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Photosensitized Isomerization of Stilbene by Phenyl Vinyl Ketone–2-Vinylnaphthalene Copolymer

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Abstract: Phenyl vinyl ketone–2-vinylnaphthalene copolymers were found to be effective polymer photosensitizers for the isomerization reaction of stilbene, especially at low concentration, compared with poly(phenyl vinyl ketone) or monomeric ketones, such as acetophenone. Phosphorescence spectra of the copolymer and its lifetime measurements revealed that the high efficiency is due to the stabilization of the triplet states of the polymer by energy transfer from the benzoyl group to naphthyl ones. The maximum rate of the photosensitized isomerization is attained by the copolymer containing 16 mol % of the 2-vinylnaphthalene unit, in which the triplet energy is completely transferred to the naphthyl group and its lifetime is rather long. The further increase of the content of the naphthalene unit, however, depressed the rate because of the destabilization of the naphthalene triplet state by dimer or excimer formation. The difference in the mechanism of photosensitization between the copolymer and poly(phenyl vinyl ketone) is also discussed.

Recently much attention has been paid to the photophysical processes in polymer systems and extensive studies concerning excimer formation and energy transfer processes have been reported.[2] One of the most interesting results obtained in these studies is that the photoexcited energy migrates along the polymer chain. The energy migrating along the chain is expected not only to bring about the chemical reaction of the polymer itself, such as bond scission,[3] but also to excite other molecules by intermolecular energy transfer. In this study we elucidate the latter process in detail to obtain an effective polymer photosensitizer.

Although several attempts have been carried out to use polymer sensitizers for isomerization reactions,[4–6] no remarkable advantage of polymers has been obtained yet. The efficiency is similar to that of the corresponding monomer and ultimate conversions are the same.

Necessary properties of an effective polymer photosensitizer are as follows: it should have (1) low singlet excited state energy and rather high triplet energy, (2) high intersystem crossing yield, (3) long lifetime in the triplet state, and (4) a favorable structure in which triplet energy migrates effectively. We used phenyl vinyl ketone–2-vinylnaphthalene copolymer, which is expected to satisfy the above properties, for the sensitization of photoisomerization of *trans*-stilbene.

Experimental Section

Phenyl vinyl ketone monomer was synthesized according to the method of Mannich and Heilner[7] and purified in vacuo by fractional distillation before use. 2-Vinylnaphthalene was recrystalized from cyclohexane twice. Copolymerizations of these two monomers were carried out in benzene at 60° using azobisisobutylonitrile as an initiator.

Zone-refined *trans*-stilbene was sublimed in vacuo before use. Benzene was fractionally distilled twice. All samples were prepared in vacuo at less than 10^{-5} mm.

Photoillumination was carried out with a mercury line of 366 nm by the use of a super high pressure mercury lamp and a monochrometer. Optical absorption and emission spectra were measured with a conventional recording spectrophotometer (Hitachi EPS-3T) and a fluorescence spectrophotometer (Hitachi MPF-2A) with a phosphorescence measurement attachment, respectively. The lifetimes of the triplet state were also determined by the use of the above phosphorescence measurement attachment and a synchroscope.

Results and Discussion

I. Poly(phenyl vinyl ketone). Aromatic ketones, such as acetophenone or benzenophenone, are effective photosensitizers of the photoisomerization of stilbene.[8] Not only monomeric ketones but also polymeric ones are expected to photosensitize the isomerization in high yield. Figure 1 shows the photoisomerization of *trans*-stilbene to the cis form in the presence of poly(phenyl vinyl ketone) (molecular weight = 40,000) as well as a corresponding monomeric ketone, acetophenone, in benzene solution at 10°. The concentrations of these two sensitizers are adjusted so as to have the same absorption at 366 nm. The isomerization was followed by optical absorption at 325 nm due to *trans*-stilbene. Poly(phenyl vinyl ketone) is an effective photosensitizer. However, its efficiency is similar to that of acetophenone. Even when the concentration of *trans*-stilbene is changed from 10^{-4} to 10^{-6} *M*, significant difference between the polymer and acetophenone is not observed. The result indicates that the advantage of polymer is not enough to bring about higher efficiency to this polymer than acetophenone, though the delocalization of the triplet excited energy may facilitate the energy transfer from the polymer to stilbene.[9]

II. Phenyl Vinyl Ketone–2-Vinylnaphthalene Copolymer. Copolymerization is a convenient way to introduce desirable photophysical and chemical properties in polymer photosensitizers. We used here 2-vinylnaphthalene as a comonomer because of the characteristic nature of the naphthalene unit. The triplet state energy of naphthalene lies between those of acetophenone and stilbene and its singlet state energy is higher than both of them. In addition the lifetime of its triplet state is much longer than

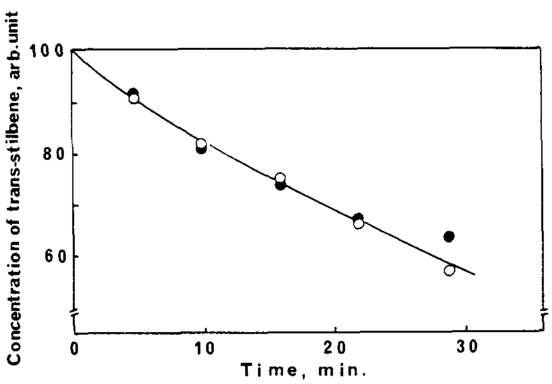

Figure 1. Photoisomerization of *trans*-stilbene to the cis form sensitized by (○) poly(phenyl vinyl ketone) and (●) acetophenone in benzene at 10° with a mercury line of 366 nm. Initial concentration of *trans*-stilbene is 1.5×10^{-5} *M*. Concentration of poly(phenyl vinyl ketone) is 5×10^{-4} *M*. Concentration of acetophenone is adjusted so as to have the same absorption as the poly(phenyl vinyl ketone) at 366 nm.

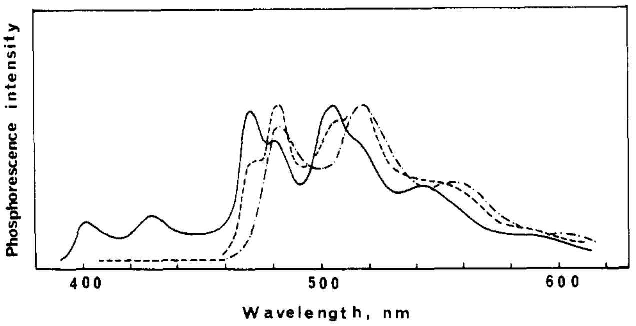

Figure 2. Phosphorescence spectra of phenyl vinyl ketone-2-vinylnaphthalene copolymers in 2-methyltetrahydrofuran at 77°K excited at 350 nm. Contents of 2-vinylnaphthalene in the copolymers are (—) 9 mol %, (- - -) 16 mol %, and (- · -) 55 mol % and the concentrations of the copolymers are 2.0×10^{-3}, 2.2×10^{-3}, and 4.0×10^{-3} *M*, respectively.

Table I
Half-Life Times of Triplet State of Phenyl Vinyl Ketone-2-Vinylnaphthalene Copolymer at 77°K[a]

PVK:VN	Half-life time[b]
100:0	9 msec
91:9	2.2 sec
84:16	2.0 sec
45:55	1.5 sec
25:75	1.3 sec
8:92	1.2 sec
0:100	1.2 sec

[a] The wavelength of excitation is 350 nm except for the 2-vinylnaphthalene homopolymer which is excited at 320 nm. [b] Half-life times of the 480 nm band except phenyl vinyl ketone homopolymer which is measured at the 400 nm band.

that of acetophenone, because of its π–π^* nature. The absorption spectrum of the copolymer has a broad n–π^* band around 340 nm due to the benzoyl group and a sharp peak at 320 nm due to the naphthyl group. These two bands are slightly red shifted compared to monomeric naphthalene.

Figure 2 depicts the phosphorescences of the copolymers with different composition ratios excited at 350 nm of the absorption of benzoyl group in 2-methyltetrahydrofuran at 77°K. They have two different phosphorescence bands around 400 and 500 nm. The former was assigned to the triplet state of the benzoyl group and the latter to that of the naphthyl group by comparing them with the corresponding monomeric compounds, acetophenone and naphthalene. Upon increasing the content of the 2-vinylnaphthalene unit in the polymer chain, phosphorescence around 400 nm disappeared. In the copolymer containing 9 mol % of the naphthalene unit both phosphorescence bands are observed. The 400 nm band, however, is no longer observed from the copolymer containing more than 16 mol % of the naphthalene unit. This result indicates that the triplet energy of the benzoyl group formed by photoabsorption at 350 nm migrates successively to the neighboring benzoyl group as far as a few units along the polymer chain and is finally transferred to the naphthyl group.

It is worthwhile to note here that the phosphorescence spectra of the copolymer around 500 nm showed a distinct red shift and became broader with the increase in the content of the 2-vinylnaphthalene units. This behavior is presumably considered due to the strong molecular interaction with the adjacent naphthyl group in the polymer chain, or triplet excimer or dimer formation, because a similar red shift and line width change are also observed in the phosphorescence spectrum of the triplet excimer of naphthalene in solution.[10] The phosphorescence peak at 469 nm is assigned due to the 0–0 band of the monomeric naphthalene unit and at 482 nm due to the dimeric one.

The half-life times of the triplet excited state increased with the introduction of naphthyl group to the polymer as shown in Table I, where apparent half-decay times are depicted because the decay of the phosphorescence is not a simple exponential one. Thus the lifetime of the copolymer containing 9 mol % of the 2-vinylnaphthalene unit is as long as 2.2 sec, though that of poly(phenyl vinyl ketone) is only 9 msec at 77°K. The ratio of the lifetimes is about 200. The remarkable increase in the lifetime is interpreted by the change of the nature of the triplet electronic state in the polymer from the n–π^* state of the benzoyl group to the π–π^* state of the naphthyl one due to energy transfer. Alkyl phenyl ketones are known to have high intersystem crossing efficiency, as high as 1,[11] but their triplet lifetime is very short. On the other hand, alkylnaphthalenes have a long lifetime in the triplet state but the intersystem crossing efficiency is low.[11] A most stable triplet state is expected to be observed in the highest yield by binding these two groups in one molecule.

Further increase of the content of 2-vinylnaphthalene units, however, reduced the lifetime. It decreased to 1.2 sec in poly(2-vinylnaphthalene). The decrease in the lifetime is possibly due to the triplet excimer or dimer formation with the adjacent naphthyl group. The lifetimes of triplet excimer or dimers are reported to be shorter than that of monomer because of the increase in rate of the nonradiative transitions.[10]

III. Photoisomerization of *trans*-Stilbene. Figure 3 shows the photoisomerization of *trans*-stilbene sensitized by phenyl vinyl ketone–2-vinylnaphthalene copolymers at 10° in benzene. The isomerization rate increases by the introduction of a small amount of the naphthyl group to the polymer, though the rate sensitized by poly(phenyl vinyl ketone) is very low for the concentration of *trans*-stilbene used.

The dependence of the rate on the contents of the 2-vinylnaphthalene unit in the copolymer is shown in Figure 4. The rate increases initially with the increase of the contents and the maximum was attained at the content of 16 mol % of the naphthalene unit. The further increase of the content, however, depresses the rate. The initial increase of the rate is probably due to the stabilization of the triplet state by energy transfer from benzoyl to naphthyl groups

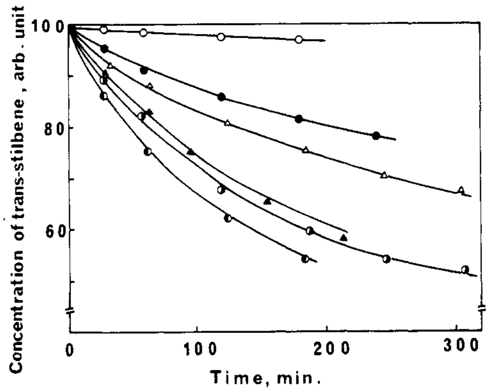

Figure 3. Photoisomerization of *trans*-stilbene to the cis form sensitized by phenyl vinyl ketone–2-vinylnaphthalene copolymers in benzene at 10° with a mercury line of 366 nm. Contents of 2-vinylnaphthalene in the copolymers are: (○) 0 mol %, (▲) 9 mol %, (◐) 16 mol %, (◑) 55 mol %, (△) 75 mol %, and (●) 92 mol %. Initial concentration of *trans*-stilbene is 1.5×10^{-5} *M*. Concentration of phenyl vinyl ketone homopolymer is 5.0×10^{-4} *M*. Concentrations of the copolymers are adjusted so as to have the same absorption at 366 nm.

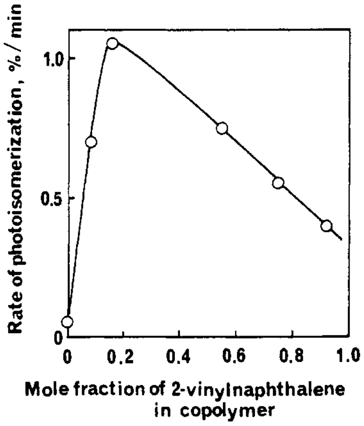

Figure 4. Dependence of the rates of photoisomerization of *trans*-stilbene to the cis form sensitized by phenyl vinyl ketone–2-vinylnaphthalene copolymers in benzene at 10° on the composition of the copolymer. Initial concentration of *trans*-stilbene is 1.5×10^{-5} *M* (concentration of polymers are the same as in Figure 3).

as indicated in Figure 2 and Table I. At 16 mol % of the naphthalene unit the triplet energy initially formed in the benzoyl group by photoillumination at 366 nm completely migrates to the naphthyl group and is most effectively transferred to *trans*-stilbene because of its rather long lifetime. The decrease of the rate at the higher contents of the naphthalene unit is accounted for by the decrease of the lifetime, as shown in Table I, even if the energy transfer from benzoyl to naphthyl groups is complete. These results indicate that the efficiency of the polymer photosensitizer depends first on the completeness of the energy transfer from benzoyl to naphthyl groups and second on the lifetime of the triplet state of naphthyl groups thus formed.

The activation energy of the isomerization is obtained to be 2.6 kcal/mol in the temperature range from 7 to 40°, as shown in Figure 5.

IV. Kinetics of the Photoisomerization. To obtain the efficiency of the polymer photosensitizer quantitatively we examined the dependence of the rate on the concentration of initial *trans*-stilbene. The isomerization rate by the copolymer depends slightly on the concentration of *trans*-stilbene, though it increases considerably with an increase of the initial concentration of *trans*-stilbene in the case of poly(phenyl vinyl ketone). This result implies that the triplet energy of the copolymer is transferred effectively to *trans*-stilbene even when the latter concentration is very low. On the other hand, the triplet energy of poly(phenyl vinyl ketone) deactivates without exciting *trans*-stilbene in the low concentration region of *trans*-stilbene because of its very short lifetime.

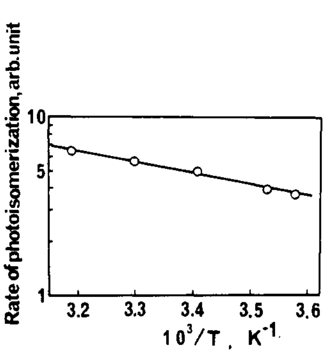

Figure 5. Dependence of the rates of photoisomerization of *trans*-stilbene to the cis form sensitized by phenyl vinyl ketone–2-vinylnaphthalene copolymer (content of 2-vinylnaphthalene is 16 mol %) in benzene on temperature. Initial concentration of *trans*-stilbene is 1.5×10^{-5} *M*. Concentration of copolymer is 6.0×10^{-4} *M*.

The photoisomerization process by the polymer photosensitizer can be represented by the following scheme

$$\mathrm{P_k} \xrightarrow{h\nu} {}^1\mathrm{P_k}^* \tag{1}$$

$${}^1\mathrm{P_k}^* \xrightarrow{k_2} {}^3\mathrm{P_k} \tag{2}$$

$${}^3\mathrm{P_k} \xrightarrow{k_3[\mathrm{N}]} {}^3\mathrm{P_n} \tag{3}$$

$${}^3\mathrm{P_k} \xrightarrow{k_4} \mathrm{P_k} \tag{4}$$

$${}^3\mathrm{P_n} \xrightarrow{k_5} \mathrm{P_n} \tag{5}$$

$${}^3\mathrm{P_k} + \text{t-S} \xrightarrow{k_6} \mathrm{P_k} + \text{c-S} \tag{6}$$

$${}^3\mathrm{P_n} + \text{t-S} \xrightarrow{k_7} \mathrm{P_n} + \text{c-S} \tag{7}$$

where P_k, P_n, t-S, and c-S indicate the benzoyl group in polymer, the naphthyl group in polymer, *trans*-stilbene, and *cis*-stilbene, respectively. 1 and 3 indicate that they are in the singlet or the triplet state. *k*'s are respective rate constants and [N] represents the content of 2-vinylnaphthalene unit in the polymer. Then the rate of isomerization is expressed by eq 8 where I_a is the rate of light absorption.

$$-\frac{\mathrm{d}[\text{t-S}]}{\mathrm{d}t} = \frac{I_a}{k_3[\mathrm{N}] + k_4 + 2k_6[\text{t-S}]} \times \left\{k_6[\text{t-S}] + \frac{k_3k_7[\mathrm{N}][\text{t-S}]}{k_5 + 2k_7[\text{t-S}]}\right\} \tag{8}$$

For poly(phenyl vinyl ketone), [N] = 0

$$\frac{1}{-\mathrm{d}[\text{t-S}]/\mathrm{d}t} = \frac{1}{I_a}\left\{2 + \frac{k_4}{k_6[\text{t-S}]}\right\} \tag{9}$$

For the copolymer containing 16 mol % of the naphthalene unit, $k_3[\mathrm{N}] \rightarrow \infty$. Then the expressions are reduced to

$$\frac{1}{-\mathrm{d}[\text{t-S}]/\mathrm{d}t} = \frac{1}{I_a}\left\{2 + \frac{k_5}{k_7[\text{t-S}]}\right\} \tag{10}$$

The dependences of the inverse rate and the inverse concentration of *trans*-stilbene are depicted in Figure 6 for poly(phenyl vinyl ketone) and the copolymer containing 16 mol % of the naphthalene unit. The experimental plots fit well with relations 9 and 10. From these slops, $k_4/k_6 = 9 \times 10^{-4}$ *M* and $k_5/k_7 = 4 \times 10^{-5}$ *M* are obtained. k_6 and k_7 are considered to be similar because they are reasonably as-

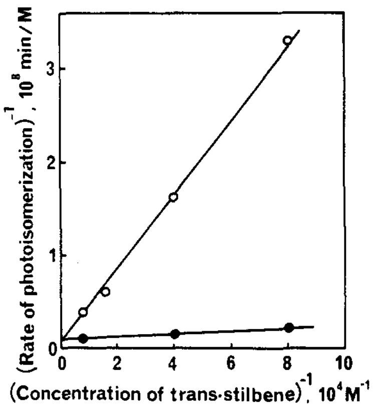

Figure 6. Dependence of the rates of photoisomerization of *trans*-stilbene to the cis form sensitized by (○) poly(phenyl vinyl ketone) and (●) phenyl vinyl ketone–2-vinylnaphthalene copolymer (content of 2-vinylnaphthalene is 16 mol %) in benzene at 10° on the initial concentration of *trans*-stilbene. The concentrations of the two polymers ($\sim 5 \times 10^{-4}$ M) are adjusted so as to have the same absorption at 366 nm.

sumed to be close to diffusion rate constants in both cases. Therefore, the increase in the efficiency observed in these two polymer photosensitizers results from the difference in the process of (4) and (5). k_4 and k_5 are estimated to be 8×10^6 sec^{-1} and 3×10^5 sec^{-1}, respectively, assuming the diffusion rate constant of 8.5×10^9 M^{-1} sec^{-1}.[11] The relative yields of the sensitized isomerization of *trans*-stilbene by poly(phenyl vinyl ketone) and the copolymer are also estimated to be 0.01 and 0.2, respectively, for the initial concentration of *trans*-stilbene of 1.25×10^{-5} M. The sensitizing efficiency of the copolymer is an order of magnitude higher than that of poly(phenyl vinyl ketone) or the corresponding monomeric ketone at the low concentration regions of the energy acceptors.

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Poly(2-vinylfluorenone). III. Photophysical and Photochemical Properties

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ABSTRACT: The absorption and emission spectra of poly(2-vinylfluorenone) are reported. The lowest lying excited electronic states for poly(2-vinylfluorenone) have been tentatively assigned as $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ in nature. The polymer exhibits both normal and excimer fluorescence when excited in the lowest $^1(\pi,\pi^*)$ state and in higher singlet states. No phosphorescence has been observed for dilute solutions or for thin films of poly(2-vinylfluorenone) when excited in the lowest $^1(\pi,\pi^*)$ state. Attempts to populate the triplet state in the polymer via energy transfer from 2,3-butanedione result in quenching of the donor emission but no phosphorescence or delayed emission from the fluorenone polymer. Phosphorescent emissions from photoproducts have been detected when poly(2-vinylfluorenone) is excited to higher excited states and chemistry occurring from a higher lying $^3(n,\pi^*)$ state is presumed to be responsible.

Fluorenone has been the subject of a number of studies because of its unusual spectroscopic properties, and because of its use as a triplet state sensitizer. Kuboyama has reassigned the lowest singlet–singlet transition in fluorenone as π–π^* on the basis of substituent effects.[1] Kearns[2] et al. have shown that the lowest singlet and triplet states are (π,π^*) in nature, and further showed the emission to be fluorescence. A number of workers have reported phosphorescence from fluorenone, but in general their experiments have not been conclusive, and it is likely that true phosphorescence has not been observed.[3-6] Solvent effects on the quantum efficiency of fluorenone fluorescence have been reported by Singer.[7] He suggested that the polarity of the medium can result in a reordering of the lower lying singlet and triplet states, thereby affecting intersystem crossing and fluorescence efficiencies.

Radiationless transitions in fluorenone have been discussed by Hunter,[8] and he classifies fluorenone as behaving like an extreme case for substituted ketones. He suggests in molecules such as fluorenone, in which the $^3(\pi,\pi^*)$ state is depressed far below the (n,π^*) states, degradations from $^3(\pi,\pi^*)$ should appear similar to those for aromatic hydrocarbons. Recently, Marchetti[9] has assigned the $^1(\pi,\pi^*)$ 0–0 band, and estimated the level of the $^1(n,\pi^*)$ state for fluorenone.

The availability of polymers having attached fluorenone chromophores[10] has prompted our investigations of the nature of the low lying excited states and the radiative and