

N-(4-Methoxyphenyl)-N-(2-methyl-1-phenylpropyl)amine (4)

Compound **4** was synthesized similarly to compound **3**, but only 0.05 mmol (0.25 g) of Sc(OTf)$_3$ was added and the reaction temperature was kept at –5 to 0 °C. A highly viscous yellow liquid was obtained in 88% yield. ^{1}H NMR (300 MHz, CDCl$_3$): 7.28 (d, 4 H, J = 4.5, H$_{Ar}$); 7.21 (m, 1 H, J = 4.5, H$_{Ar}$); 6.66 (ddd, 2 H, J = 9.0, 3.6, 2.4, H$_{Ar}$); 6.44 (ddd, 2 H, J = 9.0, 3.6, 2.4, H$_{Ar}$); 4.03 (d, 1 H, J = 6.0, CH-N); 3.85 (bs, 1 H, NH); 3.66 (s, 3 H, -OCH$_3$); 2.01 (m, 1 H, J = 6.0, 6.9, CH); 0.97 (d, 3 H, J = 6.9, -CH$_3$); 0.90 (d, 3 H, J = 6.9, -CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): 151.8 (C$_{Ar}$-O); 142.9 (C$_{Ar}$); 142.2 (C$_{Ar}$); 128.3 (4 × C$_{Ar}$H); 127.4 (2 × C$_{Ar}$H); 126.8 (C$_{Ar}$H); 114.9 (C$_{Ar}$H); 114.5 (C$_{Ar}$H); 64.8 (CH-N); 55.9 (-OCH$_3$); 35.1 (CH); 19.8 (-CH$_3$); 18.8 (-CH$_3$). For C$_{17}$H$_{21}$NO (255.4) calculated: 79.96% C, 8.29% H, 5.49% N; found: 79.38% C,

8.37% H, 5.29% N. MS, *m/z* (rel.%): 255 (50), 212 (100), 197 (23), 168 (37), 134 (30), 91 (35), 77 (15).

Oxidation of Amine 3

To a solution of amine **3** (0.2 g, 0.84 mmol) in dry CH_2Cl_2 (1 ml), a solution of mCPBA (2 equiv., 0.41 g, 2.38 mmol) in dry CH_2Cl_2 (2 ml) was added at 0 °C. The reaction mixture was stirred at room temperature under argon atmosphere for 12 h. The reaction mixture was extracted 4 times with a saturated solution of sodium carbonate. Organic phase was dried over anhydrous sodium sulfate and the solvent was evaporated. The presence of nitroxide derivatives was proved by ESR measurements (Fig. 1). However, the prepared nitroxides were unstable as described below. Decomposition products were not characterized.

Oxidation of Amine 4

Compound **4** (0.3 g, 1.17 mmol) was oxidized similarly as described above. After purification by column chromatography using hexane/ethyl acetate (10:1) as an eluent, isopropyl phenyl ketone (33%) and bis(4-methoxyphenyl)diazeneoxide (30%) as a major decomposition products were obtained.

Isopropyl phenyl ketone. ^{1}H NMR (300 MHz, CDCl$_3$): 7.97 (dd, 2 H, *J* = 6.9, 1.8, H$_{Ar}$); 7.55 (m, 1 H, H$_{Ar}$); 7.46 (ddd, 2 H, *J* = 6.9, 7.8, 1.8, H$_{Ar}$); 3.56 (m, 1 H, *J* = 6.9, CH); 1.22 (d, 6 H, *J* = 6.9, 2 × CH$_3$). MS, *m/z* (rel.%): 148 (8), 105 (100), 77 (37), 51 (14), 27 (4).

Bis(4-methoxyphenyl)diazeneoxide. ^{1}H NMR (300 MHz, CDCl$_3$): 8.27 (m, 4 H, H$_{Ar}$); 6.98 (m, 4 H, H$_{Ar}$); 3.89 (s, 3 H, OCH$_3$); 3.88 (s, 3 H, OCH$_3$). MS, *m/z* (rel.%): 258 (100), 121 (52), 107 (43), 92 (20), 77 (25), 64 (15).
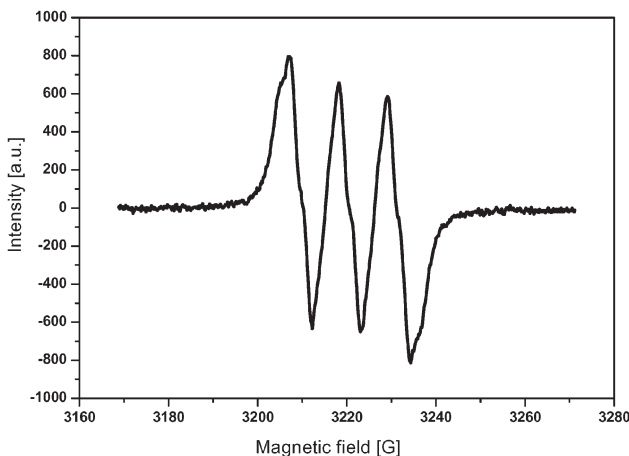

F$_{IG}$. 1
ESR spectra of the reaction mixture after oxidation of amine **3** with mCPBA in toluene (*c* = 1×10^{-2} mol/l)

RESULTS AND DISCUSSION

Synthesis

Amines **3** and **4** were obtained in high yields and purity by nucleophilic addition of isopropylmagnesium chloride using $Sc(OTf)_3$ as a catalyst in dry toluene and inert atmosphere. The catalyst $Sc(OTf)_3$ is very hygroscopic; the presence of water can decrease the reaction yield even below 30%. Half amount of $Sc(OTf)_3$ was sufficient for preparation of the methoxy derivative in compared the methyl derivative because of its higher reactivity. In both cases, an excess of organomagnesium chloride is needed. Actually, only half of the available R groups are usually used in the addition of an RMgX to aldimines[17].

Both amines **3** and **4** were oxidized in dry CH_2Cl_2 with mCPBA (2 equiv.). After work up of the crude reaction mixture, brown oil was obtained. The presence of nitroxyl radicals in the mixture was determined by EPR spectroscopy (Fig. 1). However, purification by column chromatography on silica gel or alumina led to decomposition. Similarly, EPR spectroscopy shows decomposition of the nitroxides in crude product mixture during its storing. This instability can be caused by the presence of hydrogen on the α-carbon to nitrogen[21,22].

The decomposition products formed after oxidation of amine **4** and separated by column chromatography using hexane/ethyl acetate (10:1) as an eluent, were identified by ^{1}H NMR and mass spectroscopy. They were found to be isopropyl phenyl ketone and bis(4-methoxyphenyl)diazeneoxide (Scheme 2). Beside the decomposition products, starting amine was also recovered. Decomposition products formed after oxidation of amine **3** were not separated, but on the base of TLC similar decomposition products as for amine **4** are expected.
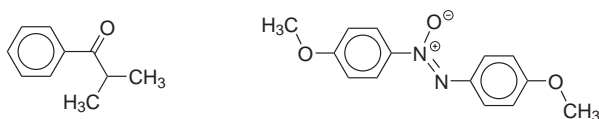
<small>Scheme 2</small>
Isopropyl phenyl ketone and bis(4-methoxyphenyl)diazeneoxide, the respective decomposition products after amine **4** oxidation

Absorption and Emission Spectra of 3 and 4

Absorption spectra of amines **3** and **4** in methanol and cyclohexane solutions as well as in PS and PMMA polymer matrices are shown in Figs 2 and 3, respectively. The spectra exhibit two maxima in both solvents and polymer matrices. The influence of environment polarity and the substituent in *para*-position of the aniline ring on the absorption spectra was observed. The short-wavelength bands of the methoxy derivative are blue shifted compared with the methyl derivative. On the other hand, the long-wavelength bands of the methoxy derivative are shifted to higher wavelengths (red shift) compared with the methyl derivative. The trend is the same in both solvents and polymer matrices (Tables I and II). Comparison of the absorption spectra of solutions in polar methanol and non-polar cyclohexane shows a slight red shift of the spectra for both compounds in methanol solution (Table I, Fig. 2). Similarly, in more polar PMMA matrix the UV absorption spectra of both compounds are red shifted compared with the spectra observed in less polar PS matrix (Table II, Fig. 3).

The emission spectra of the studied compounds were investigated in deaerated methanol and cyclohexane solutions and in the presence of air in PMMA and PS matrices. For excitation, light with the wavelength equal to the longest absorption band of the respective probe was selected. The rela-
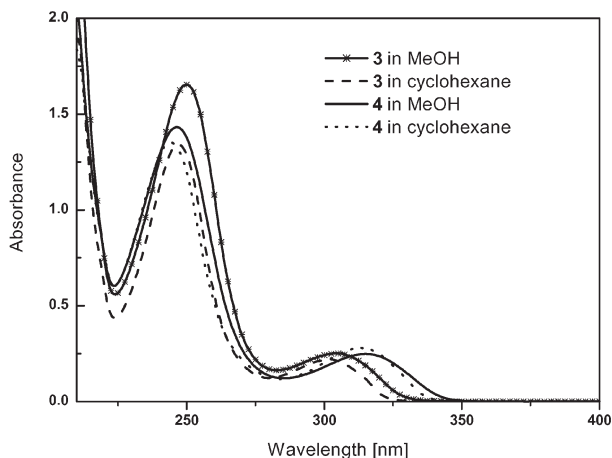

Fig. 2
UV absorption spectra of amines **3** and **4** in methanol and cyclohexane solutions ($c = 1 \times 10^{-4}$ mol/l)

tive quantum yield was calculated from the integrated observed emission spectra using anthracene as a standard. The emission band maxima and relative quantum yields are presented in Figs 4, 5 and Tables I, II. As shown in the observed emission spectra (Fig. 4) and Table I, the amine emission is strongly influenced by the substituent in *para*-position of aniline ring as well as by environment polarity. The emission spectrum of the methoxy derivative is red shifted compared with the methyl derivative in both solvents (Fig. 4, Table I). An increase in solvent polarity leads to the shift of the emission band maximum to higher wavelengths (Fig. 4, Table I). A similar influence on emission spectra of the amine derivatives by matrix polar-

TABLE I
Absorption and emission characteristics of amines **3** and **4** in solutions

Amine	Methanol			Cyclohexane		
	λ_{abs}, nm	λ_{em}, nm	Φ_{rel}	λ_{abs}, nm	λ_{em}, nm	Φ_{rel}
3	250; 304.5	355	0.4	247; 302	337	0.2
4	246.5; 315	371	0.65	244; 313.5	355	0.55

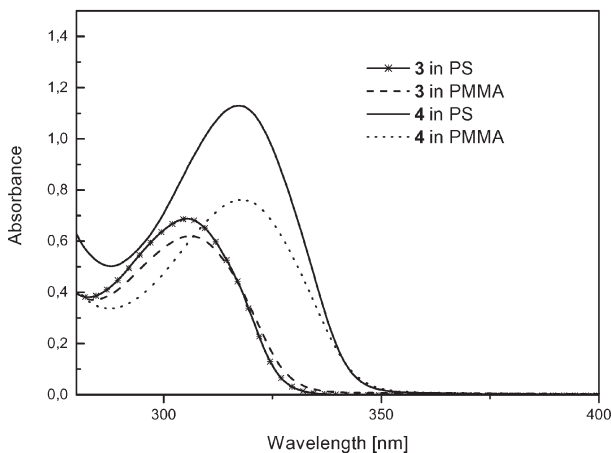

FIG. 3
Longer UV absorption bands of amines **3** and **4** in PS and PMMA matrices (c = 1 mg/20 mg polymer)

ity and substituent was observed in PS and PMMA matrices. The emission spectrum of the methoxy derivative is red shifted compared with the methyl derivative in both polymer matrices (Fig. 5, Table II) and the band maximum is more red shifted in more polar PMMA in comparison with the PS matrix. In the case of methyl derivative in the PS matrix, the longest absorption band and the emission band partially overlap.

The fluorescence quantum yields of amine derivatives were calculated according to Eq. (*1*) relative to anthracene as a standard. The results indicate the influence of the environment polarity as well as the substituent character (Tables I and II). As it can be seen from the results (Table I), a slightly

TABLE II
Absorption and emission characteristics of amines **3** and **4** in polymer matrices

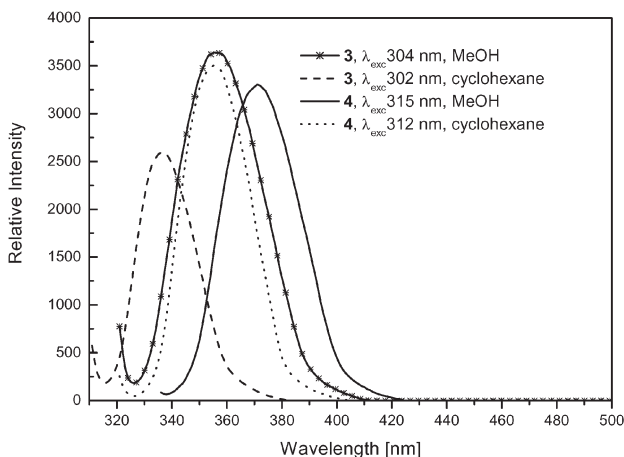| Amine	PS			PMMA		
	λ_{abs}, nm	λ_{em}, nm	Φ_{rel}	λ_{abs}, nm	λ_{em}, nm	Φ_{rel}
3	240.5; 305.5	333	<0.01	251; 306.5	336	0.05
4	238.5; 317.5	362	0.04	247.5; 318	366	0.06

FIG. 4
Emission spectra of amines **3** and **4** in deaerated methanol and cyclohexane solutions ($c = 1 \times 10^{-5}$ mol/l)

higher fluorescence quantum yield was observed for both amines **3** and **4** in methanol than in cyclohexane. Changing of methyl group in *para*-position of the aniline ring for the methoxy group leads to an increase in the quantum yield in both solvents. The effect of the substituents shows the same tendency in polymer matrices as in solutions; however, the quantum yields are about ten times lower than in solution (Table II). Even though the emission spectra in polymer matrices were measured in the presence of air, the explanation of lower quantum yields in comparison with the solution caused only by efficient fluorescence quenching by oxygen absorbed in the polymer matrix does not seem satisfactory. Oxygen concentration as well as mobility in the polymer matrix is much lower than in solution. Thus, another possible explanation could be the formation of nitroxides during irradiation of the polymer matrices in air. The formed peroxides could cause very efficient intramolecular quenching due to direct conjugation with the aromatic system. During excitation with monochromatic light in spectrofluorimeter, a change in color of the measured polymer film from colorless to red was observed. EPR spectra measured after this color change of PS film containing amine **4** showed the presence of nitroxyl radicals.

Comparing the polymer matrices, lower quantum yields were observed in the less polar PS matrix than in polar PMMA. In the case of methyl derivative measured in PS, the calculated quantum yield is strongly influenced also by a large overlap of longest-wave absorption and emission bands.
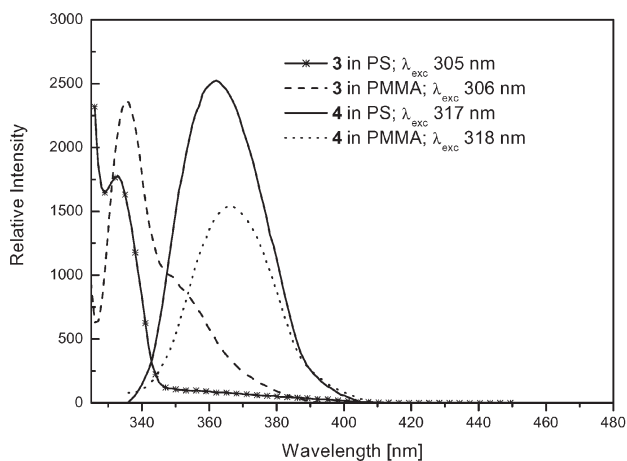

FIG. 5
Emission spectra of amines **3** and **4** in PS and PMMA matrices ($c = 1$ mg/20 mg polymer)

Irradiation of Amine 4

As already mentioned above, the nitroxides formation was detected after irradiation of amine **4** in the polymer film with monochromatic light in spectrofluorimeter. That is why we decided to follow the changes in UV-VIS and FT IR spectra of amine **4** in the PS matrix at various irradiation times. As shown in Fig. 6, the formation of a small absorption band with maximum at 505 nm was observed during irradiation with whole the spectrum of a medium-pressure mercury arc. We assume this band could belong to the formed aromatic nitroxides.

No significant changes, which could indicate decomposition of aromatic structure of the studied compound, were observed in the area below 350 nm in absorption spectra. The continued irradiation gave just very small changes in the absorption maximum at 505 nm, accompanied by an increase in absorption in the area from 370 to 450 nm, indicating some fast consecutive reactions of the formed nitroxides. UV absorption spectra of the dark reaction mixtures of the formed nitroxides are depicted in Fig. 7. We can see a slow decrease in the absorption maximum at 505 nm accompanied by an increase in absorbance below 450 nm. No significant change was observed in the absorption maximum of the studied compound in the area below 350 nm. This can indicate that during the dark reaction the
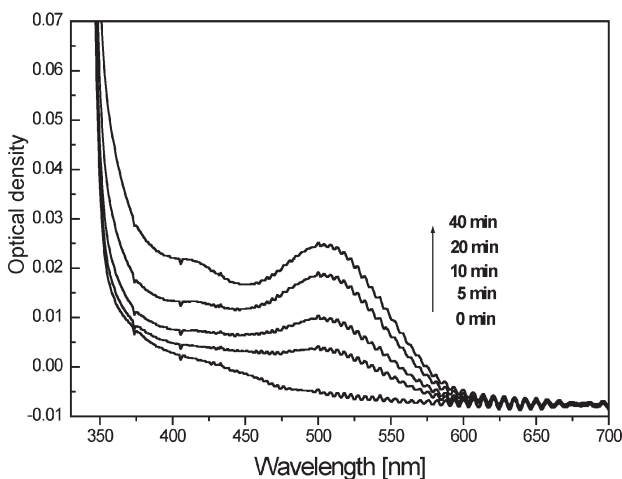

Fig. 6

UV-VIS spectra of amine **4** in PS film irradiated at ambient temperature in air for different time periods (c = 1 mg/20 mg polymer)

formed nitroxides slowly react with polymer matrix. The reaction can be much faster during irradiation in air, where various radicals from PS can be formed that can react with the formed nitroxides.

For comparison, an UV spectrum of amine **4** in PS irradiated with mono-chromatic light in spectrofluorimeter is given, in which the presence of nitroxides was proved by EPR. As we can see, the same absorption maxi-mum at 505 nm is observed in this spectrum.

In FT IR spectra the only change in the area of amine bands at 3424 cm^{-1} was observed. Thus a slight decrease in absorbance after 40-min irradiation of amine **4** in PS film and almost complete disappearance of the peak after 20-min irradiation with monochromatic light in spectrofluorimeter was observed.
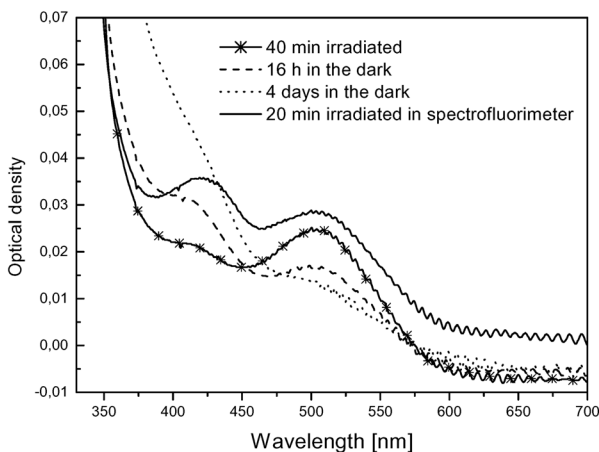

Fig. 7
UV-VIS spectra at different times of the dark reaction of PS film contaning pre-irradiated amine **4** or irradiated with monochromatic light (c = 1 mg/20 mg polymer)

CONCLUSIONS

Acyclic arylamine derivatives, **3** and **4**, have been synthesized in good yields and purity. Photophysical properties of the amines were studied in polar methanol and non-polar cyclohexane solutions as well as in PS and PMMA matrices. Their spectral characteristics are influenced by polarity as well as by the character of the substituent in *para*-position of the aniline ring. The compounds exhibit the two absorption maxima, which are shifted in dependence on the environment polarity and type of the

substituent. Fluorescence of both amines is red shifted in methanol and PMMA matrix.

Chemical oxidation of amines **3** and **4** gave the respective unstable nitroxides, which decompose during purification and storage.

Photochemical oxidation of the amines was observed in polymer matrices. The formed nitroxides dramatically decrease the fluorescence quantum yields of the studied amines by intramolecular quenching in polymer matrix compared with solutions. Preparation of more stable amine derivatives with alkyls in the α-position to nitrogen can give nitroxides with switching on/off the chromophore emission as a consequence of high intramolecular quenching.

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