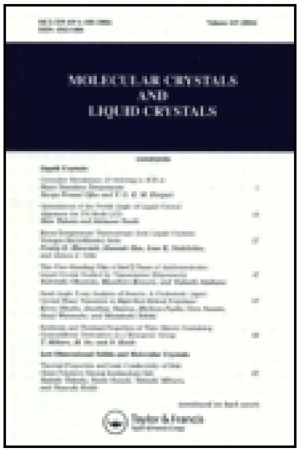

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Photoacid Catalyzed Photo-Fries Rearrangements of Poly(P-Formyloxystyrene) and Formyloxynovolac

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PHOTOACID CATALYZED PHOTO-FRIES REARRANGEMENTS OF POLY(P-FORMYLOXYSTYRENE) AND FORMYLOXYNOVOLAC

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Abstract The doping of photoacid into poly(p-formyloxystyrene) (PFS) and formyloxynovolac (FN) can catalyze their photo-Fries rearrangements to form poly(p-hydroxystyrene) and novolac respectively by exposure at 254 nm. Yields of rearrangements of PFS and FN as well as their contrasts of negative tone images are improved. Mechanism of acid catalyzed rearrangement and dark room effect of PFS are investigated.

INTRODUCTION

The uv-induced photo-Fries rearrangement of poly(p-formyloxystyrene) (PFS) has been reported.[1] The irradiation of PFS in deep uv results in the decarbonylation and therefore the formation of poly(p-hydroxystyrene) (PHS). Both PFS and PHS have maximum absorption around 265 nm. Because PHS also absorbs at the wavelength of irradiation, the sensitivity and yield are reduced. In this paper, we report that the doping of small amount of onium salt (triarylsulfonium hexafluoroarsenate, $Ph_3S^+AsF_6^-$) as photoacid into PFS and formyloxynovolac (FN) can catalyze their photo-Fries rearrangements to form PHS and novolac respectively. The exposure wavelength is based on the maximum absorption of onium salt which is about 254 nm. The PHS and novolac have much less absorption at this wavelength. The reaction mechanism and dark room effect of PFS are also studied.

EXPERIMENTAL

The PFS, FN and photoacid are prepared according to literatures.[1,2] UV irradiations were performed by using an Oriel 500 W deep uv illuminator equipped with an Oriel 254 nm narrow band interference filter. FT-IR spectra were recorded on thin films of PFS cast on KBr disks using a Bomem DA 3.002 spectrophotometer. UV spectra were recorded from films cast on thin quartz plates using a Hitachi 330 spectrophotometer. Flux doses were measured by an UVX digital radiometer with 254 nm probe. Film thickness measurements were made with a Dektak II A profilometer. Dissolution curves under various doses were measured by a home-made He-Ne laser interferometer.

RESULTS AND DISCUSSION

The addition of small amount of photoacid (PA), $ph_3S^+AsF_6^-$, to PFS can catalyze its photo-Fries rearrangement to form PHS by 254 nm deep uv exposure (Fig. 1). The more the PA is added, the higher the yield obtains. With 10 wt % PA presence, exposure at room temperature (RT) without bake, post-exposure bake (PEB) below 80°C (Fig. 2) or concurrent bake (CCB) below 80°C during exposure (Fig. 3) all at least double the yields of rearrangements as compared with no PA presence. Yields are obtained by measuring the gain of uv absorbance of hydroxyl group at 265 nm and decreasing of carbonyl (C=O) ir absorbance around 1740-1760 cm^{-1}. PEB does not effect the yield of PHS when there is no PA presence. With presence of PA, the increasing of PEB temperature will also increase the yield of PHS. Obviously, the reaction mechanisms are different. PFS + 10 wt% PA coated on Si wafers are used as samples for microlithographic studies. Average dissolution rate as a function of depth into resist thin film indicates the reduced PHS concentration

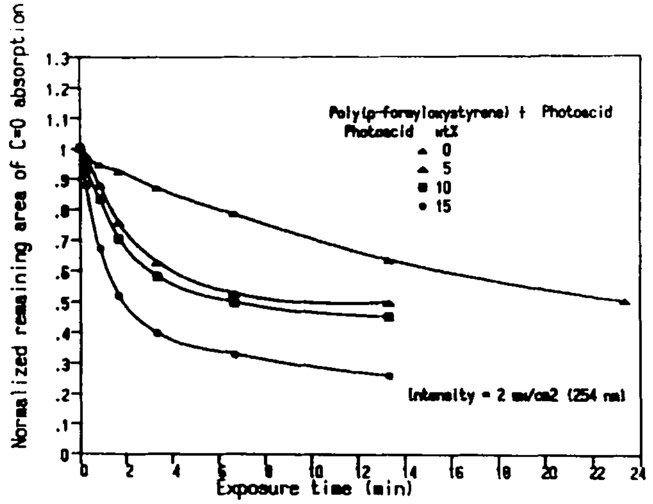

FIGURE 1 The amount of PA doping vs. the decreasing of carbonyl absorption of PFS.

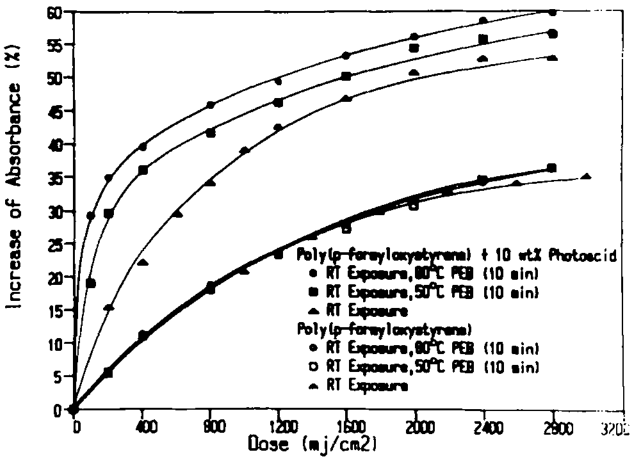

FIGURE 2 Plots of hydroxyl absorbance at 265 nm as function of exposed doses under various PEB temperature for PFS.

gradient which results from the strong absorbance of hydroxyl group around exposure wavelength of 254 nm. The contrast of negative tone image of PFS is improved from 1.69 to 2.16 using methylene chloride as developer (Fig. 4). This contrast is comparable to poly(t-butoxycarbonyloxystyrene) system.[3] Without PA presence, reaction stops right after exposure; with doping of 10 wt% PA, the rearrangement continues for more than an hour in dark room after exposure (Fig. 5), and absorbance increases more than 7%. Clearly, the acid catalyzed rearrange-

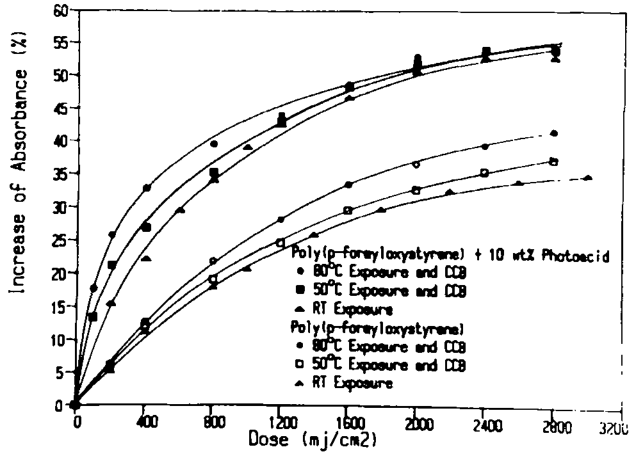

FIGURE 3 Plots of hydroxyl absorbance at 265 nm as function of exposed doses under various CCB temperature for PFS.

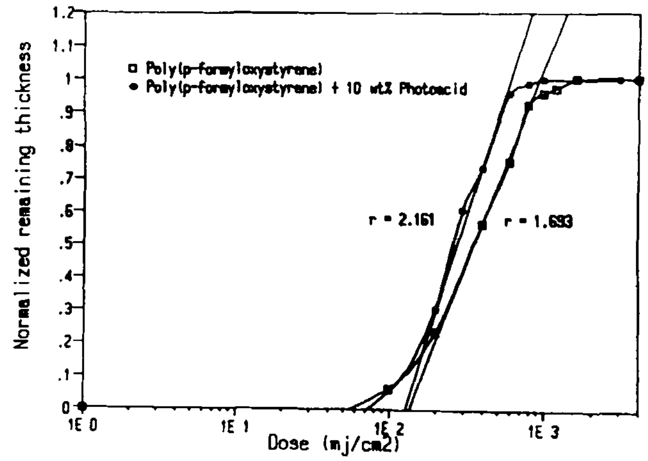

FIGURE 4 Contrast plots of negative tone images of PFS systems.

ment shows chemical amplification. When the samples are exposed to water vapor for 15 min or ammonia vapor for 10 min after exposure, dark room effect can be stopped (Fig. 6). The FT-IR spectrum taken 30 seconds after low doses of exposure shows a new C=O absorption peak at 1735 cm^{-1}, lower than th C=O absorption of more stable cis conformer at 1740 cm^{-1} (Fig. 7). The resonance of protonated formate group of cis conformer is proposed as the cause of 5 cm^{-1} shift. The mechanism of acid catalyzed rearrangement is shown in Fig. 8. Although the two

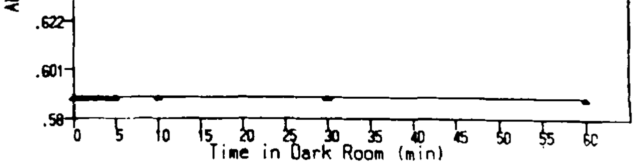

FIGURE 5 Plots of absorbance at 265 nm vs. time in dark room after exposure for PFS systems.

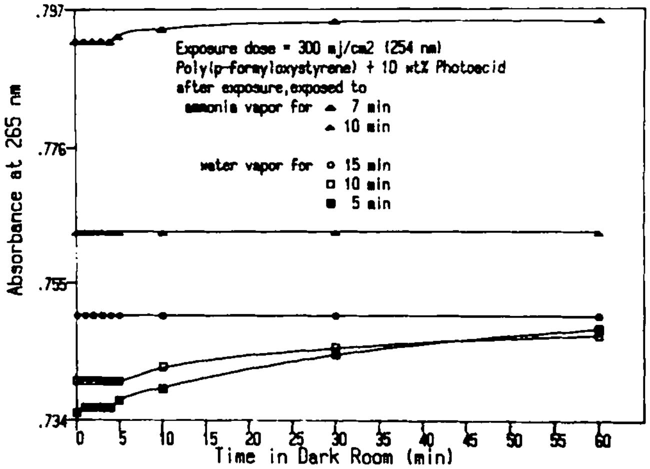

FIGURE 6 The effects of treatments of water and ammonia vapors on the hydroxyl absorbance at 265 nm in dark room after exposure for PFS.

dipoles of cis conformer are parallel, however, the nonplanarity of PFS molecules ($\theta \approx 70$), and large interaction between bulky phenyl group and oxygen atom, the trans conformer becomes less stable than that of cis conformer.[4] The 1735 cm^{-1} peak will be very difficult to detect under high doses of exposure, since the acid catalyzed rearrangement will almost complete in such case.

The preparation of FN by formylation of novolak and its deep uv-induced Fries rearrangement are shown in Fig. 9. The IR spectra of FN before

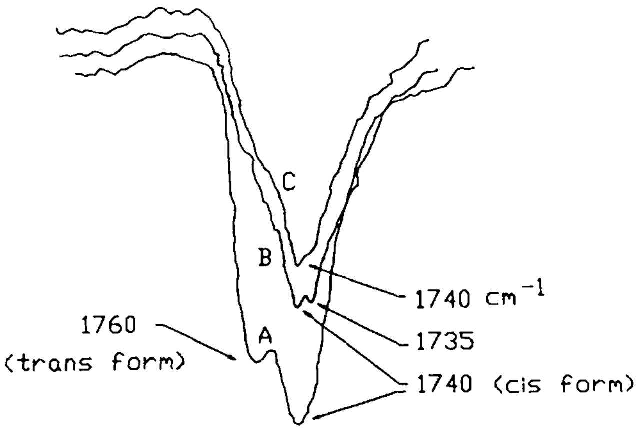

FIGURE 7 FT-IR spectra of acid catalyzed rearrangement of PFS. A) before exposure, B) 30 seconds after exposure at 254 nm, C) 2 minutes after exposure.

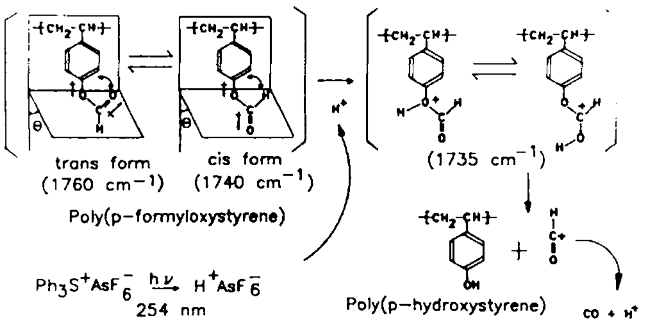

FIGURE 8 Mechanism of acid catalyzed rearrangement of PFS.

and after exposure at 254 nm are shown in Fig. 10. The decreasing of carbonyl absorption at 1716 from FN and increasing of hydroxyl absorption at 3417 cm^{-1} to form novolac are indicated. The effects of PEB (Fig.11) and CCB (Fig. 12) are similar to the PFS system after PA doping. The contrast of negative tone image is also improved from 1.781 to 2.128 using methylene chloride as developer (Fig. 13).

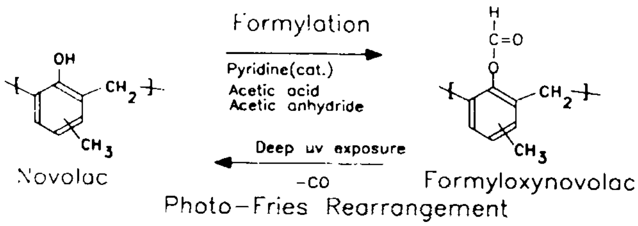

FIGURE 9 Preparation of FN and its photo-Fries rearrangement.

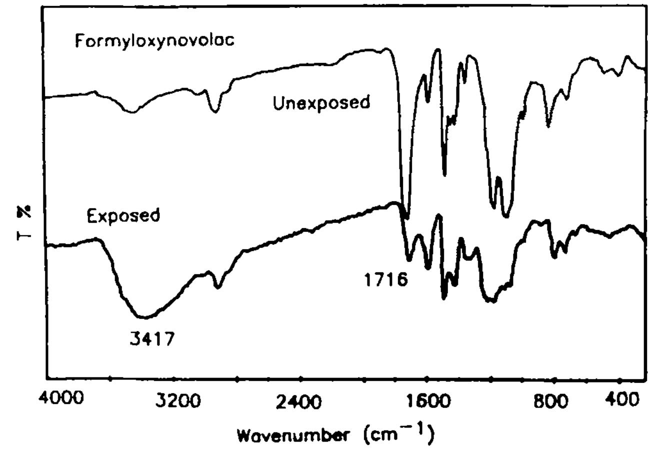

FIGURE 10 Unexposed and exposed IR spectra of FN .

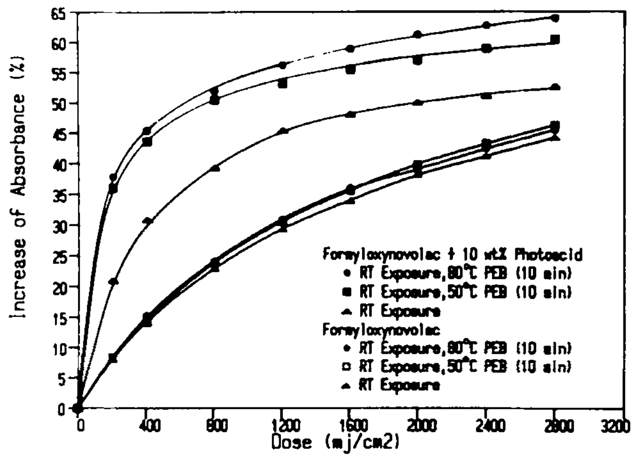

FIGURE 11 Plots of hydroxyl absorbance at 265 nm as function of exposed doses under various PEB temperature for FN.

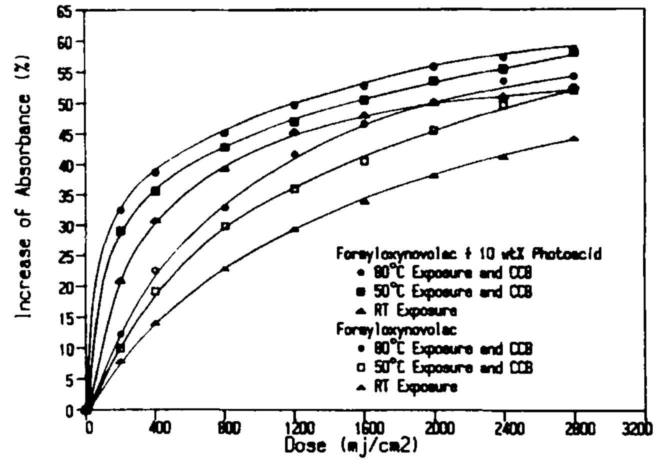

FIGURE 12 Plots of hydroxyl absorbance at 265 nm as function of exposed doses under various CCB temperature for FN.

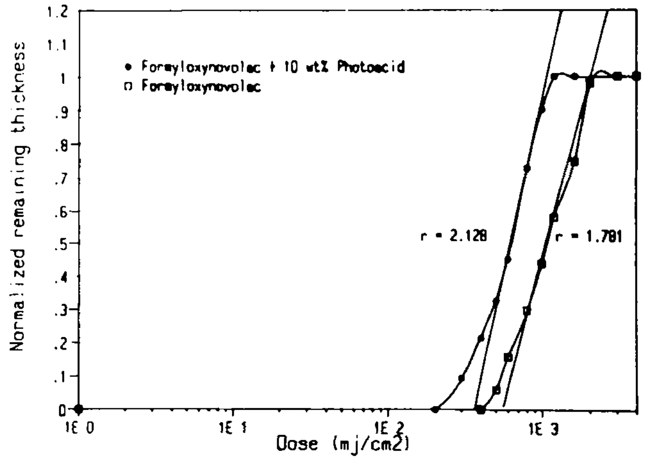

FIGURE 13 Contrast plots of negative tone images of FN systems.

CONCLUSIONS

The doping of onium salt into poly(p-formyloxystyrene) and formyloxy-novolac can catalyze their photo-Fries rearrangements. The yields and contrasts of negative tone images of these two compounds are improved.

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