Chem. Mater. **1994**, *6*, 724-726

Flash Photolysis Study of Melamine Cross-Linking Agents: Dual Role as Cross-Linker and Photosensitizer

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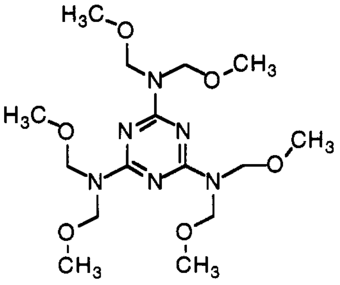
Received December 27, 1993
Revised Manuscript Received April 12, 1994

Introduction

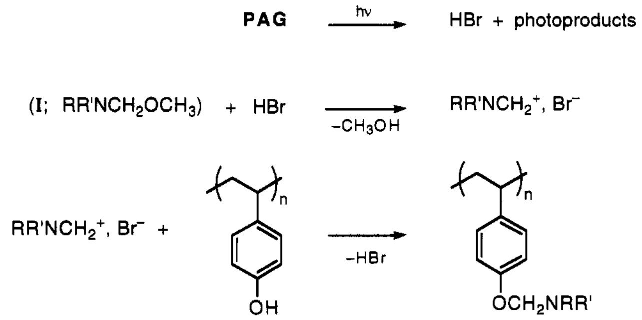
Image formation in photoresist systems usually involves changes of solubility of the exposed polymer composition. In positive resists, where the image formed is the same as on the mask, the photochemistry that occurs brings about a dissolution rate differential between the exposed and the unexposed area, leading to exposed area removal during development (e.g., diazonaphthoquinone/novolak resists). In negative resists, where the pattern formed is the reverse of the mask, the photochemistry involved renders the exposed area less soluble or insoluble in the developer.[1] Polymer insolubilization can be achieved by a variety of mechanisms; however, the great majority of negative resists are based on photo-cross-linking reactions between polymer chains. In this regard, a family of acid-hardened photoresists has been recently developed.[2] These formulations have a phenolic resin, a photosensitive acid generator (PAG) and hexamethoxymethylmelamine (I) as an acid-activated, thermally-assisted cross-linker.



I, $RR'NCH_2OCH_3$

The cross-linking process involved in these systems is similar to that found in thermoset coatings[3] and can be represented as shown in Scheme 1.

Scheme 1



The absorption spectrum of I exhibits a band in the ultraviolet region with a maximum around 220 nm. Consequently, when using deep-UV exposure tools of (i.e., $\lambda = 248$ nm) I itself may be photosensitive and therefore knowledge of its photobehavior becomes valuable. An exploratory study was thus undertaken in order to gain insight into the inherent photosensitivity of I. The results demonstrate that I also plays a role as a photosensitizer in the acid-generating process.

Results and Discussion

Laser excitation of I (266 nm) in deaerated acetonitrile solutions leads to weak absorption signals ($\Delta OD < 0.01$) having λ_{max} at 340 and 630 nm (Figure 1) and lifetime of a few microseconds ($\tau \approx 4$ μs). Several diagnostic tests lead us to conclude that these signals correspond to triplet–triplet (T–T) absorption.

Several molecules quench triplet states by an energy-transfer mechanism and are useful for diagnostic purposes.[4] Thus, molecular oxygen quenches the signals of Figure 1 readily ($\tau_{air} = 110$ ns). While oxygen is a rather nonspecific triplet quencher, conjugated dienes are frequently used as a selective triplet state quenchers. For example, 1,3-octadiene also readily quenches the signals shown in Figure 1. The rate constant for triplet decay observed in the presence of the diene (k_{obs}) is related to the rate constant of quenching by the diene (k_Q) according to eq 1, where τ_0

$$k_{obs} = \tau_0^{-1} + k_Q[\text{diene}] \qquad (1)$$

is the lifetime (in the absence of diene) of the transient being quenched. Figure 2 shows a plot according to eq 1. While this plot is based on data acquired at 630 nm, it should be noted that the same quenching behavior is also observed at 340 nm. From the slope of the plot shown in Figure 1, a k_Q value of 3.1×10^9 M^{-1} s^{-1} was obtained. This result, in combination with the oxygen quenching studies, provides firm evidence for the assignment of the transient to the triplet state of I.

In those formulations in which I is used as a cross-linker, a *gem*-dibrominated compound containing the functionality –CHBr–CHBr–, such as 1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (**II**), is used as an efficient acid (i.e., hydrogen bromide) photogenerator. In these systems the photoacid generator actually produces sequentially two bromine atoms according to reactions 2 and 3.[5,6] These bromine atoms then abstract hydrogen from the polymer matrix to yield HBr; the process is particularly facile in the case of phenolic matrices.

$$RCHBr\text{–}CH_2Br \xrightarrow{h\nu} R\dot{C}H\text{–}CH_2Br + Br^\bullet \qquad (2)$$

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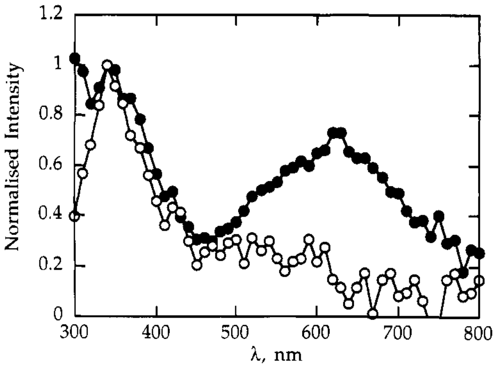

Figure 1. Triplet–triplet absorption spectra measured after 266-nm laser excitation of **I** (●) and **III** (○) in acetonitrile solutions.

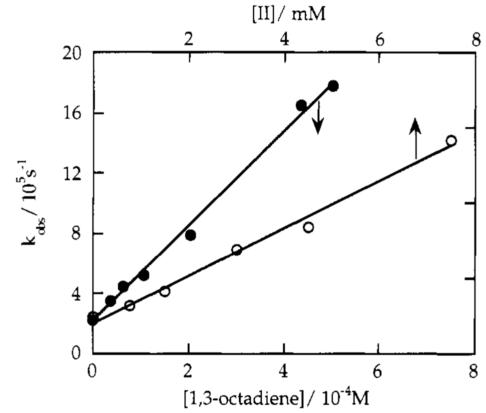

Figure 2. Plots of the observed triplet decay constant of **I** as a function of 1,3-octadiene (●) and **II** (○) concentration, monitored at 630 nm.

$$R\dot{C}H{-}CH_2Br \xrightarrow{\Delta} RCH{=}CH_2 + Br^{\bullet} \qquad (3)$$

Quenching of the triplet state of **I** by **II** was found to occur efficiently in acetonitrile solutions. The experimental approach is similar to that already described in the case of dienes (see eq 1). From the slope of a plot of k_{obs} vs concentration of **II** (Figure 2) a k_Q value of 1.6×10^8 M^{-1} s^{-1} is obtained. In these experiments, k_{obs} values were obtained by recording triplet decay traces at 630 nm since at 340 nm stronger transient signals from dibromides interfere.[6] Triplet quenching of **I** by **II** leads to the generation of bromine atoms which can be easily detected by complexation with Br^- (added as tetraethylammonium bromide) as shown in Figure 3 ($[Br^-]$ = 30 mM).[7] The quantum yield for sensitized bromine atom formation was determined using matched solutions (at 266-nm laser excitation wavelength) of **I** (having 7 mM **II**) and **II**, both in the presence of 15 mM tetraethylammonium bromide. The transient intensity at 360 nm (λ_{max} for $Br_2^{\bullet-}$) of each solution was then recorded as a function of the laser power. Direct photoexcitation of **II** produces bromine atoms with a quantum yield of 2.0.[6] Hence, from comparison of the slopes of linear plots (not shown) of intensity vs laser dose a sensitized quantum yield of 1.0 is obtained.

For comparative purposes, two other cross-linkers structurally related with **I** such as tetrahydro-1,3,4,6-tetrakis(methoxymethyl)imidazo[4,5-*d*]imidazole (**III**) and tetrakis(butoxymethyl)urea (**IV**) were also examined. Laser excitation of **III** and **IV** in deaerated acetonitrile solutions leads to similar results as in the case of **I**: i.e., weak triplet–triplet absorption spectra having in these cases only one detectable band with λ_{max} around 340 nm (Figure 1) and lifetimes on the order of microseconds (τ = 3–5 μs). The absence of a visible T–T absorption band prevented us from measuring the triplet quenching by **II** in the cases of **III** and **IV**. However, in both cases excitation exchange and consequently bromine atom generation occur as evidenced by the fact that spectra (due to $Br_2^{\bullet-}$) similar to the one shown in Figure 3 were obtained in the presence of 30 mM tetraethylammonium bromide.

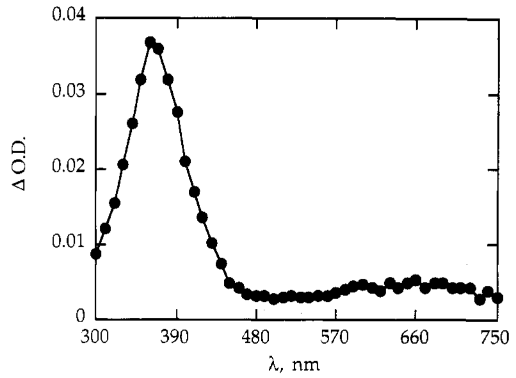

Figure 3. Transient absorption spectrum of $Br_2^{\bullet-}$ recorded after 266-nm laser excitation of **I** in acetonitrile solution in the presence of 2 mM **II** and 30 mM tetraethylammonium bromide.

To determine a relative order for sensitized decomposition of **II**, solutions of **I**, **III**, and **IV** having the same optical density at 266 nm (laser excitation wavelength) and 2 mM **II** and 20 mM tetraethylammonium bromide were prepared. The transient intensity at 360 nm (λ_{max} for $Br_2^{\bullet-}$) of each solution was then recorded as a function of the laser power. From comparison of the slopes of linear plots (not shown) of intensity vs laser dose the resulting relative efficiencies for **I**, **III**, and **IV** are 2.4:1.2:1, respectively.

In conclusion, deep-UV irradiation of **I** and related cross-linkers lead to the formation of triplet states. Sensitized decomposition of vicinal dibromides leads to the generation of bromine atoms. Two interpretations are possible for this process: in one the sensitization is attributed to energy transfer, while in the other one could involve electron transfer to the *gem*-dibromide followed by dissociative loss of Br^- to yield the radical of reaction 3. In both cases the olefin is produced, but in the electron-transfer mechanism the maximum yield of bromine atoms would be 1.0, as observed in the case of **I**. While our results do not distinguish between the two mechanisms, electron transfer is a strong possibility. In any event, it is clear that sensitized formation of bromine atoms is a very efficient process. In the presence of suitable hydrogen donors such as the phenolic resins used in photoresist applications, these bromine atoms are expected to abstract hydrogen and thus generate the HBr responsible for triggering the cross-linking process. Thus, cross-linkers such as **I** play a dual role, not just as cross-linkers but also as photosensitizers for acid generation.

Experimental Section

Materials and Apparatus. Hexamethoxymethylmelamine (**I**), tetrahydro-1,3,4,6-tetrakis(methoxymethyl)imidazo[4,5-*d*]imidazole and tetrakis(butoxymethyl)-

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urea (American Cyanamid), tetraethylammonium bromide and 1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)trione (Aldrich), and acetonitrile (Omnisolv) were used as received.

UV-absorption spectra were recorded on an HP-8451A diode array spectrophotometer.

Laser-Flash Photolysis Studies. The laser flash photolysis system will be described in detail elsewhere. Laser experiments were carried out using the pulses from the fourth harmonic of a Surelite Nd:YAG laser (266 nm, 6 ns, <15 mJ/pulse) for excitation. A flow sample cell (constructed of 7 × 7 mm^2 Suprasil tubing) was employed in order to ensure that fresh solution was irradiated by each pulse. Sample concentrations were typically 0.015 M for **I** and 0.12 M for **III** or **IV**. Solutions were deaerated by bubbling with oxygen-free nitrogen. The photomultiplier signals were captured by a Tektronix 2440 transient digitizer and transferred to a Macintosh IIci computer which was used for experiment control, data acquisition, and data processing. All laser programs were written using a LabVIEW 2.2 software package from National Instruments.