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Novel Photochemical Crosslinking Polymer Systems with High Sensitivity for Negative Resist Applications

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A process of both photochemical and thermally induced chemical amplification of the effect of primary light irradiation has been realized in the photochemical crosslinking of polyvinylethylal layers containing diphenylbenzylamine and hexabromodimethylsulphone, allowing us to obtain new highly sensitive photoresists.

Light sensitive polymer layers have various technical applications but are particularly interesting in photolithography for use in generating the high resolution elements of modern integrated circuits. As the scale of device elements moves into the submicron region, requiring the introduction of new lithographic technologies, resist layers with improved resolution and sensitivity are required. One approach to improving sensitivity involves the concept of photochemical and thermally induced chemical amplification. We now report the synthesis of new sensitive polymer layers using this techniques.

We have investigated the photochemical crosslinking of thin polyvinylethylal (PVE) layers containing the electron donor additive diphenylbenzylamine (DBPA), the electron acceptor and acid generating species hexabromodimethylsulphone (HBMS) and the photosensitizing pyrylium dye 4-(2,6-diphenyl-4*H*-pyran-4-ylidenemethyl)-2′,6′-diphenylpyryl perchlorate (PD), λ_{max} 571 nm, ϵ 1.1×10^5 mol^{-1} dm^3 cm^{-1}, which become less soluble after exposure to light due to crosslinking reactions. All the layers were cast from acetone solutions of known compositions onto a poly(ethylene terephthalate) (PETP) substrate. The layers were exposed to varying amounts of 576 nm radiation and the films developed by treatment with 62% aqueous ethanol for 2 min. The extent of crosslinking as a function of light dose is thus given by

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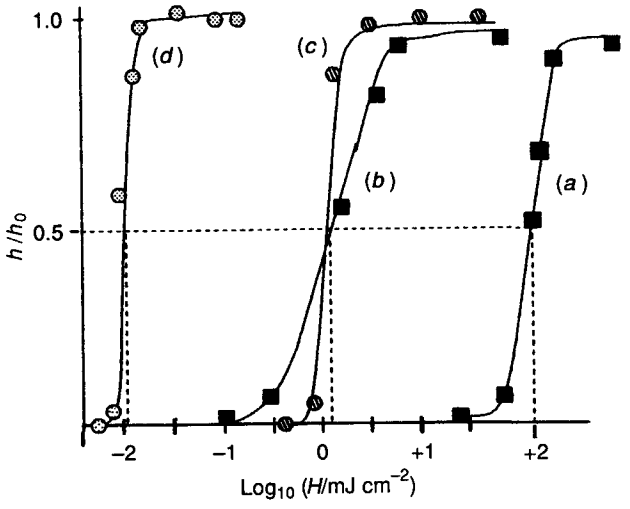


Fig. 1 Exposure response curves, λ_{ex} 576 (± 5) nm. [DPBA] = [HBMS] = 1 mol dm^{-1}; optical density of PD at 571 nm = 0.08. [DMABA] = 0 (*a*, *b*) and mol dm^{-1} (*c*, *d*). Photochemical amplification energy $H_{ph.am}$ = 0 (*a*, *c*) and 0.1 J cm^{-2} (*b*, *d*), $\lambda_{ph.am.} \geqslant 690$ nm. After exposing and amplifying the layers were heated for 4 min at 100 °C.

measuring the layer thickness (h) after such development, normalized relative to the original layer thickness (h_0) which was about 3 μm for all layers investigated. The normalized thickness was plotted as a function of $\log_{10} H$ (where H is exposure in mJ cm^{-2}) to provide the exposure response curves (Fig. 1), from which sensitivity and contrast can readily be determined. The sensitivity is H (at $h/h_0 = 0.5$), while the contrast is determined from the slope of the linear portion of the curve.

Pyrylium dye has previously been shown[1] to act as a sensitizer in the 500–600 nm region. Exposure of the layer to radiation in this region led to the generation of a coloured product (CP^+) with λ_{max} 665 nm and an acid **1** [eqn. (1)].[2]

$$^1(PD)_0 \xrightarrow[S-T]{h\nu} {}^3(PD)_1 \xrightarrow{DPBA} DPBA^{\bullet+} + PD^{\bullet-} \xrightarrow{HBMS} Br^- \cdots CBr_2{=}S(=O){-}CBr_3$$

$$+ DPBA^{\bullet+} + PD \longrightarrow CP^+Br^- + H^+[CBr_2{=}SO_2{-}CBr_3]^- \quad (1)$$

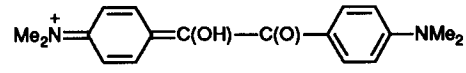
1

Polyester matrices are known[2,3] to undergo crosslinking or decomposition in the presence of acid released from the precursor, for instance the onium salts, on photolysis. Eqn. (2) shows the probable mechanism for the acid-catalysed crosslinking of polyvinylethylal, induced by the photochemically generated acid **1**. This reaction significantly accelerates on heating. Thus a sensitivity $H_{0.5} \sim 100$ mJ cm^{-2} is obtained after only 4 min at 100 °C. CP^+ acts as a spectral autosensitizer when irradiated in its visible absorption band (620–720 nm). This therefore provides the possibility of photochemical amplification of the initially formed image by subsequent secondary illumination of the exposed layer with near infrared radiation ($\lambda > 690$ nm). Unlike the two-quanta autosensitization in the absence of PD[4] the optical amplification in the layers considered is a one-quantum process, allowing us to use low-intensity irradiation. It was found[5] that on exposure to light (λ 520–600 nm) PD transforms partially to a new dye (PD') with a central =CBr— group in place of the =CH— group in PD. The structure of PD' ($C_{38}H_{24}BrClO_6$) was confirmed by elemental analyses and by the disappearance in the NMR spectrum of the proton signal in the central =CH— group. PD' has an absorption maximum at 608 nm in ethanol (ϵ_{max} 3.5 × 10^4 mol^{-1} dm^3 cm^{-1}), but at 620 nm in PVE and other polymer matrices.

In order to establish the mechanism of photochemical amplification the emission of CP^+, PD, PD' and the CP^+ emission intensity spectra were measured as a function of the concentration of PD. PD does not influence the fluorescence but quenches the phosphorescence of CP^+. Consequently photochemical amplification occurs with the participation of triplet states. From the intersection of the fluorescence excitation and emission spectra of the dyes their singlet excited state energies $^1E_1$ 2.13 eV (PD) and 1.94 eV (PD') were obtained. The singlet–triplet splitting energies were estimated as $E(S-T) = 1.24 \times 10^3 \ (1/\lambda^{fl}_{max} - 1/\lambda^{ph}_{max}) = 0.36$ eV (PD) and 0.29 eV (PD'). Hence it follows $E(T) = {}^1E_1 - E(S-T) = 1.77$ eV (PD) and 1.65 eV (PD'). The $^3(CP^+)_1$ phosphorescence spectrum is located in the region of 1.77–1.41 eV. These values allow us to propose the mechanism of eqn. (3) for the photochemical amplification,

$$^1(CP^+)_0 \xrightarrow{h\mu,\,S-T} {}^3(CP^+)_1 \xrightarrow{PD,\,PD'} {}^1(CP^+)_0 + ({}^3D_1 + {}^3D'_1) \quad (3)$$

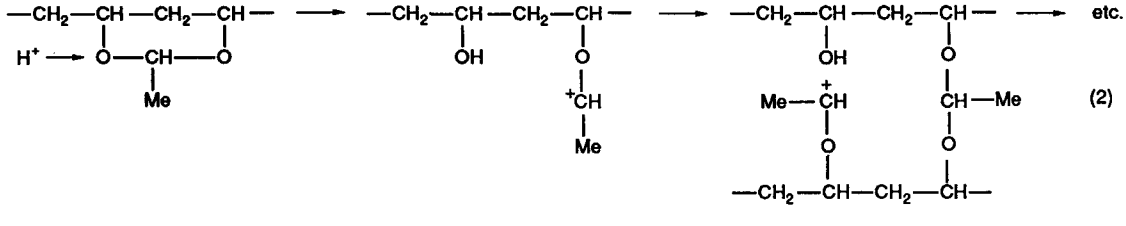
followed by reactions (1) and (2). Comparison of curves (*a*) and (*b*) in Fig. 1 shows about a hundredfold increase in resist sensitivity as a result of photochemical amplification. Curve (*c*) indicates that the addition of the chemical sensitizer 4-(*N*, *N*-dimethylamino)benzaldehyde (DMABA) to the layer produces a similar effect. Warming of the exposed layer with the addition of DMABA brings about the formation of a new product CP' (λ_{max} 430 nm) and the acid **1**. The structure of the new product



CP'

was assigned on the basis of its IR spectrum, which showed the disappearance of the —CHO peak at 1650 cm^{-1} and the appearance of new peaks at 1638 [=C—C(O)] and 1640–1680 cm^{-1} (>N=), as well as the phenyl rings (1622 cm^{-1}) and partial transformation into quinonoid structures (1590 cm^{-1}). CP' absorbs at 450 nm and is not an autosensitizer.[3]

From an analysis of the different forms of DMABA in ethanol and in aqueous acetonitrile solution in both the



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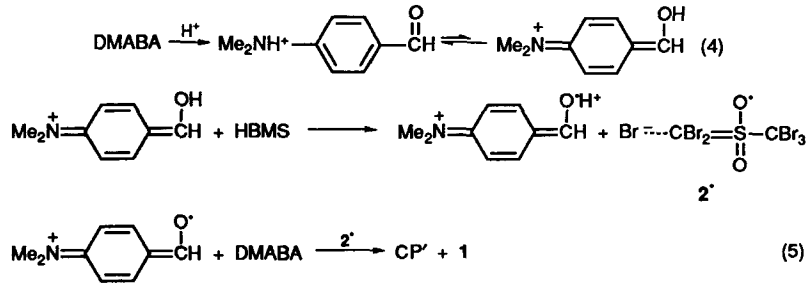

absence and presence of H_2SO_4 we can propose a mechanism for thermally induced chemical amplification. It involves initial protonation of DMABA followed by keto–enol tautomerism [eqn. (4)]. The keto- and enol- forms absorb at λ_{max} 230 nm and in the 400–415 nm region, respectively, their oxidation potentials $E^{ox}_{1/2}$ being 0.9 and 0.49 V [*vs.* saturated calomel electrode (SCE)]. The latter value corresponds to the region of potentials (< 0.65 V) in which thermal electron transfer occurs on HBMS. Indeed, the absorption spectrum of a solution of DMABA to which HMBS has been added shows the presence of CP'. The formation of CP' can be represented by eqn. (5).

Thus, in this case the thermally induced chemical amplification is probably connected with acid photogeneration followed by reactions (4) and (5) bringing about the additional formation of acid **1** and HBr. It leads to the crosslinking of the polymer [eqn. (2)] at the elevated temperature. In a polymer matrix these reactions are particularly effective at temperatures above 80 °C. Successive use of photochemical and thermally induced chemical amplifications allows to increase the sensitivity to $\sim 10^{-2}$ mJ cm^{-2}. This exceeds the highest sensitivity hitherto known for photoresists by an order of magnitude.[2,3] The contrast of the layers studied was found to be ~ 8.

It should be noted that the layers investigated are not sensitive only to light exposure. We can also obtain systems with high sensitivity to primary exposure to X-rays or electron beams.

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