Study on the Spatial Resolution of a Furfuryl Alcohol-Negative Photoresist Using a Holographic System

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ABSTRACT: A negative photoresist was obtained from furfury alcohol using methylene dichloride as a solvent and trifluoracetic acid as a catalyst. A holographic assembly with a blue laser failed to give interference patterns. However, a periodic interference pattern was printed on a film of furfuryl alcohol resin using an ultraviolet laser with a coherent beam at 360 nm. The period of the pattern was reproduced throughout the film and resulted about 0.46 μm. Thus, the resin obtained was able to reach a resolution about 0.23 m. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1749–1751, 1999

Key words: spatial resolution; furfuryl alcohol; photoresist; holographic system

INTRODUCTION

Furan resins are characterized by their dark brown or black color and capacity to crosslinking during polymerization.[1] In this context furfuryl alcohol resins (FA) have been proved to be effective as photosensitive materials.[2,3] The structure of FA resin is rather complex. It is a mixture of methylene and oxy-methylene bridges between the furan rings,[4] branching,[5] and polyconjugated sequences,[6] and no ring opening is detected under mild polymerization conditions. Experiments performed with the aim to obtain thermoplastic colorless linear chains composed only of methylene bridges between furan rings did not succeed.[5,7] Polyconjugated chains, proposed to explain the color of the resin,[5] should give visible light absorption, but these sequences are only obtained in rather small quantities and cannot be eliminated or increased at will. In fact, the resin presents an ultraviolet absorption maximum and only a tail in the visible region. On the other hand, branching occurs at the first stage of the polymerization, and crosslinking appears as a sudden process even at low molecular weight. Branching through methylene bridges of the main chain with the formation of methyne ones has been argued as a site for photocrosslinking initiation.[2,3] Their structural and mechanistic features are under study and discussion yet.[2,6] Thus, the present work is a contribution to understand the interaction of light with such a complex material.

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EXPERIMENTAL

Materials

Furfuryl alcohol (Merck) was purified as already reported.[5] Methylene dichloride (BDH), trifluoroacetic acid (Carlo Erba), and other reagents (all from BDH) were used without further purification.

Polymerization Technique

Polymerization was carried out in a three-neck flask, under reflux and stirring. Catalyst solution was dripped slowly into the monomer solution (catalyst–monomer molar ratio 1 : 20) at 40°C and reaction time of 10 h. The reaction mixture was carefully neutralized, and polymer was isolated by

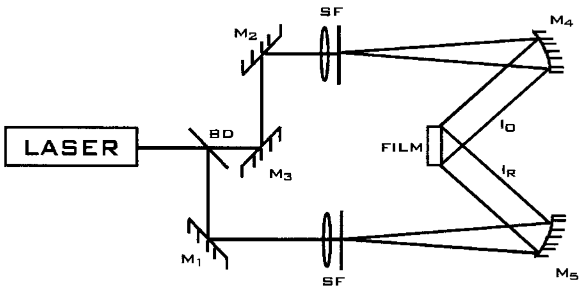


Figure 1 Holographic system.

precipitation in petroleum ether and dried under vacuum. Polyfurfuryl alcohol was dissolved in tetrahydrofuran and reacted with maleic anhydride (polymer–anhydride molar ratio 10 : 1) at 40°C for 3 h. The product was isolated by precipitation in petroleum ether and dried under vacuum.

Film Preparation

Resolution experiments were performed on FA films of about 300 nm, obtained by spin coating pouring a solution of the resin on a silicon wafer at 9000 rpm under laminar flow. Films were dried at 90°C for 25 min. Exposing time was 12 min, and developing was carried out with a mixture of toluene–petroleum ether for 2 s.

Electron Microscopy

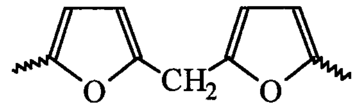
Electron micrographs were obtained with a JEOL JSM-5410 scanning electron microscope after coating the samples with approximately 10 nm of gold by sputtering.

Holographic Device

A holographic assembly used to generate and etch periodic patterns[8] is shown in Figure 1. BD is the beam divisor, M_1 to M_3 are flat mirrors, M_4 and M_5 are paraboloid mirrors and an SF spatial filter. An argon laser (λ = 360 nm) was used and its beam expanded to 50×. The angle between the beams I_o (object) and I_r (reference) was about 45° to produce patterns with a period of 0.46 μm. Gratings were etched on resin films supported on a silicon wafer.

RESULTS AND DISCUSSION

The main polymeric sequence of the furfuryl alcohol polymer is represented by:



as judged from the NMR spectra.[5] However, this monomeric unit does not absorb visible light in

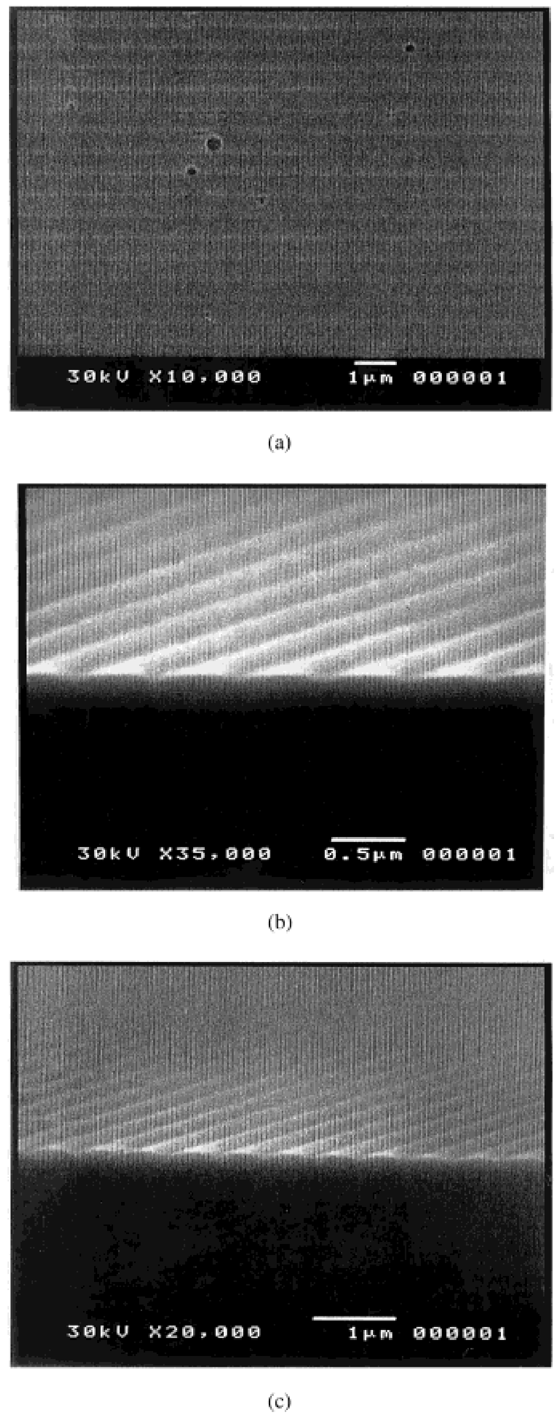
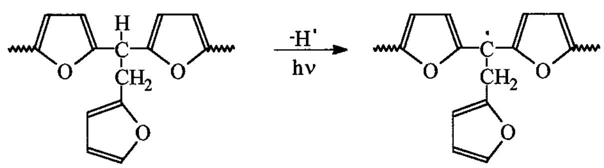


Figure 2 Photos MEV of recording periodic patternson photoresist film: (a) parallel lines, (b) lateral view, (c) frontal view.

the near ultraviolet region. Thus, photocrosslinking cannot occur at high wavelengths. Also, this is the case for the structures containing oxy-methylene bridges between furan rings. On the other hand, polyconjugated sequences could be the source of quantum uptake in the visible region, but their amount seems to be too small to be considered. This was demonstrated by trying to obtain a holographic printing with a blue laser. No interference patterns were observed at all.

Another likely site for photocrosslinking is the methyne hydrogen[9] from branching on the main chain:



Therefore, polymerization was conducted to obtain a tailored branched resin by a careful choice of the concentrations and reaction parameters. Thus, the material should possess an improved sensitivity to light. Furthermore, the resin was lightly adducted in order to increase its adhesion (see the Experimental section). Resin obtained under such experimental conditions is able to produce periodic interference patterns when using an ultraviolet laser at 360 nm. Perfect parallel lines are shown in Figure 2(a). Figures 2(b)–(c) show micrographs of the grating at several augmentations. Pattern period resulted about 0.46 μm. Therefore, the resolution attained for this material can be estimated as 0.23 μm. Micrographs show the sinusoidal profile of the patterns obtained. An ideal "square" pattern was not observed, probably due to the fact that the strength of the laser was not high enough, or resin not exposed to light was not completely removed by the developing mixture. Calibration of the laser used gave 20% of the original strength, indicating this fact as the reason for the behavior observed, but the basic physical properties of the photomaterial as a register are identified. Future work will be carried out to investigate the dependence with the exposure intensity.

CONCLUSIONS

It was possible to obtain a negative photoresist from furfuryl alcohol resin by carefully tailoring its structure. The resin was sensitive to ultraviolet light from a laser at 360 nm giving periodic interference patterns with a spatial resolution as low as 0.23 μm.

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