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Preparation of Photosensitive Polymers Containing Pendant Cinnamic Acid, Ethyl Cinnamate or Cinnamaldehyde Groups by Chemical Modification of Polystyrene

M. Jean Farrall

Ottawa-Carleton Institute for Research and Graduate Studies in Chemistry,
University of Ottawa Campus, Ottawa, Ontario, Canada KIN 9B4

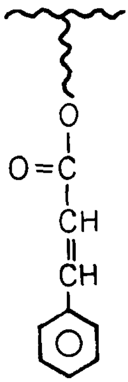
Summary

Soluble polystyrene was chemically modified to introduce pendant cinnamic acid, cinnamate ester, or cinnamaldehyde groups. The sensitivity of these polymers to crosslinking by ultraviolet light was studied by the adhesion method. Both the cinnamic acid and the cinnamaldehyde groups were found to crosslink more effectively than the cinnamate ester, the group which is commonly used in photoresists.

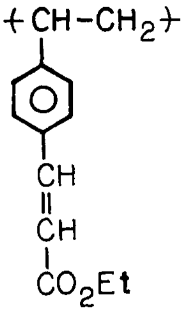
Introduction

The application of the photochemical 2+2 cycloaddition reaction of cinnamate esters to the preparation of photocrosslinkable polymer resists has been widely studied and reviewed (1). One problem with these resists, in which the cinnamate moiety is almost inevitably attached to the polymer backbone through an ester linkage as in (I), is a lack of sensitivity to UV light which requires a long exposure time to produce an acceptable image (2). Part of this problem may be due to steric crowding at the active site in structures such as (I).

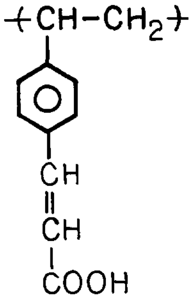
The situation could be alleviated by linking the cinnamate groups to the polymer backbone through the phenyl group and accordingly, a polymer containing pendant ethyl cinnamate moieties (II) was prepared by chemical modification of polystyrene. This sort of attachment also allows the preparation of polymers with pendant cinnamic acid (III) and cinnamaldehyde (IV) groups.



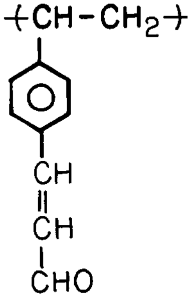
(I)



(II)



(III)



(IV)

Experimental

Soluble polystyrene (MW 20,000) was obtained from Polysciences and was precipitated once from methanol before use. Infrared spectra were taken on a Nicolet MX-1 spectrometer. Polymer films were exposed using an unfiltered General Electric 275 Watt sunlamp at a distance of 15 cm (intensity ∿ 5,000 μW cm^{-2}).

Preparation of Ⓟ-CH=CH-COOH (III)

Ⓟ-CH=CH-COOH was prepared via a Knoevagel type reaction of soluble Ⓟ-CHO, prepared as previously described (3), with malonic acid catalysed by piperidine (4). Ⓟ-CHO (2.02 g, 2-8 mequiv/g) was dissolved in 30 mL of pyridine and 1.5 g of malonic acid and 1 mL of piperidine were added. The solution was heated under N_2 in the dark for 1h at 80°C and 3h at 110°C, then cooled and poured into petroleum ether (30-60°). The precipitated polymer was redisolved in pyridine, filtered and reprecipitated in water containing sufficient HCl to give a slightly acidic solution. The solid was collected, washed with water and methanol, and dried to give 1.22 g of pale yellow polymer which was readily soluble in THF.

IR: 3600-2300 cm^{-1} (OH), 1690 cm^{-1} (C=O), 1635 cm^{-1} (CH=CH).

Preparation of Ⓟ-CH=CH-COOEt (II)

Ⓟ-CH=CH-COOH (3.35 g) was suspended in 150 mL of dry ethanol and dry HCl was bubbled into the mixture for several hours. The resulting solution was poured into ether and the precipitated polymer was dissolved in CH_2Cl_2, filtered and reprecipitated in methanol to yield, after drying, 1.72 g of white polymer.

IR: 1710 cm^{-1} (C=O), 1637 cm^{-1} (CH=CH).

Preparation of Ⓟ-CH=CH-CHO (IV)

Ⓟ-CHO (2.00 g, 2.8 mequiv/g) was dissolved in 60 mL of benzene, 2.5 g of formylmethyltriphenylphosphorane (5) was added and the reaction mixture was heated to reflux under argon in the dark for 18h. The resulting solution was cooled and poured into petroleum ether (30-60°). The precipitate was dissolved in THF, filtered and reprecipitated in petroleum ether to give, after drying, 1.56 g of bright yellow polymer. Conversion was estimated by comparing the intensities of the carbonyl bonds due to the cinnamaldehyde group (1680 cm^{-1}) and the unreacted benzaldehyde groups (1700 cm^{-1}) and in this case was approximately 80%. Complete conversion could be obtained by increasing the amount of formylmethyltriphenylphosphorane and the reaction time; however the polymer was too reactive and crosslinked on storage.

IR: 1700 cm^{-1} (benzaldehyde CHO), 1680 cm^{-1} (cinnamaldehyde CHO), 1623 cm^{-1} (CH=CH).

Determination of Percent Insolublization

A 50 mg sample of the polymer was dissolved in 3 mL of a suitable solvent ($CHCl_3$ for II and IV, THF for III) and the solution was filtered through a 5.0 μm teflon membrane filter to remove any insoluble material and spread on carefully cleaned and weighed glass slides to form films which on drying weighed 2-4 mg. The films were then exposed to UV light for the required period and then immersed in solvent for 5 min to dissolve any remaining soluble polymer. The slides were then dried at 60°C and reweighed to determine the amount of insoluble polymer and thus the % insolublization. Unexposed films of all three polymers were completely soluble in the chosen solvent.

Results and Discussion

The sensitivity of the three polymers prepared as described above to crosslinking by UV light was determined by the adhesion method, measuring the amount of insoluble polymer adhering to a glass plate after exposure for a given period and development in a good solvent for the unexposed film. The results obtained are shown in Table 1. As can be seen, all the polymers reached a maximum insolublization of $\sim$80% but their sensitivities to UV light varied greatly. The polymer with ethyl cinnamate pendant groups (II), which most closely resembles the common resist materials, was very insensitive, requiring 10 minutes exposure to reach $\sim$50% insolublization and 20 min. to reach 80%. The polymer with pendant cinnamic acid groups (III) was considerably more reactive, requiring only 2 minutes exposure to reach 50% insolublization and 10 minutes to reach its maximum value. The cinnamaldehyde polymer (IV) was even more reactive, requiring only 1 minute exposure to reach $\sim$50% insolublization and 5 minutes to reach a maximum value. This represents a significant improvement in sensitivity compared with the cinnamate ester polymer.

In order to confirm that the crosslinking was occurring via the normal 2+2 cycloaddition mechanism, infrared studies were carried out on the polymers. A polymer film was cast on a NaCl disc and the IR spectrum was taken before and after exposure to UV light for 10 min. in the case of IV and for 20 min. in the case of II and III. In all cases a significant decrease in the intensity of the carbon carbon double bond absorption was observed, as would be expected for a 2+2 cycloaddition reaction.

Table 1: Insolublization of Polymers on Exposure to U.V. Radiation

Polymer	% insolublization					
	UV exposure time (min)					
	0.5	1	2	5	10	20
Ⓟ-CH=CH-COOEt (11)	-	-	-	26	48	81
Ⓟ-CH=CH-COOH (111)	-	7	53	71	76	75
Ⓟ-CH=CH-CHO (1V)	18	48	62	80	82	-

Acknowledgements

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References

1. G.A. Delzenne, in "Encyclopedia of Polymer Science and Technology", ed. by H.F. Mark and N.M. Bikales, Interscience, New York, Supp. Vol. 1, 401 (1976); G.A. Delzenne, Adv. Photochem., 11, 1 (1979).
2. K. Jacobson and R. Jacobson, "Imaging Systems", Wiley, New York, (1976).
3. M.J. Farrall, M. Alexis and M. Trecarten, Polymer, 24, 114 (1983); M.J. Farrall and J.M.J. Fréchet, J. Org. Chem., 41, 3877 (1976).
4. I.S. Dutt, Quart. J. Chem. Soc., 1, 297 (1925).
5. S. Trippett and D.M. Walker, J. Chem. Soc., 1266 (1961).

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