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Quantum yield determination for photolysis of photoimageable polymer in thin films

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Abstract

We have established a procedure for quantum yield determination for the photolysis of photoimageable polymers in thin films. Previously, we have discovered that electron transfer in polymers bearing benzophenone ammonium borate salt pendants is followed by bond cleavage leading to the formation of the polymeric amine. A measured solid state quantum efficiency of 0.15 makes this class of compounds interesting as precursors for polymeric amine generation. © 1997 Elsevier Science S.A.

Keywords: Quantum yield; Photoimaging system; Photolysis; Polymeric amine; Thin film

1. Introduction

Photogeneration of chemically active species has been extensively utilized in a number of technologically important applications including polymer cross-linking [1] and microlithography [2]. Photogenerated acids [3] and radicals [4] have been more frequently employed as catalysts than photogenerated bases owing to the lack of efficient and reliable precursors of the latter. However, the potential significance of organic bases, amines in particular, cannot be underestimated because of their importance in various [5,6] applications.

One of the original efforts to obtain a photogenerated base was made by Willson and Kutal [7] where ammonia was formed from the photolysis of inorganic transition metal salts. Most other research in the field concentrated on UV induced photorearrangements [8] and cleavage of photolabile groups [9,10] yielding reactive amines. The latter led to the generation of several families of base photoprecursors (some of them polymeric) which have been successfully employed as curing agents in the thermally induced cross-linking of epoxy resins [11], and as agents for image reversal in well-defined microlithographical processes [12].

Recently, we have reported a positive-tone photoimaging system based on polymers bearing pendant tetraalkylammonium triphenyl-*n*-butylborate functionality where one of the groups attached to the cationic center was *p*-benzoylbenzyl. Under UV irradiation polymer **2** underwent photolysis, believed to involve electron transfer from the borate counter ions (Fig. 1) to produce polymeric amine **1** [13]. The original polymer, insoluble in aqueous acid, became acid sensitive after irradiation and could be removed in a wet development process using aqueous HCl followed by water–ethanol wash. The system yielded images of 3 μm resolution, however it was of relatively low speed.

The synthesis of a similar polymer with the tetraphenylborate anion was both easier and more reproducible than that of the triphenyl-*n*-butylborate analog. The polymer behaved similarly in the photoimaging process. Therefore, poly (2-[*N*,*N*-dimethyl-*N*-(*p*-benzoyl)benzylammonium-(tetraphenylborate)]ethyl methacrylate) (**3**) was chosen in later studies.

Herein, we report on the attempt to estimate the quantum efficiency of the photolysis of the polymer **3** in thin films.

2. Experimental details

2.1. Polymer synthesis and characterization

Poly (2-[*N*,*N*-dimethyl-*N*-(*p*-benzoyl)benzylammonium-(tetraphenylborate)] ethyl methacrylate) (**3**) was synthesized according to the scheme previously used for the synthesis of its triphenyl-*n*-butylborate analog (**2**) [14]. Radical polymerization of the appropriate monomer with AIBN

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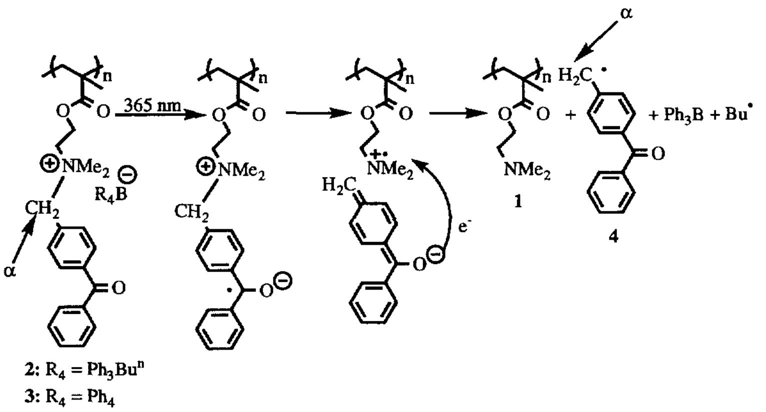

Fig. 1. Mechanism of the polymeric amine formation.

(3 mol.% of total monomer) in anhydrous acetonitrile at 60 °C for 120 h gives 58% yield (by weight) after polymer precipitation in diethyl ether. Elemental anal. Found: C, 81.26; H, 6.94; N, 2.38. $C_{46}H_{46}BNO_3$ calc.: C, 82.30; H, 6.85; N, 2.09.

Polymer molecular weight was estimated using an Ubelhode viscometer with measurements conducted in acetonitrile at 30 °C ± 1. The obtained value for the intrinsic viscosity was $[\eta] = 1.16$ dl g^{-1}. Polymer molecular weight was estimated at 80 000–90 000 [2]. Since our polymeric system is an ionomer, it is not readily amenable for molecular weight determination using conventional gel permeation chromatography. It is also worth noting that ionomers have slightly higher viscosity than nonionic polymers of similar molecular weight [15].

2.2. Sample preparation and power measurements

Polymer films were prepared from 20% by weight solution of polymer **3** in *N,N*-dimethylformamide (DMF) via spin-coating onto 22 × 22 mm square glass slides using a Headway Research Spin-coater in air at room temperature by spinning at 6000 rpm for 30 s. All films were then prebaked at 80 °C for 30 min. After carefully cutting the glass slide, the thickness of the film was measured by observing the exposed cross-section using scanning electron microscopy (SEM). The measured film thickness was thus in the range of 0.3–0.4 μm. The weight of the film was averaged over 12 films and estimated at 0.41 ± 0.05 mg. Film absorption at 365 nm, attributed to the presence of benzophenone-like chromophore, was measured by absorption spectroscopy and averaged at 0.0265 over 12 films.

UV exposures were performed on a custom made irradiation setup with a 200 W high-pressure mercury arc lamp as an irradiation source. The light was passed through a 365 nm filter (bandwidth ≈ 40 nm). The beam direction was normal to the surface of the slide bearing the film. The distance between the irradiated target and the lamp remained fixed at 11 cm. Incident dose was measured by PMT power meter with the front surface of the PMT tube positioned in the place of the slide.

After different exposure times films were carefully washed into a 4 ml vial with 1 ml of deuterated dimethylsulfoxide (d_6-DMSO). Solutions from four films for each exposure time were combined in order to obtain appreciable ^1H NMR signals. After the films were washed off, absorbance measurements were performed again on the slides to ensure completeness of the film removal.

2.3. Instrumentation

UV absorption spectroscopy was performed with the Hewlett-Packard 8452A diode array spectrometer. A Scientech 365 power meter was employed for the measurement of the incident dose. ^1H NMR (proton nuclear magnetic resonance) spectroscopy was performed on a 400 MHz Unity Plus Varian spectrometer. SEM was performed with a Hitachi S2700 scanning electron microscope. XPS (X-ray photoelectron spectroscopy) was performed with a Perkin-Elmer PHI Model 5600 MultiTechnique system. Elemental analysis was done at Atlantic Microlab, Inc. (Norcross, GA).

3. Results and discussion

In our efforts to expand the possible number of positive-tone functioning polymeric systems in which quaternary ammonium groups undergo photoreduction by organoborate anions, we have discovered that synthetic reproducibility of the originally reported system with triphenyl-*n*-butylborate as a counteranion (**2**) is poor. As a result the tetraphenylborate analog of (**2**), (polymer **3**), was tested as a prototypical positive imaging system using the procedure described elsewhere [13]. Polymer **3** displayed sensitivity values that can be calculated from the film remaining after exposure and development. The data (**x**) are shown in Fig. 2. D_0, the minimum exposure dose required to initiate observable changes in film thickness upon photoreaction and development, was equal to 1.20 J cm^{-2}, while D_c, the minimum exposure dose

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[2] K and α values for Mark–Houwink Eq. (1) were chosen for the model polymer–solvent pair according to *Polymer Handbook*. $[\eta] = KM^{\alpha}$ (1), where M is the polymer molecular weight; $K = 0.00393$ dl g^{-1}; $\alpha = 0.5$.

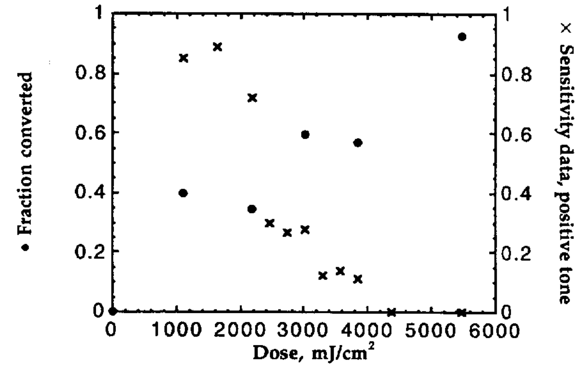

Fig. 2. Fraction of converted polymer **3** and its sensitivity vs. applied dose of incident UV irradiation.

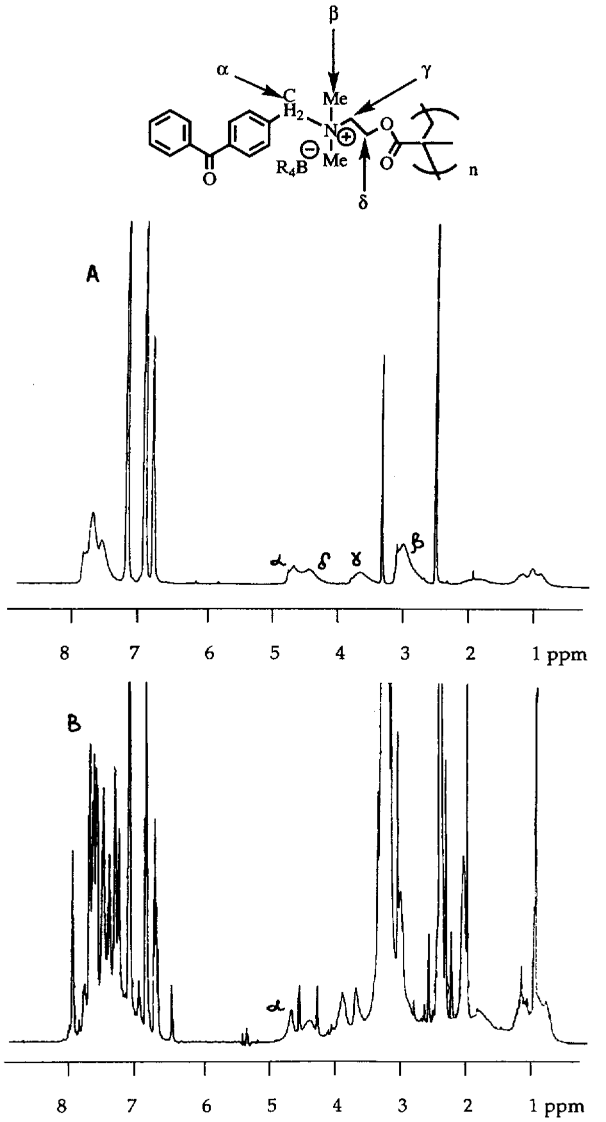

Fig. 3. ^{1}H NMR (400 MHz, d_6-DMSO) of (A) original polymer **3**; (B) film of polymer **3** irradiated (accumulated dose 3.2 J) and dissolved as described.

required to render the polymer film of the above mentioned thickness completely removable by our developing procedure, was estimated at 4.26 J cm^{-2}. These values corresponded well to those obtained for the original polymer **2**. Thus, we decided to carry out all subsequent experiments using polymer **3**.

An important determinant of the potential utility of any photoimaging system is the efficiency of the image creating photochemical reaction. Measurement of the quantum yield for photolysis of our polymer in a thin film is not a trivial problem. Since *tertiary* amine is expected to form as a result of photolysis, the well accepted IR spectroscopy methodology [16], where the disappearance of the carbamate carbonyl absorbance is monitored, cannot be employed. We have studied X-ray photoelectron spectra of polymer (**3**) before and after photolysis hoping to observe the expected shifts in the binding energy of the nitrogen atoms in **3**. Unfortunately, we were unable to design a strategy for deconvolution of the very broad signals to make an effective quantitative determination of the populations of tertiary and quaternary structures. As a result of problems with all other methods, we chose to use the NMR signals from the protons of the benzylic methylene group attached to the quaternary nitrogen atom (α-position in Fig. 1) to provide a quantitative measure. In the original quaternized polymer (**3**) the resonance signal at ca. 4.62 ppm (Fig. 3) disappears as the cleavage reaction occurs. The integrated area of the signals from the aromatic protons (8–6.6 ppm) was chosen as the reference based on the assumption that there is no change in the total number of aromatic protons. ^{1}H NMR spectra of starting polymer **3** and dissolved irradiated films (irradiated with a total of 3.2 J in this case) are shown in Fig. 3. The fraction of converted polymer (f) was expressed as:

$$f=\frac{C_0-C_\tau}{C_0},$$

where C_0 is the ratio of the area of the ^{1}H NMR signal of α-methylene hydrogens to that of the reference signal, at $t=0$ (t-irradiation time); C_τ is the ratio of the area of the ^{1}H NMR signal of α-methylene hydrogens to that of the reference signal, at $t=\tau$. After the measurements were performed with solutions of the polymeric films before and after irradiation (several exposure doses) the results (●) were plotted in Fig. 2. This figure also shows the fraction of the film removed by development after various radiation doses (**x**). The data show that the results are correlated as would be expected. It also can be seen that approximately 75% conversion of the original polymer is required for complete removal of the 0.3–0.4 μm thick films by the development process. It is also worth noting that no inner filter effect was observed since conversion ratio remained linear even for the high degree of conversion.

Quantum yields for cleavage of the polymer **3** (ϕ) were calculated from the degree of conversion and the amount of absorbed radiation as estimated from power meter readings and the measured absorbance of the films according to the following equation:

Table 1

Time (min)	Fraction converted	Number of molecules converted	Energy absorbed by film (J)	Number of photons absorbed	Quantum yield ϕ
2	0.3989	1.47×10^{17}	0.313	5.74×10^{17}	0.26
4	0.3442	1.27×10^{17}	0.626	1.15×10^{18}	0.11
5.5	0.5976	2.20×10^{17}	0.861	1.58×10^{18}	0.14
7	0.5685	2.09×10^{17}	1.096	2.01×10^{18}	0.10
10	0.9261	3.41×10^{17}	1.566	2.87×10^{18}	0.12

$$\phi=\frac{n}{N}$$

where n is the number of the converted chromophoric units and N the number of photons absorbed. The number of the converted units (n) can be determined experimentally from the product of:

$$n=n_0 f$$

where n_0 is the number of overall units of starting chromophore that can be determined from the weight of the original film. Thus, n_0 can be determined as a product of:

$$n_0=N_A\nu$$

where N_A is Avogadro's number (mol^{-1}) and ν the number of molar equivalents of the starting chromopore (mol). In its turn ν can be expressed as

$$\nu=\frac{m}{M}$$

where m is the weight of film (g); M the molecular weight of each unit containing one chromophore ($\mathrm{g\ mol}^{-1}$). For polymer **3** $M=671.25\ \mathrm{g\ mol}^{-1}$ (one monomer unit).

Substituting the symbols in the above equations with known values from Section 2 it can be calculated that $\nu=6.11\times10^{-7}$ mol and $n_0=3.68\times10^{17}$. The number of photons absorbed (N) can be calculated as

$$N=\frac{E_{\mathrm{abs}}}{E_{\mathrm{one\ photon}}}=\frac{E_{\mathrm{abs}}\lambda}{hc}$$

where E_{abs} is the energy absorbed by a film (J), $E_{\mathrm{one\ photon}}$ the energy of a single photon (J), λ the wavelength of irradiation (nm) (365 nm in our case), h Planck's constant (J s) and c the speed of light ($\mathrm{m\ s}^{-1}$). The energy absorbed by a film (E_{abs}) can be determined from the equation

$$E_{\mathrm{abs}}=I_{\mathrm{abs}}\tau$$

where I_{abs} is the absorbed dose (W) and τ the measured exposure time (s). According to Beers law

$$I_{\mathrm{abs}}=I_0(1-10^{-A})$$

where I_0 is the incident dose (W) and A the film absorbance.

The incident irradiation power flux hitting one 22 × 22 mm glass slide substrate was experimentally measured by a power meter to be 44.14 mW. Knowing the UV absorbance by the polymer film at 365 nm (see Section 2) the absorbed power flux (dose) can be determined as

$$I_{\mathrm{abs}}=44.14(1-10^{-0.0265})=2.61\ \mathrm{mW\ per\ film}$$

The energy of one photon of 365 nm wavelength is 5.45×10^{-19} J. Results of quantum yield calculations can be seen in Table 1.

Thus, the quantum yield for polymeric amine formation after UV induced photolysis can be estimated at 0.15 ± 0.02 (we estimate an NMR experimental error at 10%).

Previously, we have performed the measurements of the relative quantum efficiency of the photolysis of model ammonium tetraorganylborate salts in solution [17]. For *N*-*p*-benzoylbenzyl, *N*,*N*,*N*-tri-*n*-butylammonium tetraphenylborate which contains photoactive groups similar to those in our polymer the photolysis quantum yield was reported at 0.61. Many reasons may account for the lower quantum yield in the polymeric system, but one which is appealing is that it may be an example of a classical steric effect. In the more reactive model compound the quaternary nitrogen bears two *n*-butyl substituents whereas the corresponding substituents in the polymer are two methyl groups. The B-strain [17,18] arising from crowding of the two butyl groups would be relieved by separation of the benzylic radical breaking the C–N bond. Performing the irradiation with film surface exposed to air may have also contributed to the lowering of the quantum yield since oxygen is known to quench the excited triplet state of benzophenone [19]. Also, it is known that the efficiency of the photoprocess can be affected in solid polymeric films compared with isolated model molecules owing to the presence of impurities and chromophore self-quenching [20,21].

A solid state quantum efficiency of 0.15 is comparable to the one reported in the case of amine generation based on the photoremoval of the α,α-dimethyl-3,5-dimethoxybenzyloxycarbonyl (Ddz) group [16]. This value is considered sufficiently high for practical applications requiring the use of photogenerated polymeric tertiary amine.

4. Conclusions

Measurements of the solid state efficiency of photolysis leading to polymeric amine formation in polymeric systems with reactive benzophenone ammonium borate salts were performed. ^{1}H NMR spectroscopy was utilized for monitoring characteristic peaks disappearing upon photoreaction. The obtained value of 0.15 is considered sufficiently high to further pursue this class of compounds as photogenerated base precursors.

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