Formation of the Anti-Hirayama Excimer in a Phenylsiloxane

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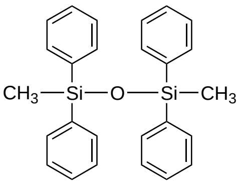
Received June 6, 1997
Revised Manuscript Received August 22, 1997

Introduction

Formation of an excimer through interaction between an excited and a ground state chromophore is widely observed for linear polymers having pendant aromatic groups.[1] Normally an intramolecular excimer is formed between two adjacent chromophores separated by just three carbon atoms, i.e., the Hirayama's rule.[2] Although this condition seems to apply also to phenylsiloxanes in which the excimer can be formed between two nearest phenyl groups separated by three atoms, Si−O−Si, additional conditions for the excimer formation may exist for phenylsiloxanes due to high flexibility of Si−O−Si chains. Recently it was reported that the copolymers consisting of dimethylsiloxane, methylphenylsiloxane, and/or diphenylsilonane units exhibit both monomer and excimer fluorescence.[3−8] It is of interest to investigate the intramolecular interaction of phenyl chromophores in phenylsiloxanes from the polymer-photophysical view point.

The present paper describes the excited-state dynamical behavior of phenylsiloxanes in dilute solution. We have measured the absorption and fluorescence spectra of 1,1,3,3-tetraphenyldimethyldisiloxane (**1**) and 1,1,5,5-tetraphenyltetramethyltrisiloxane (**2**) in a fluid solution at different temperatures, together with the emission spectra in a rigid glass at 77 K. One can recognize from a simple molecular-structure model, assuming tetrahedral bonds for Si, that for these compounds only one of the two phenyl chromophores attached to the Si atom can contribute to excimer formation. We show herein that compound **2** forms an excimer between the phenyl chromophores separated by five atoms, Si−O−Si−O−Si, i.e., the anti-Hirayama excimer. The emission of **2** in a fluid solution consists of monomer and excimer fluorescence, the relative intensity of which depends on the temperature, while that in a rigid glass at 77 K consists of the monomer fluorescence and phosphorescence, the relative intensity of which is independent of the compound structure. Analysis of the temperature dependence of the quantum yield ratio indicates the dynamical behavior which characterizes the anti-Hirayama excimer.



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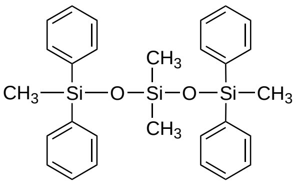

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Experimental Section

Phenylsiloxanes obtained from Petrarch Systems through Chisso, Japan, were purified by means of repeated recrystallization. Tetrahydrofuran (THF) was distilled before use and isopentane and methylcyclohexane were used as received. Emission and excitation spectra were obtained with a SPEX Fluorolog-2 (Model 211−340) fluorescence spectrophotometer, equipped with a photon-counting system, the details of which are described in a previous paper.[9] The absorption spectra were measured with a Hitachi UV-123 spectrophotometer. The temperature of the samples in a 10-mm square quartz cell was controlled by a thermostated cell holder in which either water or ethylene glycol was circulated. For the emission spectral measurements at 77 K, quartz tubes with a 3-mm diameter were used. In order to eliminate Raman scattering from the solvent, the Raman peaks were subtracted from the observed fluorescence spectra. The optical density of the sample solutions was always kept below 0.1, which corresponds to the concentration approximately below 5×10^{-5} mol/L, so that the possible intermolecular excimer formation is neglected. It was confirmed that the excitation spectrum of the emission agrees well with the corresponding absorption spectrum for all the samples investigated.

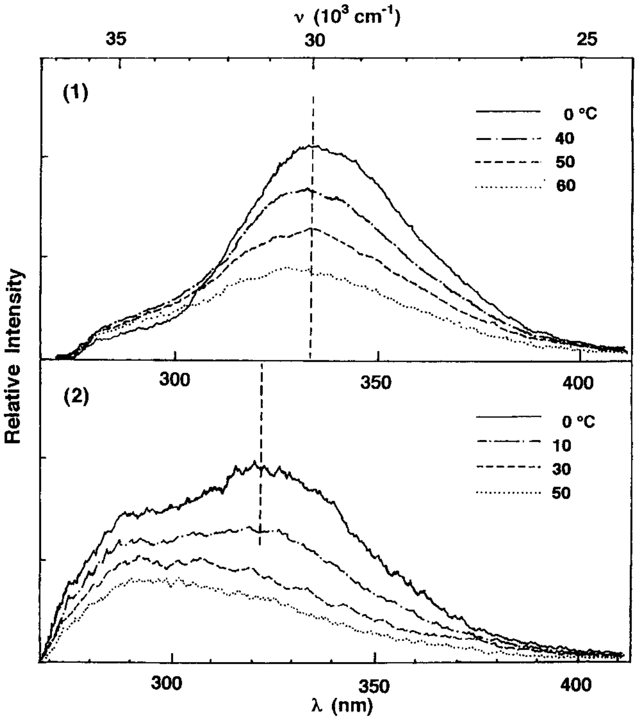

Figure 1. Fluorescence spectra of 1,1,3,3-tetraphenyldimethyldisiloxane (**1**) and 1,1,5,5-tetraphenyltetramethyltrisiloxane (**2**) in THF at different temperatures.

Results and Discussion

Figure 1 shows the fluorescence spectra of phenylsiloxanes in THF at different temperatures. The emission centered at 290 nm is regarded as the monomer fluorescence, while the broad emission centered at around 330 nm is regarded as the excimer fluorescence. At room temperature the excimer fluorescence is not observed clearly for **2**, but it appears distinctly as the temperature is lowered. It is seen that the intensity ratio of the monomer to excimer fluorescence increases with increasing temperature. Further, the intensity ratio of the excimer to monomer fluorescence at a particular temperature is markedly higher for **1** than for **2**. Closer inspection of Figure 1 reveals that the excimer fluorescence maximum, λ_{EFmax}, of **2** is observed at higher energy as compared with that of **1**.

In contrast to the emission in a fluid solution, the emission of both **1** and **2** in a rigid glass at 77 K consists only of the fluorescence and phosphorescence of the monomer; excimer fluorescence is not observed. The emission spectrum of **1** at 77 K is essentially the same

S0024-9297(97)00811-5 CCC: $14.00

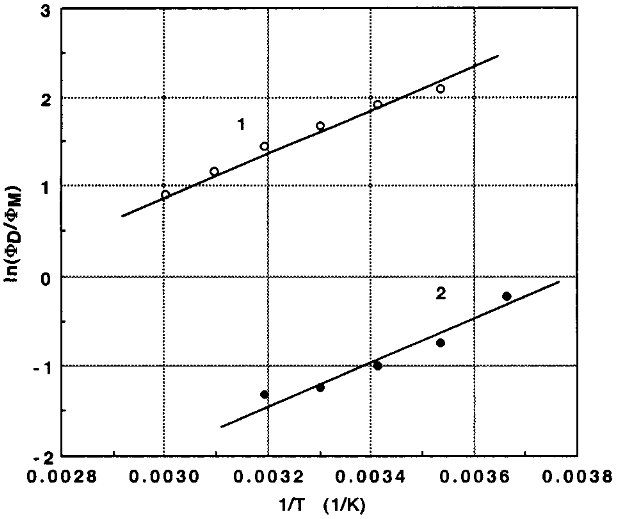

Figure 2. Values for $\ln(\Phi_D/\Phi_M)$ plotted against the reciprocal of the absolute temperature for 1,1,3,3-tetraphenyldimethyldisiloxane (**1**) and 1,1,5,5-tetraphenyltetramethyltrisiloxane (**2**) in THF.

as that reported recently.[5,8] The relative intensities of the emission for **1** and **2** at 77 K are found to be essentially identical. These observations suggest that the phenyl chromophores are not preoriented to form the excimer in the ground state and that chain folding is prevented at 77 K.

In order to analyze the observed quantum yield change, a conventional scheme is applied for the formation and dissociation of the excimer, for which the observed fluorescence quantum yield ratio is given by

$$\Phi_D/\Phi_M = [k_{FD}k_{DM}/(k_{FD} + k_{ND} + k_{MD})]/k_{FM} \qquad (1)$$

where k_{DM} and k_{MD} are respectively the rate constants for formation and dissociation of the excimer, k_{FM} and k_{NM} are respectively the radiative and nonradiative rate constants of the monomer, and k_{FD} and k_{ND} are those for the excimer. If we further assume $k_{MD} >> k_{FD} + k_{ND}$, then we have

$$\Phi_D/\Phi_M = k_{FD}k_{DM}/k_{FM}k_{MD} \qquad (2)$$

where k_{DM}/k_{MD} is proportional to $\exp(\Delta E/kT)$, with k being the Boltzmann constant and T the absolute temperature. The binding energy of the excimer, ΔE, is obtained from the slope of the plots of $\ln(\Phi_D/\Phi_M)$ versus reciprocal of the absolute temperature. As is shown in Figure 2, the ΔE values thus obtained are found to be 4.5 and 5.0 kcal/mol, respectively, for **1** and **2** in THF.

According to the scheme in Figure 3 for excimer formation, one can obtain the relation

$$\Delta E_s = \Delta E + \Delta E_{ex} + \Delta E_g \qquad (3)$$

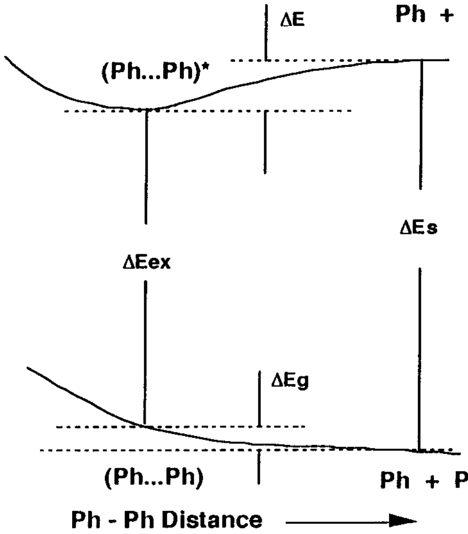

Figure 3. Energy level scheme related to the excimer formation for the present systems.

where ΔE_g is the energy difference between the ground states in the excimer and nonexcimer geometry, and ΔE_s and ΔE_{ex} correspond to the monomer excited singlet energy and the excimer transition, respectively. The overlapping center of the absorption and monomer fluorescence emission is estimated to be ΔE_s, which is 104 kcal/mol (275 nm) for both of **1** and **2**. Due to the broadness of the excimer emission, it is normally difficult to estimate the exact values for ΔE_{ex} . If the energies at the excimer emission maxima, 3×10^4 (85.8) and 3.1×10^4 cm^{-1} (88.6 kcal/mol) for **1** and **2**, respectively, are tentatively used for the ΔE_{ex} values, then apparent ΔE_g values of 13.7 and 10.4 kcal/mol which are obtained for **1** and **2**, respectively, can be compared with quantum chemical calculations for the ground-state molecules. Although there is uncertainty in the ΔE_{ex} values, it is not unreasonable to consider that ΔE_g of **1** is larger than that of **2**, since the anti-Hirayama excimer emission of **2** appears at higher energy than the excimer emission of **1** and since the ΔE values are almost the same for **1** and **2**. The anti-Hirayama excimer of the present system is likely to be formed at lower temperatures.

References and Notes

(1) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: New York, 1985.

(2) Hirayama F. *J. Chem. Phys.* **1965**, *42*, 3163−3171.

(3) Macanita, A. L.; Danesh, P.; Peral, F.; Horta, A.; Pierola, I. F. *J. Phys. Chem.* **1994**, *98*, 6548−6551.

(4) Macanita, A. L.; Horta, A., Pierola, I. F. *Macromolecules* **1994**, *27*, 958−963.

(5) Hamanishi, K.; Shizuka, H. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 3007−3013.

(6) Macanita, A. L.; Pierola, I. F.; Horta, A. *Macromolecules* **1991**, *24*, 1293−1298.

(7) Salom, C.; Semlyen, J. A.; Clarson, S.; Hernandez-Fuentes, I.; Macanita, A. L.; Horta, A.; Pierola, I. F. *Macromolecules* **1991**, *24*, 6827−6831.

(8) Itoh, T.; Yang, H. M.; Chou, C. *J. Chem. Soc., Faraday Trans.* **1996**, 3593−3597.

(9) Itoh, T.; Mita, I. *Macromolecules* **1992**, *25*, 479−483.

MA970811W