Polymer Bulletin 50, 227–234 (2003)

Polymer Bulletin

Synthesis of poly[methyl(phenyl)silanediyl] containing 1,3,4-oxadiazole electron-transporting moieties

Rudolf Kotva, Věra Cimrová, and Drahomír Výprachtický(✉)

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
Tel.: +420-296809251, Fax: +420-296809410, e-mail: vyprach@imc.cas.cz

Received: 10 February 2003/Revised version: 8 April 2003/Accepted: 8 April 2003

Summary

The new oxadiazole derivative containing amino group, 2-(4-aminophenyl)-5-(biphenyl-4-yl)-1,3,4-oxadiazole (Oxad-NH_2), was synthesized and attached to formylated poly[methyl(phenyl)silanediyl] (PMPSi) by acid-catalyzed condensation of the aldehyde with the amino group yielding a Schiff base. The aldehyde groups were incorporated into the parent PMPSi by the reaction with dichloromethyl methyl ether in the presence of Lewis acid ($SnCl_4$). GPC analyses before and after modification reaction revealed that the attachment of Oxad-NH_2 proceeded without degradation of the silicon backbone. We reached 75 % conversion of aldehyde groups to oxadiazole Schiff base. The condensation reaction was followed and the prepared compounds and polymers were characterized by ^1H NMR, UV-vis, FT IR, GPC and elemental analyses. Fluorescence behavior of oxadiazole-modified PMPSi was studied in tetrahydrofuran. Broad emission band with maximum at 440 nm was observed. Fluorescence quantum yield of modified polysilanes increases with the increasing content of the attached oxadiazole moiety.

Introduction

Recently, oxadiazole-containing polymers have received a great deal of interest in the field of polymeric light-emitting devices (LED). Low-molecular-weight oxadiazoles like 2-(biphenyl-4-yl)-5-(*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) have been used as electron-transporting and emitting moieties in LEDs. To overcome the diffusion and crystallization of low-molecular-weight oxadiazoles in the polymer layers, the oxadiazole-containing polymers, such as poly(methyl methacrylate) [1], polystyrene [2], polyfluorene [3], polythiophene [4], poly(1,4-phenylenevinylene) [5], poly(1,4-phenylene) [6], polyether [7], poly(*N*-vinylcarbazole) [8], have been synthesized. Synthesis of oxadiazole-modified polysilanes has not been reported yet. In our previous papers [9-11], we have shown that the electroluminescence efficiency and time stability of polymer LEDs can be improved using polymer blends based on an electroluminescent polymer and hole-transporting polysilane. Addition of electron-transporting PBD further increased the electroluminescence efficiency. Therefore, we focused on the synthesis of polysilane modified with 1,3,4-oxadiazole derivative

(Fig. 1). The functionalization or modification of polysilanes is a problem because not all reactive functional groups present in the dichlorosilane monomer ($R^1R^2SiCl_2$; R^1, R^2 = alkyl or aryl) before polymerization can withstand drastic conditions of the Wurtz coupling reaction. A very useful chemical modification of aryl-containing polysilanes is the Friedel-Crafts chloromethylation [12]. Four reaction steps, however, were necessary to accomplish the transformation of chloromethyl groups into aldehyde ones [13]. Here we used the new one-step synthesis of poly[(4-formylphenyl)methylsilanediyl] (PMPSi-CHO) developed in our laboratory recently [14]. The synthesis of new oxadiazole derivative containing amino group is described as well.

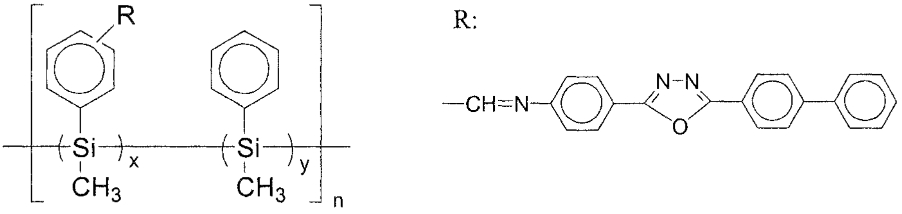

Fig. 1: Structure of the polymer under study

Experimental

Organic Synthesis

The oxadiazole derivative containing amino group (Oxad-NH_2) was prepared via a multistep synthesis (Fig. 2).

4-Nitrobenzohydrazide was prepared according to the known procedure [15]. Yield 62.7 g (86 %); mp 210-212 °C (lit. [15] 210 °C). Anal. calcd for $C_7H_7N_3O_3$ (181.16): C, 46.41; H, 3.90; N, 23.19 %. Found: C, 46.65; H, 3.92; N, 22.97 %.

1-(Biphenyl-4-carbonyl)-2-(4-nitrobenzoyl)hydrazine. Biphenyl-4-carbonyl chloride (Fluka, 8.67 g, 0.04 mol) was dissolved in 40 mL of dry pyridine and 7.25 g (0.04 mol) of 4-nitrobenzohydrazide in 30 mL of dry pyridine was added dropwise under stirring and with exclusion of air humidity. The orange reaction mixture was refluxed (1 h), then poured into water and left in a fridge overnight. The crude product was filtered off, dried, recrystallized from acetic acid, washed with water, and dried. Yield 10.88 g (75 %); mp 261-262 °C. Anal. calcd for $C_{20}H_{15}N_3O_4$ (361.36): C, 66.48; H, 4.18; N, 11.63 %. Found: C, 66.60; H, 4.16; N,11.81 %. ^1H NMR (DMF-d_7): 7.37-7.51 (m, 3H, C_6H_5), 7.72-7.81 (m, 4H, i.e., 2H of C_6H_5 and 2H of C_6H_4), 8.09 (m, 2H, C_6H_4), 8.23 (d, 2H, C_6H_4-N), 8.35 (d, 2H, C_6H_4-N), 10.52 ppm (s, 2H, NH). FT IR (KBr pellet): 3211 (N-H stretching); 3037 (aromatic C-H); 1643 (C=O stretching); 1606 (N-H bending); 1528 (NO_2 asym. stretching); 1344 (NO_2 sym. stretching); 1278, 1110, 1010 (aromatic C-H, in-plane); 850 (Ph-N); 751, 720, 695 (aromatic C-H, out-of-plane); 601 (N-C=O bending); 569, 503 (ring deformation); cm^{-1}.

2-(Biphenyl-4-yl)-5-(4-nitrophenyl)-1,3,4-oxadiazole (Oxad-NO_2). 1-(Biphenyl-4-carbonyl)-2-(4-nitrobenzoyl)-hydrazine (9.03 g, 0.025 mol) and 170 mL of $POCl_3$ (Aldrich) were stirred and refluxed for 24 h under dry conditions. The reaction mixture was poured on crushed ice (vigorous reaction), the precipitate was filtered off, washed with water and dried. The crude product was crystallized from acetic acid (950 mL). Yield 7.36 g (86 %); mp 270-272 °C. Anal. calcd for $C_{20}H_{13}N_3O_3$ (343.35): C, 69.96; H, 3.82; N, 12.24 %. Found: C, 69.85; H, 4.02; N,12.15 %. ^{1}H NMR (DMF-d_7): 7.43-7.54 (m, 3H, C_6H_5), 7.78-7.81 (m, 2H, C_6H_5), 7.96 (m, 2H, C_6H_4), 8.27 (m, 2H, C_6H_4), 8.48 ppm (m, 4H, i.e., 4H of C_6H_4-N). FT IR (KBr pellet): 3078 (aromatic C-H); 1607, 1070 (B_1 of oxadiazole ring); 1520 (NO_2 asym. stretching); 1480, 1104 (A_1 of oxadiazole ring); 1340 (NO_2 sym. stretching); 1275, 1185, 1006 (aromatic C-H, in-plane); 850 (B_2 of oxadiazole ring and Ph-N); 771, 735, 713 (aromatic C-H, out-of-plane); 547, 508 (ring deformation); cm^{-1}.

2-(4-Aminophenyl)-5-(biphenyl-4-yl)-1,3,4-oxadiazole (Oxad-NH$_2$). The Oxad-NO_2 (7.27 g, 0.021 mol) and 40 mL of phenylhydrazine were stirred and heated slowly. At 135 °C the solution became dark red and the temperature suddenly increased to 175 °C. The reaction mixture was refluxed (2 h), then cooled, and poured into benzene (200 mL) for crystallization. The crystals formed in a fridge overnight were filtered off, washed with benzene and petroleum ether and dried. Yield 4.55 g (69 %). The crude product was crystallized from toluene-ethanol (2:1 by vol.), mp 227-229 °C. Anal. calcd for $C_{20}H_{15}N_3O$ (313.36): C, 76.66; H, 4.83; N, 13.41 %. Found: C, 76.71; H, 4.85; N,13.51 %. ^{1}H NMR (THF-d_8): 5.27 (s, 2H, NH_2), 6.69 (m, 2H, C_6H_4-N), 7.01 (m, 2H, C_6H_4), 7.43 (m, 3H, C_6H_5), 7.69-7.96 (m, 4H, i.e. 2H of C_6H_5 and 2H of C_6H_4-N), 8.16 ppm (m, 2H, C_6H_4). FT IR (KBr pellet): 3458, 3317 (NH_2, stretching); 3005 (aromatic C-H); 1609 (NH_2, scissoring); 1592, 1072 (B_1 of oxadiazole ring); 1491, 1093 (A_1 of oxadiazole ring); 1313 (Ph-N); 1269, 1178, 1011 (aromatic C-H, in-plane); 844 (B_2 of oxadiazole ring); 765, 737, 701 (aromatic C-H, out-of-plane); 597, 485 (ring deformation); cm^{-1}. UV-vis (THF): $\lambda_{max} = 330$ nm, $\varepsilon = 36\,500$ L mol^{-1} cm^{-1}.

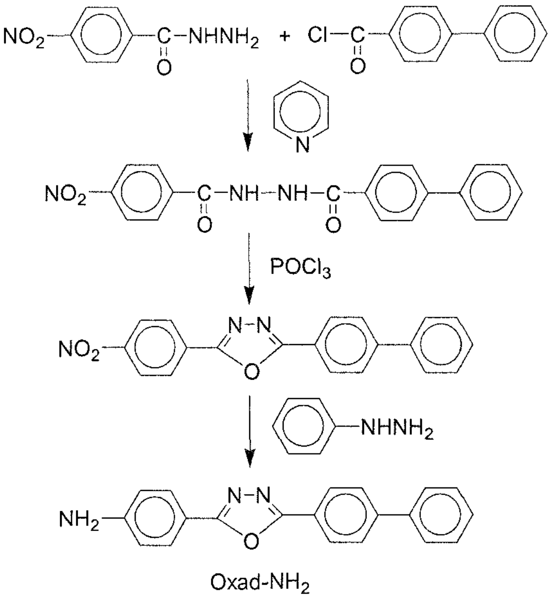

Fig. 2: Synthesis of 2-(4-aminophenyl)-5-(biphenyl-4-yl)-1,3,4-oxadiazole (Oxad-NH$_2$)

2-[4-(Benzylideneamino)phenyl]-5-(biphenyl-4-yl)-1,3,4-oxadiazole (Oxad-Ph). The Oxad-NH_2 (0.31 g, 1 mmol) was dissolved in 25 mL THF (dried with $LiAlH_4$) and 10 mL of benzaldehyde was added. After addition of 4-methylbenzene-1-sulfonic acid (0.01 g) the color was changed from yellow to brown. The reaction mixture was filtered with charcoal and its volume reduced to one half. Crystallization in a freezer gave yellow crystals. Yield 0.191 g (48 %); mp 188-190 °C. Anal. calcd for $C_{27}H_{19}N_3O$ (401.47): C, 80.78; H, 4.77; N, 10.47 %. Found: C, 80.80; H, 4.80; N,10.39 %. ^{1}H NMR (THF-d_8): 6.68 (d, 2H, C_6H_4), 7.30-7.52 (m, 6H, i.e., 3H of C_6H_5-Ph and 3H of C_6H_5-C), 7.65-7.97 (m, 6H, i.e., 2H of C_6H_5-Ph and 4H of C_6H_4-N), 8.12-8.25 (m, 4H, i.e., 2H of C_6H_5-C and 2H of C_6H_4), 8.59 ppm (s, 1H, N=CH) (Fig. 3d, signal at 9.95 ppm belongs to traces of benzaldehyde CHO). UV-vis (THF): λ_{max}= 330 nm, ε = 42 000 L mol^{-1} cm^{-1}.

Polymer Synthesis

Poly[(4-formylphenyl)methylsilanediyl], PMPSi-CHO, was synthesized from PMPSi according to the published procedure [14]. M_w = 27 000, M_n = 12 800 (GPC). ^{1}H NMR (THF-d_8): −1.1 to 0.6 (broad peak, 3H, CH_3), 6.1-7.6 (broad peak, 5H, C_6H_5), 9.5-9.9 ppm (peak, 1H, CHO) (Fig. 3a). From ^{1}H NMR spectrum the content of aldehyde groups in PMPSi-CHO was determined as 12 mol %. UV-vis (THF): λ_{max}= 328 nm, ε = 7 170 L mol^{-1} cm^{-1} (Fig. 4a). FT-IR (film on KBr): 3070, 3050 and 3020 (aromatic C–H); 2960 and 2895 (aliphatic C–H); 2926 (aldehyde C-H); 1702 (aldehyde C=O); 1950, 1890 and 1815 (aromatic); 1485 (skeletal ring breathing); 1430 and 1100 (Si–Ph); 1250 (Si–Me); 730 (aromatic C–H, out-of-plane); 696 (Si–C); 462 (Si–Si); cm^{-1}.

Polymer Modification

PMPSi-Oxad(1)-(4). 1.00 g (1.0 mmol of CHO groups) of PMPSi-CHO was dissolved under argon in 100 mL of a dry solvent (toluene or THF) and 1.00 g (3.2 mmol) of Oxad-NH_2 was added in 50 mL of the solvent. 4-Methylbenzene-1-sulfonic acid (0.02 g) was added and the reaction mixture was refluxed for a certain time (Table 1) with (in toluene) or without (in THF) a Dean-Stark adapter. The solvent was evaporated (20 mL) and the residue precipitated into methanol (400 mL). The polymer was reprecipitated from THF (20 mL) into methanol (400 mL) and dried to constant weight. Yields: 50-60 %. M_w and M_n (GPC) were the same as for parent PMPSi-CHO. ^{1}H NMR (THF-d_8): see Figs. 3b and 3c as a very good superposition of Figs. 3a and 3d. UV-vis (THF): see Fig. 4a and Table 1. FT IR (film on KBr): 3067, 3048 (aromatic C-H); 2956 (aliphatic C-H); 2894 (aldehyde C-H); 1700 (C=O); 1611 (HC=N); 1590 (B_1 of oxadiazole ring); 1484, 1098 (A_1 of oxadiazole ring); 1427 (δ_{as} of Si-CH_3); 1326 (Ph-N); 1247 (δ_s of Si-CH_3); 1186, 1067 (aromatic C-H, in-plane); 847 (Si-CH_3, rocking); 781, 753, 733 (aromatic C-H, out-of-plane); 698 (Si-C); 464 (Si-Si); cm^{-1}.

Polymer characterization

Molecular weights of the polymers were determined using GPC chromatograph (Laboratory Instruments, CZ) equipped with RI and UV 254 nm detectors, column 8 × 600 mm (PSS 10 000, PSS, Germany) and data collection and treatment (Data

Monitor, Watrex, CZ). Polystyrene standards (PL Laboratories, UK) were used for calibration. The samples were measured in tetrahydrofuran (THF), which was dried over molecular sieve 4A and distilled.

UV-vis spectra were taken on a Perkin-Elmer Lambda 20 spectrometer in THF (for UV-spectroscopy, Fluka) in a quartz cuvette (0.1 or 1.0 cm).

^{1}H NMR spectra were taken on a Bruker ACF-300 spectrometer at 300.1 MHz in deuterated tetrahydrofuran (THF-d_8) or dimethylformamide (DMF-d_7) using hexamethyldisiloxane as an internal standard.

FT IR spectra were measured using a Perkin-Elmer Paragon 1000 PC Fourier transform infrared spectrometer in KBr pellets or as a film on KBr pellet.

Fluorescence spectra of solutions were measured with a Hitachi Perkin-Elmer MPF-2A spectrometer in L-format and corrected [16] for the calculation of the fluorescence quantum yields (Q_{FL}).

Results and Discussion

The starting poly[methyl(phenyl)silanediyl] (PMPSi) was prepared by Wurtz coupling polymerization of dichloromethyl(phenyl)silane using refluxing toluene-sodium dispersion and characterized as described [14]. The prepared PMPSi possessed a largely unimodal but broad molar mass distribution (M_w = 45 000, M_n = 18 000). The characteristic $\sigma \rightarrow \sigma^*$ transition for the silicon backbone of PMPSi was measured at λ_{max}= 335 nm as ε = 8 300 L mol^{-1} cm^{-1}. The poly[(4-formylphenyl)methylsilanediyl] (PMPSi-CHO) was synthesized reacting PMPSi and dichloromethyl methyl ether in the presence of Lewis acid ($SnCl_4$). The formylation reaction was in competition with the silicon backbone degradation (cleavage) and a decrease in molecular weight (ca. 50 %) and polydispersity was observed. The ratio M_w/M_n dropped from 2.5 to 2.1 for PMPSi and PMPSi-CHO, respectively. This is a very good result in comparison with the above mentioned four-step synthesis [13], where larger molecular weight decreases (90 %) were reported. In general, the random degradation cleavage of a polymer with $M_w/M_n > 2$ leads to the material with polydispersity limiting to 2. The decrease in molar absorption coefficient ($\sigma \rightarrow \sigma^*$ transition) of formylated PMPSi is in agreement with a decrease in σ-conjugation of the silicon backbone caused by the lower average molecular weight. The synthesized PMPSi-CHO was further utilized as a functionalized polymeric precursor. The aldehyde protons (1H) in PMPSi-CHO were clearly detected by ^{1}H NMR spectroscopy at 9.75 ppm, and by comparison with a broad signal of aromatic protons (5H) at 6.1 – 7.6 ppm, the content of aldehyde groups in the polymer was determined as 12 mol % (Fig. 3a). The aldehyde C-H (2926 cm^{-1}) and C=O (1702 cm^{-1}) vibrations in addition to those of PMPSi were detected by FT IR spectroscopy. The aldehyde groups are assumed to be attached in the *para* positions of benzene rings for steric reasons, like in chloromethylation of PMPSi [12]. The oxadiazole derivative containing amino group, 2-(4-aminophenyl)-5-(biphenyl-4-yl)-1,3,4-oxadiazole (Oxad-NH_2), was synthesized and attached to PMPSi-CHO by acid-catalyzed condensation of the aldehyde with the amino group yielding a Schiff base (Fig. 1). The Oxad-NH_2 was prepared by a multistep synthesis starting from 4-nitrobenzohydrazide and biphenyl-4-carbonyl chloride (Fig. 2). Modification of PMPSi-CHO with Oxad-NH_2 used in excess (mole ratio 1:3) under different reaction conditions is summarized in Table 1.

The content of oxadiazole structure units in modified polysilanes PMPSi-Oxad(1)-(4) increases with increasing reaction time (equilibrium reaction). The reaction water was

Table 1: Modification of PMPSi-CHO with Oxad-NH_2 used in excess (NH_2/CHO = 3) under different reaction conditions yielding PMPSi-Oxad(1)-(4)

expt no.	solvent	reaction time (min)	molar absorption coeff. at 328 nm (L mol^{-1} cm^{-1})		N analysis (wt. %)	oxadiazole content (mol %)	
			ε_{calc}	ε_{exp}		ex N	^{1}H NMR
1	toluene	15	7 800	7 700	0.59	1.7	1.9
2	THF	30	8 370	8 290	1.08	3.4	3.5
3	THF	240	8 950	8 700	1.55	5.0	5.2
4	toluene	240	9 960	10 090	2.24	7.7	8.5

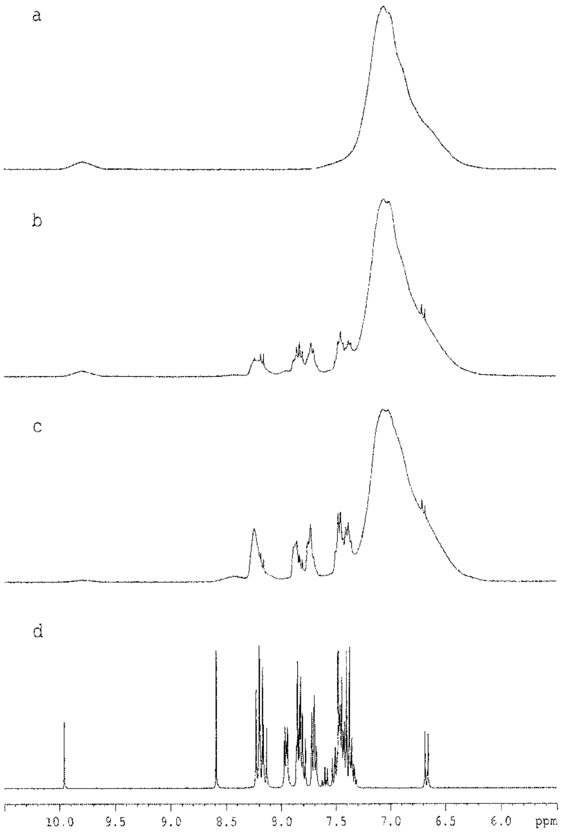

Fig. 3: ^{1}H NMR spectra of PMPSi-CHO (a), PMPSi-Oxad(3) (b), PMPSi-Oxad(4) (c), and Oxad-Ph (d) in THF-d_8.

removed by refluxing in excess of dry tetrahydrofuran or using an azeotropic Dean-Stark adapter for the refluxing toluene reaction mixture. The latter procedure was more efficient and we reached ca. 8 mol % of aldehyde groups replaced by Oxad-NH_2 for PMPSi-Oxad(4). The content of oxadiazole moieties in polymer was determined both from elemental analysis (ex N) and ^1H NMR spectroscopy. The measured values were in good agreement. ^1H NMR spectra of modified polymers show increasing signals of oxadiazole aromatics at 7.3 – 8.6 ppm accompanied by a decreasing aldehyde signal around 9.7 ppm as the content of oxadiazole structures in polysilane increases (Figs. 3b,c). The spectrum of model compound 2-[4-(benzylideneamino)-phenyl]-5-(biphenyl-4-yl)-1,3,4-oxadiazole (Oxad-Ph) is shown for convenience modeling the oxadiazole moiety in modified polysilane (Fig. 3d). UV-vis absorption of PMPSi-Oxad(1)-(4) at λ_{max} = 328 nm increases with increasing degree of modification (Table 1). This is reasonable taking into account the molar absorption coefficients (λ_{max} = 328-330 nm) of PMPSi-CHO ($\sigma \rightarrow \sigma^*$) and Oxad-Ph ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$) as ε = 7 170 and 42 000 L mol^{-1} cm^{-1}, respectively. Molar absorption coefficient, ε_{exp}, was determined from experimental UV-vis spectra (Fig. 4a) using an average molecular weight <M> of the structure unit of modified polymer. Molar absorption coefficient, ε_{calc}, was calculated using the 7 170 and 42 000 values and the average contents of oxadiazole units in modified polymers. For the <M> and ε_{calc} calculations, the average contents of oxadiazole units in PMPSi-Oxad(1)-(4) were taken as 1.8, 3.45, 5.1, and 8.0 mol %, respectively (average from N analysis and ^1H NMR values). Very good agreement of ε_{calc} and ε_{exp} values suggests that the σ-conjugation of silicon backbone is not decreased by modification reaction. The attachment of Oxad-NH_2 yielding a Schiff base proceeded smoothly and without degradation of the main chain. This result was confirmed by GPC analyses of polysilanes before and after modification. GPC curves for the PMPSi-CHO and modified PMPSi-Oxad(1)-(4) nearly matched each other. The presence of oxadiazole units in modified PMPSi was confirmed also by FT IR spectroscopy. The 1,3,4-oxadiazole belongs [17] to the point

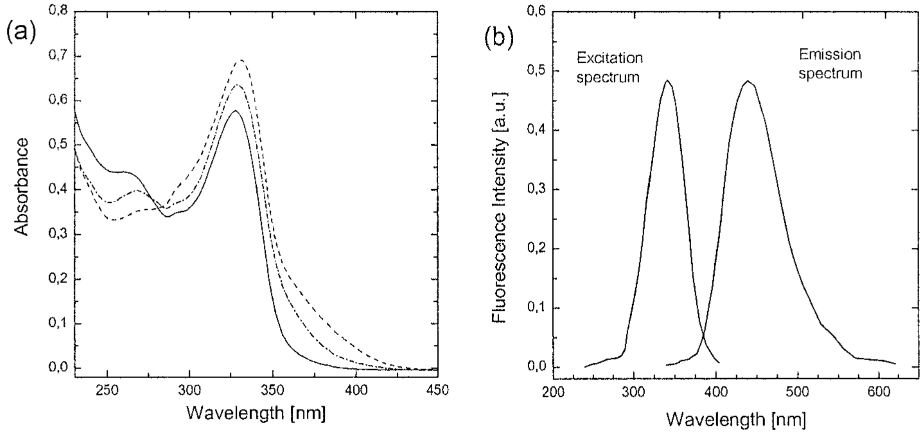

Fig. 4: (a) UV-vis spectra of PMPSi-CHO (solid line), PMPSi-Oxad(3) (dashed and dotted line), and PMPSi-Oxad(4) (dashed line) in THF (0.1 cm, c = 0.1 g L^{-1}); (b) Fluorescence excitation (em = 440 nm) and emission (ex = 340 nm) spectra of PMPSi-Oxad(2) in THF (c = 5.88 × 10^{-3} g L^{-1}).

group C_{2v} expecting 15 fundamental vibrations ($6A_1 + 5B_1 + 2A_2 + 2B_2$). The strongest A_1 (at 1484 and 1098 cm^{-1}) and B_1 (at 1590 cm^{-1}) were detected in the modified polymers. The A_2 fundamentals are infrared inactive and B_2 at 844 cm^{-1} (observed in Oxad-NH_2) was overlapped by Si-CH_3 rocking vibration at 847 cm^{-1}.

Fluorescence behavior of the synthesized polysilanes modified with electron-transporting and emitting oxadiazole moieties was studied in tetrahydrofuran. PMPSi-Oxad(1)-(4) exhibited broad emission spectra with a maximum located at 440 nm. Excitation spectra showed a maximum at 340 nm. The typical fluorescence spectra are displayed in Fig. 4b. Sharp near-ultraviolet emission of PMPSi at 350-360 nm was not detected and fluorescence spectra of modified polymers matched those of Oxad-Ph. This indicates that an efficient energy transfer from polysilane to oxadiazole fluorophores occur as a consequence of exciton mobility in PMPSi [18]. Fluorescence quantum yields (Q_{FL}) of the modified polysilanes and Oxad-Ph were evaluated using carbazole in cyclohexane [16] as a standard compound (Q_S = 0.38). The "inner filter effect" was eliminated using solutions at the same absorbance (A) at excitation (λ_{ex} = 340 nm, A_{340} = 0.4). Oxad-Ph exhibited a high fluorescence quantum yield, Q_{FL} = 0.82. Fluorescence quantum yield in oxadiazole-modified polysilanes increases with the increasing content of the attached oxadiazole units. The Q_{FL} values of 0.09, 0.11, 0.26, 0.36 were determined for PMPSi-Oxad(1)-(4), respectively.

Acknowledgments. We are grateful to the Grant Agency of the Czech Republic for supporting the project by grants No. 102/98/0696 and No. 203/01/0512.

References

[1] Meier M, Buchwald E, Karg S, Pösch P, Greczmiel M, Strohriegl P, Rieß W (1996) Synth Met 76:95.

[2] Sato H, Sakaki Y, Ogino K, Ito Y (1997) Polym Adv Technol 8:454.

[3] Ding J, Day M, Robertson G, Roovers J (2002) Macromolecules 35:3474.

[4] Huang W, Meng H, Yu WL, Heeger AJ (1998) Adv Mater 10:593.

[5] Song SY, Ahn T, Shim HK, Song IS, Kim WH (2001) Polymer 42:4803.

[6] Wang C, Kilitziraki M, Palsson LO, Bryce MR (2001) Adv Funct Mater 11:47.

[7] Shu CF, Wu FI (2001) J Polym Sci, Part A: Polym Chem 39:3851.

[8] Jiang X, Register RA, Killeen KA, Thompson ME, Pschenitzka F, Sturm JC (2000) Chem Mater 12:2542.

[9] Cimrová V, Neher D, Remmers M, Kmínek I (1998) Adv Mater 10:676.

[10] Cimrová V, Výprachtický D, Pecka J, Kotva R (2000) Proc SPIE 3939:164.

[11] Cimrová V, Výprachtický D (2003) Appl Phys Lett 82: 642.

[12] Jones RG, Benfield RE, Swain AC, Webb SJ, Went MJ (1995) Polymer 36:393.

[13] Kmínek I, Brynda E, Schnabel W (1991) Eur Polym J 27:1073.

[14] Výprachtický D, Cimrová V (2002) Macromolecules 35:3463.

[15] Flowers WT, Taylor DR, Tipping AE, Wright CN (1971) J Chem Soc C 1986.

[16] Výprachtický D, Cimrová V, Machová L, Pokorná V (2001) Collect Czech Chem Commun 66:1473.

[17] Christensen DH, Nielsen JT, Nielsen OF (1967) J Mol Spectrosc 25:197.

[18] Tokura H, Tachibana H, Kishida H, Morimoto Y, Matsumoto M (1994) J Phys Soc Jpn 63(Suppl. B):30.