

Notes

Photosensitive Polymer Containing Nitro Aromatics

INTRODUCTION

A number of light-catalyzed intramolecular rearrangements of ortho-substituted nitro aromatics are known in which the nitro group is reduced to a nitroso function.¹

Belyakova et al.² introduced nitrophenyl groups in poly(vinyl alcohol) (PVA) by benzaldehyde with nitrobenzaldehyde (*o*-, *m*-, *p*-). They found that the PVA modified with *o*-nitrobenzaldehyde was susceptible to the photochemical intramolecular rearrangement.

In the present study, color development of the modified PVA was investigated using the nitroso group generated by irradiation. Furthermore, preparation of a photodegradable polymer containing *o*-nitrophenyl was attempted.

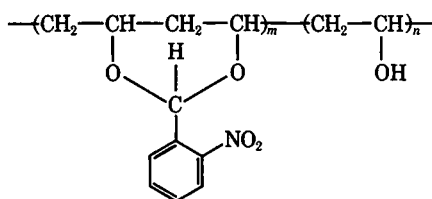
EXPERIMENTAL

A commercially available PVA was used without further purification. *o*-Nitrobenzaldehyde was synthesized by the oxidation of *o*-nitrotoluene.³ 2-(*o*-Nitrophenyl)-1,3-dioxolane was prepared by the reaction of *o*-nitrobenzaldehyde with ethylene glycol using *p*-toluenesulfonic acid as a catalyst.⁴ *o*-Nitrobenzal (polymer I) has prepared by the reaction of PVA with *o*-nitrobenzaldehyde. In a solution of *o*-nitrobenzaldehyde in 1,2-dichloroethane, PVA (P = 2000) was suspended, and concentrated HCl was added as a catalyst.⁵ After stirring for 68 hr at 40°C, the mixture was filtered to separate the remaining polymer. The filtrate was evaporated to dryness, and the residual polymer was extracted thoroughly with ethyl alcohol to remove the unreacted *o*-nitrobenzaldehyde. The polymer was then purified by dissolving in *N,N*-dimethylformamide followed by pouring into water and drying in a brown desiccator in vacuo. A film was made by coating a solution of the polymer in 1,2-dichloroethane on a glass plate. The film was irradiated with a 100-watt high-pressure mercury lamp (Toshiba SHL-100 UV) at room temperature.

A copolymer (polymer II) was obtained from a cationic copolymerization of styrene with 2-(*o*-nitrophenyl)-1,3-dioxolane. In a glass ampoule, a mixture of styrene and 2-(*o*-nitrophenyl)-1,3-dioxolane was placed and cooled in a Dry Ice-methanol bath. To the solution, methylene chloride containing $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ was added. After replacing the atmosphere with nitrogen, the ampoule was sealed and kept at room temperature for 24 hr in the dark. By pouring the reaction mixture into a large amount of methyl alcohol, a yellow, viscous liquid was separated. The liquid was redissolved in benzene and the solution was poured into methanol. A yellow powder having a relatively low molecular weight was obtained.

RESULTS AND DISCUSSION

The IR spectrum of polymer I showed the presence of nitro group (1520 cm^{-1}) and ether linkage (1100 cm^{-1}). Assuming the structure as below, the *m*:*n* ratio of the polymer was calculated to be 85:15 from the elemental analysis:



A film of polymer I was made to crosslink on exposure to ultraviolet radiation. The sensitivity of the polymer increased with the degree of benzalization.

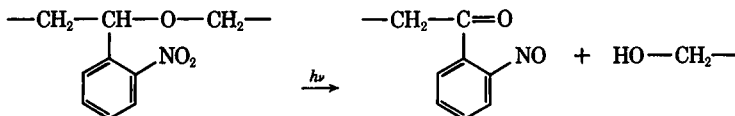
Belyakova et al. found no nitroso group in the irradiated polymer and assumed that the crosslinking of the polymer was caused by the photodecomposition of the nitro group generated by the intramolecular rearrangement of the nitro group. In our case, however, IR (1280 cm^{-1}) and UV (315 nm) evidences for nitroso group were found in the irradiated polymer. This discrepancy may be due to the difference in experimental conditions.

Upon immersing the irradiated film into a solution containing *p*-toluidine for a few minutes at room temperature, a brown image appeared in the exposed part. The development of color was influenced considerably by the nature of solvents used. A solvent that swelled the film strongly favored rapid color development but was unsuitable because it weakened the film and obscured the image. Among the solvents investigated, a mixture of acetic acid and carbon tetrachloride was best, as seen in Table I.

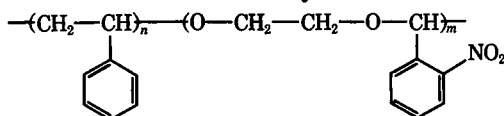
TABLE I
Nature of Solvent

Solvent	Color development	Swelling of film
$\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}:\text{AcOH}$ = 30:5	rapid	strong
$\text{H}_2\text{O}:\text{AcOH} = 5:1$	very slow	none
$\text{H}_2\text{O}:\text{AcOH} = 5:3$	slow	none
$\text{CCl}_4:\text{AcOH} = 5:1$	rapid	slight

A polymer containing a nitro aromatic unit in the main chain is expected to undergo photogradation as follows:



To obtain such a type of polymer, we attempted a cationic copolymerization of styrene with 2-(*o*-nitrophenyl)-1,3-dioxolane, although it has been known that 2-substituted 1,3-dioxolane does not give a ring-opening polymer but a polybenzyl-type polymer in cationic homopolymerization at high temperature.⁶ In the copolymerization of styrene with 2-(*o*-nitrophenyl)-1,3-dioxolane at room temperature, a yellow powder was obtained. The IR spectrum of the product showed the presence of a nitro group (1520 cm^{-1}) and ether linkage (1100 cm^{-1}). Assuming the structure as below, the $m:n$ ratio of the product was calculated to be 18:82 from the elemental analysis:



A brittle film made from a benzene solution of the product was exposed to ultraviolet radiation. Conversion of the nitro group to the nitroso group was observed from the UV spectrum after the irradiation. During the irradiation of a benzene solution of the product with ultraviolet light, however, no change in viscosity was observed. This may be due to the relatively low molecular weight of the original polymer and/or the nitro aromatic unit combined only to the end of the polymer. Many attempts to obtain the high molecular weight copolymer were unsuccessful.

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