Studies of Photosensitive Resins. II. The Electron Spin Resonance Spectra of Light-irradiated Polyvinyl Cinnamate[1]

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In the previous paper,[2] the photo-isomerization and photo-dimerization of cinnamic acid were discussed from the standpoint of the electronic structures, and it was shown that the radical reactivities at α- and β-carbons of cinnamic acid were increased by the electronic excitation. It seems reasonable to assume on the basis of these results, that the radical is produced by the irradiation of polyvinyl cinnamate with ultraviolet light, since the electronic structure of the cinnamoyl group in polyvinyl cinnamate and that of cinnamic acid are essentially identical. In the present paper the ESR spectra of light-irradiated polyvinyl cinnamate will be studied.

In recent years many studies have been made of the ESR spectra of polymers,[3] but most of them are related to γ-irradiated polymers; there have been few studies of light-irradiated polymers. The ESR spectrum of the irradiated polymer often consists of more than two species of radicals. The ESR spectrum, consisting of more than two species of radicals, can be resolved into each component by keeping the sample at various temperatures. Therefore, the experiments were carried out at 77—243°K.

Results and Discussion

Polyvinyl cinnamate was prepared by the pyridine method.[4] The synthesized resin was dissolved in methyl cellosolve acetate, precipitated by pouring it into water, and then washed with methanol, after with the solvent was decanted off. The samples sealed in quartz tubes were exposed to ultraviolet light at 77°K with a 500 W high pressure mercury lamp. A filter of Toshiba UV-D25, transparent from 240 mμ to 350 mμ, was used. Polyvinyl cinnamate has two absorption bands, the K-band and the E-band of the cinnamoyl group.[2] The light used to irradiate the resin was in the region of the K-band. Minsk *et al.*[4] have reported that the crosslinking is produced by the light-irradiation of polyvinyl cinnamate. Light in the regions of both the K-band and E-band is effective in the photo-crosslinking of the resin. It is said that the photo-crosslinking of polyvinyl cinnamate is initiated by the free radical.

The observed ESR spectrum of polyvinyl cinnamate irradiated at 77°K for an hour is shown in Fig. 1. The unexposed polyvinyl cinnamate gave no ESR signal. The spectroscopic splitting factor of the spectrum was found to be 2.003. The spectrum appears to consist of two components, a broad singlet and a quartet. The component of the broad singlet is stable at 77°K. When the resin was kept in the dark at 77°K for several hours after exposure, the quartet signal was found to disappear, while the intensity of the singlet signal did not decrease, The ESR spectrum of the resin left in the dark at 77°K for several hours after exposure is shown in Fig. 2. The quartet signal decayed to a great extent, but the intensity of the singlet signal is as large as that in Fig. 1. These facts suggest that two species of radicals are produced by the irradiation of the resin.

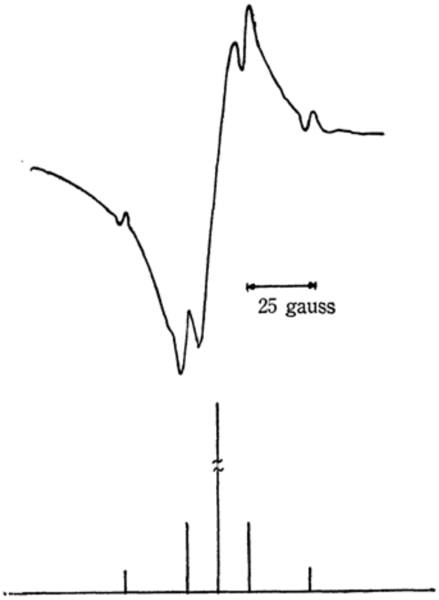

Fig. 1. ESR spectrum of the light-irradiated polyvinyl cinnamate at 77°K: irradiated for an hour.

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[3] D. H. Whiffen, *Makromol. Chem.*, **34**, 170 (1959).

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[5] N. Tamura, *J. Chem. Phys.*, **37**, 479 (1963).

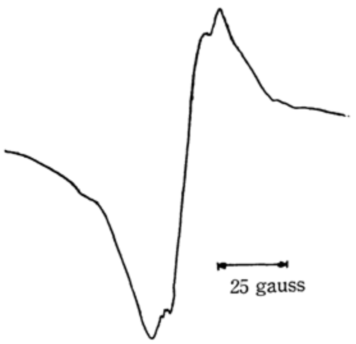


Fig. 2. ESR spectrum of the light-irradiated polyvinyl cinnamate at 77°K: left in dark for an hour after exposure.

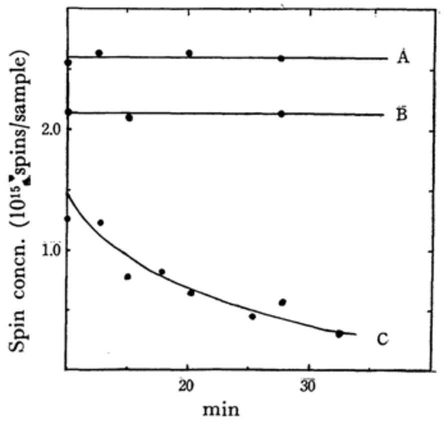


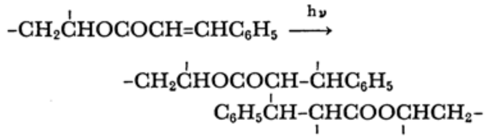
Fig. 3. Decay curves of the singlet at various temperatures.

A: at 153°K
B: at 203°K
C: at 243°K

The value of the $\varDelta H_{msl}$ of the broad singlet was found to be 15.8 gauss. As is shown in Fig. 3, the concentration of the broad singlet signal does not decrease at 153°K or at 203°K, but it does gradually decrease at 243°K. At room temperature, it decreases more rapidly. Tamura[5] reported that, when the molecular chain is in the rigid state at low temperature, the spectrum, which has a fine structure at higher temperatures, changes to a dull, broad spectrum. Therefore, the observed singlet spectrum may be the smeared-out spectrum of a hyperfine structure. Using the data of molecular orbital coefficients calculated by the LCAO-SCF-MO method,[2] the ESR signals of the cinnamoyl radical may be expected to be as shown in Fig. 4. The hyperfine splitting, a_i, is evaluated by:

$$a_i = Q\rho_i$$

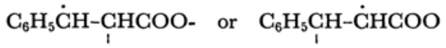
where Q is 23 gauss and ρ_i is the electron density of the i atom, as calculated from the MO coefficient of the upper occupied molecular orbital for the cinnamoyl cation radical. The broken curve in Fig. 4 is the absorption curve calculated by assuming that the resolving power of the spectrum is 5 gauss. The value of $\varDelta H_{msl}$ was estimated to be 13 gauss. This is in reasonable agreement with that of the observed value for the broad singlet. When polyvinyl cinnamate is irradiated by ultraviolet light, a crosslinking reaction arises and the polymer become insoluble to any solvent:



$$-\mathrm{CH_2}\overset{|}{\mathrm{C}}\mathrm{HOCOCH{=}CHC_6H_5} \xrightarrow{h\nu}$$

$$\begin{array}{l} -\mathrm{CH_2}\overset{|}{\mathrm{C}}\mathrm{HOCOCH{-}}\overset{|}{\mathrm{C}}\mathrm{HC_6H_5} \\ \quad\quad\quad \mathrm{C_6H_5}\overset{|}{\mathrm{C}}\mathrm{H{-}}\underset{|}{\mathrm{C}}\mathrm{HCOO}\underset{|}{\mathrm{C}}\mathrm{HCH_2}- \end{array}$$

Therefore, the species of the broad singlet may be the crosslinked cinnamoyl radical produced by the light-irradiation:



$$\mathrm{C_6H_5\dot{C}H{-}}\underset{|}{\mathrm{C}}\mathrm{HCOO}- \quad \text{or} \quad \mathrm{C_6H_5}\underset{|}{\mathrm{C}}\mathrm{H{-}\dot{C}HCOO}$$

The hyperfine splitting of the quartet was found to be 23.0 gauss. It is reasonable to assume that the splitting is caused by the α- and β-hydrogen atoms. Therefore the quartet signal seems to be due to the main chain radical of polyvinyl cinnamate, $-\underset{|}{\mathrm{C}}\mathrm{H\dot{C}H}\underset{|}{\mathrm{C}}\mathrm{H}-$. It seems that this radical is produced by the hydrogen-abstraction of the cinnamoyl radical.

It may be concluded from the results of this investigation that two species of radical, the cinnamoyl radical and the main-chain radical, are produced by the irradiation of polyvinyl cinnamate by ultraviolet light.

The authors wish to thank the Japan Electron Optics Lab. Co., Ltd., for measuring the ESR spectra.

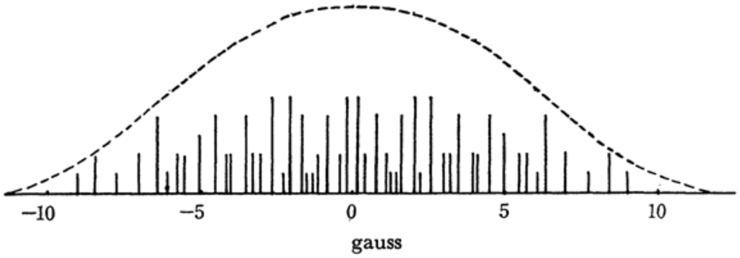


Fig. 4. The calculated signals of cinnamoyl radical.