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The Temperature Effect on the Formation of Excimer in Siloxanes and Polystyrene Solutions

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Introduction

Formation and dissociation of an excimer in solution occurs in two temperature ranges (KLÖPFFER, 1973):

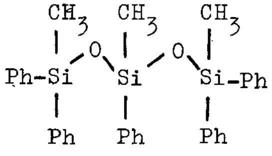
(i) At low temperature; formation of an excimer depends on the viscosity of the solvent. Increasing the temperature reduces viscosity and thus favours an excimer formation.

(ii) At high temperatures; the growth of a temperature favours the dissociation of excimers.

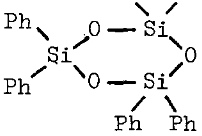
The transition temperature between two regions depends on the thermodynamic parameters: enthalpy, free energy and entropy of the excimer. From the thermodynamic point of view, the lower temperatures will favour an exeimer formation. From other side, the amount of an excimer formation depends strictly on a temperature region in which molecules may posses required sandwich geometry. Since in solution the formation of excimers is diffusion-controlled (FÖRSTER, 1969), the viscosity of the solvent plays an important role. Increasing the temperature therefore favours association, but at high temperatures the situation is reversed and thermal dissociation to excited and non-excited monomers predominates.

Experimental

Siloxanes: pentaphenyltrimethyltrisiloxane (I) and hexaphenylcyclotrisiloxane (II), (chem-pur.), were kindly supplied by the Laboratory of Silicone Chemistry, Institute of Chemistry, Academy Sinica, Pekin, China:



(I)



(II)

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Polystyrene (PS)(synthetized by the cationic polymerization) with $\bar{M}_w$ = 41 000 was purified by dissolving in benzene and precipitating with ethanol in nitrogen atmosphere. This procedure was repeated once.

1,2-Dichloroethane (anal.pure) was additionally purified by fractionation destillation two times.

Fluorescence emission spectra were measured using the Hitachi MPF-4 (Japan) fluorescence spectrophotometer. All of the fluorescence spectra were measured with 260 nm excitation radiation. The following concentration were used: 1.2x10^{-3}M(I); 1.6x10^{-3}M (II) and 5.8x10^{-3}M (PS) in 1,2-dichloroethane. The temperature control of the spectrophotometric cell was carried out by a dewar thermostat (Type 2160, Forma Scientific, USA) in the region -17°C to +15°C, and with common laboratory thermostat (temperature regulation better than ± 1°C) in the region above +15°C.

Results and discussion

The fluorescence spectra of (I),(II) and (PS) at various temperatures are shown in Figs 1,2 and 3, respectively.

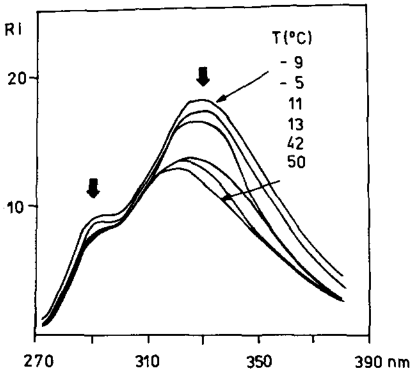

Fig.1. Fluorescence spectra of (I) at different temperatures.

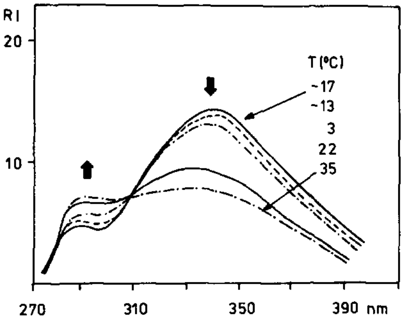

Fig.2. Fluorescence spectra of (II) at different temperatures.

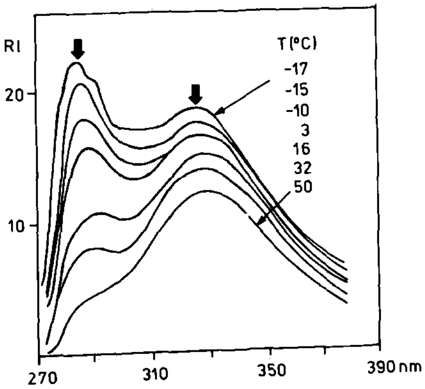

Fig.3. Fluorescence spectra of (PS) at different temperatures.

The shape of these spectra change during increasing temperature:

(i) Peak maximum characteristic for the excimer formation for (I) at 330 nm, for (II) at 340 nm and (PS) at 330 nm decreases.

(ii) Peak maxima characteristic for the monomer presence at 290 nm for (I) and (PS) decreases, whereas for (II) increase.

The silicone (II) spectrum (Fig.2) shows formation of the isosbestic point at 310 nm, whereas is not influenced by the changing a temperature. The silicone (I) and (PS) spectra do not show formation of isosbestic points, (Fig.1 and Fig.2, respectively), because both peaks at 290 nm and 330 nm decrease simultaneously.

The simplest mechanism which describes excimer formation and its dissociation (GHIGGINO et al, 1978) can be presented as follow:

$$M + h\nu \longrightarrow {}^1M^* \qquad (1)$$

$${}^1M^* + M \xrightarrow{k_1} {}^1D^* \qquad (2)$$

$${}^1D^* \xrightarrow{k_2} M + M + \text{dimer fluorescence} \qquad (3)$$

$${}^1D^* \xrightarrow{k_3} M + M + \text{heat} \qquad (4)$$

$${}^1D^* \xrightarrow{k_4} {}^1M^* + M \qquad (5)$$

The concentration of excimer in the steady-state condition is given by:

$$\frac{d\left[{}^1D^*\right]}{dt} = k_1\left[{}^1M^*\right] - (k_2+k_3+k_4)\left[{}^1D^*\right] \qquad (6)$$

and

$$\frac{\left[{}^1D^*\right]}{\left[{}^1M^*\right]} = \frac{k_1}{k_2+k_3+k_4} \qquad (7)$$

where: M and ${}^1M^*$ are monomer molecules in the ground and an excited state, respectively; D^* is an excited dimer molecule.

Fluorescence intensities of monomer (I_M) and excimer (I_D) molecules, are proportional to $[{}^1M^*]$ and $[{}^1D]$, respectively. Measurements of the ratio I_D/I_M or I_M/I_D can not yield absolute values of k_1, k_2, k_3 and k_4, but allows for the calculation of an activation energy for intramolecular excimer formation and excimer dissociation according to the equation:

$$\frac{\partial \ln(I_D/I_M)}{\partial(1/T)} = -E_a/R \qquad (8)$$

assuming that processes (4) and (5) are negligible.

The data plotted in this form (eq.8) are shown in Figs 4, 5 and 6.

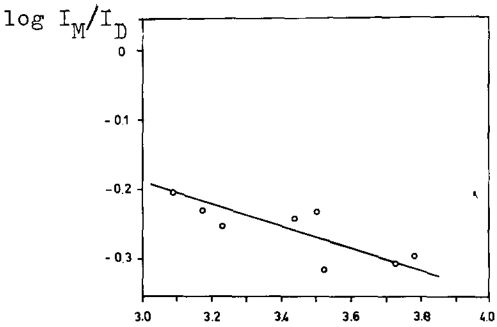

Fig.4. Arrhenius plot of I_M/I_D versus inversion temperature for (I).

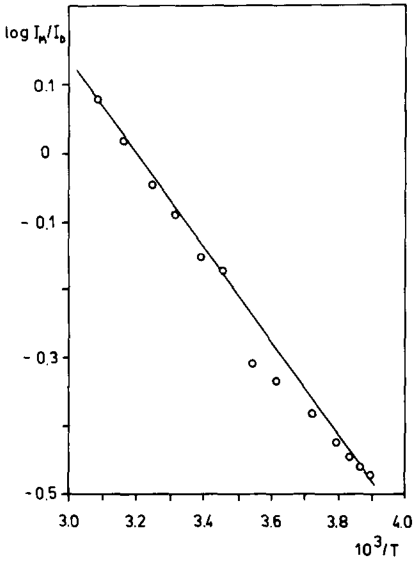

Fig.5. Arrhenius plot of I_M/I_D versus inversion temperature for (II).

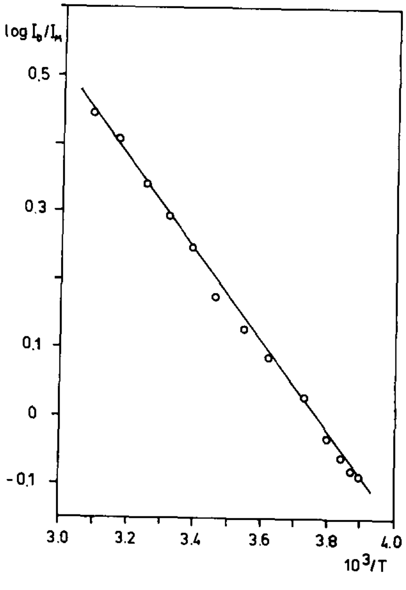

Fig.6. Arrhenius plot of I_D/I_M versus inversion temperature for (PS).

The following activation energies for dissociation of an excimer to a monomer for (I) 0.64 kcal/mol and for (II) 3.18 kcal/mol were found. For the (PS) energy activation for an excimer formation was calculated 3.05 kcal/mol. Very low activation energy for (I) shows for very easy rotation around Si-O bond, whereas activation energies for (II) and (PS) are comparable to the rotation energies in a methylene chain (CHANDROS AND DEMPSTER, 1970). However, one cannot preclude the possibility of small rotations and/or translations during conversion to the excimer or in dissociation process. The activation energy associated with excimer formation can be interpreted as that required to depopulate the shallow traps, or that required to rotate phenyl rings about methylene bridge between them (FOX et al, 1972).

There has been little work done on geometry of the excimer state in fluid solutions (VALA et al, 1965, HIRAYAMA, 1965, NISHIHARA and KANEKO, 1969 and DAVID et al, 1976).

The entropy and enthalpy of the (II) excimer formation were calculated directly from fluorescence spectra as a function of temperature (Fig.2)(by method given by STEVENS and BAN, 1964) and are $\Delta S=-3.04$ cal/mol°C and $\Delta H=3.38$ kcal/mol. The low value of entropy may shows for the intramolecular process of the (II) excimer formation. The entropy values for the photoassociation of dissolved aromatic hydrocarbons are much higher (from -17 to -21 cal/mol°C)(STEVENS AND BAN, 1964).

X-ray diffraction measurements of cyclotrisiloxane indicate a planar molecule, with all phenyl groups located at the same side of a ring (LICHTENWALNER and SPRUNG, 1970). This particular geometric configuration probably facilitates the (II) excimer formation by the intramolecular process.

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