

Photosensitivities and Rates of Photocrosslinking of Poly(vinyl α -Cyanocinnamate) and Poly(vinyl α -Cyanocinnamoxy Acetate)

T. NISHIKUBO, T. ICHIJYO, AND T. TAKAOKA, *Chemical Research and Development, Nippon Oil Seal Co., Ltd., Fujisawa-Shi, Kanagawa, Japan 251*

Synopsis

The photosensitivities and the rates of photocrosslinking of poly(vinyl α -cyanocinnamate) and poly(vinyl α -cyanocinnamoxyacetate) were investigated. The photocrosslinkings of these polymers proceeded mainly through radical addition, and these polymers showed higher photosensitivities than poly(vinyl cinnamate) and poly(vinyl cinnamoxyacetate), in spite of lower rates of photocrosslinking of the former polymers.

INTRODUCTION

Poly(vinyl cinnamate) (PVC) is a photopolymer^{1,2} which has been used widely as a photoresist in electrical industries. However, the photosensitivity of this polymer is not very high in the absence of a sensitizer.

Tsuda et al.³⁻⁵ reported some photopolymers similar to PVC, such as poly(vinyl 2-furylacrylate), poly(vinyl β -styrylacrylate), and poly(vinyl *p*-azidecinnamate). All these polymers showed higher photosensitivities than PVC in the absence of a sensitizer.

In the previous paper, we reported the preparation of some photopolymers with pendant α -cyanocinnamic ester groups⁶⁻⁸ showing high photosensitivities in the absence of a sensitizer.

In this paper, the photosensitivities and the rates of photocrosslinking of poly(vinyl α -cyanocinnamate) (PVCC) and poly(vinyl α -cyanocinnamoxyacetate) (PVCCA) were investigated and, further, they were compared with the sensitivities and the rates of PVC, poly(vinyl cinnamoxyacetates) (PVCA), and poly(vinyl β -styrylacryloxyacetate) (PVSAA).

EXPERIMENTAL

Material

Hexamethyl phosphoramidate (HMPA), pyridine, and *n*-hexane were dried by using calcium hydride and then distilled for purification before the use. Graduated pure-grade cinnamoyl chloride and other solvents were further used. Potassium α -cyanocinnamate, potassium cinnamate, and

potassium β -styrylacrylate were prepared in methanol from potassium hydroxide and α -cyanocinnamic acid, cinnamic acid, and β -styrylacrylic acid, according to the methods reported in the previous paper.⁷ α -Cyanocinnamoyl chloride was prepared as follows; α -cyanocinnamic acid (52 g, 0.3 mole) was added in thionyl chloride (80 ml) and the mixture was reacted at 80°C for 4 hr. After the reaction, an excess of thionyl chloride was distilled under reduced pressure, and the product was washed with dried *n*-hexane and collected by suction filtration. α -Cyanocinnamoyl chloride was obtained in quantitative yield (57.5 g).

PVCC. PVCC was prepared as follows: Poly(vinyl alcohol) (degree of polymerization, 1700; degree of acetate saponification, 99.8%) (3.0 g, 0.068 mole) was suspended in pyridine (150 ml), and α -cyanocinnamoyl chloride (15 g, 0.078 mole) was added to the suspension. The mixture was reacted at 50°C for 5 hr, and acetone (100 ml) was then added to the solution. The reaction was further continued for 2 hr at the same temperature. The insoluble matters in the reaction mixture was filtered with suction and the solution was poured into 2 lit of water. The obtained polymer was sucked dry to give PVCC (9.6 g, 71.0%) (degree of esterification, 99.8%).

PVC. PVC was prepared from poly(vinyl alcohol) (degree of polymerization, 1700; degree of acetate saponification, 99.8%) and cinnamoyl chloride in HMPA, according to the method reported in the previous paper⁹ (degree of esterification, 99.8%).

PVCCA. PVCCA was prepared from poly(vinyl chloroacetate) (intrinsic viscosity, 0.10) and potassium α -cyanocinnamate in HMPA, according to the method reported in the previous paper⁷ (degree of esterification, 94.0%).

PVCA. PVCA was prepared from poly(vinyl chloroacetate) (intrinsic viscosity, 0.10) and potassium cinnamate in the same condition as the preparation of PVCCA (degree of esterification, 99.8%).

PVSAA. PVSAA was prepared from poly(vinyl chloroacetate) (intrinsic viscosity, 0.10) and potassium β -styrylacrylate at the same condition as the preparation of PVCCA (degree of esterification, 94.8%).

Measurement of Photosensitivities

The relative photosensitivities of the obtained polymers, assuming the sensitivity of PVC which was sensitized by 5-nitroacenaphthene (5 wt-% for PVC) to be valued at 100, were measured by the gray-scale method.

Each of PVCC (1 g) and PVC (1 g) was dissolved in ethyl methyl ketone (10 ml). Films of PVCC and PVC, about 1 μ thick, were formed on copper plates from the polymer solutions by using a rotary applicator. The step tablet no. 2 (manufactured by Eastman Kodak) was piled up on the films, which were exposed by a chemical lamp (20 W \times 6) for 5 min at a distance of 10 cm, and the exposed films were then developed by methylcellosolve acetate for 2 min.

Each of PVCCA (1 g), PVCA (1 g), and PVSAA (1 g) was dissolved in tetrahydrofuran (10 ml). The PVCCA, PVCA, and PVSAA films, about

1 μ thick, were formed on the copper plate by the same method for the preparation of PVCC film. Those films were exposed by the chemical lamp (20 W \times 6) under the same conditions of exposing PVCC film. The exposed films were then developed by tetrahydrofuran for 2 min.

Measurement of Rates of Photocrosslinking

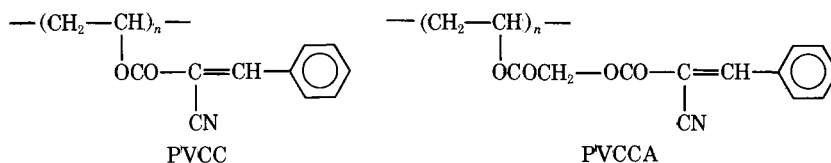
The rates of photocrosslinking were measured as follows: The polymer solutions were applied on KRS plates and dried. The films obtained on the plates were irradiated by a high-pressure mercury lamp (manufactured by Ushio Electric Co., USH-500D) at a distance of 30 cm. The decrease in the absorbance of the C=C band at 1640 cm^{-1} was measured by IR spectrophotometry (Hitachi EP-1-G2 Model), and the rates of photocrosslinking of the polymers were estimated with a second-order equation to which the obtained results applied.

RESULTS AND DISCUSSION

The solubilities of PVCC and of PVCCA are similar to or greater than that of PVC, and similar to those of PVCA and PVSAA, before irradiation.

The relative photosensitivities (which are understood to be the degree of the insolubilities of the crosslinked polymers) of PVCC, PVC, PVCCA, PVCA, and PVSAA are 71, 0, 71, 7, and 50, respectively (Table I).

On the other hand, the rates of photocrosslinking of PVCC and PVCCA are lower than that of PVC (Fig. 1) and those of PVCA and PVSAA (Fig. 2):



Although Tanaka¹⁰ reported that the rates of photocrosslinking of polymers with pendant *p*-substituted α -cyanocinnamic ester groups were lower

TABLE I
Solubilities and Relative Photosensitivities of Polymers

	PVCC	PVC	PVCCA	PVCA	PVSAA
Solubilities:					
acetone	○	△	△	△	△
ethyl methyl ketone	⊙	⊙	△	△	△
methylcellosolve acetate	⊙	⊙	△	△	△
tetrahydrofuran	⊙	⊙	⊙	⊙	⊙
HMPA	⊙	⊙	⊙	⊙	⊙
Relative photosensitivities ^a	71	0	71	7	50

^a The relative values when the sensitivity of PVC with 5-nitroacenaphthene (5 wt-% for PVC) is assumed to be 100.

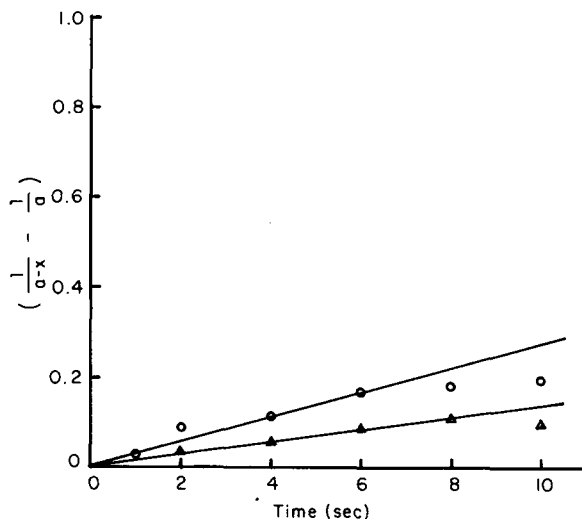


Fig. 1. Rate of photocrosslinking of PVCC and PVC: (Δ) PVCC; (○) PVC.

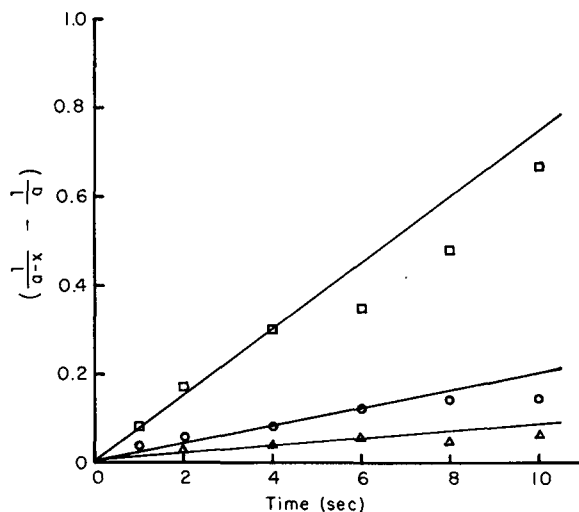


Fig. 2. Rate of photocrosslinking of PVCCA, PVCA, and PVSAA: (Δ) PVCCA; (○) PVCA; (□) PVSAA.

than those of polymers with pendant cinnamic ester or pendant β -styryl-acrylate ester groups and that the photosensitive double bonds of these polymers were isomerized from *trans* to *cis* by ultraviolet irradiation, the results concerning the relative photosensitivities obtained by us do not agree with his results.

It was reported that cinnamic esters were not polymerized radically¹¹ and that the photocrosslinking of PVC proceeded through cyclobutane formation.¹²

Also, in copolymerization of butadiene with α -cyanocinnamic esters and with cinnamic esters, the amount of α -cyanocinnamic esters contained in the polymers obtained from the copolymerization of the former was higher than that of cinnamic ester contained in the polymers obtained from the copolymerization of the latter.¹³

It was also reported¹⁴ that methyl α -cyano- β -styrylacrylate which was controlled topochemically gave a cyclobutane addition compound by ultraviolet irradiation and that ethyl α -cyano- β -styrylacrylate which was not controlled topochemically gave a radical addition compound.

In the previous paper, rubbery poly(glycidyl cinnamate)¹⁵ which was not controlled topochemically showed a higher photosensitivity than PVC.

From these results, it seems that photopolymers with a pendant cinnamic ester group and similar ester groups are not only crosslinked through the formation of cyclobutane but also through the radical addition by ultraviolet irradiation, and that in the case of the photopolymers with a pendant α -cyanocinnamic ester group, which are hindered sterically, the photocrosslinkings proceed mainly through radical addition and that one double bond gives one gelation point in the cyclobutane forming but one double bond gives two or more gelation points in the radical addition.

It can, therefore, be concluded that polymers with pendant α -cyanocinnamic ester groups show higher photosensitivities than polymers with pendant cinnamic ester groups, in spite of lower rates of photocrosslinking of the former polymers than that of the latter polymers.

References

1. L. M. Minsk, J. G. Smith, W. P. Van Deusen, and J. F. Wright, *J. Appl. Polym. Sci.*, **2**, 302 (1959).
2. E. M. Lobertson, W. P. Van Deusen, and L. M. Minsk, *J. Appl. Polym. Sci.*, **2**, 308 (1959).
3. M. Tsuda, *J. Polym. Sci. A-1*, **7**, 259 (1969).
4. H. Tanaka, M. Tsuda, and H. Nakanishi, *J. Polym. Sci., A-1*, **10**, 1729 (1972).
5. A. Yabe, M. Tsuda, K. Honda, and H. Tanaka, *J. Polym. Sci., A-1*, **10**, 2379 (1972).
6. T. Nishikubo, Y. Tomiyama, K. Maki, Y. Imamura, T. Ina, and T. Takaoka, Germ. Pat. 2060873 (1971).
7. T. Nishikubo, Y. Tomiyama, K. Maki, and T. Takaoka, *Kobunshi Kagaku (Japan)*, **29**, 295 (1972).
8. T. Takaoka, T. Nishikubo, and Y. Imamura, Jap. Pat. 4736513 (1972).
9. T. Nishikubo, M. Imaura, and T. Takaoka, *Nippon Kagaku Kaishi (Japan)*, **1974**, 185.
10. H. Tanaka, *Nippon Shashin Gakukaishi (Japan)*, **35**, 288 (1972).
11. T. Otsu, B. Yamada, and T. Nizaki, *Kogyo Kagaku Zasshi (Japan)*, **70**, 1941 (1967).
12. K. Nakamura, Doctoral Thesis, Tykyo University, 1967.
13. C. S. Marvel, G. H. Mc Cain, M. Passer, W. K. Taft, and B. G. Labbe, *Ind. Eng. Chem.*, **45**, 2311 (1953).
14. M. C. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, **1964**, 1996.
15. T. Nishikubo, T. Ichijyo, and T. Takaoka, *Nippon Kagaku Kaishi (Japan)*, **1973**, 35.

Received December 14, 1973