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Studies of Photosensitive Resins. III. The Thermal Hardening of Polyvinyl Cinnamate

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The thermal hardening of polyvinyl cinnamate was investigated. The IR spectrum of the thermally-hardened polyvinyl cinnamate was measured, and the change of its structure by heat was studied. The results showed that the structure of the resin hardened by heat was the same as that of the illuminated resin. The kinetics of the crosslinking by heat was also evaluated; the activation energy for the crosslinking was estimated to be 25.4 kcal/mol. The critical hardening value of polyvinyl cinnamate was also measured and estimated to be about 1.3 crosslinking per polymer molecule.

It is well-known that polyvinyl cinnamate is crosslinked by ultraviolet light[1] and becomes insoluble to any solvent. However, its thermal character has not yet been made clear. Therefore, the mechanism and kinetics of thermal hardening were studied by measuring the IR spectra.

Inami and Morimoto[2] measured the IR spectra of polyvinyl cinnamate before and after light-irradiation, and concluded that the α,β double bond of the cinnamoyl group was broken to the single bond by light. Kirsh *et al.*[3] also measured its IR spectra and obtained the quantum yield and the critical hardening exposure. They estimated that the hardening ratio at the critical point was 0.02%. However, such a method may not be the best way of estimating the critical hardening value, for the resin is not hardened uniformly by light, but is, rather, hardened exponentially with

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[1] L.M. Minsk, J.Q. Smith, W.P. Van Deusen and J.F. Wright, *J. Appl. Pol. Sci.*, **2**, 302 (1959).

[2] A. Inami and K. Morimoto, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **65**, 293 (1962).

[3] Yu. E. Kirsh, K.S. Lyalikov and L. Kalnins. *Zh. Fiz. Khim.*, **39**, 1886 (1965).

the depth. On the other hand, the resin is hardened uniformly by heat. Therefore, the present authors also tried to ascertain the hardening ratio at the critical point.

In a previous paper,[4] the ESR spectrum of the irradiated polyvinyl cinnamate was investigated and it was established that two free radicals, the main-chain radical and the cinnamoyl radical, were produced by the irradiation of the resin. The photocrosslinking mechanism has been made fairly clear by such studies as have been described above, but its thermal hardening is still the subject of frequent discussion.

The sensitized polyvinyl cinnamate is sensitive to light in the ultraviolet and visible regions, while the nonsensitized one is sensitive only in the ultraviolet region. Tsuda[5] discussed the sensitization mechanism of the resin on the basis of the triplet-state mechanism. When a sensitizer is added to the resin, it is hardened by light in the region with longer wavelengths than intrinsic ones. The critical and activation energies for the hardening will be kinetically investigated. The thermal hardening of the photosensitive resin is important for the "afterhardening" process and for preservation in the dark. Therefore, the authors also intend to obtain data on such a process.

Experimental

Polyvinyl cinnamate was synthesized by the pyridine method.[1] The synthesized resin was dissolved into a cellosolve acetate solution, and coated on KBr tablet. The samples were heated at various temperatures, and their IR spectra were measured with a Nippon Bunko infrared spectrophotometer, DS-301. When the heated samples were introduced into water after IR measurements, the thin films of resin remained on the surface of the water. These films were put into the solvent, and their residual weights were measured in order to get information on their solubilities.

The authors estimated the hardening rate of the resin by measuring the concentration of the α,β double bond. The amount of the double bond was evaluated by means of the integrated area of the IR absorption signal at 1640 cm^{-1}. The calibration curve was obtained by means of the IR spectra of films with various depths. Beer's law could be applied to them fairly well.

Results and Discussion

The IR Spectrum of the Heated Polyvinyl Cinnamate. The IR spectra of polyvinyl cinnamate before and after illumination are shown in Fig. 1. The resin was exposed for 160 min with a 1000 W Xe lamp. The IR spectrum of the irradiated polyvinyl cinnamate has already been measured by Inami and Morimoto,[2] who reported that absorption band resulting from the double bond, $\nu_{C=C}$ (1640cm^{-1}), δ_{CH} (1315 cm^{-1}), and δ_{CH} (975 cm^{-1}), disappeared and the $\nu_{C=O}$ (1718cm^{-1}) band shifted to a higher frequency band upon exposure. However, they could not detect any newly-appeared band becaus eof the photocrosslinking.

Figure 1 also shows evidence for the disappearance of the absorption bands resulting from the double bond and the shift of the $\nu_{C=O}$ band. The results agree with those

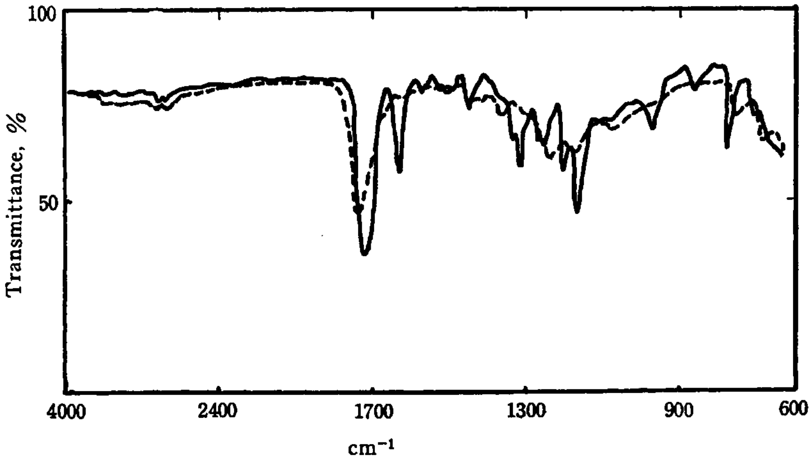

Fig. 1. IR spectra of polyvinyl cinnamate.
—— before illumination, ---- after illumination

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[4] K. Nakamura and S. Kikuchi, This Bulletin, **40**, 2684 (1967).

[5] M. Tsuda, *J. Soc. Sci. Phot. Japan*, **28**, 7 (1965)

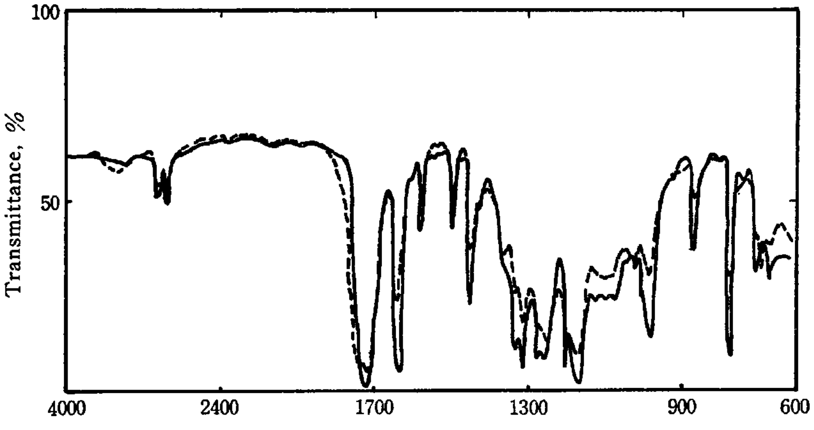

Fig. 2. IR spectra of polyvinyl cinnamate.
—— before heating, ---- after heating

obtained by Inami *et al.*, but Fig. 1 shows that the δ_{CH} band newly appears at 1375 cm^{-1} and that the absorption strengths of all the bands decrease upon exposure to light. It seems that the band is due to the bending vibrational absorption of the saturated CH, which is produced by light-irradiation. Kirsh *et al.*[8] reported that all the absorption bands decreased upon illumination, and concluded that this was caused by the change in electronic structure.

The IR spectrum of the heated polyvinyl cinnamate is shown in Fig. 2. The IR spectra after light-irradiation and after heating are the same. It may, therefore, be concluded that there is no difference between the thermal hardening and photo-hardening of polyvinyl cinnamate with regard to the crosslinking reaction. The disappearance of the $\nu_{C=C}$ (1640 cm^{-1}), and δ_{CH} (1315, 980 cm^{-1}) bands, the decrease of all absorption bands, and the appearance of a new absorption band (1375 cm^{-1}) may also be seen in Fig. 2.

Kinetics of the Thermal Hardening. The rate of the thermal hardening of polyvinyl cinnamate is estimated by measuring the IR spectra. The extent of the double bond was determined by means of the absorption of $\nu_{C=C}$ (1640 cm^{-1}). In the IR spectra of polyvinyl cinnamate, the absorption of the bands resulting from the double bond disappears upon heating, while all the other absorption bands decrease with illumination, as has been described previously. When the sensitized polyvinyl cinnamate was irradiated by a 350 mμ light, the same IR spectral results as with a non-sensitized one were obtained. The light may not be sufficient to decompose the resin, for its energy is only about 82 kcal/mol, while more than 100 kcal/mol may be necessary to decompose it. Therefore, it seems reasonable to assume that the decrease in the spectrum is not due to the decomposition of the resin, but is caused by the change in electronic

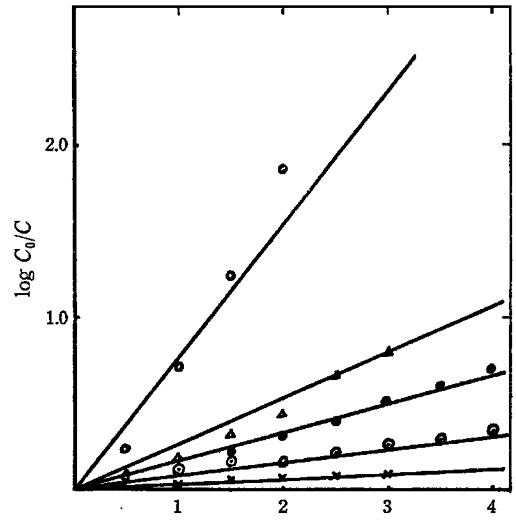

Fig. 3. Decay of cinnamoyl group.
× 182°C ◉ 195°C ● 200°C
△ 220°C ○ 235°C

TABLE 1. RATE CONSTANTS, α AT VARIOUS TEMPERATURES

T	$\log k$
508 °K	0.254
493	−0.212
473	−0.416
455	−1.036

structure proposed by Kirsh.[3] The electronic structural change can be found only in the crosslinked group, and the non-crosslinked group is not affected by it. Therefore, the authors concluded that the IR-determining method of the double bond might be useful.

Relations between the heating times and the rates of the non-crosslinked cinnamoyl group at various temperatures are shown in Fig. 3 and Table 1.

The thermal hardening of polyvinyl cinnamate can be expressed by the formula:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -aC \qquad (1)$$

where a is a rate constant and C is the concentration of the non-crosslinked cinnamoyl group. Therefore, we obtained the following expression:

$$\log x = \log \frac{C_0}{C} = at \qquad (2)$$

where C_0 is the initial concentration of cinnamoyl groups. This formula shows that there is a linear relation between $\log x$ and t. In Fig. 3, the linear relation is satisfactory, so it may be concluded that, in the thermal-hardening process, the reaction can be expressed by the first order, as is shown in formula (1).

When polyvinyl cinnamate was heated to more than 250℃, the decomposition reaction took precedence over the crosslinking and the sample was colored, while the resin is rapidly hardened at more than 200℃. Therefore, in the "afterhardening process" it is better to keep the temperature at about 200℃. After the values at various temperature were estimated by means of formula (2), they were plotted against $1/T$. The relation is shown in Fig. 4. In Fig. 4 the good linear relation between them can be seen. The activation energy of the thermal crosslinking reaction can be obtained from the slope of the line: it is evaluated as 25.4 kcal/mol. About one hundred kcal per mole is necessary to harden polyvinyl cinnamate by light, but a much smaller energy is sufficient to harden it by heat. The energy level of the lowest triplet state of polyvinyl cinnamate was inferred to be 57.2 kcal/mol from the ground state by measuring the phosphorescence spectrum of cinnamic acid.[6] The activation energy is smaller than the triplet state energy. The critical energy of the sensitization should correspond to the triplet-state energy.[7] The above results suggest that the critical energy of sensitization can be diminished to 25.4 kcal/mol if the triplet-state energy is degraded by some methods such as introduction of substitutional groups to the benzene ring of the cinnamoyl group. The following expression can be derived from data in Table 1:

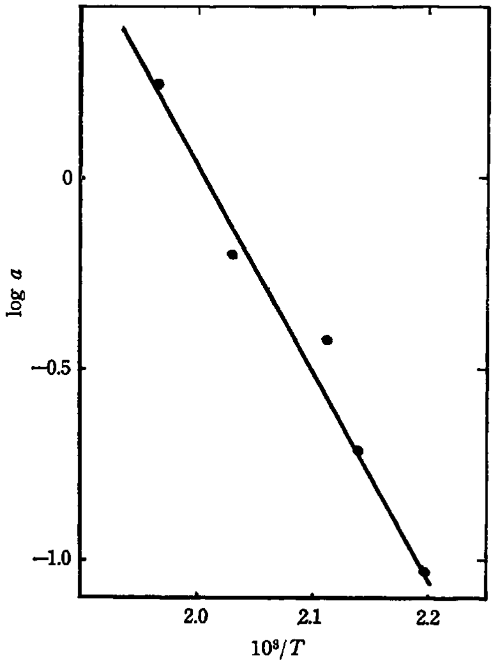

Fig. 4. Rate constants against $1/T$.

$$y = 1 - \exp(-at) \qquad (3)$$

where y is a hardening ratio and where:

$$a = a_0 \exp(-E/\boldsymbol{k}T)$$
$$a_0 = 4.22 \times 10^7\ \mathrm{sec}^{-1}$$
$$E = 25.4\ \mathrm{kcal/mol}$$

When the hardening ratio is very small, formula (3) can be expressed by:

$$y = at \qquad (4)$$

The solubilities of the thermally-hardened resin were investigated, thus making it clear that all the resins, which had been ascertained by IR measurements to be hardened, were insoluble in any solvent.

The critical hardening ratio of polyvinyl cinnamate was evaluated from formula (4). The resin become insoluble in the solvent when kept at 147℃ for 10 min. The average degree of polymerization of the resin was 2000, and the degree of esterification was estimated to be 76.5% by the method proposed by Tsuda.[8] The critical hardening ratio was

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6) K. Nakamura and S. Kikuchi, This Bulletin, in press.

7) M. Tsuda, International Conference on Photographic Science, Tokyo, 1967.

8) M. Tsuda, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **66**, 1365 (1963).

calculated to be 7.68×10^{-4} by formula (4). Therefore, the number of crosslinked cinnamoyl groups per polymer molecule was computed to be 1.17. On the other hand, the critical value of the resin (the degree of polymerization was 1400, and the degree of esterification was 68.5 %) was found to be 15.36×10^{-4}, and the number of hardening groups was 1.47 groups per polymer molecule. Therefore, it seemed that the critical hardening value of polyvinyl cinnamate was about 1.3.

Formerly, the present authors showed that the minimum exposure time, $t_{\min}$, for the photo-crosslinking of the resin could be expressed by[9]:

$$t_{\min} = \frac{2\gamma_c Cd}{S_\phi \lambda} \qquad (5)$$

where γ_c is the critical hardening value, C is the concentration of the cinnamoyl group, d is the depth of the polymer layer, λ is average degree of polymerization, and S_ϕ is the quantum photosensitivity. The quantum photosensitivity can be evaluated by using the critical hardening value.

On the basis of above results, it was concluded that the most suitable temperature for the "afterhardening process" was about 200°C, that the activation energy for the thermal hardening was 25.4 kcal/mol, and that the critical hardening value was about 1.3 groups per polymer molecule.

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[9] K. Nakamura, S. Kikuchi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 930 (1966).