Luminescence Study of *cis*- and *trans*-Stilbenes in the Sol-Gel System

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The emission spectra of *cis*- and *trans-* stilbene molecules doped in sol-gels(tetraethoxysilane system) have been measured during the sol-gel transformation. Changes in the emission spectra of both molecules were observed as the system changed from sol stage to dried glass over a period of 14 days. Our results indicate that the motion of the *cis→trans* photoisomerization decreases in accord with the rigidity changes of the surrounding system. Although the *trans→cis* photoisomerization was not observed in the sol-gel system, the twisting motion of the single bond between the phenyl group and the ethylene moiety during the photoexcitation was detected in this system. The existence of the transient intermediates will be discussed to interpret the subtle changes of the emission spectra of the stilbene molecules encapsulated in the sol-gel system.

KEY WORDS: Fluorescence; stilbenes; sol-gel.

INTRODUCTION

Stilbene (1,2-diphenyl ethylene) has been considered a prototype system for studying the *cis-trans* photoisomerization (Fig. 1) in olefins. Because of the important role of the photoinduced *cis-trans* isomerization of ethylenic double bonds in biological and material systems, the interest to both theoretical and experimental chemists in this field remains [1–12]. During past years, many studies have been carried out under different conditions, such as in inert gas clusters [13–14], viscous solutions [15–16], and zeolites systems [17], trying to understand the effects of the chemical environment on the physical properties of this type of molecule. Collectively, the results of these experiments demonstrated that the excited states of the stilbene system are sensitive to the chemical environments. However, the properties of the transient states in the *cis-trans* photoisomerization of the stilbene system are still not well understood because of the conditional

limitations in those experiments. To obtain a more detailed assessment of the photophysical properties of the stilbene system, a sol-gel technique was introduced to this system based on its intrinsic properties of systematic changes of the chemical environments during the sol-gel process.

Basically, The sol-gel process is a synthesis technique of preparing oxide glasses from metal alcoholates through hydrolysis and polycondensation at normal temperature [18–20]. In this process, the phase of the system will change gradually from its initial solution phase to the eventual dried xerogel. Consequently, the accompanied property of the chemically induced phase transitions of the sol-gel system provides a new approach to investigate the environmental effects on the electronic structure as well as the molecular conformation of the encapsulated molecules [21–25].

In this work, we investigated the effects of the chemical environment on stilbenes by monitoring the changes in the luminescence of the encapsulated stilbenes in the sol-gel system. Our results indicate that the *cis-trans* photoisomerization of stilbenes in the excited states could be explored by monitoring the luminescence spectrum of

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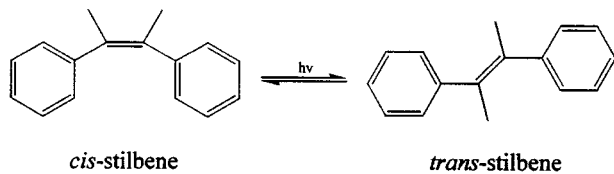
Fig. 1. The photoisomerization of stilbene.

stilbenes in different stages of sol-gel transformations. All these observations will be discussed in terms of the rigidity effect of the environment on the conformational change of stilbenes in the different stages of the sol-gel process.

EXPERIMENTAL

Tetraethoxysilane (TEOS), *cis-* and *trans*-stilbenes were purchased from Merck and Aldrich, respectively. The sol-gel doped with stilbene was prepared by adding TEOS, alcohol/stilbene solution, and distilled water into a quartz cuvette. The mole ratio of TEOS:H_2O:C_2H_5OH was 1:6.2:3.8. The final concentration of stilbene in the sol solution was approximately 10^{-5} M. The cuvette was then covered with aluminum foil. A couple of pin holes were pierced in the foil to allow slow evaporation of alcohol and water for 2 weeks. The experiments were carried out at neutral pH without any addition of catalyst.

The luminescence and spectra were taken at room temperature with a spectrofluorometer (Perkin-Elmer LS-50) in rectangular excitation. The excitation wavelength for the luminescence was 250 nm for each of the samples in this study.

RESULTS

The luminescence spectra of *cis-* and *trans*-stilbenes doped in TEOS sols are recorded at regular intervals (every day). The changes of the emission spectra as a function of time are shown in Figs. 2 and 3, respectively. The emission spectra of *cis-* and *trans*-stilbenes recorded right after the mixing of the sol solutions are similar to each other in the liquid state, except the emission quantum yield of *cis*-stilbene is much lower than that of *trans*-stilbene. The band maximum is centered at ~350 nm in both cases. However, the changes of the spectra in these two isomers proceed in different routes as the polymerization and condensation of TEOS sols start to take place. As shown in Fig. 2, the luminescence spectra of the *cis*-stilbene molecule changes not only the peak position but also the band width during the sol-gel-xerogel process.

Fig. 2. The changes of emission spectrum of *cis*-stilbene in the sol-gel system: (a) initial liquid, (b) dried gel. The peak labeled with the asterisk is due to the second-order signal of the excitation line.

The luminescence maximum shifts from ~350 nm to ~420 nm smoothly in conjunction with the intensity growth (by 5 times) during the sol-gel transformation. This shift is parallel to the environmental changes from the liquid state of sols to the rigid state of xerogels. In addition to the shift of the emission band, some vibronic peaks are also observed in the rigid state of xerogels. The peak positions are at 376 nm, 406 nm, 422 nm, and 484 nm.

In the case of the *trans*-stilbene system, the sol-gel transformation does not change the whole band position and the band width of the luminescence spectrum except that the vibronic structures with the long progression in $\Delta v \simeq 1330$ cm^{-1} become more prominent as the rigidity of the system is increased. The peak positions are deconvoluted to the best fit with maxima at 334, 350, 366, 385, 406, and 429 nm. It is also observed that the intensity distribution of vibronic peaks is changed significantly during the sol-gel transformations. The main intensity of the luminescent spectrum changed from the second peak of the progression to the third member of the progression as the system changes from the liquid state of sols to the
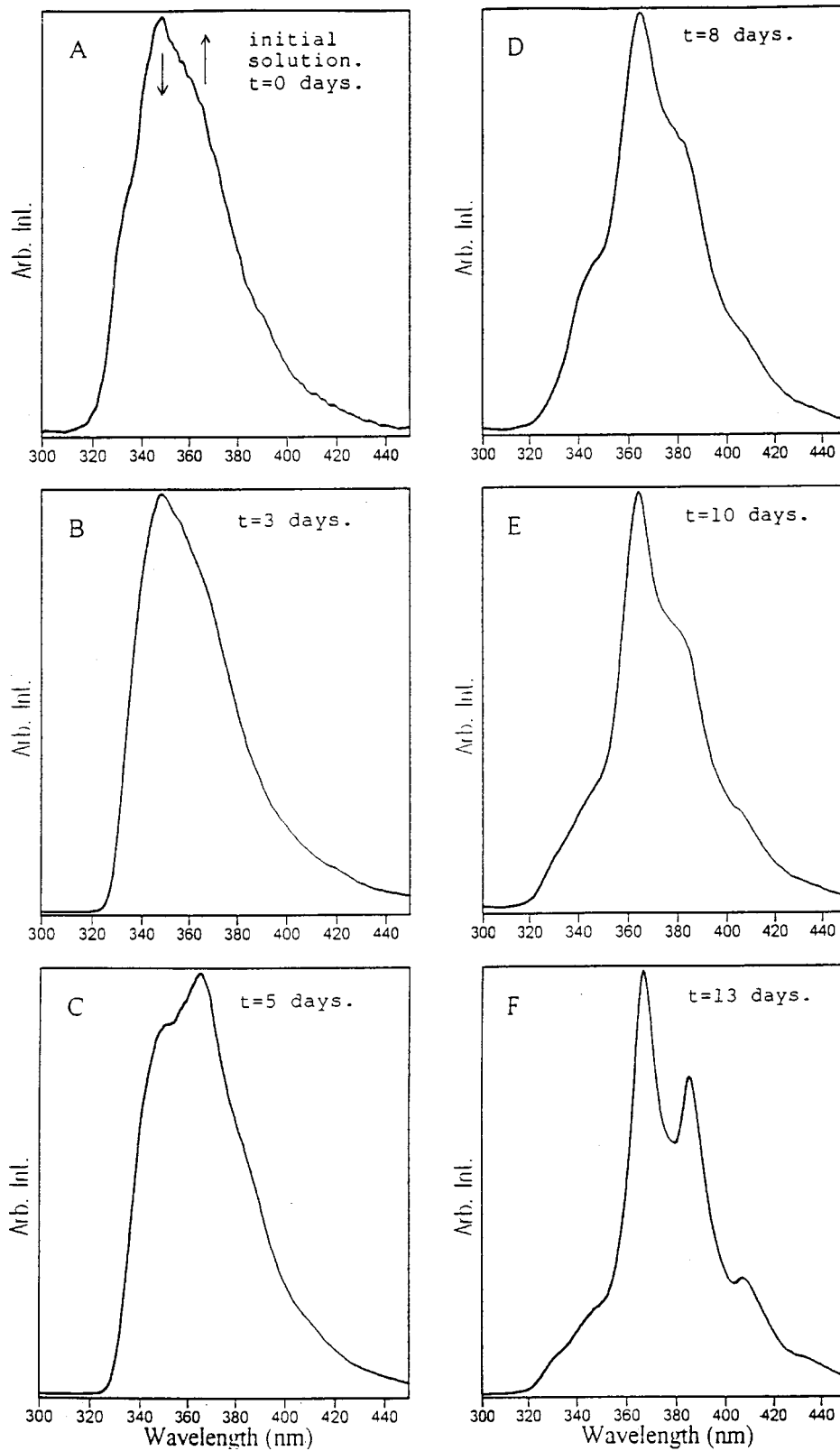
Fig. 3. The changes of emission spectrum of *trans*-stilbene during the sol-gel-xerogel process: (A) initial liquid, (B) - (E) aged gel, (F) dried gel. The arrows indicate the direction of the intensity changes during the sol-gel transformation.

rigid state of xerogels. This observation is not identical with that obtained from the temperature-dependent experiment in which the intensity distribution of the vibronic bands is not affected as the phase changes from the liquid state to the solid state [26].

DISCUSSION

The *cis-trans* photoisomerization of stilbene is considered to proceed mainly via torsional motion about the central c=c double bond in the excited states [9–11]. Various spectroscopic studies have shown that the electronic structure as well as molecular structure of *trans*-stilbene is sensitive to the environment [3,7]. Consequently, the dynamic properties of the conformational changes of the stilbene system during the photoexcitation are of fundamental importance to reveal the photoisomerization mechanisms. Because the stilbene molecules display an intense luminescent signal when they are irradiated to the excited states, the technique of the luminescence spectroscopy is widely used to monitor the physical properties of stilbene system in its excited states.

Normally, the emission spectrum of *trans*-stilbene displays an ambiguous vibronic structure in organic solvents at room temperature, whereas the well-resolved vibronic structure is obtained as the temperature is lowered and the solvent becomes a clear glass [26]. Although the subtle changes in the ultraviolet and fluorescence spectra of *trans*-stilbene at low temperatures have recently been observed and attributed to the aggregation of the *trans*-stilbene molecule [27], the essentially similar contour and the band width of the luminescent spectra at different temperatures indicate that the configurations of the *trans*-stilbene molecule are not affected by the temperature of the solvent. However, as the molecule is trapped in the sol-gel system, the intensity distribution of vibronic bands is changed significantly during the sol-gel transformations. The similar result is also observed as the *trans*-stilbene is trapped in the cavity of cyclodextrin [28]. These results indicate that the microenvironments of glass and xerogel have different effects in extent on the configurations of the *trans*-stilbene molecule in its emitting states. Because the xerogel is generated by the covalently linked molecules during the sol-gel transformations, the restrictions of the xerogel cavity on the motions of the *trans*-stilbene molecules are expected to be larger than those in the solid glass, which is formed physically by lowering the temperature of the organic solvents. It has also been demonstrated that as gelation begins, the progress of shrinkage of the

system leads to an increase in the number of pores, with a decrease in the diameter of each pore [25]. As a result, it is reasonable to believe that the harder restrictions of the xerogel cavity on the motions of the *trans*-stilbene molecules could maintain the conformation of the *trans*-stilbene molecule unchanged during the photoexcitation. In addition, the photoexcitation of the *trans*-stilbene molecule does not exhibit a detectable luminescent signal from the *cis*-stilbene molecule in both solution phase and dried glass. The change of the intensity distribution of vibronic peaks observed in the sol-gel system is then attributed to the different conformations of the *trans*-stilbene molecule in the excited state. This change can also be interpreted as a result of the shrinkage of the entangled O−Si−O network upon drying. However, any further attempt to correlate this change to the pore size of the matrix would be very difficult, because the nature of the entrapment is still not fully understood.

Structural studies have indicated that *trans*-stilbene is planar in both the solution and the solid phases. However, in the gas phase, a non-planar structure of the *trans*-stilbene molecule is reported by the fact that both benzene rings in the *trans*-stilbene molecule are tilted by $\tau = 32.5$ degrees with respect to the vinyl group [5]. These results indicate that the twisting motion (Fig. 4) of the single bond between the phenyl group and the ethylene moiety is sensitive to the physical states of the environment.

Furthermore, the *trans*-stilbene derivatives with the rigid molecular structure in respect to the phenyl twisting mode have been obtained by linking phenyl ortho positions to α or β positions of the ethylene moiety in the molecule [29]. In addition to the red-shifts of the absorption and emission spectra of these structurally rigid *trans*-stilbene derivatives, the maximum absorption changes from the third peak of the progression for *trans*-stilbene to the second member of the progression for the chemically frozen *trans*-stilbene derivatives. These observations were attributed to the resonance
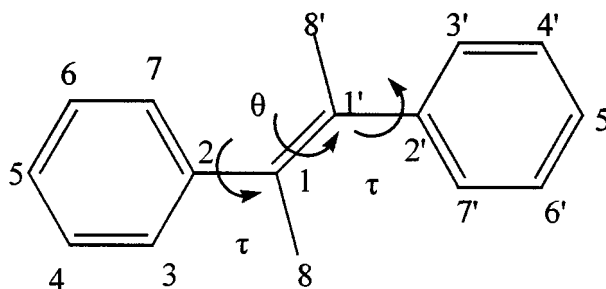

Fig. 4. Molecular structure of *trans*-stilbene, which shows the numbering of the atoms and the twisting and the torsional motion of the molecule.

effects and the changes in the relative location of the potential energy minimum for the excited molecules caused by the chemical modification. As a result, the similar trend of the spectroscopic properties between the chemically frozen *trans*-stilbene derivatives and the *trans*-stilbene molecule encapsulated in the xerogel cavity indicates that the planar structure is maintained in the excited state for the *trans*-stilbene molecule. Conversely, the blue-shifts of the emission spectrum of the *trans*-stilbene molecule in solution phases imply the existence of the non-planar structure in the excited state. Collectively, the spectral changes of the *trans*-stilbene molecule in the sol-gel system are reflecting the extent of the twisting motion of the single bond between the phenyl group and the ethylene moiety instead of the torsional motion about the central $c=c$ double bond in the excited state during the sol-gel transformation. Additionally, the extent of the frequency shift of the emission spectrum in solution is weaker than those obtained in the jet-cooled experiments [13]; this make us believe that the conformational change of the *trans*-stilbene molecule in the excited state is relatively small in the solution phases.

In contrast to the high emission quantum yield of the *trans*-stilbene molecule, the luminescence spectrum of *cis*-stilbene recorded right after the mixing of the sol solutions is relatively weak and appears identical with a *trans*-stilbene emission spectrum because of *cis*→*trans* photoisomerization. However, the band position, intensity, and band-width of the luminescence spectrum change smoothly as the polymerization and condensation of TEOS sols start to take place. The luminescence spectrum recorded in the rigid state of xerogels is similar to the *cis-stilbene* $S_1 \rightarrow S_0$ emission spectrum reported by other groups [30]. Our results indicate that the *cis*→*trans* photoisomerization is inhibited gradually during the sol-gel transformations. In addition, the smooth shift of the spectrum implies that the *cis* form of the stilbene molecule may go through several intermediate states with different conformations before ending at the *trans* form of the stilbene molecule during the photoisomerization. This interpretation is supported by the fact that the changes of the emission spectrum during the sol-gel transformations cannot be simply deconvoluted to the combination of the emission spectra of *cis*- and *trans*-stilbene. Even though it is difficult to deduce the number of the transient intermediates and their corresponding conformations in the process of the *cis-trans* photoisomerization at the current stage, the results indicate that this photoisomerization is not a simple reversible process through the torsional motion about the $\rangle c=c\langle$ double bond in the excited state. In other words, the steric effects between the phenyl groups and the rotation of the phenyl ring with respect to the vinyl group in the excited state might also play an important roll in the process of the photoisomerizations.

CONCLUSIONS

The *cis*- and *trans*-stilbene molecules doped in sol-gels have been studied by luminescence spectroscopy. The subtle changes in the emission spectra induced by the sol-gel transformation are attributed to the contributions of the transient intermediates in the process of the *cis-trans* photoisomerization. The significant change of the emission spectrum of *cis*-stilbene and the relatively minor change of the emission spectrum of *trans*-stilbene in the sol-gel system indicate that this system can provide a suitable environment to retard both the twisting of the electronically excited $\rangle c=c\langle$ double bond and the torsional motion of the benzene rings with respect to the vinyl group during the photoexcitation. These results also imply that the steric repulsion between the benzene rings might play an important role in the process of the photoisomerization of the stilbene molecules.

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