Synthesis and photophysical properties of novel fluorescent silicones

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Abstract

Six fluorescent polysiloxanes have been synthesized by dehydrogenative coupling of fluorescent alcohols or phenols with poly(methylhydrosiloxane), using several different coupling catalysts. The absorption and emission spectra for the polymers have been studied; emission from both monomer and excimer states appears to take place.
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1. Introduction

Fluorescent polymers have been of interest for many years [1]. They are now receiving increased attention because many such polymers are also electroluminescent [2], and so may be useful in polymeric light emitting diodes for display technology [3–9]. A limited amount of research has been done on fluorescent polysiloxanes. The fluorescence of poly(phenylmethylsiloxane) was studied by Dias et al., and both monomer and excimer emitting states were identified [10]. The emission spectra of cyclic phenylsiloxanes have been carefully investigated by Pernisz and co-workers [11]. Polysiloxanes with pendant carbazolyl groups were observed to show strong fluorescence, also from monomer and excimer sites [12,13]. Polysiloxanes grafted with pyrene or carbazolyl groups were shown to have electroluminescent properties by Gaudiana and co-workers [14], and a recent study reports the grafting of both charge-transporting and nonlinear optical functionalities onto polysiloxanes [15].

In this paper we report the synthesis of six fluorescent polysiloxanes, **2a**–**7a**, and a preliminary study of their electronic absorption and emission. The polysiloxanes were all made by dehydrocoupling of alcohols or phenols with poly(methylhydrosiloxane), **1** [16] (Scheme 1).

2. Results and discussion

To bring about the dehydrocoupling reaction we employed a variety of catalysts, as shown in Table 1. Triethylamine, H_2PtCl_6 and Karlstedt's catalyst ('Pt⁰') are all quite active catalysts for this reaction. However all three gave a small amount of insoluble, apparently crosslinked material as a byproduct. With potassium carbonate the dehydrocoupling takes place very rapidly, but is accompanied by extensive crosslinking which sets the entire mixture into a gel. The best results were obtained with $RhCl(PPh_3)_3$, as recommended by Boudjouk and co-workers [16]. Although the coupling is slower with this catalyst, requiring about 24 h at 70 °C for completion, the product is free of any detectable crosslinked material. Phenols reacted somewhat more rapidly than carbinols, note the results for Pt⁰ in Table 1.

All polymers were characterized by ²⁹Si- and ¹H-NMR, and by UV–vis and fluorescence spectroscopy. The data are summarized in Table 2.

Emission from excimer states is expected for these polymers with multiple fluorescent substituents, and in methylene chloride solution we observe long wavelength fluorescence attributable to excimers in the emission spectra for **2a**–**5a**. An example is the spectra of the 1-

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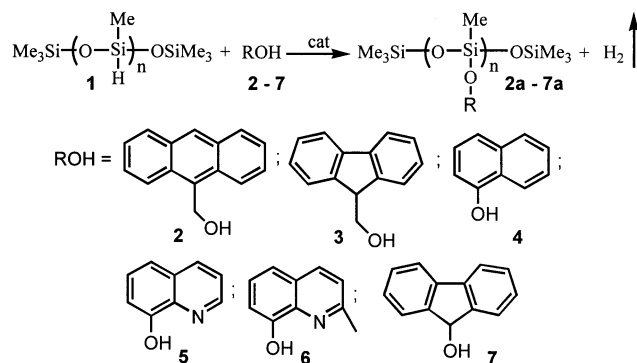
Scheme 1. Synthesis of fluorescent polysiloxanes.

Table 1
Effect of type of catalysts on alcoholysis of PMHS

Catalyst / Alcohol	RhCl(PPh$_3$)$_3$ benzene	K$_2$CO$_3$ benzene	Et$_3$N benzene	"Pt^o" benzene	H$_2$PtCl$_6$ benzene
(quinaldine, 8-hydroxy-2-methyl)	70°C 24 h	24 °C crosslinked insoluble	70°C 3 h trace crosslink	24°C 18 h trace crosslink	70°C 4 h trace crosslink
(anthracene methanol)	70°C 24 h	24 °C crosslinked insoluble	70°C 4.5 h trace crosslink	70°C 4 h trace crosslink	70°C 4h trace crosslink

Table 2
Yields, ^{29}Si-NMR (δ), UV–vis and fluorescence (Fl) for silicones **2a**–**7a**

Alcohol (2 – 7)	(2a)	(3a)	(4a)	(5a)	(6a)	(7a)
Yield (%)	90	94	92	90	87	92
^{29}Si NMR	-57.41 +10.32[a]	-56.35 -57.51 +9.71[a]	-60.70 -61.29 +11.01[a]	-62.70 -62.96 +8.50[a]	-61.98 -63.18 -63.76 +8.68[a]	-56.77 -57.87 -58.09 +9.804[a]
UV-vis $\lambda_{max}/\varepsilon$	256/14664 332/505 348/1125 366/1767 386/1577 (c-hexane)	256/21700 280/6950 290/7654 (c-hexane)	295/5760 326/2710 (c-hexane)	244/67929 322/4232 (c-hexane)	248/58150 316/3144 (c-hexane)	276/12975 288/9189 310/2647 (CH$_2$Cl$_2$)
Fl λ_{max}/Φ^c	450[b]/0.04 (c-hexane)	375[b]/0.33 (CH$_2$Cl$_2$)	410[b]/0.03 (c-hexane)	415[b]/0.015 (c-hexane)	326/0.02 (c-hexane)	320/0.34 (CH$_2$Cl$_2$)
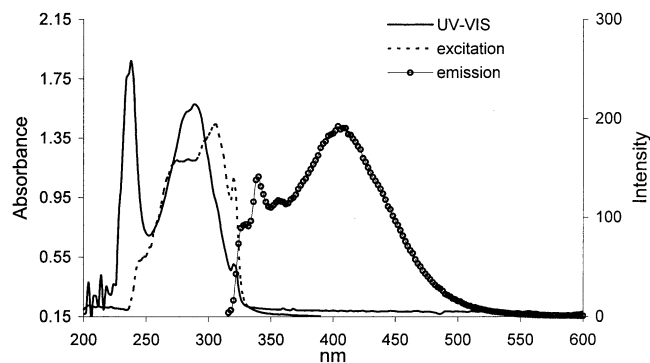
Fig. 1. UV–vis, excitation, and emission, spectra of polymer **4a** in CH$_2$Cl$_2$ solution.

naphthol-substituted polymer **4a** (Fig. 1). No long wavelength emission was however seen for **6a** and **7a**. Fig. 2 shows the absorption and emission spectra for the 8-hydroxyquinaldine-substituted siloxane, **6a**. It is interesting to note that this polymer does not give an excimer band, although the corresponding polymer differing only in the lack of a methyl group, **5a**, does show excimer-type emission. Possibly the methyl group in **6a** prevents close association of the 8-quinaldyloxy rings so that excimer formation is prevented. Perhaps a conformational restriction also accounts for the lack of excimer emission in the other non-excimer polymer, **7a**.

The emission spectra of our polymers also show strong solvent dependence. Fig. 3 shows the absorption and emission spectra of **3a** in three different solvents. The excimer band is absent in cyclohexane, weak in THF and becomes strong in methylene chloride. Increasing intensity of the long wavelength band with solvent polarity has been observed for other polyaromatic polymers [17,18], and is consistent with a polar, charge-transfer nature of the low-energy emitting state.

Intensity and structure of the emission of polymer **3a** depends on the excitation wavelength applied during recording. When **3a** was excited at 268 nm in methylene chloride the structure of spectra changed and emission
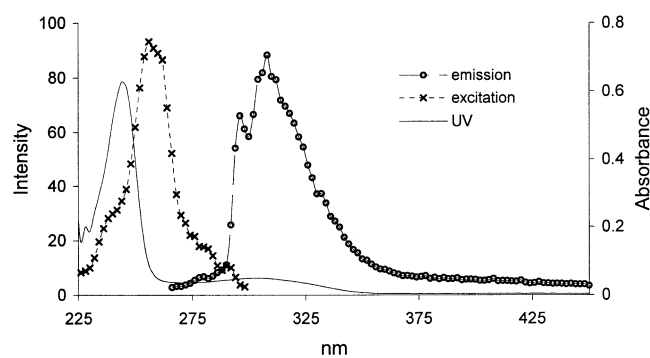
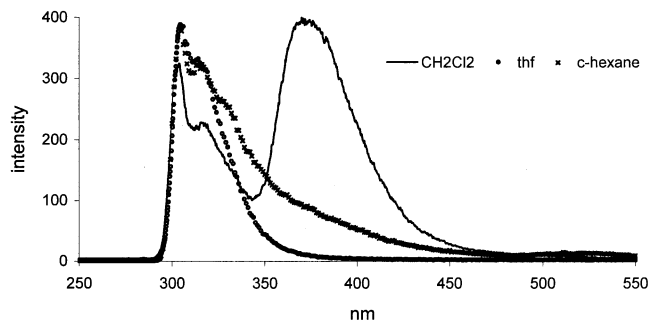Fig. 2. UV–vis, excitation, and emission, spectra of polymer **6a** in CH$_2$Cl$_2$ solution.

Fig. 3. Emission spectra of **3a** ($c = 0.25 \times 10^{-5}$ mol l^{-1}) in different solvents (excited at 299 nm).
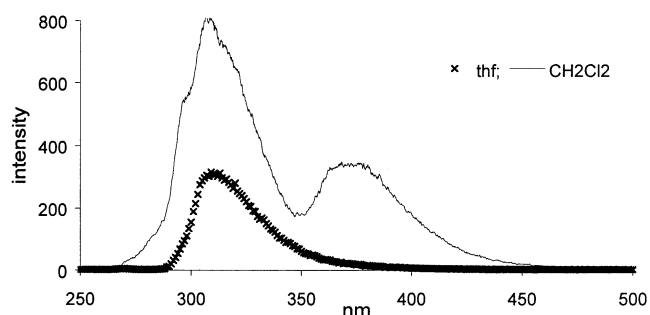

Fig. 4. Emission spectra of **3a** ($c = 0.25 \times 10^{-5}$ mol l^{-1}), excited at 268 nm.
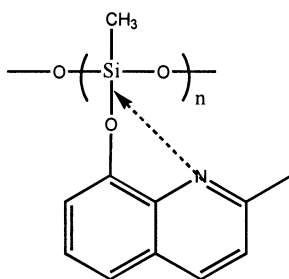

Fig. 5.

at 316 nm increased dramatically. In tetrahydrofuran, the intensity of emission of **3a** decreased when it was excited at 268 nm Fig. 4.

We noticed that polysiloxanes, **5a** and **6a**, grafted with 8-hydroxyquinoline (**5**) and 8-hydroxyquinaldine (**6**), have their ^{29}Si signals shifted upfield by 7 ppm (at $-63 \, -64$ ppm) compare to those of polysiloxanes **2a**, **3a**, **4a** and **7a** (at -56 to -57 ppm). The reason for this upfield shift in the ^{29}Si resonance can be the coordination of the nitrogen in 8-oxyquinoline (or 8-oxyquinaldine) substituents to silicon atom of the backbone chain of the polymers Fig. 5.

To confirm this suggestion we synthesized the model molecules triphenyl(8-quinaldyloxy)silane (**8**) and triphenyl(1-naphthoxy)silane (**9**) by the reaction of triphe-
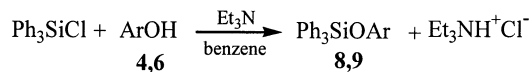
Scheme 2. Reaction of triphenylchlorosilane with phenols **4**, **6**.

nylchlorosilane with aromatic alcohols **4** and **6** (Scheme 2).

The ^{29}Si signal of triphenyl(8-quinaldyloxy)silane (**8**) is -13.52 ppm, shifted upfield by 1.96 ppm compared to that of triphenyl(1-naphthoxy)silane (**9**) (-11.56 ppm). This shift can likewise be explained by an additional coordination of the Si atom in **8** by nitrogen.

3. Experimental

3.1. General

All reactions were carried out using a standard Schlenk line under nitrogen or argon gas atmosphere. All solvents were dried and distilled from sodium/benzophenone solutions. Poly(methylhydrosiloxane), (PMHS), ($M_w \sim 2000$; $n = 33–35$) and RhCl(PPh$_3$)$_3$ (99.99%) were obtained from Aldrich and used as received. Commercially available alcohols were used without further purification.

All polymers **2a–7a** were analyzed by ^{1}H-, ^{13}C- and ^{29}Si-NMR, UV–vis, fluorescent and FT-IR spectroscopy.

Infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer (film on KBr disk).

^{1}H-, ^{13}C- and ^{29}Si-NMR spectra were determined in CDCl$_3$ at 20 °C on a Varian INOVA-500 spectrometer working at 500.0 MHz for ^{1}H, 99.38 MHz for ^{29}Si. The chemical shifts are expressed in parts per million using TMS as an internal standard (^{1}H, ^{29}Si data). Electronic absorption and fluorescence spectra were recorded on a HP 8452 UV–Visible Spectrophotometer and F-4500 fluorescence spectrophotometer, respectively. The quantum yields for **2a–7a** were measured in cyclohexane solution. Anthracene, naphthalene and quinine sulfate in 0.1 N sulfuric acid were used as standards [19].

3.1.1. Synthesis of polymers 2a–7a

The method of synthesis of grafted silicones earlier described by Boudjouk and co-workers [16] was modified by employing a smaller amount of RhCl(PPh$_3$)$_3$ (0.18 mg, 0.02 mmol instead of 0.36 mg, 0.04 mmol).

The synthesis of **2a** is described as an example. PMHS (0.12 ml, 2 mmol), RhCl(PPh$_3$)$_3$ (0.18 mg, 0.02 mmol) and anthracenemethanol (**2**) (0.42 g, 2 mmol) were placed in a Schlenk flask and air was removed by pumping during 0.5 h at room temperature (r.t.). The flask was flashed with argon, dry benzene (0.8 ml) was added and this mixture was heated at 78 °C for 24 h. After the reaction was complete, the mixture was passed

through a silica gel pad with CHCl$_3$: benzene (1:10) eluent. Solvent was removed under vacuum and polymer **2a** was obtained in 90% yield. Polymers **3a–7a** were obtained by using similar technique and molar ratios.

No evidence of Si–H bond was observed in FT-IR spectra of polymers **2a–7a**.

3.1.2. Poly[methyl(9-anthrylmethoxy)siloxane] (2a)

^{1}H-NMR (CDCl$_3$): δ 0.06 (s, broad, OSiMe$_3$); 0.13 (s, broad, SiMe); 5.53 (s, broad, OCH$_2$); 7.28–8.31 (broad, aromatics). ^{29}Si-NMR (CDCl$_3$): -57.41 (SiMe); $+10.32$ (terminal OSiMe$_3$). GPC (toluene/polystyrene): $M_w = 17190$ ($M_w/M_n = 1.15$).

3.1.3. Poly[methyl(9-fluorenylmethoxy)siloxane] (3a)

^{1}H-NMR (CDCl$_3$): δ 0.06 (s, OSiMe$_3$); 0.31–0.54 (s, broad, SiMe); 5.66 (s, broad, OCH$_2$); 7.28–8.74 (broad, aromatics). ^{29}Si-NMR (CDCl$_3$): -56.35, -57.51 (SiMe); $+9.71$ (terminal OSiMe$_3$). GPC (toluene/polystyrene): $M_w = 9652$ ($M_w/M_n = 1.03$).

3.1.4. Poly[methyl(1-naphthoxy)siloxane] (4a)

^{1}H-NMR (CDCl$_3$): δ 0.15 (s, OSiMe$_3$); 0.30 (s, broad, SiMe); 7.14–8.29 (broad, aromatics). ^{29}Si-NMR (CDCl$_3$): -60.70, -61.29 (SiMe); $+11.01$ (terminal OSiMe$_3$). GPC (toluene/polystyrene): $M_w = 10\,650$ ($M_w/M_n = 1.06$).

3.1.5. Poly[methyl(8-quinolinoxy)siloxane] (5a)

^{1}H-NMR (CDCl$_3$): δ 0.13 (s, OSiMe$_3$); 0.30 (s, broad, SiMe); 7.14–7.32 (broad, aromatics). ^{29}Si-NMR (CDCl$_3$): -62.70, -62.96 (SiMe); $+8.50$ (terminal OSiMe$_3$). GPC (toluene/polystyrene): $M_w = 11\,130$ ($M_w/M_n = 1.31$).

3.1.6. Poly[methyl(8-quinaldyloxy)siloxane] (6a)

^{1}H-NMR (CDCl$_3$): δ 0.03(s, OSiMe$_3$); 0.13–0.49 (s, broad, SiMe); 2.61–2.66 (s, broad, CH$_3$); 7.14–8.48 (broad, aromatics). ^{29}Si-NMR (CDCl$_3$): -61.98, -63.18, -63.76 (SiMe); $+8.68$ (terminal OSiMe$_3$). GPC (toluene/polystyrene): $M_w = 9875$ ($M_w/M_n = 1.22$).

3.1.7. Poly[methyl(9-fluorenyloxy)siloxane] (7a)

^{1}H-NMR (CDCl$_3$): δ 0.13 (s, OSiMe$_3$); 0.30 (s, broad, SiMe); 7.14–7.32 (broad, aromatics). ^{29}Si-NMR (CDCl$_3$): -56.77, -57.87, -58.09 (SiMe); $+9.80$ (terminal OSiMe$_3$). GPC (toluene/polystyrene): $M_w = 14\,530$ ($M_w/M_n = 1.1$).

3.1.8. Investigation of dehydrocoupling reactions of PMHS with alcohols in presence of different catalysts

Triethylamine, H$_2$PtCl$_6$, Karlstedt's catalyst ('Pt^0') and K$_2$CO$_3$ were used as catalysts for these reactions.

A catalyst (0.5% of H$_2$PtCl$_6$ (or Karlstedt's catalyst ('Pt^0'), or K$_2$CO$_3$, or 20% of triethylamine) was placed in a Schlenk flask and degassed by freeze-pump cycle three times. A solution of an air free mixture of PMHS (2 mmol) with an alcohol (2 mmol) in dry benzene (1 ml) was transferred into the flask with the degassed catalyst. A vigorous evolution of hydrogen was observed at r.t. For most catalysts the reaction was complete after 3–4 h at r.t. The completion of the reaction was monitored by ^{1}H-NMR spectroscopy. After removing solvent the polymer was analyzed by ^{29}Si-NMR and unidentified signals in the -40 to -50 ppm region were observed, in addition to the signals of polymers **2a–7a**. We assume that the new signals at -40 to -50 ppm are due to crosslinked products.

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