concentration, the percentage of intrablob links is constant. It must be noted that the small intrablob loops involved here differ from the loops found in the cyclizations investigated by Dušek, K., Gordon, M., and Ross-Murphy, S. B.,[10] in the sense that they only occur on a short scale and thus do not affect the critical properties of the transition. In conclusion, the results presented in Figure 1a can be compared without any assumption to the classical and percolation models of gelation.

The exponent of the viscosity (κ) and that of the elastic modulus (θ) have been calculated by plotting $\eta^{-1/X}$ and $G^{1/Y}$ versus c_1. We retain the values of X and Y for which the experimental points fall on straight lines intercepting the c_1 scale inside the range where $c_{1,c}$ is located. From such plots (see Figure 1b), we have deduced

$$\kappa = 0.9 \pm 0.2$$

$$\theta = 1.9 \pm 0.1$$

These values are quite different from the predictions of the classical theory (0 and 3, respectively) but are in good agreement with those of the percolation model (0.75 and 1.9, respectively). Investigations on various systems (radical copolymerization,[11] vulcanization in semidilute solutions,[12] and thermoreversible gelation[13]) also showed good agreement with the percolation predictions for θ. But, in some cases, discrepancies have been observed which may be attributed to the influence of chain rigidity[14] or to the failure of the assumption of linearity between the experimental parameter and the theoretical one.

The width of the critical region which corresponds to the range of the cross-link concentration where power laws are observed is found to be very large, greater than 60% of the relative distance from the critical point. In contrast to time-dependent studies for which the width of the critical range can be drastically reduced because of the nonlinear variation of the cross-link concentration versus time, the value which is determined here is perfectly reliable. Moreover, it is in good agreement with the Daoud's predictions concerning vulcanization in semidilute solutions.[15]

In conclusion, our study of the sol–gel transition as a function of the concentration in cross-links shows that a large number of intrablob links exist at the threshold but that the mechanical properties are well described by the percolation model. A more detailed study of chromium(III) cross-linking in hydrolyzed polyacrylamide solutions is in progress and will be reported later.

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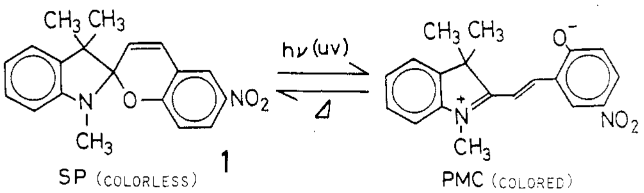
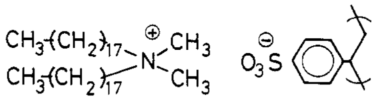
Rate Control of Thermal Isomerization of a Spirobenzopyran Embedded in Bilayer-Immobilized Cast Film by the Phase Transition

It is widely known that photochromism of spirobenzopyran derivatives is largely influenced by the physical state of the surrounding matrices due to a large steric requirement during the isomerization. A typical example is the effect of the glass transition of polymer matrices on the thermal decoloration (isomerization of UV-induced merocyanine (PMC) to starting spiropyran (SP)).[1-5] Our recent work revealed that when spirobenzopyrans were incorporated into an aqueous bilayer membrane, the decoloration kinetics was strongly dependent on the membrane fluidity which is altered by the crystal to liquid crystal phase transition.[6] In light of the development of photoresponsive materials and devices, photochromic phenomena taking place in the solid phase would be of considerable interest. It has been shown by Kunitake and his co-workers that bilayer-immobilized solid films are obtainable by simple casting methods.[7-9] A noteworthy feature of these films is that the immobilized bilayers maintain considerably well the characteristics of bilayers dispersed in water and show clearly the crystal to liquid crystal phase transition.[7-9] In this paper we report the thermal decoloration of a spirobenzopyran compound 1 embedded in a bilayer cast film which consists of an ion complex between dioctadecyldimethylammonium and poly(styrene sulfonate) (M_w = 500 000) ($2C_{18}N^+2C_1$–PSS^-). It is found that the crystal to liquid crystal phase transition of the bilayer cast film brings about an abrupt increase in the reaction rate.



1



$2C_{18}\overset{+}{N}2C_1$-$PSS^-$

The bilayer-immobilized cast film was prepared in a similar method described by Kunitake et al.[8] The polyion complex, $2C_{18}N^+2C_1$–PSS^-, was dissolved in chloroform together with 0.5 mol % of 1 and cast onto a quartz plate (film thickness, 10 μm). The cast film was then allowed to stand for 1 h at 60 °C at relative humidity of 100% and dried under vacuum before kinetic measurements. This

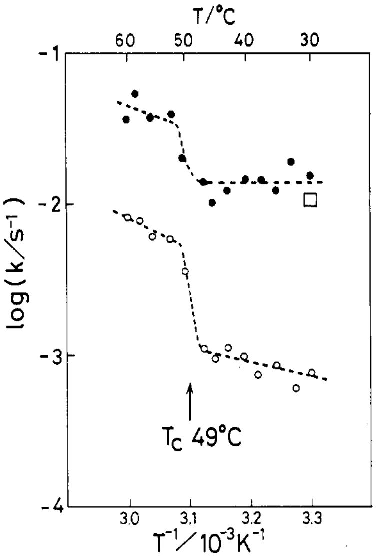


Figure 1. Arrhenius plots for the thermal decoloration rate of 1: (○) slow process; (●) fast process. The rate constants were determined by fitting the experimental data to the equation $(A_t - A_\infty)/(A_0 - A_\infty) = F \exp(-k_{\text{fast}}t) + (1 - F) \exp(-k_{\text{slow}}t)$, where A_t, A_0, and A_∞ are the absorbances at 568 nm at time t, zero, and infinite time, respectively, and F and $1 - F$ are the fractions of PMC decaying with rate constants k_{fast} and k_{slow}, respectively. (□) The datum observed in 1,4-dioxane/water (97/3 by volume) mixed solvent.

annealing procedure was found to be essential to give a well-structured multibilayer, which was proved by differential scanning calorimetry (DSC) and X-ray diffraction analyses[10] and gave rise to a significant effect on the reaction behavior. The X-ray (Ni-filtered Cu Kα) pattern of the annealed film showed the lamellar bilayer structure (spacing, 3.8 nm) whose membrane plane was preferentially oriented parallel to the film surface. The thermal decoloration was followed by measuring the absorbance change with time at 568 nm of PMC in the dark immediately after UV irradiation ($\lambda < 366$ nm, with a 500-W high-pressure mercury lamp and a glass filter).

At all temperatures examined the first-order plots of the reaction showed strong deviation from linerity and were satisfactorily analyzed as being the sum of two first-order processes. Figure 1 shows the temperature dependence of the rate constants of the two processes ("fast" and "slow") expressed in terms of Arrhenius plots. As shown in the figure, the rate constants (k/s^{-1}) for both processes were increased in a narrow temperature region near the crystal to liquid-crystal phase transition temperature (T_c = 49 °C, determined as the endothermic peak top of the DSC measurement in the heating scan). The rate constants increased by a factor of approximately 3 (fast process) to 7 (slow process) with rising temperature from 47 to 53 °C as the result of increased molecular mobility in the bilayer matrix.

In contrast to the kinetics observed in this solid film, the decoloration obeyed strictly first-order kinetics when 1 was incorporated into an aqueous bilayer membrane formed by dioctadecyldimethylammonium bromide.[6] At least two factors are responsible for the deviation from first-order kinetics in the solid system: (i) nonuniformity of micropolarity around PMC and (ii) nonhomogeneous steric restriction by the matrix which may involve the factors of both local order of the bilayer structure and free volume in the film. In general the visible absorption maximum of PMC ($\lambda_{\max}$) is blue-shifted and the thermal isomerization is retarded in polar media.[11] If PMC is located in sites of varying micropolarity, $\lambda_{\max}$ should show a blue shift in the dark after UV irradiation as the result of faster decaying of PMC molecules located in a less polar environment. However, such a spectra shift was not observed. It seems thus reasonable to assume that the factor of steric restriction is more important for the origin of the plural decaying processes. In order to estimate the magnitude of the restriction in the bilayer film, the reaction rate was compared with that observed in a homogeneous solution. 1,4-Dioxane/water (97/3 by volume) mixed solvent was chosen for this purpose whose polarity based on $\lambda_{\max}$ is equivalent to the micropolarity of PMC in the film and the rate at 30 °C is also indicated in Figure 1. Rates of the fast process were almost comparable to that observed in solution, suggesting that the restriction from the surrounding matrix contributing to this process resembles that from the liquid medium. Rates of the slow process were reduced nearly 10 times relative to those of the fast one. This implies the strong restriction from the matrix leading to the slowly isomerizing PMC.

In conclusion, the thermal isomerization rate of a spirobenzopyran embedded in the bilayer-immobilized cast film was considerably controlled by the crystal to liquid crystal phase transition. The discontinuity of the rate change by the phase transition of the bilayer was more pronounced than that by the glass transition of most polymer matrices.[2,4,5]

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