

# PHOTOPOLYMERIZATION OF PROPARGYL ACETATE WITH MICHLER'S KETONE AS PHOTOINITIATOR

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## ABSTRACT

Photopolymerization of propargyl acetate (PAT) with Michler's ketone (MK) as photoinitiator in benzene has been investigated for the first time. Some features of the PAT photopolymerization with MK as photoinitiator is described.

## INTRODUCTION

Michler's ketone (MK) behaves as a high susceptibility to ultraviolet light (UV). The photochemical reactivity and an interesting solvent effect of Michler's ketone have received a great deal of attention in the past thirty years. There have been some reports of Michler's ketone as photoinitiator for the photopolymerization of vinyl unsaturates<sup>[1]</sup>, yet none for that of propargyl acetate (PAT). In general, PAT can be polymerized with the radical initiators and/or a  $\text{PdCl}_2$ -catalyst<sup>[2,3]</sup>. It has been reported that polypropargyl acetate (PPAT) shows paramagnetism and semiconductor characteristics<sup>[3]</sup>. This paper reports the first research results of propargyl acetate polymerization by UV irradiation in the presence of Michler's ketone.

## EXPERIMENTAL

PAT photopolymerizations with MK as photoinitiator in benzene were carried out in 20ml ampoules under nitrogen atmosphere at 20°C. The ampoules were placed at a constant distance (8cm) and a UV high-pressure mercury lamp (500W) was used for irradiation. After the photopolymerization for a definite time, the resulting polymer was

precipitated by adding ether, centrifugalized, and dried at 50°C under vacuum. The polymerization conversion was calculated by gravimetry.

## RESULTS AND DISCUSSION

Propargyl acetate (PAT) can not be polymerized by UV irradiation without the presence of photoinitiator. The polymerization in the presence of Michler's ketone (MK) as the photoinitiator is confirmed by the IR spectrum of the product (Fig. 1), showing the characteristic absorption peak of conjugated C=C bonds ( $1650\text{cm}^{-1}$ ), of C=O groups ( $1740\text{cm}^{-1}$ ), and of C-O-C groups ( $1230\text{cm}^{-1}$ ) and missing monomeric triple bond ( $\text{C}\equiv\text{C}$ ) peak of  $2120\text{cm}^{-1}$ . This indicates that MK is an effective photoinitiator and the product is polypropargyl acetate (PPAT). The polymer obtained is a deep yellow powder and insoluble in most organic solvents.

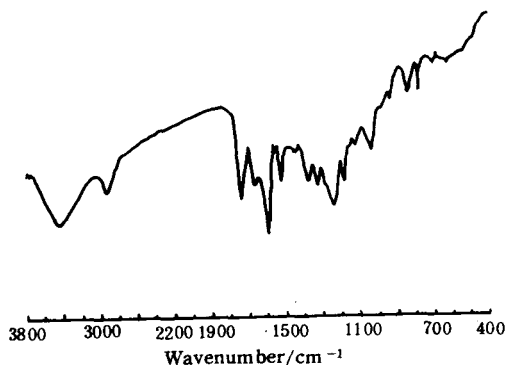


Fig. 1 Infrared spectrum of polypropargyl acetate

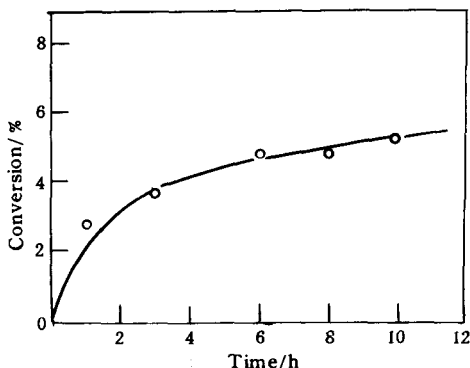


Fig. 2 A typical example of time-conversion curves for the polymerization of propargyl acetate  
Conditions:  $[\text{PAT}] = 6.0 \text{ mol/L}$ ;  $[\text{MK}] = 6 \times 10^{-2} \text{ mol/L}$ , in benzene

Effect of reaction time on the conversion for the propargyl acetate polymerization is shown in Fig. 2. It is seen that the conversion increases quickly up to 3h, subsequently goes upward slowly. The overall activation energy of propargyl acetate photopolymerization in the presence of MK was calculated from the plot of  $\ln R_p$  vs.  $1/T$  (Fig. 3) and was found to be  $8.3 \text{ kJ} \cdot \text{mol}^{-1}$ .

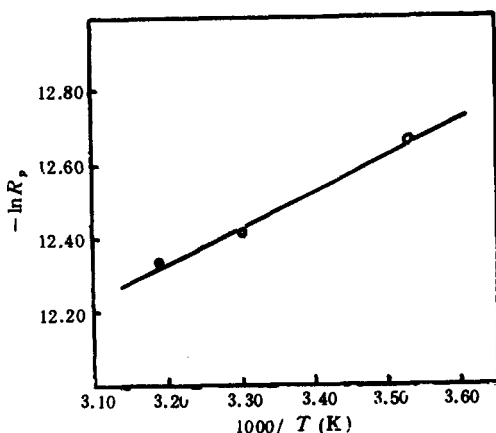


Fig. 3 Effect of temperature on PAT polymerization rate. Conditions:  $[\text{PAT}] = 4.12 \text{ mol/L}$ ;  $[\text{MK}] = 5 \times 10^{-3} \text{ mol/L}$ , in benzene

A certain amount of a triethylamine or triphenylamine, amine/MK mol ratio of 3, added to the polymerization system respectively was found to raise the polymer yield by a factor of 2, as compared with that without adding amine, which is similar to that reported in the literature<sup>[4,5]</sup>. The rate of polymerization increased with the increasing of the solvent dielectric constant ( $\epsilon$ ) under the experimental conditions used, as shown in Table 1. This may be due to increasing of photochemical reactivity of MK in more polar solvent<sup>[6,7]</sup>. The polymerization was suppressed by addition of hydroquinone or introduction of oxygen gas, showing the existence of free radicals in the system. Further investigations are in progress.

Table 1 Effect of solvents on the PAT photopolymerization

| Solvent         | Dielectric constant ( $\epsilon$ ) | $R_p \times 10^6 \text{ (mol L}^{-1} \text{S}^{-1})$ |
|-----------------|------------------------------------|------------------------------------------------------|
| Benzene         | 2.28                               | 1.43                                                 |
| Chloroform      | 4.81                               | 2.01                                                 |
| Dichloromethane | 8.93                               | 2.15                                                 |

Conditions:  $[\text{PAT}] = 4.21 \text{ mol/L}$ ;  $[\text{MK}] = 5 \times 10^{-3} \text{ mol/L}$ ;  $20^\circ \text{C}$

**Keywords:**

Propargyl acetate; Photopolymerization; Michler's ketone photoinitiator

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