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The Photogeneration of Polymeric Amines:
Synthesis and Photocrosslinking of Copolymers
Containing Photoactive Carbamate Pendant Groups

by

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THE PHOTOGENERATION OF POLYMERIC AMINES: SYNTHESIS AND PHOTOCROSSLINKING OF COPOLYMERS CONTAINING PHOTOACTIVE CARBAMATE PENDANT GROUPS.

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ABSTRACT

Two families of copolymers containing 4-[(2-nitrobenzyloxy)-carbamoyl]-styrene as the photoactive component, with styrene or methyl methacrylate as the other component are described. The polymers are prepared by chemical modification of copolymers of 4-amino-styrene with styrene and methyl methacrylate, respectively, using 2-nitrobenzyl chloroformate. The photoactive carbamate groups of both copolymers can be removed by irradiation with UV light below 320nm. Quantum yield measurements and comparisons with small molecule model compounds confirm that attachment to the polymer has no effect on the photolability of the 2-nitrobenzyl carbamoyl protecting group. Quantum yield values near 0.10 also compare favorably with those obtained for related small molecules. The photoactive polymers have been tested successfully in the UV induced crosslinking of formulations containing epoxy groups.

INTRODUCTION

The chemistry of amines has been of particular significance in several areas of polymer chemistry[1] as some commercially important adhesives, foams, thermosets, etc., have relied on the reactivity of amines for chain formation, chain extension, or crosslinking.

Previous work from this laboratory has reported new designs for efficient photo-precursors of amines. Following earlier work on the use of photoactive protecting groups for alcohols[2], carboxylic acids[3], or amino-acids[4], we have studied two families of photo-precursors of amines[5,6]. The first is based on carbamates containing the photo-active Ddz (α,α-dimethyl-3,5-dimethoxybenzyl carbamoyl group)[7], and the second is based on carbamates incorporating the well-known 2-nitrobenzyl or related chromo-phores. In all cases, removal of the photolabile protecting groups from their carbamate precursors has been demonstrated in the solid state through experiments in which polymer films containing small amounts of the carbamates were exposed to UV light[6,8]. While the Ddz chemistry affords quantum yields near 0.10, higher quantum yields vary-ing from 0.11 to 0.62 are obtained with 2-nitrobenzyl carbamate chemistry through changes in the structure of the basic 2-nitrobenzyl chromophore. For example, substitu-tion of the ´ 6-dinitrobenzyl for the 2-nitrobenzyl chromophore produced a more than five-fold increase in quantum yield, while the introduction of an α-methyl-benzyl group resulted in both increased quantum yield and reactivity enhancements in some applica-tions[9].

This work has concentrated on polymers containing the simple 2-nitrobenzyl chromophore due to its ready availability and since the structural modifications elucidat-ed earlier in the model studies could be implemented into polymeric systems. In view of the potential use of a polymer containing photolabile amino protecting groups as a curing agent, this report will focus on both the preparation of the photoactive polymers and their use in a model crosslinking reaction involving epoxides. We have recently reported on the use of amines photogenerated from low molecular weight precursors in chemically amplified imaging systems.[9]

RESULTS AND DISCUSSION
Design and Synthesis

2

The initial synthetic strategy used to form copolymers containing *o*-nitrobenzyloxycarbonyl protected amine functionalities involved the preparation of the photoactive monomer, N-(2-nitrobenzyloxycarbonyl)-4-aminostyrene. This photosensitive carbamate was prepared from *p*-amino styrene and 2-nitrobenzyl chloroformate. However attempts at radical polymerization of this monomer were less successful than expected as only very low molecular weight compounds could be isolated due to significant inhibition by the *o*-nitro substituent. Such inhibition phenomenon is well-known for nitroaromatics, though the radical polymerization or copolymerization of 4-nitrostyrene has been described[10]. An alternative route to the desired photoactive polymers involving the modification of amine containing polymers was explored.

Poly(4-aminostyrene) itself is not an attractive starting material due to its low solubility in most organic solvents. In contrast, copolymers of 4-aminostyrene and styrene or methyl methacrylate show better solubilities depending on the 4-aminostyrene content. The copolymers are therefore suitable starting materials for the preparation of photoactive polymer systems. The first copolymer was prepared by radical copolymerization of 4-aminostyrene and styrene in a 15:85 molar ratio. The reactivity ratios[10] of the two comonomers (r_1=0.220 and r_2=0.410, respectively) are favorable for the formation of a random copolymer and ^{1}H NMR, as well as elemental analysis, confirmed that 14% of the 4-aminostyrene moiety had indeed been introduced into copolymer **1**.

Similarly, 4-aminostyrene and methyl methacrylate were copolymerized in a 1:9 molar ratio. The reactivity ratios[10] of a similar system, *p*-N,N-dimethylaminostyrene and methyl methacrylate, are r_1=0.101 and r_2=0.204, respectively. Incorporation of 10% 4-aminostyrene into copolymer **2** was again confirmed by ^{1}H NMR and elemental analysis.

Introduction of the photoactive carbamate group on both of the copolymers was achieved by polymer modification (Scheme I). Reaction with 2-nitrobenzyl chlorofor-

mate in the presence of triethylamine and N,N-dimethylaminopyridine resulted in essentially quantitative formation of the desired photoactive polymeric carbamates **3** and **4** as confirmed by ^{1}H NMR spectroscopy which showed the expected resonances for the *o*-nitrobenzyl group as well as the correct integration data. Additional confirmation of the successful functionalization was provided by FT-IR spectrometry with the appearance of nitro and carbonyl bands at 1525 and 1740 cm^{-1}.

As all of the photoactive carbamates we had described previously[5,6,8,9] were derived from aliphatic amines, the corresponding N-(*o*-nitrobenzyloxycarbonyl)-aniline **5** was prepared to allow a direct comparison of the photo-cleavage of the polymeric carbamates with a small molecule having a similar structure. The model compound itself was synthesized by the lithium alkoxide catalyzed addition of *o*-nitrobenzyl alcohol to phenylisocyanate (Scheme II).

Photochemistry

As described previously by DeMayo[11], the 2-nitrobenzyl photo-rearrangement is an intramolecular process[4,6,12] (Scheme III) in which the nitro group is reduced to a nitroso group and an oxygen atom is inserted into the ortho benzylic carbon hydrogen bond. The primary photochemical process in this oxidation-reduction scheme is an intramolecular hydrogen abstraction by the excited nitro group. This is followed by an electron redistribution process to the aci-nitro form, which rearranges to the nitroso product with concomitant liberation of the free amine. Since the *o*-nitrobenzyl photo-rearrangement is an intramolecular process, the deprotection of the amino moiety can be accomplished in the solid state as well as in solution. Thus, the photo-deprotection of all three systems, the small molecule model and both polymeric amines (Scheme IV), was explored in the solid state and in solution.

^{1}H NMR spectroscopy was used to monitor the solution photolysis of photoactive carbamates **3-5** in deuterated dichloromethane. The extent of conversion of carbamate

4

to free amine was determined by NMR monitoring of the disappearance of the 2-nitro-benzyl methylene resonances near 5.6 ppm. Figure 1 documents these changes for a solution of **3** in CD_2Cl_2; similar observations were made for the model compound **5** and for copolymer **4**. Formation of free amino groups upon irradiation was provided by a positive ninhydrin test for the polymer after irradiation, while the starting polymer did not react with ninhydrin. As was the case for comparable photoactive model compounds[6] no evidence of formation of imine (structures **6** or **7**) arising by recombination the photo-by-products was seen in the ^1H NMR spectra. As demonstrated earlier imine forma-tion by recombination of the photoproducts is favored in a weakly acidic medium[4,9].

The solid state photoreaction was also monitored by infrared spectroscopy. For both polymers **3** and **4** the asymmetric NO_2 stretching frequency (1525/1528 cm^{-1}) disappears upon exposure to increasing doses of UV light as the 2-nitrobenzyl carba-mate is photolyzed to 2-nitrosobenzaldehyde. Similarly, the carbamate band of polymer **3** at 1742 cm^{-1} also disappears upon exposure (Figure 2). In the case of polymer **4**, the carbamate band is obscured by the large ester bands of the methacrylate moieties and its loss cannot be monitored. In all cases, the strong C=N absorption band near 1630 cm^{-1} that would arise from imine structures **6** or **7** was not observed.

Detection of the free 2-nitrosobenzaldehyde photoproduct was accomplished by GC-MS analysis of films of irradiated **3-5**. As expected, a peak corresponding to 2-nitrosobenzaldehyde at m/e 135 was detected for the irradiated films but was absent in a parallel GC-MS study of unirradiated films. This finding supports the formation of the free amine by irradiation of the photoactive copolymers.

Quantum Yield

The quantum efficiency of the photoreaction in the solid state was monitored by infrared spectroscopy. For these studies, copolymers **3** and **4** were cast as thin films on

5

appropriate substrates while model compound **5** (10 mol%) was incorporated into a thin film poly(methyl methacrylate) matrix to simulate the copolymer systems. The quantum yields, Φ, were evaluated experimentally using the following equation.

$$\Phi = \frac{\text{No. of moles of 2-nitrobenzyl substrate consumed}}{\text{No. of Einsteins absorbed}} \qquad \text{[Eq. 1]}$$

$$\Phi = \frac{\text{Starting Film Concentration (mol/cm}^2\text{)} \times \% \text{ Conversion}}{\text{Radiation Flux (Einsteins/s cm}^2\text{)} \times \text{Time(s)} \times \% \text{ Absorbed}} \qquad \text{[Eq. 2]}$$

The % conversion was determined by measuring quantitatively the disappearance of the nitro stretch (1525 cm^{-1}) relative to a constant intensity reference band with increasing doses of UV radiation[8]. Only the data corresponding to 5-20% conversion was used to determine the quantum yield. At higher conversion values an inner filter effect due to the photoproducts is observed. At lower conversion, observed values show significant scatter due to the limited sensitivity of the quantitative infrared measurement. The quantum yield was evaluated by plotting the log of quantum yield against the number of quanta absorbed, followed by back extrapolation to the point of zero quanta absorbed after correction for any internal filtering by the o-nitrosobenzaldehyde by-product.

Figures 3 and 4 show the data used for quantum yield measurements at 254 and 313 nm respectively for both polymers **3** and **4**. The values that are obtained are in good agreement with those obtained for model compound **5** which shows quantum yields of 0.10 at 254nm and 0.06 at 313nm. This suggests that the different copolymer backbones do not interfere in the photocleavage of the o-nitrobenzyl pendant group. All of the various quantum yields are also in agreement with those measured previously for aliphatic based 2-nitrobenzyl carbamates[6]. It might therefore be possible to increase the quantum yield of deprotection for polymers derived from **1** and **2** through incorpora-

6

tion of the more efficient 2,6-dinitrobenzyl chromophore[6] which has afforded quantum yields as high as 0.62.

Imaging

The introduction of photocrosslinkable groups in polymers has been used for a large number of curing or imaging processes. While low molecular weight amines[13] or acids[14] have frequently been used to crosslink reactive polymers, there are no previous examples of photoactivated *polymeric* amines as curing agents. Having demonstrated that both polymers **3** and **4** can be activated photochemically to structures **1** and **2** containing free amino groups, imaging of the two polymers was attempted using a simple *bis*-epoxide as the crosslinking agent. Since the two photoactive copolymers contain a relatively high proportion of photolabile carbamate groups, their photocuring should be easily achieved by exposure to light of the appropriate wavelength. Films containing copolymer **3** or **4** as well as the *bis*-epoxide **8** (Scheme IV) in 2-methoxy-ethyl ether were spin-coated onto silicon wafers and the solvent was evaporated. The molar ratio of photoactive carbamate groups to *bis*-epoxide **8** was chosen as 4:1. The films were then exposed to UV light (below 300 nm) to free the amino groups. Cross-linking occurs in a subsequent heating step during which the exposed film is heated to 120°C for 10 minutes. Development of resulting negative image was accomplished using a 1:1 mixture of 2-propanol and chlorobenzene to remove the unexposed film. Dosages equivalent to 15-25% deprotection of the amino groups were required to retain 90% of the film thickness upon image development. In addition, line-widths as small as 0.5 μm were formed using copolymer **4**. For example figure 5 shows a negative image obtained by UV crosslinking of polymer **4** with the *bis*-epoxide **8**, followed by solvent development. As expected similar imaging results were also obtained with copolymer **3**.

CONCLUSIONS.

The use of photolabile amino protecting groups in functional polymers has been demonstrated. Attachmnent of classical chromophores such as the 2-nitrobenzylcarbamoyl group to a polymer backbone does not appear to affect their subsequent photochemical cleavage in solution and in the solid state. The quantum yields for the cleavage of polymer-bound chromophores is essentially the same as is observed for corresponding model compounds. The usefulness of polymeric amines has been demonstrated in their application as a radiation-sensitive imaging system. Other applications as curing promoters or catalysts in a variety of photoactive systems are under investigation

EXPERIMENTAL PROCEDURES

General

Melting points were recorded on Gallenkamp melting point instrument and are uncorrected. Infrared spectra were obtained on KBr disks using a Nicolet FTIR/44 Spectrometer. Ultraviolet-visible spectra were measured in THF solution using a Nicolet 9430 Spectrometer. ^{1}H NMR and ^{13}C spectra were recorded using $CDCl_3$ or CD_2Cl_2 solutions with an IBM-Bruker AF 300 FT-NMR spectrometer (300.13 MHz and 75.47 MHz for ^{1}H and ^{13}C nuclei, respectively) using the solvent proton signal as standard. Spectral assignments were made according to the structural representations given in Scheme V. GC-MS spectra were obtained from a Hewlett-Packard 5890 GC-MS.

Size exclusion chromatography was carried out on a Nicolet LC/9560 Liquid Chromatograph connected to a Milton Roy refractoMonitor IV refractive index detector, data analysis was performed using Viscotek GPC-PRO software. Five PL gel 10μm GPC/SEC columns (300x7.7 mm Polymer Laboratories) connected in series in order of

decreasing pore size were used with THF as solvent, and column calibration involved the use of narrow dispersity polystyrene standards. Solution photolyses were performed in ESR quartz tubes using a Rayonet photochemical chamber reactor (RPR100) equipped with 300 nm ultraviolet lamps. Microanalyses were performed by M.H.W. Laboratories, Phoenix, AZ.

Quantum Yield Determination

a)Sample Preparation

The samples used to determine quantum yields were prepared in the following manner. For the model compound, poly(methyl methacrylate) (20 wt%) was dissolved in 2-methoxyethyl ether and 10 mol% (relative to polymer repeating unit) of N-(2-nitrobenzyloxycarbonyl)aniline was added. Copolymers **3** and **4** were used as 20% solutions in 2-methoxyethyl ether. Films were prepared from all of the polymer solutions by spin-coating onto standard 25 mm diameter sodium chloride, silicon, and quartz disks with a Headway Research spin-coater. All films were dried at 90°C for 30 min and then in *vacuo* for 12h. Film thicknesses were measured on a Tencor Alpha-Step and were between 0.9-1.1μm.

Evaluation of Quantum Yield

Quantum yield measurements were performed using quantitative infrared spectroscopy as detailed previously[6]. The asymmetric nitro absorbance (1525 cm^{-1}) was measured with respect to the carbonyl absorbance (1775-1765 cm^{-1}) for the model compound **5** and for copolymer **4**. For copolymer **3**, the same nitro band was monitored with respect to the out of plane aromatic ring bending absorbance (698 cm^{-1}).

Preparation of N-(2-nitrobenzyloxycarbonyl)aniline. 5

To a solution of 2-nitrobenzyl alcohol (3.06g, 20.0mmol) in dry tetrahydrofuran (10mL) under nitrogen was added an ethereal solution of methyl lithium (1.5M, 1.35mL, 2.02mmol) dropwise. The reaction mixture was stirred for 4h and a solution of phenyl isocyanate (2.28mL, 2.46g, 20.6mmol) in dry tetrahydrofuran (10mL) was then added dropwise. After addition was complete, the mixture was heated at reflux for 10h. After cooling to room temperature, the reaction mixture was concentrated in vacuo, dissolved in ether (50mL) and washed with water (2x20mL) and brine (1x20mL). The crude product was purified by recrystallization (hexanes/ether) to yield the desired carbamate $\underline{5}$ as a light brown solid (2.82g, 51%): mp 124-127°C.

Analysis(%): Calculated for $C_{14}H_{12}N_2O_4$(272.26): C, 61.76; H, 4.44; N, 10.29. Found C, 62.00; H, 4.53; N, 10.43.

IR: 3342 (m, N-H str), 1727 (s, C=O str), 1528 (s, asym. N-O str), 1343 cm^{-1} (m, sym. N-O str).

^{1}H NMR (See Scheme V); δ (ppm): 5.61 (2H, s, H_g), 6.73-6.85 (1H, br s, H_e), 7.10 [1H, t (J=7 Hz), H_a], 7.33 [2H, t (J=7 Hz), H_b], 7.39 [2H, d (J=9 Hz), H_c], 7.46-7.51 (1H, m, H_j), 7.64 [2H, d (J=6 Hz), H_k,H_i], 8.11 [1H, d (J=8 Hz), H_l].

^{13}C NMR; δ (ppm): 63.46 (C_g), 118.72 (C_c), 123.69 (C_a), 124.96 (C_l), 128.35-129.07 (C_b, C_i, C_k), 132.51 (C_j), 133.74 (C_h), 137.40 (C_d), 147.33 (C_m), 152.80 (C_f).

Preparation of poly(p-aminostyrene-co-styrene). 1

To a solution of p-amino styrene (1.04g, 8.73mmol) and styrene (6.98g, 67.0mmol) in dry tetrahydrofuran (8.0mL) was added 2,2'-azobis(2-methylpropionitrile) (0.60g, 0.365mmol). The reaction mixture was stirred for two hours under nitrogen and then heated at 73°C for 24h. The resulting copolymer was purified by precipitation into hexanes, filtered and dried in vacuo for 12h to yield the desired copolymer $\underline{1}$ as a white powder (5.26g, 66%). GPC: M_n = 23000; M_w = 45000.

10

Analysis(%): Calculated for $(C_8H_9N)_{0.14}(C_8H_8)_{0.86}$: C, 90.31; H, 7.84; N, 1.97. Found C, 90.12; H, 7.85; N, 1.95.

IR: 3360 (m, asym. N-H str), 3374 cm^{-1} (m, sym. N-H str).

^{1}H NMR (See Scheme V); δ (ppm): 0.73-1.69 (H_b,$H_{b'}$), 1.69-2.36 (H_a, $H_{a'}$), 3.18-3.63 (H_g), 6.09-6.86 (H_e, H_i), 6.86-7.24 (H_d, H_j, H_k).

^{13}C NMR; δ (ppm): 39.32-40.21 (C_a, $C_{a'}$), 40.21-46.31 (C_b, $C_{b'}$), 115.01 (C_e), 125.60 (C_k), 126.86-129.54 (C_d, C_i, C_j), 136.33 (C_c), 143.91 (C_f), 145.37 (C_h).

Preparation of poly(p-aminostyrene-co-methylmethacrylate). 2

To a solution of p-aminostyrene (0.80g, 6.71mmol) and methylmethacrylate (6.66g, 66.5mmol) in dry tetrahydrofuran (7.1mL) was added 2,2'-azobis(2-methylpropionitrile) (0.12g, 0.731mmol). The reaction mixture was stirred for two hours under nitrogen and then heated at 73°C for 24h. The resulting polymer was purified by precipitation into methanol, filtered and dried in vacuo for 12h to yield the desired copolymer **2** as a white powder (6.14g, 82%). GPC: M_n = 22500; M_w = 36000.

Analysis(%): Calculated for $(C_8H_{10}N)_{0.096}(C_5H_8O_2)_{0.904}$: C, 62.24; H, 8.09; N, 1.32. Found C, 62.10; H, 7.96; N, 1.29.

IR: 3445 (m, asym. N-H str), 3375 (m, asym. N-H str), 1731 cm^{-1} (s, C=O str).

^{1}H NMR (See Scheme V); δ (ppm): 0.48-1.36 (H_h), 1.36-2.05 (H_b, $H_{b'}$), 2.23-3.76 (H_a, H_g, H_j), 6.41-6.57 (H_e), 6.66-6.79 (H_d).

^{13}C NMR; δ (ppm): 16.32-21.13 (C_h), 44.38-45.56 (C_a, $C_{a'}$), 50.56-54.49 (C_b, $C_{b'}$), 51.68 (C_j), 114.34-115.10 (C_e), 128.67-129.42 (C_d), 136.54 (C_c), 144.44 (C_f), 176.23-178.11 (C_i).

Preparation of the N-(2-nitrobenzyloxycarbonyl) derivative of poly(p-aminostyrene-co-styrene). 3

To a solution of poly(p-aminostyrene-co-styrene) (**1**, 3.02g, 23.0mmol) in dry tet-

11

rahydrofuran (10mL) under nitrogen at 0˚C was added dropwise a solution of 2-nitro-benzylchloroformate (2.51g, 8.41mmol) in dry tetrahydrofuran (10mL). After addition was complete, a solution of triethylamine (1.13g, 11.2mmol) and dimethylaminopyridine (0.0683g, 0.560mmol) in dry tetrahydrofuran (10mL) was added dropwise. The reaction was then stirred at 0˚C for 2h, slowly brought to room temperature, and refluxed for 1h. The resulting material was purified by precipitation into methanol, filtered, reprecipitated, and dried in vacuo for 12h to yield the desired copolymer $\underline{3}$ as a white powder (1.74g, 84%). GPC: M_n = 30000; M_w = 60000.

Analysis(%): Calculated for $(C_{16}H_{14}N_2O_4)_{0.14}(C_8H_8)_{0.86}$: C, 84.75; H, 6.89; N, 3.03. Found C, 84.84; H, 6.80; N, 3.10.

IR: 3394 (m, N-H str), 1743 (s, C=O str), 1524 (s, asym. N-O str), 1345 cm^{-1} (m, sym. N-O str).

^{1}H NMR (See Scheme V); δ (ppm): 0.73-1.69 (H_b, $H_{b'}$), 1.69-2.36 (H_a, $H_{a'}$), 5.51-5.73 (H_m), 6.20-6.87 (H_d, H_i), 6.87-7.39 (H_e, H_g ,H_j, H_k), 7.39-7.51 (H_p), 7.51-7.72 (H_o, H_q), 8.04-8.18 (H_r).

^{13}C NMR; δ (ppm): 39.54-41.60 (C_a, $C_{a'}$), 40.60-47.05 (C_b, $C_{b'}$), 63.51 (C_m), 118.25 (C_e), 125.09 (C_r), 125.70 (C_k), 126.86-128.54 (C_d, C_j, C_i), 128.80-129.10 (C_o, C_q), 132.92 (C_p), 133.78 (C_n), 135.43 (C_f), 145.11-145.72 (C_c, C_h), 147.96 (C_s), 152.94 (C_l).

Preparation of the N-(2-nitrobenzyloxycarbonyl) derivative of poly(*p*-aminosty-rene-co-methylmethacrylate), 4

To a solution of poly(*p*-aminostyrene-co-methylmethacrylate) (**2** 5.02g, 49.2mmol) in dry tetrahydrofuran (20mL) under nitrogen at 0˚C was added dropwise a solution of 2-nitrobenzylchloroformate (2.12g, 7.11mmol) in dry tetrahydrofuran (10mL). After addition was complete, a solution of triethylamine (0.95g, 9.39mmol) and dimeth-ylaminopyridine (0.083g, 0.66mmol) in dry tetrahydrofuran (10mL) was added dropwise. The reaction was then stirred at 0˚C for 2h, slowly brought to room temperature, and

12

refluxed for 1h. The resulting polymer was purified by precipitation into hexanes, filtered and dried in vacuo for 12h to yield the desired copolymer **4** as a white powder (5.31g, 83%). GPC: M_n = 31000; M_w = 47000.

Analysis(%): Calculated for $(C_{16}H_{14}N_2O_4)_{0.096}(C_5H_8O_2)_{0.904}$: C, 61.05; H, 7.26; N, 2.26. Found C, 60.91 H, 7.25; N, 2.09.

IR: 3343 (m, N-H str), 1727 (s, C=O str), 1526 (s, asym. N-O str), 1345 cm^{-1} (m, sym. N-O str).

^{1}H NMR (See Scheme V); δ (ppm): 0.48-1.36 (H_h), 1.36-2.10 (H_b, $H_{b'}$), 2.23-3.76 (H_a, H_j), 5.52-5.60 (H_l), 6.81-7.03 (H_d), 7.06-7.34 (H_e, H_g), 7.47-7.56 (H_o), 7.62-7.71 (H_n, H_p), 8.08-8.16 (H_q).

^{13}C NMR; δ (ppm): 15.73-19.82 (C_h), 43.50-46.01 (C_a, $C_{a'}$), 50.01-55.35 (C_b, $C_{b'}$) 51.72 (C_j), 63.40 (C_l), 118.57 (C_e), 125.00 (C_q), 128.18-129.55 (C_d, C_n, C_p), 132.63 (C_o), 133.77 (C_m), 135.62 (C_f), 141.32 (C_c), 147.83 (C_r), 153.05 (C_k), 176.91-178.32 (C_i).

Imaging Experiments

Films of polymers **3** or **4** were spin coated onto silicon wafers from 20wt% solution containing *bis*-epoxide **8** (25 mol% with respect to photoactive carbamate groups in **3** or **4**) in 2-methoxyethyl ether. After pre-baking at 90°C for 30 min the films were exposed to 254nm light through a quartz mask. Postbaking was done at 120°C for 10 min. Development was achieved by dipping the wafers in a 1:1 mixture of 2-propanol and chlorobenzene until the unexposed areas of the film were removed.

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zation facility.

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FIGURE CAPTIONS

Figure 1. Change in NMR spectra of **3** in CD_2Cl_2 solution with increasing dose (310nm). *(a)* starting material; *(b)* 54% conversion; *(c)* 74% conversion; *(d)* 100% conversion.

Figure 2. Change in infrared carbonyl and nitro absorption of **3** in the solid state with increasing dose (313nm). *(a)* Prior to irradiation *(b)* After $0.65J/cm^{-2}$ *(c)* After $1J/cm^{-2}$ *(d)* After $1.5J/cm^{-2}$ *(e)* After $3J/cm^{-2}$ *(f)* After $4J/cm^{-2}$ *(g)* After $8J/cm^{-2}$.

Figure 3. Quantum yield determination in the photolyses of **3** and **4** at 254nm.

Figure 4. Quantum yield determination in the photolyses of **3** and **4** at 313nm.

Figure 5. Scanning electron micrograph of a negative-tone image obtained by irradiation of polymer **4** and *bis*-epoxide **8** in the deep UV.

Scheme I

Scheme II

HO—CH₂–(2-NO₂-C₆H₄) + C₆H₅–NCO →[MeLi] C₆H₅–NH–C(=O)–O–CH₂–(2-NO₂-C₆H₄)

5
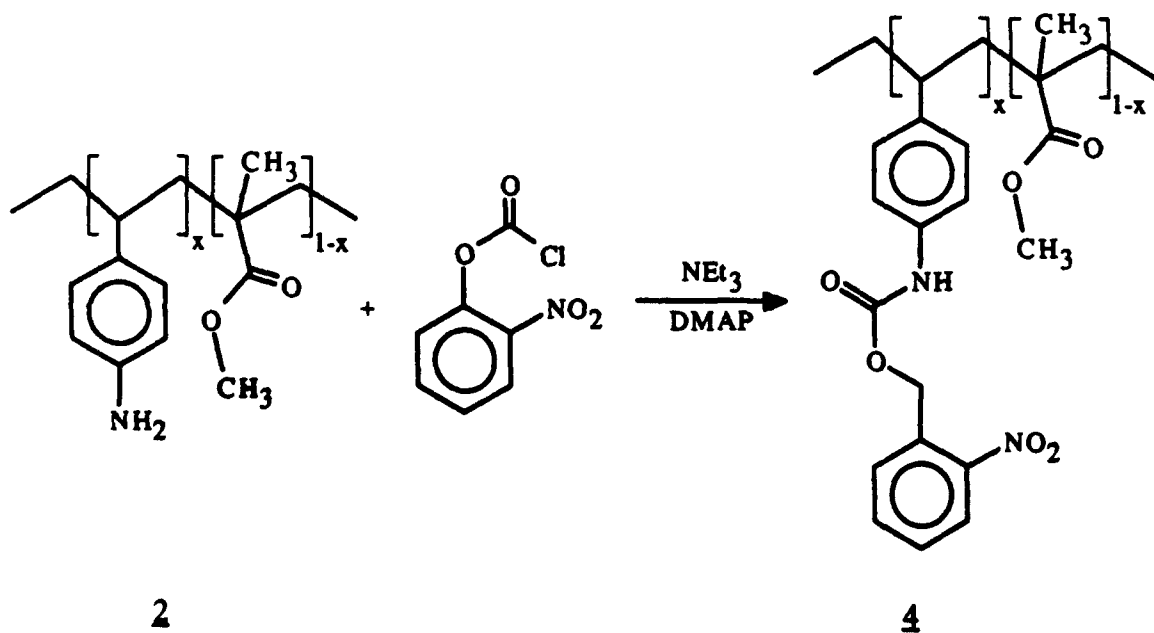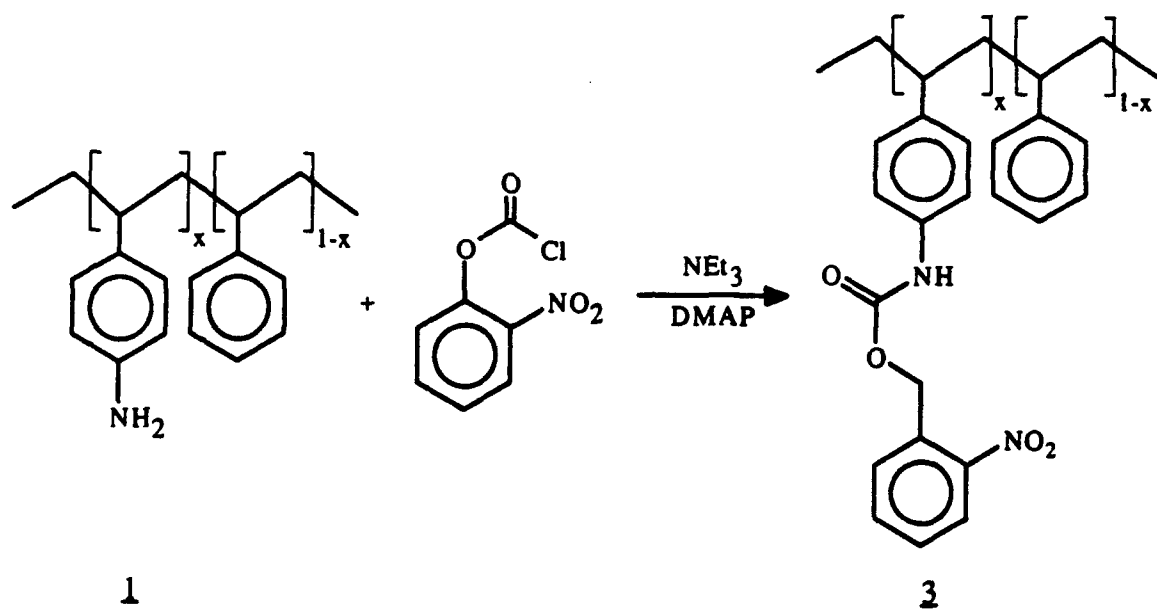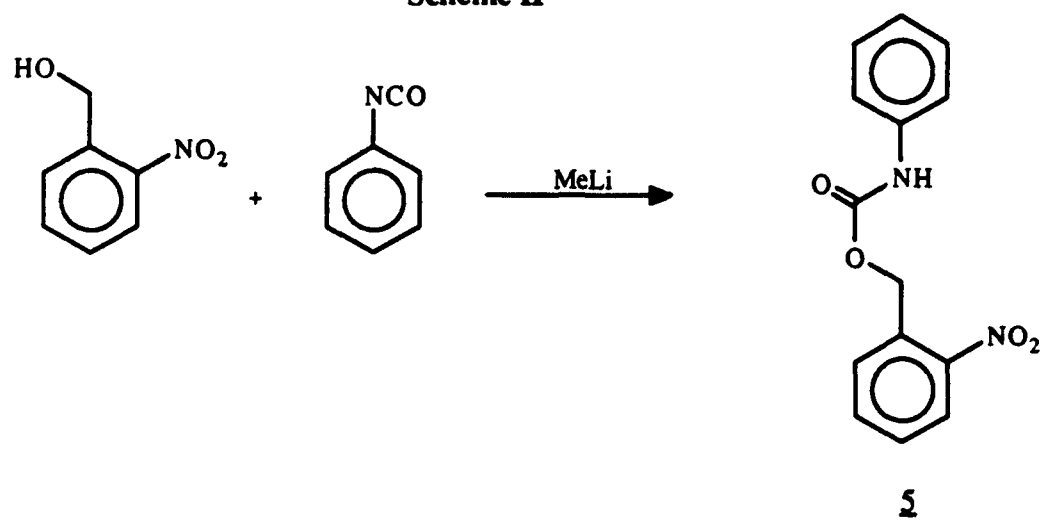
Scheme III

Scheme IV

$$CO_2 + $$

3, 4

1, 2
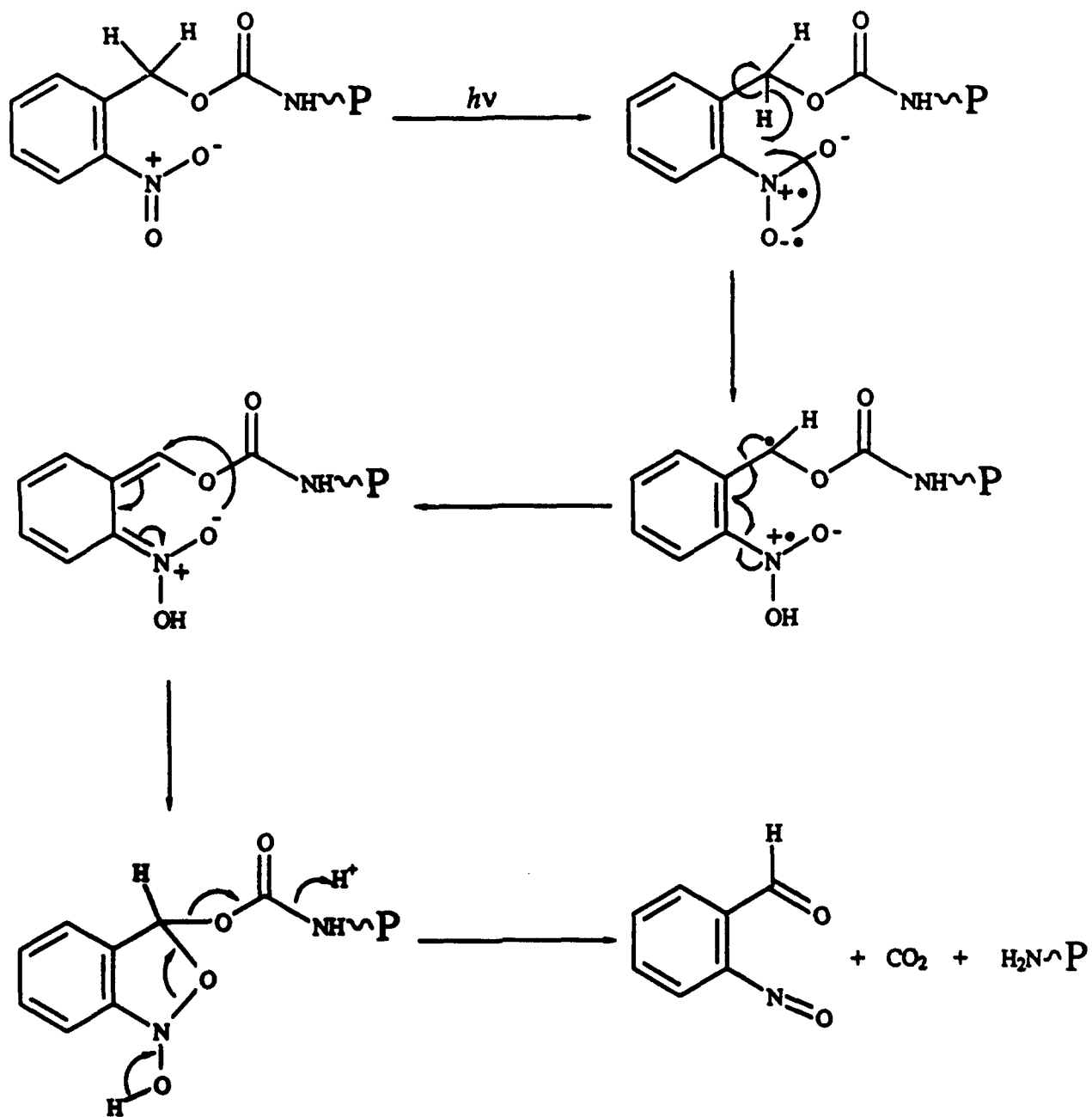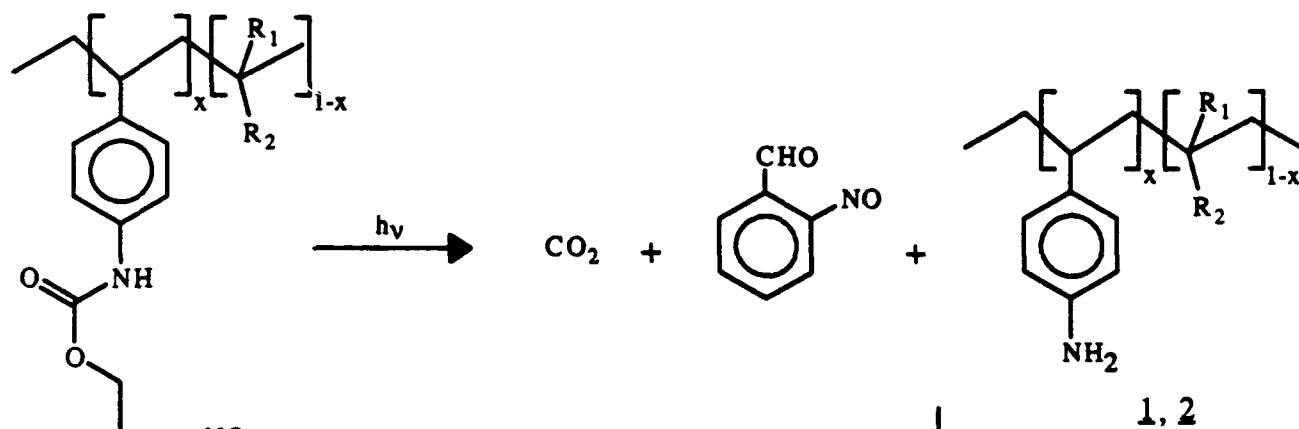
1, 3, 6 : $R_1 = H$, $R_2 = Ph$
2, 4, 7 : $R_1 = CH_3$, $R_2 = COOCH_3$

6, 7

8

Scheme V

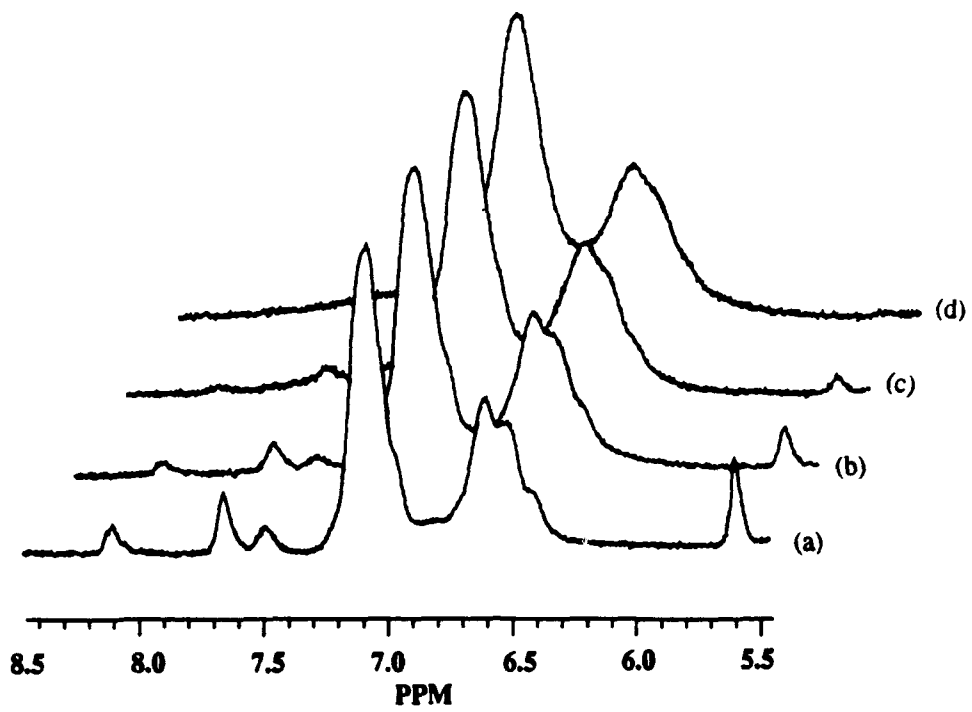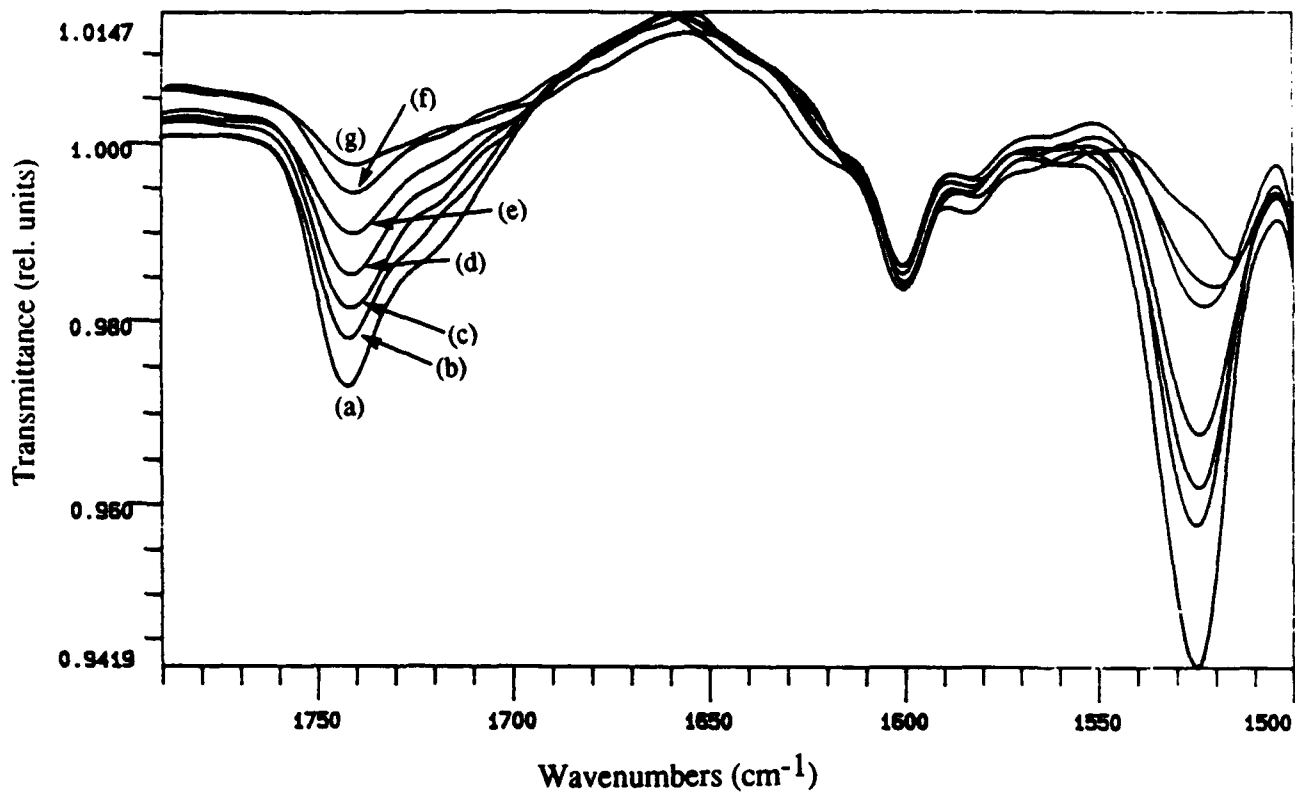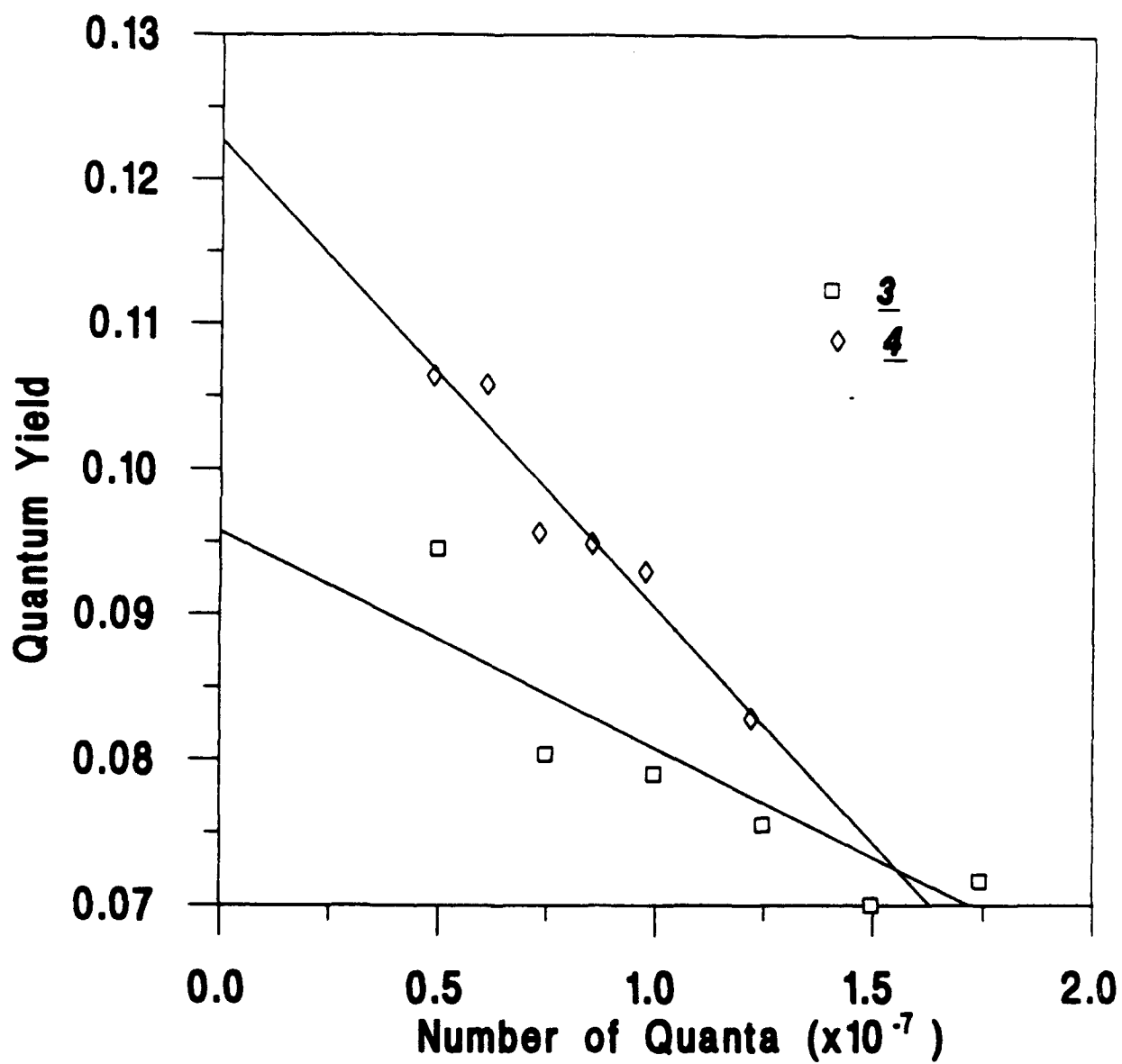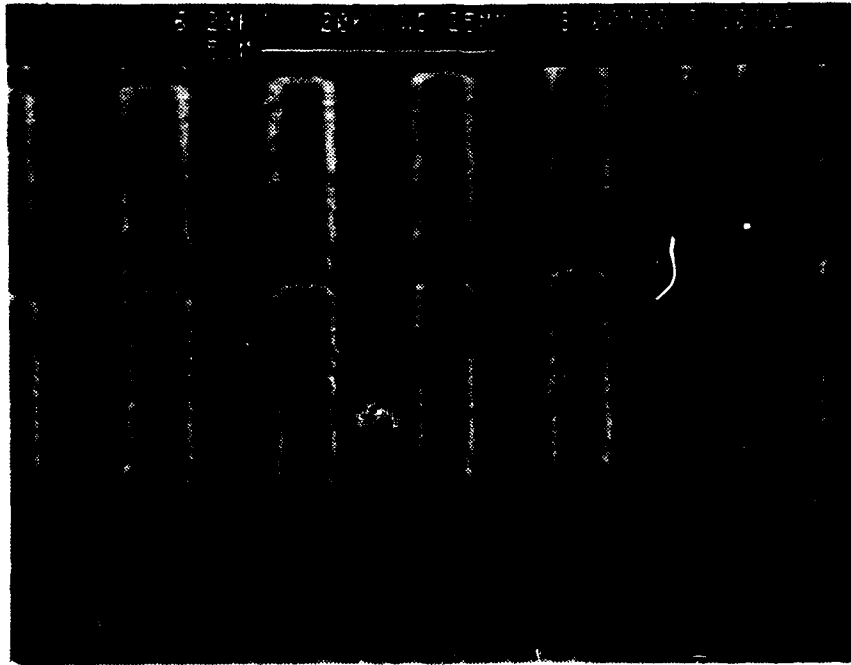8.5   8.0   7.5   7.0   6.5   6.0   5.5

PPM
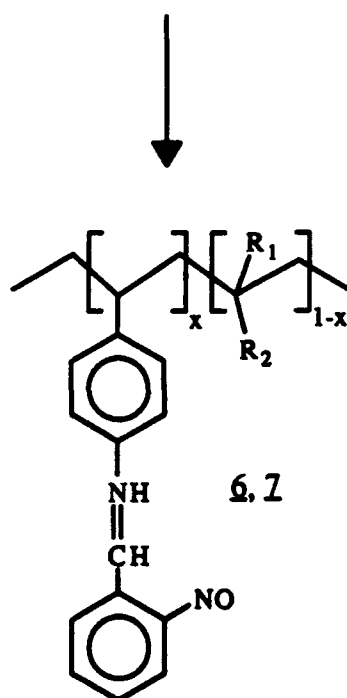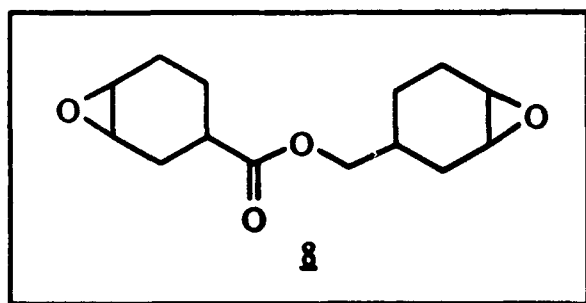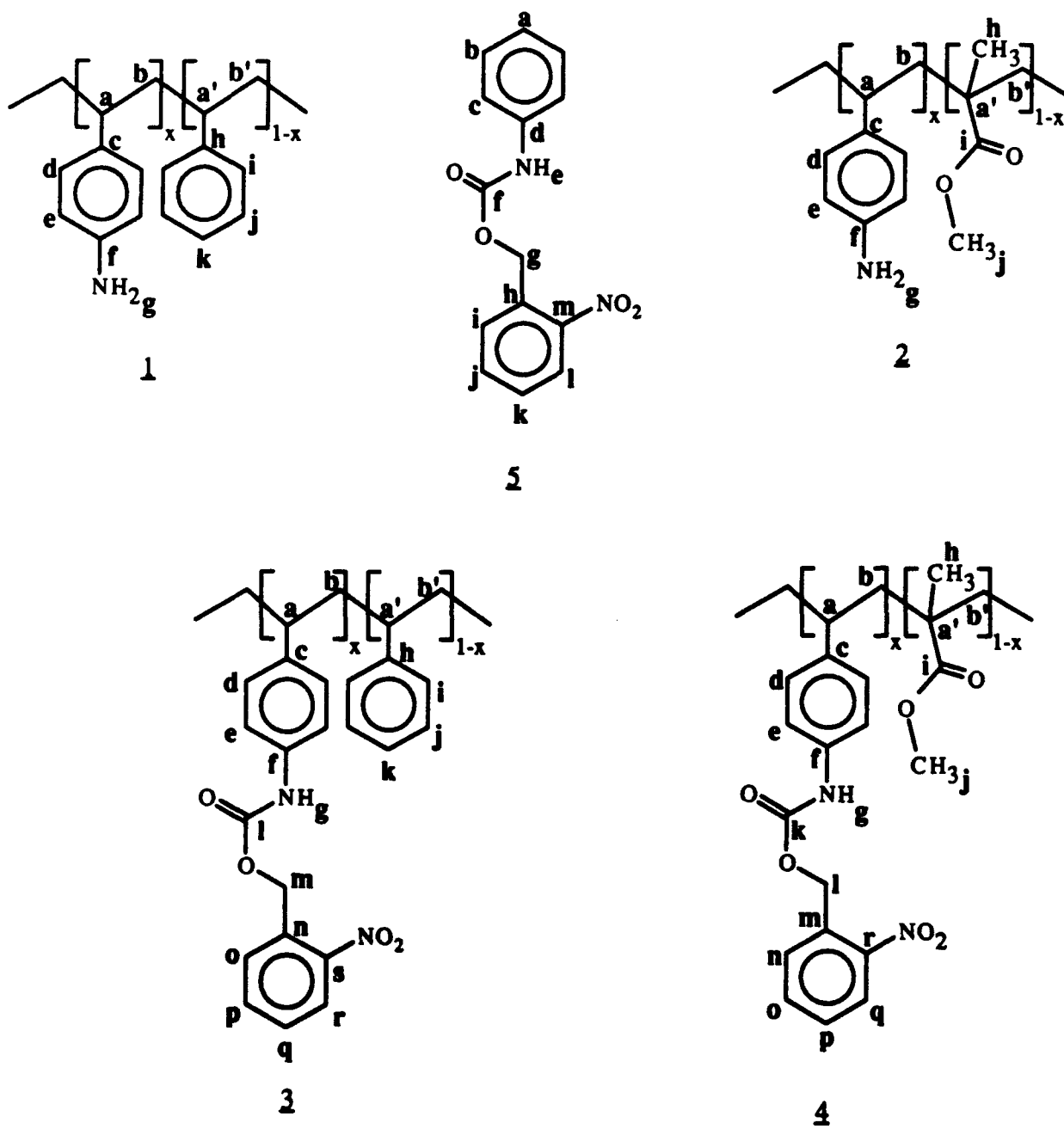
Figure 1

Figure 2

Figure 3

Figure 4

FIGURE 5