

Syntheses of Photocrosslinkable Polymer from Modified Poly(methyl Vinyl Ketone)

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Synopsis

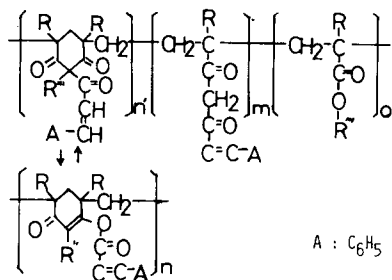
Photocrosslinkable polymer is prepared from amorphous poly(methyl vinyl ketone) (A-PMVK) obtained by anionic polymerization of methyl vinyl ketone. The reaction of A-PMVK with cinnamoyl chloride proceeds in pyridine at 50°C. The photosensitivity of the polymer obtained is measured by infrared and Ultraviolet photometry. The polymer is of a crosslinkable type and forms cyclobutane linkage by ultraviolet irradiation. The polymer is coated on a lithographic aluminum plate and exposed to arc and high-pressure mercury lamps. Development is with benzene, and standard inking by lithography is applied. The imaging area on the plate is stable and harder than poly(vinyl cinnamate), due to intra- and intermolecular cyclization of the main chain. Many good reproductions are produced in the lithographic proofing machine. The photosensitive polymer obtained by A-PMVK is very useful in relief plates requiring etching.

INTRODUCTION

Agnihotri¹ published that the cinnamated diacrylylmethane copolymer was a photosensitive polymer. He suggested the polymer has a structure as shown in Scheme I.

However, we considered that the *m*-unit structure of (I) in the case of poly-diacrylylmethane is not reactive to cinnamoyl chloride, but an *n*-unit is reacted easily with cinnamoyl chloride. We had studied anionic polymerization of methyl vinyl ketone (MVK)²; much of the polymer obtained was poly(methyl vinyl ketone) (PMVK) containing OH groups (3500 cm⁻¹) after initiation by organic metallic compounds, as shown in Figure 1.

So, we have synthesized a photosensitive polymer from amorphous PMVK (A-PMVK) containing the OH group obtained by anionic polymerization of MVK, and have suggested its photosensitivity for lithographic plate making.



Scheme I.

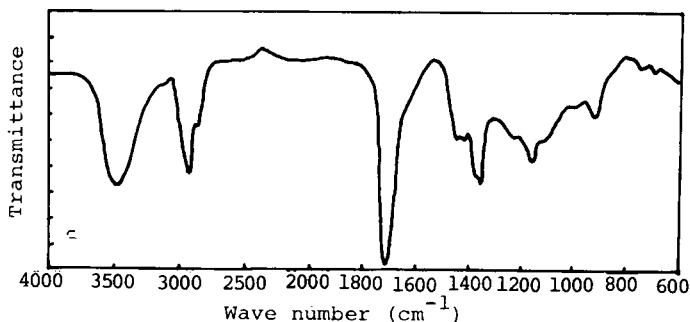


Fig. 1. Infrared spectrum of A-PMVK obtained from the anionic polymerization of MVK.

We have extended our investigations for the application of the photosensitive polymer mentioned in our previous paper.³

EXPERIMENTAL

Reaction of PMVK with Cinnamoyl Chloride

PMVK was dissolved in pyridine at 50°C for 4 h. The solution was cooled in room temperature, added to cinnamoyl chloride, and heated to 50°C for 4 h. The reaction mixtures were left at room temperature, added to acetone, and filtered for the insoluble part of PMVK. When the mixtures were precipitated with water, a pale yellow polymer was obtained. The purifying operation of this polymer was done three times by acetone and water shown in flow chart of Figure 2.

The vinylketone polymers have also used polyisopropenylketone (PMIK), poly-*tert*-butylvinylketone (P-*tert*-BuVK) instead of PMVK, and MIPK monomer was reacted with cinnamoyl chloride as low molecular weight model.

Infrared Spectra

Infrared spectra were measured on a Beckman IR-10 spectrophotometer by film using KBr tablets.

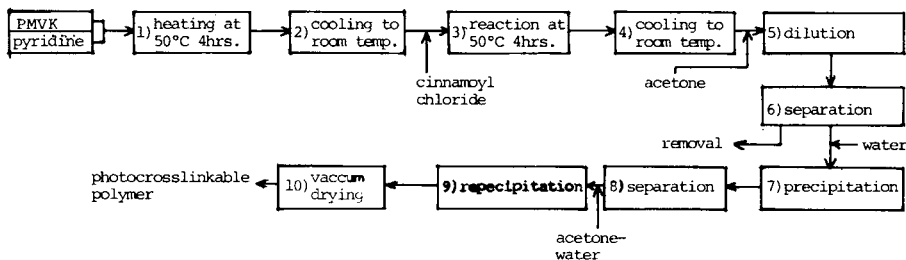


Fig. 2. Flow chart of preparing photocrosslinkable polymer from A-PMVK with cinnamoyl chloride.

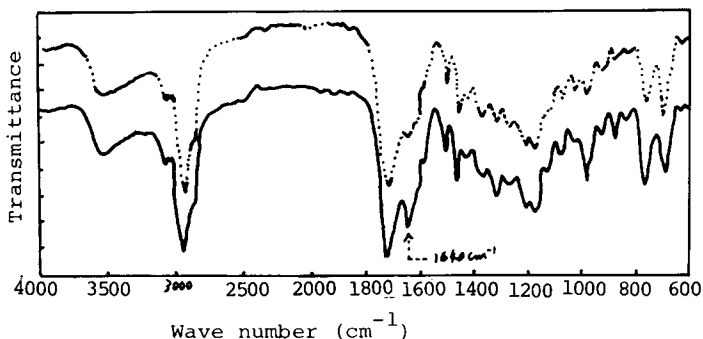


Fig. 3. Infrared spectra of photosensitive polymer of esterifying A-PMVK with cinnamoyl chloride: (—) spectrum before irradiation; (---) spectrum after 2-h irradiation.

Ultraviolet Spectra

Ultraviolet spectra were recorded on a Shimadzu SV-50A type spectrometer in films using a quartz cell.

Apparatus of Photoirradiation

The film sample for infrared or ultraviolet measurement were irradiated by a super high pressure mercury lamp 100 W (Toshiba SMLS 2B type) from a distance of 50 cm from the light source at room temperature.

Practical Tests for Lithographic Plate

The photosensitive polymer obtained was coated on aluminum plate by using a whirler, and dried in room temperature. The coated polymer in the printing frame was exposed to a high pressure mercury lamp 400 W from a distance of 40 cm and developed by benzene. Sensitivity of the polymer was measured by the grey scale method. A standard substance for sensitivity evaluation⁴ was used in poly(vinyl cinnamate) obtained by the alkaline water solution method.⁵

RESULTS AND DISCUSSION

Results of Synthesis

A-PMVK was reacted with cinnamoyl chloride. The polymer obtained shows absorption for the ethylenic double bond at 1640 cm^{-1} in the IR spectrum, shown in Figure 3.

R-PMVK obtained by the radical polymerization of MVK was reacted by the same method, but the polymer shows slight absorption by the ethylenic bond, shown in Figure 4.

In the case of reaction with A-PMVK, there is a decreasing absorption at 3500 cm^{-1} of the hydroxyl group as shown in Figure 1. Moreover, absorptions appear at 1170 cm^{-1} for the ester group of carboxylic acids, and at 980 cm^{-1} for *trans*-olefins.

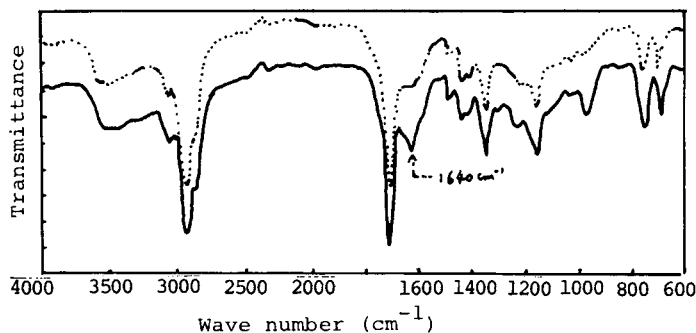


Fig. 4. Infrared spectra of R-PMVK-cinnamoyl chloride: (—) spectrum before irradiation; (---) spectrum after 2-h irradiation.

From these facts, it was confirmed that the hydroxyl group in A-PMVK was reacted with cinnamoyl chloride, and the ethylenic bond was formed in side chains. When reaction times for the esterification were increased, higher sensitivity polymer was obtained. This was identified from the IR spectrum. In the case of R-PMVK, if long esterification times were applied, a slightly sensitive polymer was obtained. The reason is that R-PMVK was modified by inter- and intramolecular aldol condensation due to alkaline media.

Figure 5 shows IR absorptions of untreated R-PMVK and treated R-PMVK by pyridine at 50°C for 5 h. The figure clearly distinguished the absorption of the OH group at 3500 cm⁻¹.⁶

It is supposed that the molecular structure was formed by aldol condensation.⁷ PMIK and P(*tert*-BuVK) were proceeded by the same reaction. In any case photosensitive polymers were obtained. The former shows higher esterification than the latter due to the steric effect of the *t*-butyl group.

Photoirradiation of Polymer

IR spectrum of the photosensitive polymer obtained from A-PMVK was shown in Figure 3. The solid line denotes IR spectrum before irradiation and dotted line after irradiation by means of the super high pressure mercury lamp, re-

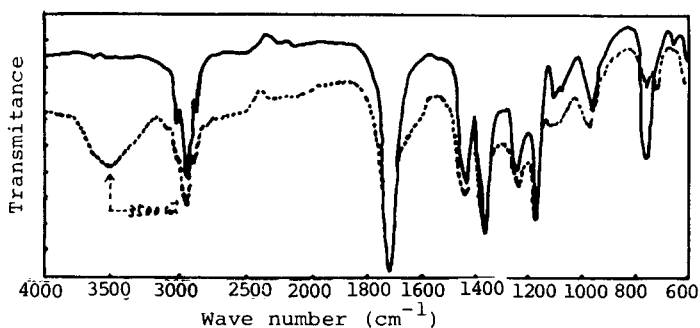


Fig. 5. Infrared spectra of R-PMVK: (—) spectrum before treatment of R-PMVK; (---) spectrum treated at 50°C for 4 h in pyridine.

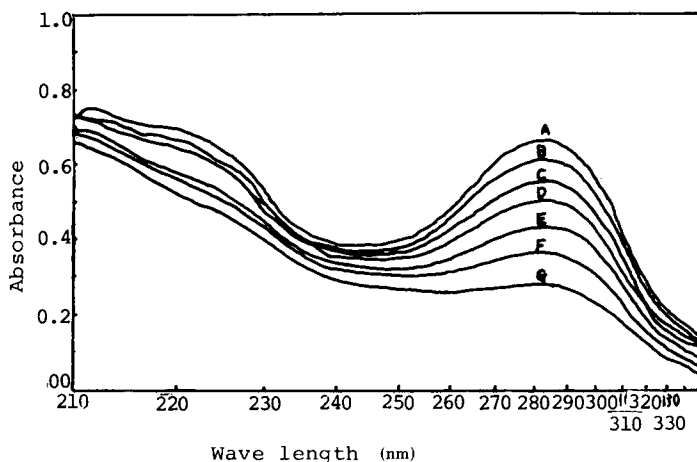


Fig. 6. Ultraviolet spectra in each hour by irradiating photocrosslinkable polymer obtained from A-PMVK. Irradiation time (min): (A) 0; (B) 2; (C) 8; (D) 15; (E) 30; (F) 60; (G) 100.

spectively. The spectra of the polymer showed absorption bands at 1715 cm^{-1} for the characteristic of the ester group, and at 1640 cm^{-1} and 980 cm^{-1} for the ethylenic double bond. After irradiation, two peaks at 1640 cm^{-1} and 980 cm^{-1} almost disappear and a peak at 1715 cm^{-1} slightly decreases. It did not appear to shift to higher wavelength shown usually in the photocrosslink of poly(vinyl cinnamate).

It is thought that there are two reasons that steric hindrance of six-membered ring due to intra- and intermolecular condensation and low esterification obstructed the shift of the absorption of the carbonyl group to the higher wavelength.

The change of the ultraviolet spectrum of the photosensitive polymer obtained from A-PMVK and R-PMVK by irradiation is given in Figure 6 and Figure 7

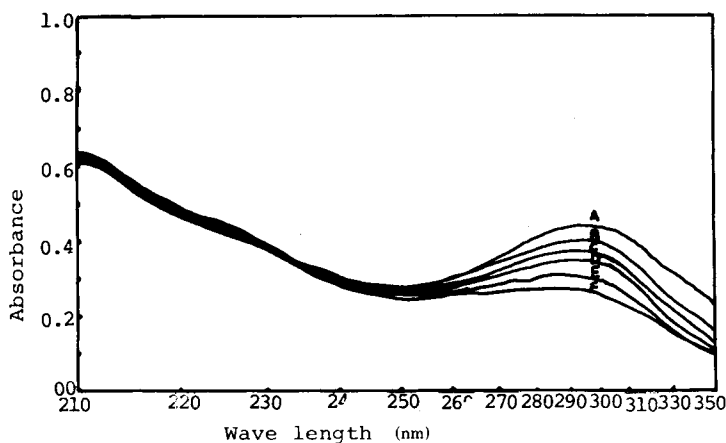


Fig. 7. Ultraviolet spectra in each hours by irradiating photocrosslinkable polymer obtained from R-PMVK. Irradiation time (min): (A) 0; (B) 15; (C) 25; (D) 35; (E) 60; (F) 100.

respectively. In the spectrum of Figure 6, λ_{\max} of the K band is 285 nm (ϵ_{\max} 8600) and the limited wavelength is 350 nm. In Figure 7 obtained from R-PMVK, λ_{\max} is 290 nm (ϵ_{\max} 4200). Films of these polymer on a quartz plate were irradiated with the super high pressure mercury lamp. After irradiation, both absorptions of the K band were decreased and were slightly shifted to a longer wavelength. From the measurements of absorption spectra before and after irradiation of the polymers, it is confirmed that the ethylenic bonds in the side chain disappear and the cyclobutane linkage is formed by irradiation. However, isosvestic points do not appear in both figures, so some of the crosslinking is by free radical reactions.⁸

Practical Tests of the Photosensitive Polymer

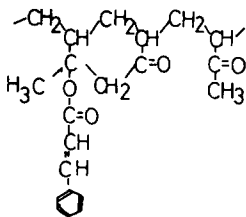
Photosensitive polymer obtained from A-PMVK was dissolved in acetone and coated on lithographic aluminum plate. The coated plate was exposed through the negative by a super high pressure mercury lamp (400 W) at a distance of 15 cm, and then developed in benzene. The image on the plate was formed clearly and the plate was desensitized by arabic gum solution. Many good reproductions were impressed by a lithographic proofing machine. The imaging area on the plate is more stable and firm than that obtained from polyvinyl cinnamate.

Sensitivity of the polymer was increased by adding a sensitizer such as Micher's ketone and *p*-benzoquinone, and plate making can be performed easily by practical light sources such as an arc lamp and a mercury lamp. The photosensitive polymer is useful for relief plates required for etching. The acid resist coating due to six-membered ring formation of inter- and intramolecular aldol condensation did not damage in strongly acid solutions such as hydrochloric acid, nitric acid and iron (III) chloride. If the burning treatment⁹ before etching was done at 200°C for 30 min, more stable acid resist film was formed.

CONCLUSION

A-PMVK is produced by anionic polymerization of MVK. The structure of A-PMVK is of an inter- and intramolecular aldol condensation type. The hydroxyl group in A-PMVK was reacted with cinnamoyl chloride, and highly photosensitive polymer was obtained.

On the other hand, when R-PMVK was treated by alkaline solvents, condensation products were obtained, and then by further treatment a hard and brittle polymer was formed. Even in the R-PMVK, a photosensitive polymer was obtained after a long reaction time with cinnamoyl chloride. Both these polymers have sensitivity for ultraviolet light due to the structure shown in Scheme II.



Scheme II.

The polymer becomes insoluble in various organic solvents by ultraviolet irradiation due to formation of cyclobutane linkages, as observed for poly(vinyl cinnamate). The sensitivity of the polymer increases with increasing degree of esterification reaction time. The wavelength limit of photosensitivity of the polymer is about 350 nm. A partial radical reaction is involved in the cross-link.

In a practical test, the imaging area is hard due to intra- and intermolecular cyclization of the polymer chain. It is confirmed that the final structure of photocrosslinked polymer by ultraviolet irradiation is more network due to cyclobutane linkage.

The effect of different kinds of cinnamoyl chloride and a variety of sensitizers on sensitivity are very interesting, and their investigation will be published in the future.

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