

Effect of the Polysilane Structure on Its Solution Fluorescence Quenching

GAOQUAN LI, JIAN TAN, HEJIAN FU, HONG MA, DEBEN CHEN, ZHONGHUA ZHOU

Department of Chemistry, Sichuan University, Chengdu, 610064, People's Republic of China

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ABSTRACT: We studied the solution fluorescence quenching of poly(methylphenethylsilane) (1[#]), poly(dimethylsilane-*co*-methylphenethylsilane) (2[#]), poly(*n*-hexylmethylsilane) (3[#]), and poly(dimethylsilane-*co*-*n*-hexylmethylsilane) (4[#]) by such quenchers as CCl₄, CHCl₃, Cl₂CHCHCl₂, and methyl benzoate. We treated the fluorescence quenching data using the equations $F_0/F = 1 + K_{SV}[Q]$, $F_0/F \exp(-NV[Q]) = 1 + K_{SV}[Q]$, and $\ln(F_0/F) = NV[Q]$, where F and F_0 are the fluorescence intensity with and without the addition of a quencher, respectively; K_{SV} , the Stern–Volmer constant; $[Q]$, the quencher concentration; N , Avogadro's constant; and V , the volume of the active sphere. For the systems with both static quenching and dynamic quenching, we calculated their contributions and the critical quencher concentration $[Q]_C$ and determined the nature of the fluorescence quenching in different quencher concentration ranges. We observed that, under the condition of the same quencher, the fluorescence quenching of the polysilane homopolymer is smaller than that of its corresponding polysilane copolymer, that is, $1^{\#} < 2^{\#}$ and $3^{\#} < 4^{\#}$, and that for the fluorescence quenching of the same polysilane by different chlorohydrocarbons the fluorescence quenching ability of CCl₄ is larger than that of CHCl₃ and Cl₂CHCHCl₂. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 133–139, 2000

Key words: polysilane; fluorescence quenching; static quenching; dynamic quenching; active sphere; critical quencher concentration; energy transfer

INTRODUCTION

Polysilane, because of its Si–Si σ conjugation, has many unique electrical and optical properties and several potential applications such as high-resolution photoresists,¹ optical waveguide films,² and nonlinear optical materials.³ In a wide wavelength range (about 280–350 nm), polysilane displays strong absorption. After ultraviolet absorption, it emits strong fluorescence ($\phi = 0.1$ – 0.8) and undergoes photodegradation.^{4–6} However, the quantum yield of the photodegrada-

tion in the solid state is 50–100 times lower than that in solution.^{7–9} Miller et al. added aromatic sensitizers with $-\text{CCl}_3$ to the poly(methylphenethylsilane) film and greatly improved the photodegradation rate.¹⁰ This is of both theoretical and practical importance in the study of polysilane microlithography. Moreover, they studied the fluorescence quenching of poly(methylpropylsilane) by CCl₄, calculated the volume of the active sphere (V) and the Stern–Volmer constant (K_{SV}) according to the equation $F_0/F \exp(-NV[Q]) = \tau_0/\tau = 1 + K_{SV}[Q]$, and proposed that the fluorescence quenching includes both static quenching and dynamic quenching but is dominated by static quenching.^{11–13}

We previously studied the fluorescence quenching of poly(dimethylsilane-*co*-methylphenethylsi-

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Table I Structures, Copolymerization Ratios (m/n), and Molecular Weights (M_n) of the Four Polysilanes

Parameter	Polysilanes			
	1 [#]	2 [#]	3 [#]	4 [#]
Structures	—(SiMePe) _n —	—(SiMe ₂) _m — —(SiMePe) _n —	—(SiMeHex- <i>n</i>) _n —	—(SiMe ₂) _m — (SiMeHex- <i>n</i>) _n —
m/n	—	0.92/1	—	1.07/1
M_n ($\times 10^4$)	1.49	1.47	0.85	0.65

Pe, Me, and Hex-*n* represent phenethyl, methyl, and *n*-hexyl, respectively.

lane) and poly(dimethylsilane-*co*-cyclohexylmethylsilane) by CCl₄, CHCl₃, Cl₂CHCHCl₂, and Cl₃CCCl₃ and treated the fluorescence quenching data according to the equations $F_0/F \exp(-NV[Q]) = 1 + K_{SV}[Q]$ and $\ln(F_0/F) = NV[Q]$. In combination with the fluorescence lifetime quenching measurements, we proposed that the fluorescence quenching of polysilane by chlorohydrocarbon includes both static quenching and dynamic quenching. At least mathematically, there exists a critical quencher concentration $[Q]_C$. When $[Q] > [Q]_C$, the fluorescence quenching is dominated by static quenching; when $[Q] < [Q]_C$, it is dominated by dynamic quenching.¹⁴ In this article, we studied the solution fluorescence quenching of poly(methylphenethylsilane) (1[#]), poly(dimethylsilane-*co*-methylphenethylsilane) (2[#]), poly(*n*-hexylmethylsilane) (3[#]), and poly(dimethylsilane-*co*-*n*-hexylmethylsilane) (4[#]) by such quenchers as CCl₄, CHCl₃, Cl₂CHCHCl₂, and methyl benzoate. Our aim was to investigate the effect of the polysilane structure on its fluorescence quenching and obtain some understanding of the relationship between the fluorescence quenching and the photodegradation of polysilane added with sensitizers with —CCl₃.

EXPERIMENTAL

Materials

All the polysilanes were synthesized by Wurtz-type reductive condensation of their corresponding disubstituent dichlorosilanes^{15,16} and purified according to the literature procedures. Table I shows the structures, copolymerization ratios, and molecular weights of the four polysilanes.

Cyclohexane, CCl₄, CHCl₃, Cl₂CHCHCl₂, and methyl benzoate, all analytically pure, were further purified before use according to the reported

methods¹⁷ and have no absorption at the excitation wavelength. Cyclohexane was used as a solvent. The concentrations of the polysilanes were calculated according to the number of the Si atoms, all 1.0×10^{-4} mol/L. The concentrations of the quenchers are shown in Table II.

Instrumentation

We used a Shimadzu UV-240 spectrophotometer to determine the UV spectra (the solvent was used as a reference) and a Shimadzu RF-540 fluorescence spectrophotometer to record the steady-state fluorescence spectra. During the measurement, the excitation light caused no obvious photodegradation to the polysilane solution. We conducted the experiment at about 7°C, and the excitation wavelength was 310 nm.

RESULTS AND DISCUSSION

There are two kinds of fluorescence quenching: static quenching and dynamic quenching. The dynamic quenching conforms to the Stern–Volmer equation:

$$F_0/F = 1 + K_{SV}[Q] = \tau_0/\tau = 1 + k_q\tau_0[Q] \quad (1)$$

where F , F_0 , and τ , τ_0 represent, respectively, the fluorescence intensity and the fluorescence lifetime with and without the addition of a quencher; K_{SV} , the Stern–Volmer constant; k_q , the fluorescence quenching rate constant, $K_{SV} = k_q\tau_0$; and $[Q]$, the quencher concentration. For static quenching, there exists a similar relationship:

$$F_0/F = 1 + K[Q] \quad (2)$$

Table II Polysilanes, Quenchers, and Concentrations of the Quenchers (mol/L) for All the Fluorescence Quenching Systems

Polysilanes	Quenchers	Concentrations						
		1	2	3	4	5	6	7
1 [#]	CHCl ₃	0.000	1.500	3.000	4.500	6.000	7.500	9.000
2 [#]	CHCl ₃	0.000	1.000	2.000	3.000	4.000	5.000	6.000
3 [#]	CHCl ₃	0.000	1.500	3.000	4.500	6.000	7.500	9.000
4 [#]	CHCl ₃	0.000	1.000	2.000	3.000	4.000	5.000	6.000
1 [#]	CCl ₄	0.000	0.080	0.160	0.240	0.320	0.400	0.480
2 [#]	CCl ₄	0.000	0.080	0.160	0.240	0.320	0.400	0.480
3 [#]	CCl ₄	0.000	0.040	0.080	0.120	0.160	0.200	0.240
4 [#]	CCl ₄	0.000	0.080	0.160	0.240	0.320	0.400	0.480
1 [#]	Cl ₂ CHCHCl ₂	0.000	0.500	1.000	1.500	2.000	2.500	3.000
2 [#]	Cl ₂ CHCHCl ₂	0.000	0.500	1.000	1.500	2.000	2.500	3.000
3 [#]	Cl ₂ CHCHCl ₂	0.000	0.500	1.000	1.500	2.000	2.500	3.000
4 [#]	Cl ₂ CHCHCl ₂	0.000	0.500	1.000	1.500	2.000	2.500	3.000
1 [#]	Methyl benzoate	0.000	0.800	1.600	2.400	3.200	4.000	4.800
2 [#]	Methyl benzoate	0.000	0.075	0.150	0.225	0.300	0.375	0.450
3 [#]	Methyl benzoate	0.000	0.150	0.300	0.450	0.600	0.750	0.900
4 [#]	Methyl benzoate	0.000	0.075	0.150	0.225	0.300	0.375	0.450

where K is the formation constant of the complex formed between the fluorophore and the quencher molecule.

The measurement of fluorescence lifetime is the decisive method to distinguish static quenching and dynamic quenching. In static quenching, the quencher does not change the fluorescence lifetime, that is, $\tau_0/\tau = 1$. However, in dynamic quenching, the quencher quenches both the fluorescence intensity and the fluorescence lifetime, that is, $\tau_0/\tau = F_0/F$.

Usually, there exist both static quenching and dynamic quenching in the same fluorescence quenching system, the fluorescence quenching curve ($F_0/F - [Q]$) bends upward, and the fluorescence quenching data conforms to the following equation:

$$F_0/F = (1 + K_D[Q])(1 + K_S[Q]) \\ = 1 + (K_D + K_S)[Q] + K_D K_S [Q]^2 \quad (3)$$

where K_D and K_S represent the dynamic quenching constant and the static quenching constant, respectively. This equation can be rearranged to

$$(F_0/F - 1)/[Q] = (K_D + K_S) + K_D K_S [Q] \quad (4)$$

Plotting $(F_0/F - 1)/[Q] - [Q]$ yields a straight line, the slope of which is $K_D K_S$ and the intercept

of which is $(K_D + K_S)$. K_D can be determined by the measurement of the fluorescence lifetime according to the equation $\tau_0/\tau = 1 + K_D[Q]$. In this way, we can obtain both K_D and K_S .

Furthermore, there exists a special static quenching which is due to the quencher molecule being adjacent to the fluorophore at the moment of excitation instead of the complexation between the fluorophore and the quencher molecule.^{18,19} To describe it, we introduce a concept, the active sphere, in which the probability of fluorescence quenching is unity. When the fluorescence quenching is simply this kind of static quenching, there exists the following relationship between the fluorescence intensity quenching (F_0/F) and the volume of active sphere (V):

$$F_0/F = \exp(NV[Q]) \text{ or } \ln(F_0/F) = NV[Q] \quad (5)$$

where N is Avogadro's constant. We can draw an $\ln(F_0/F) - [Q]$ straight line.

If there exist both this kind of static quenching and dynamic quenching in the same fluorescence quenching system, we can describe it by the following equation:

$$F_0/F = (1 + K_{sv}[Q])\exp(NV[Q]) \quad (6)$$

This equation can be changed to

Table III Radii r (Å) and Volumes V (Å³) of the Active Sphere and the Stern–Volmer Constants K_{SV} (L/mol) for All the Fluorescence Quenching Systems

Polysilanes	Quenchers	r (Å)	V (Å ³)	K_{SV} (L/mol)
1 [#]	CHCl ₃	—	—	—
2 [#]	CHCl ₃	3.5	179.6	1.50
3 [#]	CHCl ₃	4.37	349.6	—
4 [#]	CHCl ₃	4.5	381.7	0.195
1 [#]	CCl ₄	—	—	1.84
2 [#]	CCl ₄	7.0	1437	2.32
3 [#]	CCl ₄	9.0	3053	3.62
4 [#]	CCl ₄	7.0	1437	4.45
1 [#]	Cl ₂ CHCHCl ₂	2.9	102.2	0.0023
2 [#]	Cl ₂ CHCHCl ₂	4.3	333.0	0.213
3 [#]	Cl ₂ CHCHCl ₂	4.4	356.8	0.010
4 [#]	Cl ₂ CHCHCl ₂	6.0	904.8	0.029
1 [#]	Methyl benzoate	—	—	0.360
2 [#]	Methyl benzoate	—	—	2.762
3 [#]	Methyl benzoate	—	—	1.413
4 [#]	Methyl benzoate	—	—	4.133

$$F_0/F \exp(-NV[Q]) = 1 + K_{SV}[Q] \quad (7)$$

where V and K_{SV} are adjustable parameters. Through experiment, we can obtain many groups of $(F_0/F)-[Q]$ values and find a volume of active sphere (V) to obtain a best-fit least-square $F_0/F \exp(-NV[Q])-[Q]$ straight line and determine K_{SV} . After determining V and K_{SV} , we can divide eq. (6) into two parts, that is, the dynamic quenching part:

$$(F_0/F)_D = 1 + K_{SV}[Q] \quad (8)$$

and the static quenching part:

$$(F_0/F)_S = \exp(NV[Q]) \quad (9)$$

Of course, the total fluorescence quenching equals the product of these two parts:

$$F_0/F = (F_0/F)_D(F_0/F)_S \quad (10)$$

Nearly all the fluorescence emission spectra showed that with increase of the quencher concentration the fluorescence intensity of polysilane is quenched step by step. Only for the 1[#]-CHCl₃ system can the fluorescence intensity not, obviously, be quenched. In this article, we studied only the fluorescence quenching of polysilane at the maximum emission wavelength (332 nm).

From the fluorescence emission spectra, we drew the $F_0/F-[Q]$ curves. For the 1[#]-CCl₄ system and the four methyl benzoate systems, we obtained $F_0/F-[Q]$ straight lines. For the other systems, the $F_0/F-[Q]$ curves all are bent upward. These results are consistent with refs. 11–14.

For all the $F_0/F-[Q]$ curves, we treated the fluorescence quenching data according to eqs. (1), (5), and (7). The 1[#]-CCl₄ system and all the methyl benzoate systems conform to eq. (1), the 3[#]-CHCl₃ system conforms to eq. (5), and all the other nine systems conform to eq. (7). Moreover, we obtained the volumes (V) and radii (r) of the active sphere and the Stern–Volmer constants (K_{SV}) for all the fluorescence quenching systems, as shown in Table III.

The systems with both dynamic quenching and static quenching are all chlorohydrocarbon systems. They are competitive fluorescence quenching systems and are consistent with eq. (6). For these systems, generally speaking, there exists a critical quencher concentration $[Q]_C$, at least mathematically. When $[Q] = [Q]_C$, the contribution of dynamic quenching equals that of static quenching; when $[Q] < [Q]_C$, the fluorescence quenching is dominated by dynamic quenching; and when $[Q] > [Q]_C$, the fluorescence quenching is dominated by static quenching. After we obtained K_{SV} and V , we calculated $[Q]_C$ by the

Table IV Critical Quencher Concentrations $[Q]_C$ (mol/L) for All the Competitive Fluorescence Quenching Systems and the Contributions of the Dynamic Quenching Part $(F_0/F)_D$ and the Static Quenching Part $(F_0/F)_S$ to the Total Fluorescence Quenching When $[Q] = 1.00$ mol/L

Polysilanes	Quenchers	$[Q]_C$ (mol/L)	$(F_0/F)_D$	$(F_0/F)_S$
2 [#]	CCl ₄	2.00	3.320	2.375
3 [#]	CCl ₄	0.67	4.612	6.284
4 [#]	CCl ₄	3.12	5.434	2.375
2 [#]	CHCl ₃	37.5	2.50	1.11
4 [#]	CHCl ₃	0.50	1.22	1.26
1 [#]	Cl ₂ CHCHCl ₂	-17.0	0.94	1.06
2 [#]	Cl ₂ CHCHCl ₂	Nonexistent	1.19	1.22
3 [#]	Cl ₂ CHCHCl ₂	-0.12	0.97	1.72
4 [#]	Cl ₂ CHCHCl ₂	-0.11	0.99	1.24

equation $1 + K_{SV}[Q]_C = \exp(NV[Q]_C)$ for the nine systems conforming to eq. (7) and determined the nature of the fluorescence quenching. The results are shown in Table IV.

According to Table IV, for the 2[#]-Cl₂CHCHCl₂ system, because the $(F_0/F)_S-[Q]$ curve is always over the $(F_0/F)_D-[Q]$ straight line across the whole quencher concentration range, $[Q]_C$ is non-existent and the fluorescence quenching is dominated by static quenching. For the other eight systems, we calculated their corresponding $[Q]_C$ values. For the 1[#]-, 3[#]-, and 4[#]-Cl₂CHCHCl₂ systems, their $[Q]_C$ values are all negative. Of course, it is practically impossible. This indicates that the fluorescence quenching for these systems is dominated by static quenching over the whole quencher concentration range.

For the 2[#]-CHCl₃ system, we obtained $[Q]_C = 37.5$ mol/L. However, according to the room-temperature density of CHCl₃ (1.484),²⁰ we know that the maximum room-temperature solution concentration $[Q]_{\max}$ of CHCl₃ is 12.43 mol/L. Therefore, $[Q]_C$ is much larger than is $[Q]_{\max}$, and the fluorescence quenching for this system is dominated by dynamic quenching.

Table IV also shows the contributions of dynamic quenching $(F_0/F)_D$ and static quenching $(F_0/F)_S$ to the total fluorescence quenching when $[Q] = 1.00$ mol/L. For the 2[#]- and 4[#]-CCl₄ and 2[#]-CHCl₃ systems, because $[Q] = 1.00$ mol/L is always smaller than their corresponding $[Q]_C$: 2.00, 3.12, and 37.5 mol/L, the fluorescence quenching is dominated by dynamic quenching. For the 3[#]-CCl₄, 4[#]-CHCl₃, and 1[#]-, 3[#]-, and 4[#]-Cl₂CHCHCl₂ systems, because $[Q] = 1.00$ mol/L is larger than their corresponding $[Q]_C$: 0.67, 0.50, -17.0, -0.12, and -0.11 mol/L, the

fluorescence quenching is dominated by static quenching.

From Table III, we can see a general phenomenon: the Stern-Volmer constants (K_{SV}) and the radii of the active sphere (r) for 2[#] by the same quencher are always larger than those for 1[#]. The situation is the same for 4[#] and 3[#]. The only exception exists for the systems 4[#]-CCl₄ and 3[#]-CCl₄, where $r(4^{\#}\text{-CCl}_4) = 7.0 \text{ \AA} < r(3^{\#}\text{-CCl}_4) = 9.0 \text{ \AA}$. This phenomenon is caused by the polysilane side-group structure. 1[#] is a homopolymer and 2[#] is a copolymer, $m/n = 0.923/1$. For 1[#], phenethyl/methyl = 1/1; for 2[#], phenethyl/methyl = 0.351/1. Obviously, the spatial obstruction of the side groups of 1[#] is larger than that of 2[#]. This makes it more difficult for the quencher molecule to reach the Si-Si main chain of 1[#] to quench the S_1 state and results in a smaller fluorescence quenching. Similarly, for 3[#] and 4[#], n -hexyl/methyl = 1/1 and 0.318/1, respectively, that is, the spatial obstruction of the side groups of 3[#] is larger than that of 4[#], and this results also in a smaller fluorescence quenching.

According to Table III, for the same polysilane, when it is quenched by different chlorohydrocarbons, the order of the fluorescence quenching ability is $n^{\#}\text{-CCl}_4 > n^{\#}\text{-CHCl}_3$ and $n^{\#}\text{-CCl}_4 > n^{\#}\text{-Cl}_2\text{CHCHCl}_2$, where $n = 1-4$. This phenomenon is caused by the structural difference of chlorohydrocarbons: CCl₄ has one more Cl atom than has CHCl₃, and the Cl atom functions both as electron-withdrawing and as a "heavy-atom effect,"²¹ so the fluorescence quenching ability of CCl₄ is larger than that of CHCl₃. However, the fluorescence quenching of polysilane by chlorohydrocarbons is related not only to the Cl atom, but also to the positive

charge of the carbon nucleus of the quencher.¹⁴ The number of the Cl atoms of $\text{Cl}_2\text{CHCHCl}_2$ is the same as that of CCl_4 , but the charge of its carbon nucleus is not so positive as that of CCl_4 , and this also makes the fluorescence quenching ability of CCl_4 larger than that of $\text{Cl}_2\text{CHCHCl}_2$. Of course, compared with $\text{Cl}_2\text{CHCHCl}_2$, CCl_4 has a smaller volume and can reach the Si—Si main chain more easily to quench the fluorescence of polysilane.

The chromophores of polysilane are various individual *trans* segments with different lengths and different energy levels.^{22,23} Under ultraviolet irradiation, the polysilane segments absorb photons and then produce excitons by $\sigma \rightarrow \sigma^*$ transfer. These excitons are effectively transmitted to the longest and lowest *trans* segments, part of which fall into oblivion by emitting fluorescence via a radiational process and part of which are decomposed into free electrons and holes and break the Si—Si bonds via a nonradiational process.^{24,25}

The dynamic quenching part of the fluorescence quenching of polysilane by CCl_4 is energy-transfer quenching,^{11,12} that is, after the polysilane main chains absorb photons and produce excitons, part of the excitons produce rapid energy transfer to the CCl_4 molecules gathered around the main chains. According to the fluorescence lifetime measurement of $4^\#$ (226 ps),¹⁴ calculated by the equation $K_{SV} = k_q\tau_0$, the rate constant of this energy transfer k_q can reach the $10^{10}\text{M}^{-1}\text{s}^{-1}$ scale. According to references 14 and 26, the dynamic quenching part of the fluorescence quenching of polysilane by halohydrocarbons is caused mainly by the positive charge of the carbon nucleus in the quencher molecule, while the static quenching part is caused by the "heavy-atom effect" of the halo element. The fluorescence quenching of polysilane by bromohydrocarbons is simply static quenching. Possibly, the large atomic number of the Cl and Br elements leads to a strong interaction between the spin angular momentum and the orbital function angular momentum of the σ conjugation along the polysilane segments, that is, spin-orbital function coupling. This coupling increases the probability of such processes as the $S_0 \rightarrow S_1$ absorptional transition, the $S_1 \rightarrow T_1$ intersystem crossing, phosphorescence, and the $T_1 \rightarrow S_0$ intersystem crossing. However, among all these, the probability of the $S_1 \rightarrow T_1$ intersystem crossing increases most, so the population of the S_1 excited state decreases. This weakens the room-

temperature solution fluorescence intensity ($S_1 \rightarrow S_0$) and even makes it disappear.²¹

We previously used the XeCl excimer laser to irradiate the CHCl_3 solution of $1^\#$ and $2^\#$, measured the laser energy absorbed by the polysilane macromolecules, determined the GPC molecular weights of the polysilane macromolecules both before and after irradiation, and calculated their corresponding apparent quantum yields.²⁷ The apparent quantum yield of laser degradation of the $1^\#$ - CHCl_3 solution is two orders of magnitude larger than that of the $2^\#$ - CHCl_3 solution. This result is opposite to the fluorescence quenching result. Possibly, in the photodegradation of the CHCl_3 solution of polysilane, the radical chain-transfer process^{5,6} is more important than is the fluorescence quenching.

Miller et al. showed that the fluorescence quenching of polysilane by methyl benzoate is electron-transfer quenching, different from that by chlorohydrocarbon. It is carried out mainly by the overlap of the electron clouds between the fluorophore and the quencher molecule and the exchange of the excited electrons.^{28,29}

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