

TEMPERATURE DEPENDENCE OF THE FLUORESCENCE SPECTRA OF LADDERLIKE POLYPHENYLSILSESQUIOXANE AND LADDERLIKE 1,4-PHENYLENE-BRIDGED POLYVINYLSILOXANE*

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Abstract Fluorescence spectra of ladderlike polyphenylsilsesquioxane (LPPS) and ladderlike 1,4-phenylene-bridged polyvinylsiloxane (LPPVS) have been measured as a function of temperature (4–55°C), in dilute tetrahydrofuran solution. The excimer (I_E) to monomer (I_M) intensity ratio (I_E/I_M) of LPPS dilute solution shows a double linear Arrhenius plot with a break point ascribable to a transition temperature T_i . This behavior has not been found for single chain polyorganosiloxanes. When $\ln I_E$ of LPPS was plotted against $1/T$, it also gave a double linear plot with one break point, which was found in single chain polyorganosiloxanes. The different behaviors between LPPS and single chain polyorganosiloxanes may be mainly attributed to the relatively rigid double-chain macromolecular backbone of LPPS. However, the $\ln(I_E/I_M)$ of dilute LPPVS solution versus $1/T$ shows a simple linear variation with a positive slope which confirms our proposition. The difference between the fluorescence results of LPPS and those of LPPVS may possibly derive from their structure differences and cooperative motion in backbone chain bonds.

Keywords Ladderlike polyphenylsilsesquioxane, Ladderlike 1,4-phenylene-bridged polyvinylsiloxane, Fluorescence spectra, Temperature dependence

INTRODUCTION

The formation and dissociation of an excimer of aromatic synthetic polymer in solution is temperature dependent^[1]. Excimers are excited-state complexes formed by a couple of chromophores in aromatic synthetic polymer placed face to face (i.e. sandwich geometry) at a short distance. Excimers have red-shifted emission with respect to “monomer” or single chromophore emission. The excimer-to-monomer intensity ratio (I_E/I_M), called the fluorescence ratio, depends on intrinsic and extrinsic characteristics of the system (solvent, temperature, polymer tacticity, molecular weight, etc.^[2a–2c]).

Temperature-dependent fluorescence measurements are particularly interesting in that, through steady-state experiments, they can yield information on coil dynamics^[2e]. The I_E/I_M of aromatic synthetic polymers is temperature dependent. Arrhenius plots of I_E/I_M in a broad temperature range usually show^[3–10] a crossover with two limits of linear behavior. One linear curve displays the behavior in the low temperature region. The other one reflects the behavior in the high temperature region. At low temperature, it is generally assumed that excimer dissociation is negligible and the slope of the I_E/I_M Arrhenius plot provides the activation energy for excimer

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formation. In the high-temperature limit, it is supposed that there is an apparent excited state equilibrium between monomers and excimers and therefore the excimer binding enthalpy is calculated from the I_E/I_M Arrhenius plot; however this assumption was only accepted for small molecules that exhibited an isoemissive point^[3]. In polymer solutions radiationless decay of monomer and excimer plays an important role and the isoemissive point is usually not observed at high temperature because the apparent excited state equilibrium is disturbed.

Up to now, many works concerning excimer formation in siloxanes and polyorganosiloxanes in dilute solution have been presented^[11–18]. Additionally, the temperature dependence of polyorganosiloxanes was investigated extensively by Pi  rola *et al.*^[19–21]. However, only few publications^[22–24] related to the investigation of excimer formation in polysilsesquioxanes with double-chain ladderlike structure have appeared. Moreover, to our knowledge, there has been no report on temperature dependence of the ladderlike polysilsesquioxanes till now.

In the present work, polyphenylsilsesquioxane with siloxane-bridged ladderlike structure and polyvinylsiloxane with 1,4-phenylene-bridged ladderlike structure were prepared by stepwise coupling polymerization. The temperature (4–55   C) dependence of fluorescence spectra of ladderlike polyphenylsilsesquioxane (LPPS) and ladderlike 1,4-phenylene-bridged polyvinylsiloxane (LPPVS) was investigated.

EXPERIMENTAL

Materials

All the solvents were commercially available and of analytical grade. Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Toluene was dried over CaH_2 . Phenyltrichlorosilane (PhSiCl_3), vinyltrimethoxysilane ($\text{ViSi}(\text{OCH}_3)_3$), trimethylchlorosilane, phenyltriethoxysilane ($\text{PhSi}(\text{OC}_2\text{H}_5)_3$), methanol, ethanol, pyridine, 1,4-phenylenediamine (PDA), diethylamine, triethylamine (TEA), CaH_2 and anhydrous Na_2SO_4 were obtained from the Beijing Chemical Factory and were of analytical grade. 1,4-Dibromobenzene and 1,1,3,3-tetramethyldisiloxane (HMM) were purchased from Acros Organics Company and were of analytical grade. Pyridine and TEA were dried over CaH_2 prior to use.

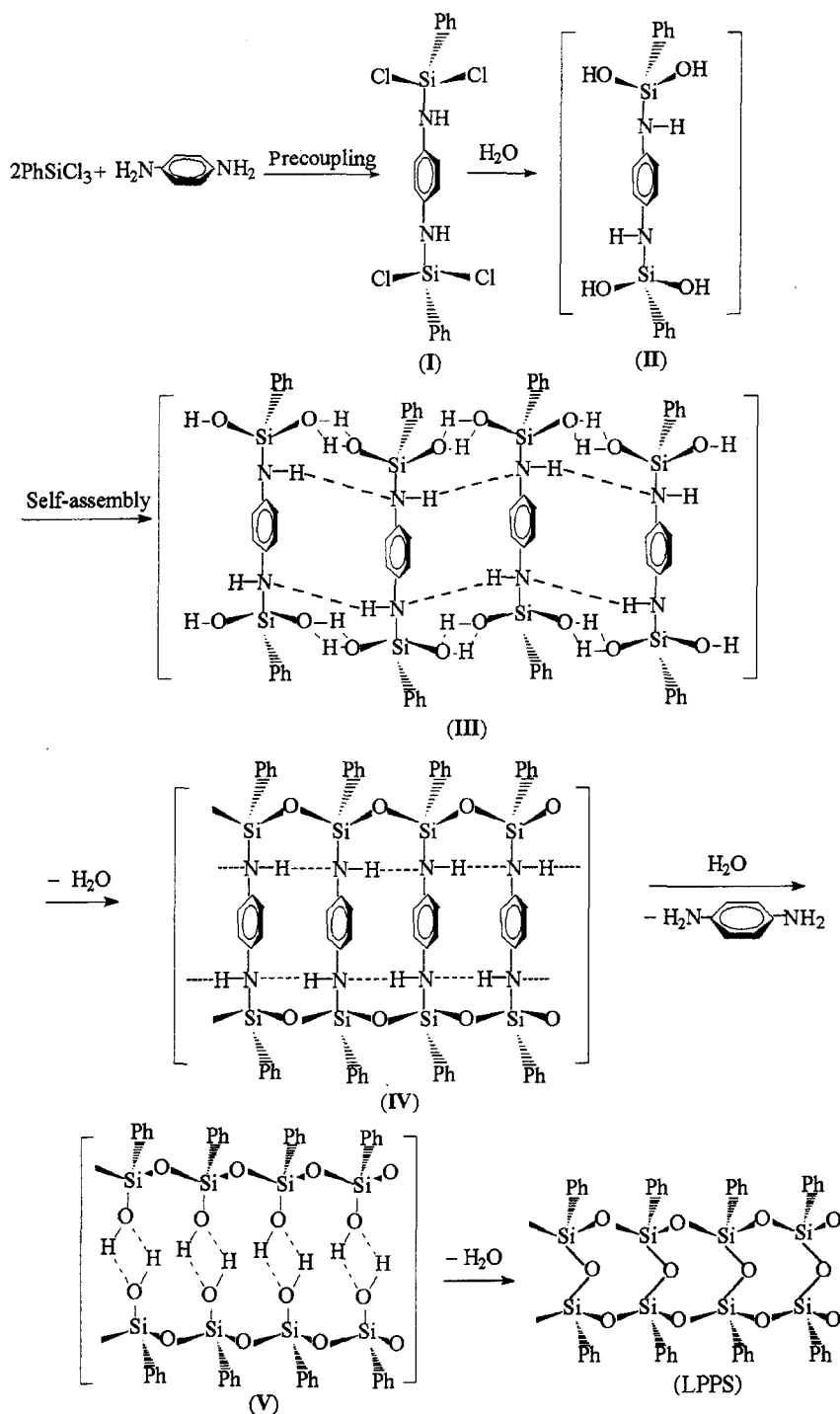
Physical Characterization

Number-average molecular weights (M_n) of the polymers were determined using a Knauer vapor pressure osmometer. Fluorescence emission spectra were obtained from a Hitachi F-4500 fluorescence spectrometer with a temperature controller. Refined UV pure THF was used as solvent, and no interference fluorescence was observed under the experimental conditions. The intensities of excimer emission and monomer emission were measured at 323 nm and 285 nm for LPPS and at 310 nm and 290 nm for LPPVS in dilute THF solution, respectively.

Synthesis of LPPS

Scheme 1 shows the synthetic route for LPPS. (1) Preaminolysis. A solution of 5.4 g (0.05 mol) of PDA and 140 mL THF was added dropwise to a 1000 mL three-necked flask containing 21.3 g (0.1 mol) PhSiCl_3 , 20.2 g (0.2 mol) TEA, and 200 mL toluene with stirring at -5 to -10°C within a period of 4 h. The rate of addition was controlled to keep the reaction temperature below -5°C . This reaction solution was stirred for another 30 min at -5 to -10°C . (2) Hydrolysis. A solution comprised of 3.6 mL water and 100 mL THF was added dropwise to the flask kept below 0°C within a period of 5 h. Then the reaction solution was stirred at room temperature for 6 h, after which the prepolymer solution was filtered to remove the $\text{TEA}\cdot\text{HCl}$ and $\text{PDA}\cdot 2\text{HCl}$ salts. The THF in the solution was removed by vacuum distillation. (3) Polycondensation. The above mentioned concentrated toluene solution of the hydrolate was subjected to condensation reaction in the presence of diethylamine catalyst and anhydrous Na_2SO_4 . The solution was stirred at about 50°C for 72 h. The polymer solution was then washed with distilled water until neutral and dried over anhydrous Na_2SO_4 . For capping the end silanol ($\text{Si}-\text{OH}$) of the product, silylation was carried out by using trimethylchlorosilane as an endcapper. The procedure was as follows. A solution of 0.63 mL pyridine, 1 mL trimethylchlorosilane, and 30 mL toluene was added dropwise to the reaction mixture at room temperature with stirring. The solution became turbid gradually. The mixture was

stirred at room temperature for 24 h. The remaining trimethylchlorosilane and pyridine in the solution were removed by vacuum distillation. The solution was washed with diluted HCl and water until neutral and then dried over anhydrous Na_2SO_4 . The solution was concentrated to about 20 mL. 80 mL methanol was added to the concentrated solution to precipitate the product. The precipitate was dried in a vacuum oven. The product is a white solid, which can be dissolved in toluene, acetone, THF and chloroform *etc.*, with a yield of 90%. The M_n of



Scheme 1 Synthetic route for ladderlike polyphenylsilsesquioxane (LPPS)

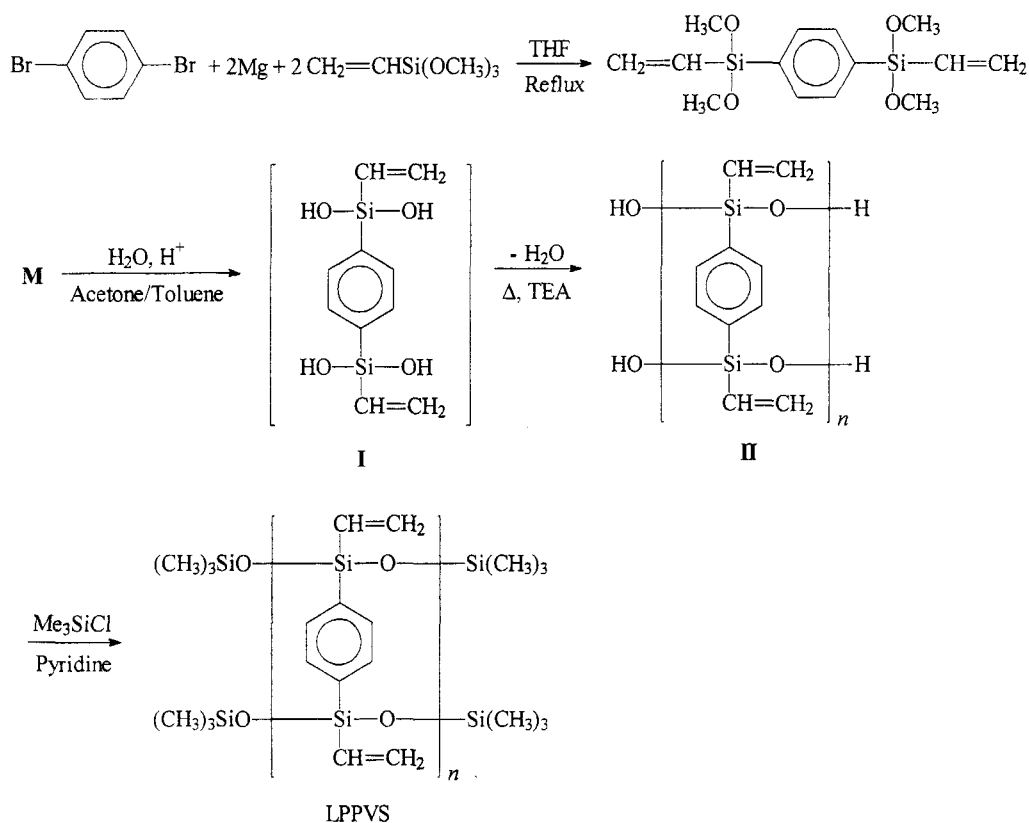
LPPS measured by VPO was 2.6×10^4 . X-ray diffraction (XRD), molecular simulation, calculation and fluorescence spectroscopy were used to elucidate the steric structure of LPPS and which was found predominately to be a *cis*-isotactic polymer^[24].

Synthesis of LPPVS

Synthesis of monomer **M**

A mixture of 19.2 g (0.8 mol) magnesium powd, 400 mL THF and 222 g (1.5 mol) vinyltrimethoxysilane was placed in a 1000 mL round bottomed flask. A solution consisting of 47.2 g (0.2 mol) 1,4-dibromobenzene and 200 mL THF was added dropwise into the flask with stirring and refluxed for 5 h. A small amount of iodine was used to initiate the reaction. The reaction mixture was kept for another 4 h and vacuum distilled to remove the solvent. Hexane (500 mL) was added in portions to precipitate magnesium salts in the solution and the upper clear liquid was collected, and hexane and the remaining vinyltrimethoxysilane were distilled off. The remaining yellow oil was vacuum distilled to give a clear colourless product (130–132 °C/ 39.9 Pa). Yield: 67%.

Synthesis of LPPVS



Scheme 2 Synthetic routes for monomer **M** and ladderlike 1,4-phenylene-bridged polyvinylsiloxane (LPPVS)

Scheme 2 shows the synthetic route for LPPVS. A mixture of 2 mL concentrated HCl, 30 mL THF, and 15 mL methanol was added dropwise slowly into a flask containing 4.5 g (14 mmol) **M**, 50 mL toluene, and 20 mL THF and held at 0 to -10°C for 6 h. The reaction mixture was stirred at room temperature for 24 h. For polycondensation, THF in the reaction solution was distilled off under vacuum. The condensation reaction was carried out using TEA as a catalyst. The solution was stirred at about 50°C for 48 h and then it was washed with water until neutral and dried over anhydrous Na_2SO_4 . For endcapping the terminal silanol group ($\text{Si}-\text{OH}$) of the

polymer, silylation was carried out using trimethylchlorosilane as an endcapper. The procedure was as follows. 39.5 mg (0.5 mmol) pyridine and 54.3 mg (0.5 mmol) trimethylchlorosilane in 20 mL toluene was added dropwise to the reaction mixture at room temperature with stirring. The solution became turbid gradually. The mixture was stirred at room temperature for another 24 h. The remaining trimethylchlorosilane and pyridine were removed by vacuum distillation. The solution was washed with diluted HCl and water until neutral and then dried over anhydrous Na_2SO_4 . The solution was concentrated to about 20 mL. 80 mL methanol was added to the concentrated solution to precipitate the product. The precipitate was dried in a vacuum oven. The product is a white solid product with a yield of 81%. The M_n measured by VPO was 2.2×10^4 .

RESULT AND DISCUSSION

Ladderlike Polyphenylsilsesquioxane (LPPS)

Figure 1 shows the emission spectra of LPPS and its model compound $\text{PhSi}(\text{OC}_2\text{H}_5)_3$, from which it can be seen that the fluorescence spectrum of $\text{PhSi}(\text{OC}_2\text{H}_5)_3$ at a concentration of 5.0×10^{-5} Ph mol/L has an emission peak at 285 nm. Under the same conditions, LPPS shows a new broad band ($\lambda_{\text{max}} = 323$ nm) besides the shoulder peak at 285 nm. Therefore, it is reasonable to attribute the emission band with maximum at 285 nm to the skeleton of $\text{Ph}-\text{Si}-$ and the broad band at 323 nm to the excimer formed by phenyl chromophores in the side chains of LPPS. It is noted that these two bands overlap to some extent. It is quite difficult to resolve them under the present conditions. Therefore the fluorescence intensities of the two peaks, corresponding respectively to I_E and I_M , were taken.

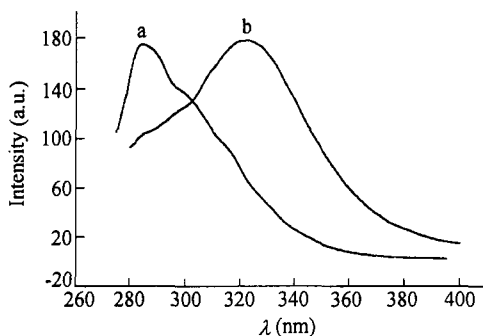


Fig. 1 Fluorescence spectra of (a) model compound $\text{PhSi}(\text{OC}_2\text{H}_5)_3$ and (b) LPPS

Excimer emission in the dilute solution of LPPS is often observed, while a shoulder peak corresponding to monomer emission still appears. The effect of polymer concentration on the fluorescence spectrum of LPPS was investigated elsewhere^[24].

Figures 2–3 show the temperature dependence of LPPS fluorescence intensity. Both the excimer to monomer intensity ratio (I_E/I_M) and excimer intensity (I_E) show a double linear Arrhenius plot (see Fig. 2 and Fig. 3) with an inflection point ascribed to the transition temperature T_t , implying that formation and dissociation of an excimer in solution occur in two temperature ranges. The temperature dependence of single chain polyphenylsiloxane (PPS) fluorescence was extensively investigated by Piérola *et al.*^[19–21]. However, for PPS, no transition point was found from the Arrhenius plot of I_E/I_M versus reciprocal temperature. It is well known that the transition temperature between two regions depends on the thermodynamic parameters such as enthalpy, free energy and entropy of the excimer. From the thermodynamic point of view, lower temperature will favor excimer formation. On the other hand, the amount of excimer formation depends strictly on a temperature region in which chromophores may possess the so-called sandwich geometry.

The simplest mechanism of excimer formation and dissociation can be expressed as follows^[11, 25]:



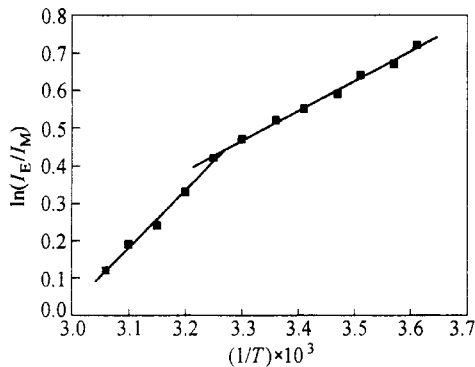


Fig. 2 Arrhenius plot of the excimer to monomer intensity ratio for LPPS

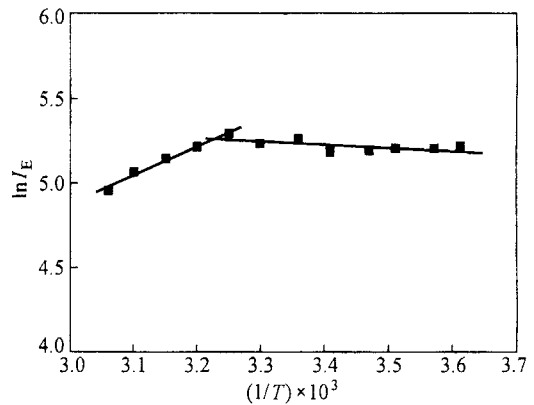


Fig. 3 Arrhenius plot of the excimer emission intensity of LPPS

The concentration change of excimer is written as:

$$\frac{d[{}^1\text{E}^*]}{dt} = k_1[{}^1\text{M}^*] - (k_2 + k_3 + k_4)[{}^1\text{E}^*] \quad (6)$$

Under the steady-state condition, *i.e.* Eq. (6) equals zero.

$$\frac{[{}^1\text{E}^*]}{[{}^1\text{M}^*]} = \frac{k_1}{k_2 + k_3 + k_4} \quad (7)$$

where M and ${}^1\text{M}^*$ are the monomer molecules in the ground and excited state, respectively; E^* stands for excimer. If k_2 and k_4 are negligible and assuming that the fluorescence intensities of monomer (I_M) and excimer (I_E) molecules are proportional to the concentrations of ${}^1\text{M}^*$ and ${}^1\text{E}^*$, respectively, the calculation of activation energy for excimer formation and excimer dissociation can be carried out by the Arrhenius equation:

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

In fact, the left part of Eq. (8) is the slope of the linear plot in Fig. 2. Then,

$$E_a = -\text{Slope} \times R \quad (9)$$

A low activation energy, to some extent, indicates easy rotation around the Si—O bond and vice versa. It is noteworthy that the concentration of LPPS and LPPVS is so low that the possibility of forming an intermolecular excimer may be eliminated. For LPPS, in the low temperature region, *i.e.* $T < T_b$, there exists an excited state equilibrium between the excimers and monomers in the first singlet excited state. That is the reason why isoemission points are frequently observed (see Fig. 4). In this case, excimer formation and dissociation are thermally activated processes, while the rate constant for nonradiative decay is independent of temperature^[19, 20]. In the present temperature range, the behavior of LPPS is almost the same as that of PPS observed by Pi  rola *et*

al. Moreover, in the low temperature range, the formation of excimer usually leads to a decrease of the monomer concentration. Thus, the linear plot of $\ln(I_E/I_M)$ versus temperature is steeper compared with that of $\ln I_E$ with decreasing temperature. In the high temperature region, i.e. $T > T_b$, two factors which determine the excimer formation and dissociation should be taken into account. First, above T_b , the excited state equilibrium is lost because the thermal energy is sufficient to activate the excimer nonradiative decay by dissociation to ground state. It is also worthy of mention that the intensification of molecular motion would lead to a lower rate of excimer formation in the high temperature range and the intensity corresponding to the excimer emission shows a marked decrease with increasing temperature. As a consequence, the isoemission point disappears. Second, it should be kept in mind that LPPS has a double chain macromolecular backbone different from that of PPS. Moreover, the optimized geometry of LPPS with lower energy proves to be doubly stranded^[24]. With increasing temperature, the geometry is probably changed and the spiral-like molecular chain of LPPS will be extended, which may possibly result in high activation energy for excimer formation (see Fig. 2). Therefore, we consider that the cooperative motions in backbone chain bonds may be a possible factor to explain the observed phenomenon in ladderlike polyphenylsilsequioxane.

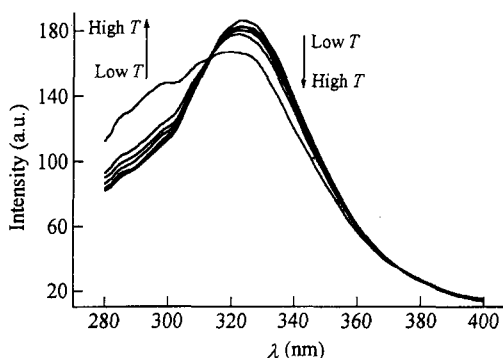


Fig. 4 Fluorescence emission spectra of LPPS at different temperatures (4–35°C)

Ladderlike 1,4-Phenylene-Bridged Polyvinylsiloxane (LPPVS)

To confirm the above proposition and presentation, it is straightforward to synthesize one ladderlike polysiloxane, in which the chromophores are almost fixed. From Scheme 2, ladderlike 1,4-phenylene-bridged polyvinylsiloxane may be a good candidate. Correspondingly, its model compound **M** was prepared.

Figure 5 gives the emission spectra of monomer **M** and LPPVS. It can be seen that the fluorescence spectrum of monomer **M** (5.0×10^{-5} Ph mol/L) displays only one emission peak at 290 nm. LPPVS has a new broad band at 310 nm in addition to a shoulder peak at 290 nm. The 310 nm peak may be ascribed to the excimer emission. It is obvious that the excimers in LPPVS are formed by the adjacent face to face 1,4-phenylene chromophores in the bridge of LPPVS as shown in Scheme 2.

Figure 6 presents the temperature dependence of LPPVS fluorescence intensity. The Arrhenius plot of I_E/I_M ratio gives a simple linear variation with a positive slope similar to that of PPS (Fig. 6).

It should also be mentioned that the temperature dependence behaviors of LPPVS with 1,4-phenylene-bridged double main chain are different from those of LPPS with siloxane-bridged double main chain. There are two possible causes. One is that the bridge in LPPVS is different from that in LPPS (although both of them have double chain structure), which results in different flexibility of the double chain backbone. The other cause is that the flexibility of 1,4-phenylene chromophores in the bridge of LPPVS is lower than that of the phenyl chromophores in the side chains of LPPS. In this way, the molecular motion of LPPVS is quite different from that of LPPS at high temperature. Thus, no transition point is observed in the Arrhenius plot of I_E/I_M of LPPVS versus the reciprocal of temperature.

In this study, the temperature range chosen is 4–55°C. Due to the boiling point of tetrahydrofuran, a further temperature increase was not carried out. It should be emphasized that k_2 in Eq. (7) can not be negligible if the

temperature is very high. In that case, the temperature effect is too complex. Further investigation is in progress.

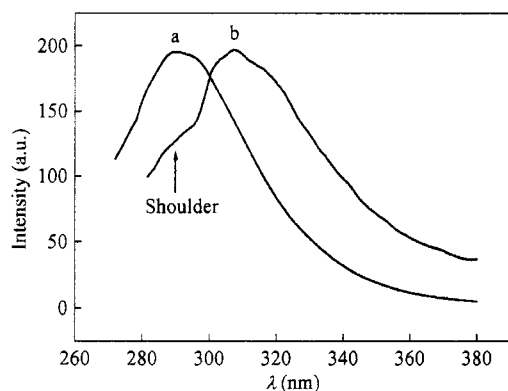


Fig. 5 Fluorescence spectra of (a) monomer **M** and (b) LPPVS

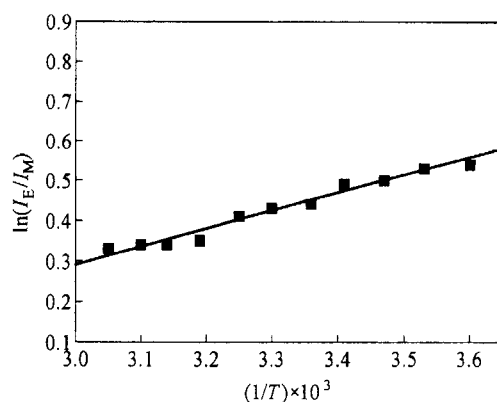


Fig. 6 Arrhenius plot of the excimer to monomer intensity ratio for LPPVS

CONCLUSION

The temperature dependence of ladderlike polyphenylsilsequioxane (LPPS) and ladderlike 1,4-phenylene-bridged polyvinylsiloxane (LPPVS) fluorescence was investigated. The excimer to monomer intensity ratio (I_E/I_M) of dilute LPPS solution shows a double linear Arrhenius plot with a break point ascribable to a transition temperature T_i dissimilar to that of single chain polyorganosiloxane (PPS). This difference may be mainly attributed to the relatively rigid double-chain macromolecular backbone of LPPS. When $\ln I_E$ of LPPS was plotted versus $1/T$, a linear plot with one break point was found, which is the same as that of PPS. However, the Arrhenius plot of I_E/I_M of ladderlike 1,4-phenylene-bridged polyvinylsiloxane (LPPVS) in dilute solution versus $1/T$ presented a simple linear variation with a positive slope, which confirmed our proposition. The difference between the properties of fluorescence spectra of LPPS and LPPVS may possibly derive from their structure differences and cooperative motion in backbone chain bonds.

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