group IV element present had greatly diminished compared with that present before oxidation.

Since chemical oxidation apparently resulted in cleavage of the group IV element, it was anticipated that electrochemical oxidation would produce a similar outcome; this proved to be the case. The solid poly(2,5-(dimethylsilyl)thiophene, poly(2,5-(dimethylgermyl)thiophene and poly(2,5-(dimethylstannyl)thiophene) dissolved in $CHCl_3$ to give nonconductive solutions. With $TBAPF_6$ as supporting electrolyte, cyclic voltammetric scans to as high as 2.8 V failed to produce a film on a Pt electrode. However, in $TBAPF_6$/nitrobenzene, the polymers (except poly(2,5-(dimethylstannyl)thiophene)) underwent electrooxidation, showing a typical nucleation loop similar to that observed for monomeric thiophenes, which resulted in the formation of free-standing films that were easily removed from the ITO electrodes. The electrochemical data are shown in Table I. The electrochromic polymers are red in the reduced state and deep blue in the oxidized state with conductivities in the range of 2.1–9.2 S cm^{-1}. EDAX studies on the films show that there is no measurable Si or Ge present in the oxidized materials in contrast to the original polymers (Table II). These results indicate that the polymer is probably made up of thiophene units only; the measured sulfur/phosphorus ratios are consistent with a doping level of about 20%. On the basis of our experience with thiophenes substituted with groups containing group IV elements and the work of Lemaire et al.[9] in which 2,5-bis(trimethylsilyl)thiophene was used as a precursor for the formation of well-defined polythiophene, these results are not surprising and raise questions concerning the nature of the material prepared by chemical oxidation by $NOBF_4$.[16]

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The support of the Wake Forest Research and Creative Activities Fund is gratefully acknowledged. We thank Mr. Tim Prater of Micromed, Bowman Gray School of Medicine, Wake Forest University, for instruction in the use of the scanning electron microscope equipped with EDAX.

Registry No. H_3GeCl, 13637-65-5; $(CH_3)_3PbCl$, 1520-78-1; $(CH_3)_3SiCl$, 75-77-4; 3-(trimethylgermyl)thiophene, 100099-21-6; 3-bromothiophene, 872-31-1; bromotrimethylgermane, 1066-37-1; 3-germylthiophene, 141930-56-5; 3-(trimethylplumbyl)thiophene, 141930-57-6; $((CH_3)_2GeCl_2)$(2,5-dibromothiophene) (copolymer), 141930-59-8; $((CH_3)_2GeCl_2)$(2,5-dibromothiophene) (SRU), 141930-65-6; $((CH_3)_2SnCl_2)$(2,5-dibromothiophene) (copolymer), 141930-60-1; $((CH_3)_2SnCl_2)$(2,5-dibromothiophene) (SRU), 141930-66-7; 3-methylthiophene, 616-44-4; iodomethane, 74-88-4; 3-(trimethylsilyl)thiophene, 18245-17-5; 3-(trimethylstannyl)-thiophene, 70161-87-4; chlorotrimethylstannane, 1066-45-1; 2,5-bis(trimethylsilyl)thiophene, 17906-71-7; (2,5-dibromothiophene)$((CH_3)_2SiCl_2)$ (copolymer), 141930-61-2; (2,5-dibromothiophene)$((CH_3)_2SiCl_2)$ (SRU), 130904-62-0; thiophene, 110-02-1; thiophene (homopolymer), 25233-34-5; 3-bromothiophene (homopolymer), 84928-93-8; 3-methylthiophene (homopolymer), 84928-92-7; 3-trimethylsilylthiophene (homopolymer), 100099-19-2; 3-trimethylgermylthiophene (homopolymer), 141930-62-3; 3-germylthiophene (homopolymer), 141930-63-4; 2,5-bis(trimethylsilyl)thiophene (homopolymer), 141930-64-5.

Introduction of Functional Groups into Polymer Films via Deep-UV Photolysis or Electron-Beam Lithography: Modification of Polystyrene and Poly(3-octylthiophene) by a Functionalized Perfluorophenyl Azide

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Received February 12, 1992. Revised Manuscript Received May 18, 1992

A general method for the covalent attachment of functional groups to polymer films is described. The key step likely involves a C–H bond insertion reaction of a highly reactive nitrene intermediate derived from a functionalized perfluorophenyl azide (PFPA). The nitrene can be generated either by photolysis or during electron-beam lithography. Since a *N*-hydroxysuccinimide (NHS) active ester group is present elsewhere in the nitrene intermediate, this group also becomes attached covalently to the polymer and is capable of further reaction with a variety of reagents containing an amino group by way of amide formation. The methodology is illustrated by the following examples: Photolysis of a polystyrene (PS) or poly(3-octylthiophene) (P3OT) film containing 8–10 wt % of NHS-functionalized PFPA (1) resulted in the installment of the NHS groups into the polymers. Reaction of the NHS modified polymer films with amino azide **3** resulted in the introduction of azide groups into the polymers as determined by IR spectroscopy. Alternatively, electron-beam lithography of PS or P3OT films containing **1** resulted in both the introduction of NHS groups and the cross-linking of the polymers in a single step. Micron-size patterns incorporating the NHS functional groups could be produced. Treatment with amino fluorescein **7** resulted in the covalent attachment of fluorescent groups into the polymer structure.

Introduction

Functionalized polymers have been the subject of intensive research, owing to their wide application in chemistry and biology and in technologies involving ion-exchange resins, immobilized enzymes, and electrically conductive polymers.[1] Functionalized polymers can be prepared either by polymerization of functionalized monomers or by modification of polymers. Modification of polymer films or film surfaces with concomitant introduction of functional groups is important for the development of new

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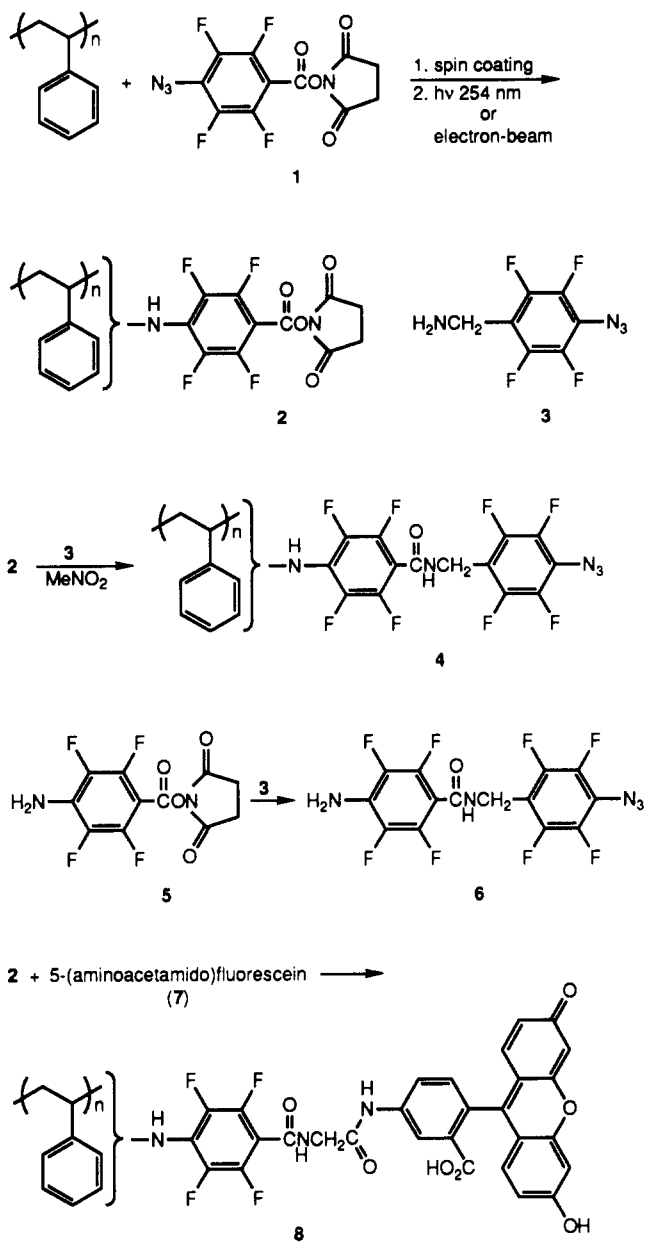
Scheme I



materials such as novel composites,[2] resist materials,[3] and biomaterials.[4] Existing methods for the modification of polymer films include sulfonation of polystyrene[5] and poly(aryloxy)phosphazenes,[6] plasma treatment of polyester,[7] base hydrolysis of polyimide[8] and polyphophazenes,[9] and base treatment of poly(vinylidene fluoride).[10]

Nitrene and carbene intermediates generated in the gas phase have been reported to modify the surface of hydrocarbon polymers such as polyethylene, presumably by a CH insertion reaction.[11,12] Difluorocarbene generated

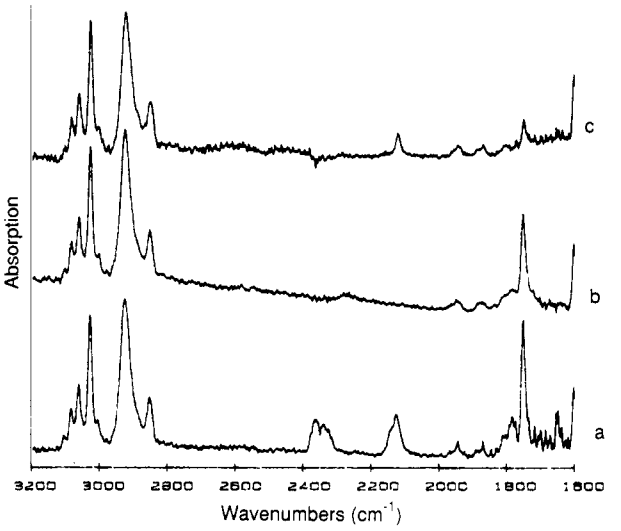


Figure 1. IR spectra of polystyrene containing 8 wt % of NHS-PFPA 1: (a) before photolysis; (b) after photolysis; (c) after treatment with amine 3. Absorption values for b and c are offset. The peaks at 2300 cm^{-1} are from CO_2.

in solution has been reported to modify 1,4-polybutadienes.[13] We[14,15] and others[16,17] have demonstrated the improved CH insertion efficiency of perfluorophenyl azides (PFPAs) over their nonfluorinated analogues when they are photolyzed in hydrocarbon solvents such as cyclohexane or toluene. Initially the PFPAs were developed as efficient photolabeling reagents.[18-20] We have recently demonstrated that bis(PFPAs) are efficient cross-linking agents for polystyrene[21] (PS) and poly(3-octylthiophene)[22] (P3OT) and have shown their application in deep-UV and electron-beam lithography. Herein we report a general method for the introduction of functional groups into CH-bond-containing polymer films using functionalized PFPAs. We report that photolysis of either PS or P3OT films containing a few weight percent of PFPA *N*-hydroxysuccinimide (NHS) active ester 1 (Scheme I) results in the introduction of the NHS active ester functional groups into the polymers. We also report that under electron-beam lithographic conditions the polymers can be functionalized and cross-linked in a single step, resulting in micron size patterns incorporating these functional groups.

Results and Discussion

Our first objective was to determine whether functionalized PFPAs can be used to modify hydrocarbon polymer such as PS and P3OT by CH insertion of the photochemically generated nitrene intermediates in the solid state. The active ester 1, formed by esterification of *N*-hydroxysuccinimide (NHS) with 4-azido-2,3,5,6-tetra-

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fluorobenzoic acid, was selected among our available functionalized PFPAs[15] because NHS active esters react readily with amine-containing reagents to form amides. This general reaction might then permit ready synthesis of a host of functionalized polymers depending on which functional groups were present elsewhere in the amine-containing molecules.

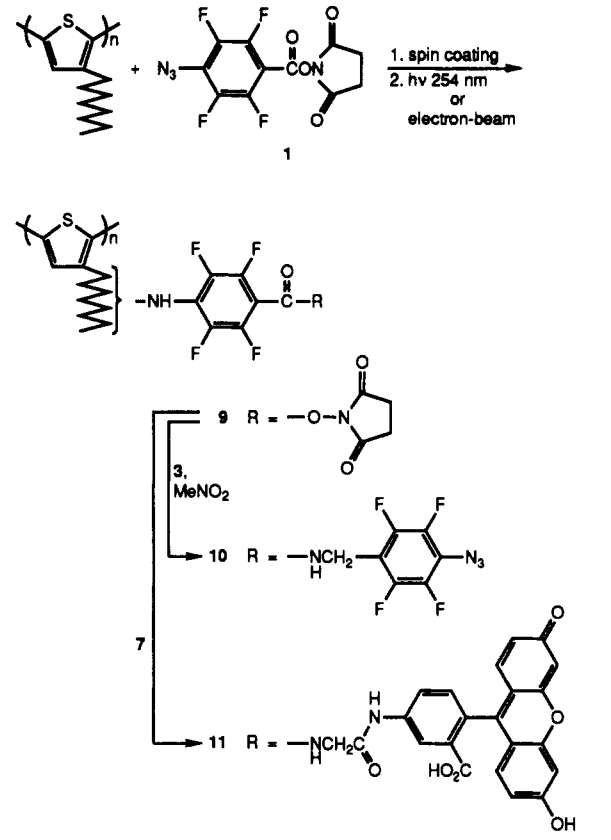
In the event, photolysis (254 nm) of a PS film containing 8 wt % of 1 resulted in the smooth decomposition of the azide group in 1 over 1.5 min with concomitant formation of the functionalized polymer 2 derived from a C–H insertion reaction. The photolysis was monitored by the disappearance of the azide absorption at 2124 cm^{-1} (Figure 1, part a vs b). The active ester carbonyl absorption around 1750 cm^{-1} was not affected by the photolysis reaction. Next, the photolyzed film 2 was treated at room temperature over 2 h with a solution of 4-azido-2,3,5,6-tetrafluorobenzylamine (3)[15] in nitromethane, a solvent which does not dissolve the polymer. The coupling reaction was monitored by IR spectroscopy which revealed the reappearance of azide absorption at 2121 cm^{-1} and a decrease in the absorption at 1750 cm^{-1} attributed to the carbonyl group of the active ester (Figure 1, part b vs c). The IR spectra confirm that amine 3 has reacted with the NHS-active esters resulting in the further modification of the polymer by incorporation of the perfluorophenylazide groups along the chain to give 4. IR intensity comparison of the azide absorptions (Figure 1, part c vs a) suggest that about 40% of the original number of azide groups became incorporated as a result of the treatment of 2 with 3. This is probably due to the fact that photolysis of azide 1 in PS results in less than a 100% yield of CH insertion. It is also possible that some of the NHS groups were sterically unaccessible to amine 3 or else some of the NHS groups may have been cleaved by adventitious hydrolysis during the treatment with the solution of amine 3 in nitromethane.

The following control experiments were performed. A PS film was photolyzed in the absence of NHS-active ester 1 and treated with a solution of amine 3 in nitromethane. No azide absorption was observed in the IR spectra (not shown). Another PS film containing active ester 1 was not photolyzed but treated directly with a solution of amine 3 in nitromethane. IR spectra (not shown) revealed the disappearance of the absorption at 2124 and 1750 cm^{-1}, showing that the nitromethane had extracted essentially all of the active ester 1 or the corresponding amide out of the polymer since neither species was covalently attached to the polymer. These two control experiments showed that both the NHS-active ester 1 and photolysis are needed for the modification of the PS film with NHS-active ester groups.

We have reported previously that photolysis of methyl 4-azidotetrafluorobenzoate in toluene gave products derived from CH insertion into the aromatic ring and the methyl group.[15] Therefore it seems likely that both kinds of CH insertion have also occurred in PS as depicted in structure 2. Using *N*-succinimidyl 4-amido-tetrafluorobenzoate (5) as a model for 2, active ester 5 was allowed to react with amine 3 in $CDCl_3$. The reaction between 3 and 5 was monitored by ^1H NMR spectroscopy at room temperature. Amide 6 was isolated in 94% yield. The IR spectrum of 6 showed an azide absorption at 2124 cm^{-1}, which was the same as that observed in the polymer film after photolysis and reaction with amine 3.

The generality of our new polymer film functionalization methodology could be extended to the conducting polymer P3OT (Scheme II). We have demonstrated previously

Scheme II



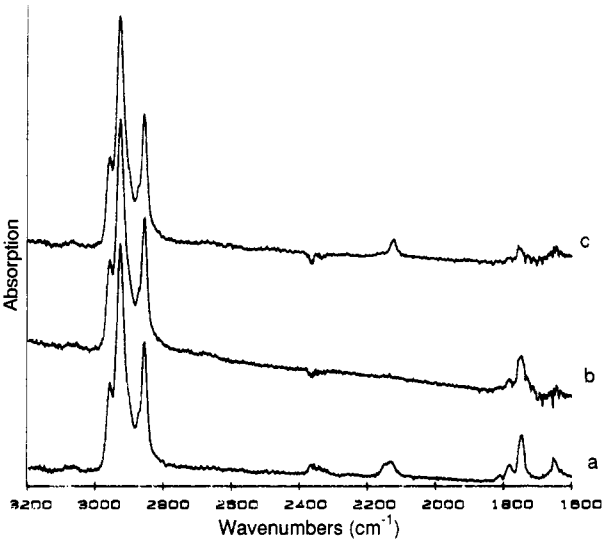


Figure 2. IR spectra of poly(3-octylthiophene) containing 10 wt % of NHS-PFPA 1: (a) before photolysis; (b) after photolysis; (c) after treatment with amine 3. Absorption values for b and c are offset.

that P3OT can be photochemically cross-linked by a bis-PFPA and that P3OT can be used for the direct production of conducting structures via cross-linking under electron-beam lithographic conditions.[22]

Photolysis of a film of P3OT containing 10 wt % 1 resulted in the decomposition of the azide group (Figure 2, part a vs b) giving functionalized polymer 9. Treatment of 9 with a solution of amino azide 3 in nitromethane resulted in polymer 10 in which amide formation between 3 and the NHS active esters (Figure 2, part b vs c) with concomitant covalent attachment of a new set of azide groups to the polymer had taken place. A control experiment involving photolysis of a P3OT film in the absence

of 1 and subsequent treatment with 3 gave no detectable incorporation of amine 3 into the polymer.

We suggest that the C–H insertion reaction giving 9 has taken place along the octyl side chain without involvement of the thiophene ring. This is based on our earlier observation that photolysis of a simple PFPA ester, methyl 4-azidotetrafluorobenzoate in cyclohexane/thiophene gave methyl 4-(cyclohexylamino)tetrafluorobenzoate as the only isolated CH insertion product.[22]

Earlier,[22] we demonstrated that P3OT could be cross-linked directly by electron-beam lithography. It occurred to us that it might be possible to use electron-beam lithography to accomplish both the cross-linking of a polymer and the introduction of NHS-active ester groups in the polymer in a single step. In the event, micron size patterns were drawn in a PS film containing 8 wt % NHS ester 1 using an electron beam. Cross-linking occurred at a dosage of about 50 μC cm^{-2}, which is lower than the dosage required for the cross-linking of PS alone (about 90 μC cm^{-2}). After observing the cross-linked sample using an optical microscope (Figure 3a), the sample was treated with a solution of 5-(aminoacetamido)fluorescein (7) in ethanol with the aim of introducing an easily visible fluorescent marker at the active ester sites. The fluorescence pattern observed under fluorescence microscope was similar to that observed under an optical microscope (Figure 3, part a vs b). As a control, micron size patterns were drawn in a PS film in the absence of 1 using an electron beam. The cross-linked sample was treated with amino-fluorescein 7 under identical conditions. No fluorescence pattern was observed under the fluorescence microscope. This control experiment demonstrated that the presence of NHS-active ester 1 was needed for the attachment of the amino fluorescein label 7 to the polymer.

Micron size patterns were drawn in a P3OT film containing 7 wt % NHS active ester 1 using an electron beam and the sample was similarly treated by fluorescein 7. It was found that P3OT itself is strongly fluorescence at the rhodamine excitation wavelength and only weakly fluorescence at the fluorescein excitation wavelength; thus, both wavelengths were used to observe the sample. An essentially identical pattern with strong fluorescence both at the rhodamine excitation wavelength (Figure 4A(a)) and fluorescein excitation wavelength (Figure 4A(b)) was observed. Last, micron size patterns were drawn in a P3OT film in the absence of 1 using an electron beam, and the sample was similarly treated with fluorescein 7. Strong fluorescence was observed at the rhodamine excitation wavelength (Figure 4B(a)), but only weak fluorescence was observed at the fluorescein excitation wavelength (Figure 4B(b)). This control experiment showed that little fluorescein 7 became attached to P3OT in the absence of the active ester groups, and thus the presence of NHS-active ester 1 is needed for the covalent attachment of 7 to P3OT.

Conclusions

We have found that photolysis of films of PS or P3OT containing 8–10 wt % of NHS-active ester 1 resulted in the covalent modification of these polymers by the NHS active ester groups. The presence of NHS groups and their accessibility for further reaction with amine-containing reagents were demonstrated by treatment of the photolyzed films with amino-PFPA 3, which resulted in the introduction to the polymer films of a new set of azide groups as determined by the IR spectroscopy. We have found that electron-beam lithography of films of PS and P3OT in the presence of NHS-active ester 1 results in both cross-linking and functionalization of these polymers in a single step, thus producing micron size patterns incorporating the NHS-active ester groups. The NHS groups were used to react with an amino fluorescein 7 and resulted in the modification of the micron size patterns by attachment of a fluorescence dye as observed under fluorescence microscope. This general method of modification of polymer films by functionalized PFPAs via photolysis or electron-beam exposure should find wide application for the introduction of functional groups into polymer films as well as for the attachment of reagents or active molecules to conducting polymer films for the preparation of conducting polymer based microelectronic devices.

Experimental Section

General Methods. Polystyrene (MW 125 000–250 000) was purchased from Polysciences Inc. Poly(3-octylthiophene) was prepared from 3-octylthiophene as reported.[22] 5-(Aminoacetamido)fluorescein (7) was purchased from Molecular Probes. IR spectra were recorded on a Nicolet 5DXB FTIR spectrometer. Photolysis was carried out in a Rayonet photoreactor with 254-nm lamps. Spin coating was done with a photoresist spinner (Headway Research Inc.) set a 1000 rpm. Films thichness was measured by ellipsometer (Rudolph Research) to be about 0.7 μm. Electron-beam exposure was carried out with a scanning electron microscope (JEOL-SEM) modified for lithography.[23] Fluorescent micrographs were obtained with a Zeiss microscope equipped with epifluorescence optics and a rhodamine filter set (excitation wavelength 510–560 nm, emission wavelength >590 nm) or a fluorescein filter set (excitation wavelength 450–490 nm, emission wavelength 515–565 nm).

***N*-Succinimidyl 4-Aminotetrafluorobenzoate (5).** A mixture of 214 mg (1.00 mmol) of 4-aminotetrafluorobenzoic acid, 119 mg (1.00 mmol) of *N*-hydroxysuccinimide, and 211 mg (1.00 mmol) of dicyclohexylcarbodiimide in 10 mL of CH_2Cl_2 was stirred for 24 h. The mixture was filtered, and the solid was dried. The solid was then stirred with acetone (6 mL), the mixture was filtered, and the filtrate was evaporated to leave 262 mg (83%) of 5 as a white solid, mp 200–201 °C: ^{1}H NMR, δ 2.899 (s, 4), 4.665 (s, 2); IR 3522, 3418, 1779, 1749, 1683, 1530, 1507, 1317 cm^{-1}; MS 306 (M$^+$, 2), 192 (100), 164 (30).

***N*-(4-Azidotetrafluorobenzyl)-4-aminotetrafluorobenzamide (6).** A mixture of 11 mg (0.036 mmol) of 5 (not all the 5 dissolved in $CDCl_3$) and 6.9 mg (0.031 mmol) of amine 3 in $CDCl_3$ (0.5 mL) was prepared, and the reaction was followed by ^{1}H NMR. New signals at δ 4.7 (d) were observed. A clear solution was obtained in 24 h, and the ^{1}H NMR spectrum shown no more signal at δ 3.941 for 3 and δ 2.899 for 5. The mixture was separated by preparative TLC (hexane–THF 1:1) to give 12 mg (94%) of 6 as a white solid, mp 155–156 °C (decomposition): ^{1}H NMR δ 4.286 (s, 2), 4.701 (d, 2), 6.402 (m, 1); IR 3411, 2122, 1686, 1668, 1497, 1314, 1239 cm^{-1}; MS 411 (M$^+$, 1), 383 (20), 192 (100), 164 (18).

Procedure for the Modification of Polystyrene Film by NHS-Active Ester 1 and the Subsequent Reaction with Amine 3. A solution of 50.2 mg of PS and 4.0 mg of NHS ester 1[15] in 1.0 mL of xylene was spin coated on a NaCl disk and then dried at 50 °C for 1 h. The film was photolyzed for 1.5 min, after which IR spectrum showed no more azide absorption in the region of 2120 cm^{-1}. This sample of film 2 was immersed in a solution of 5.4 mg of amine 3[15] (hydrochloride salt) and 10 mg of Et_3N in 1.4 mL of $MeNO_2$ for 2 h, then removed from the solution, immersed in 40 mL of $MeNO_2$ for 10 min, rinsed by $MeNO_2$, and air dried. The IR spectrum of the resulting film 4 showed a moderately strong absorption at 2121 cm^{-1} for the azide group (Figure 1).

In a control experiment, a solution of 100 mg of PS in 2 mL of xylene was spin coated, dried, photolyzed, and treated with amine 3 under identical conditions as above. The IR spectrum showed no azide absorption.

Procedure for the Modification of Poly(3-octylthiophene) Film by NHS-Active Ester 1 and the Subsequent Reaction with Amine 3. A solution of 25.8 mg of P3OT and 2.6 mg of NHS

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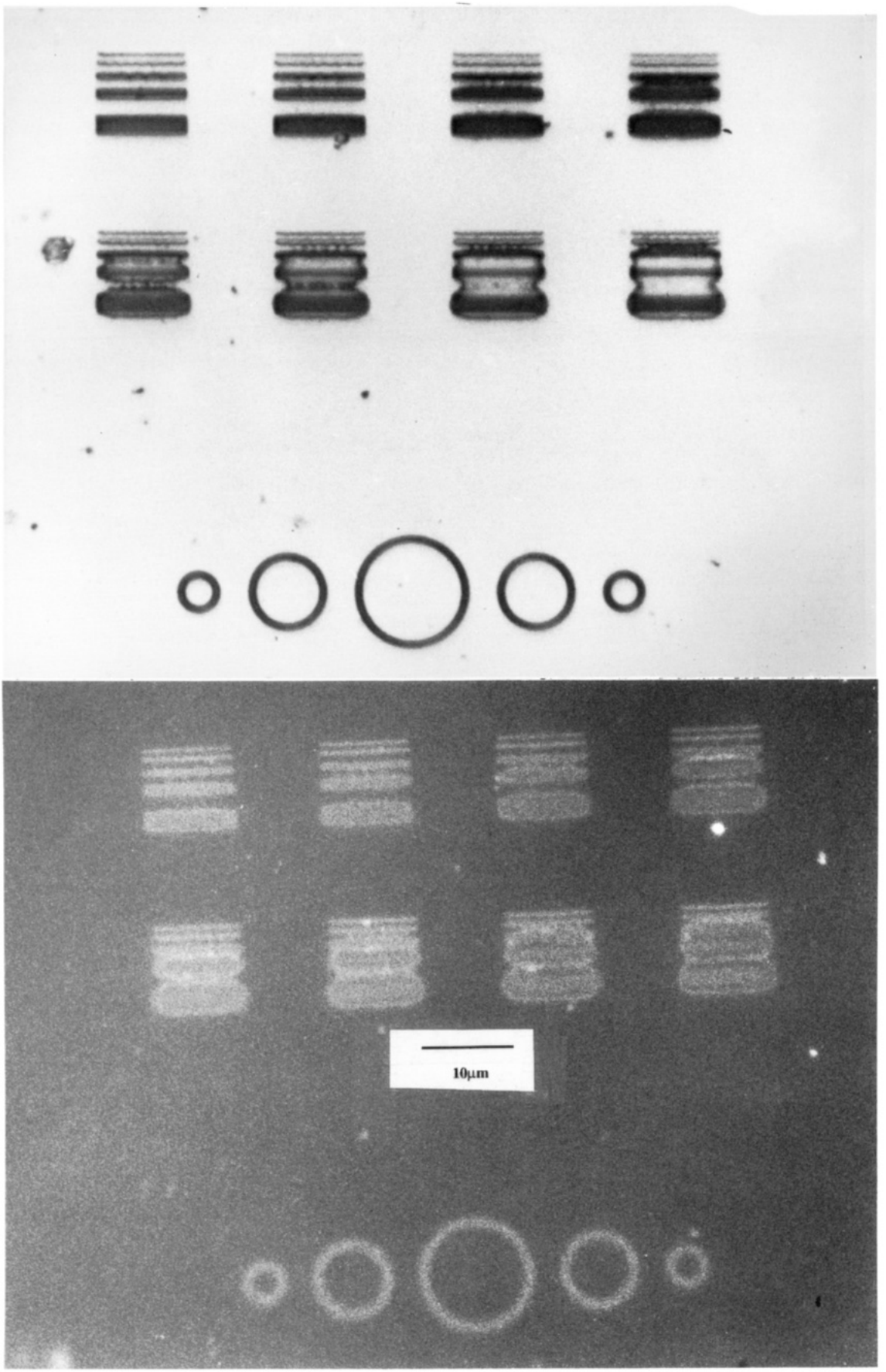

Figure 3. Micrographs taken (a, top) under an optical microscope showing the patterns produced from polystyrene containing 8 wt % 1 by electron beam lithography and (b, bottom) under a fluorescence microscope with a fluorescein filter set showing the patterns after treatment with amino fluorescein 7. The micrograph consists of eight five-line patterns. Within each pattern, the drawn line thickness are 0.1 (top), 0.2, 0.5, 1.0, and 2.0 μm. EB doses increased from left to right: top row, 50, 60, 70 and 80 $\mu C/cm^2$; bottom row, 90, 100, 110, 120 $\mu C/cm^2$. The drawn line thickness for the circles are 0.5 μm and doses are 60 $\mu C/cm^2$.

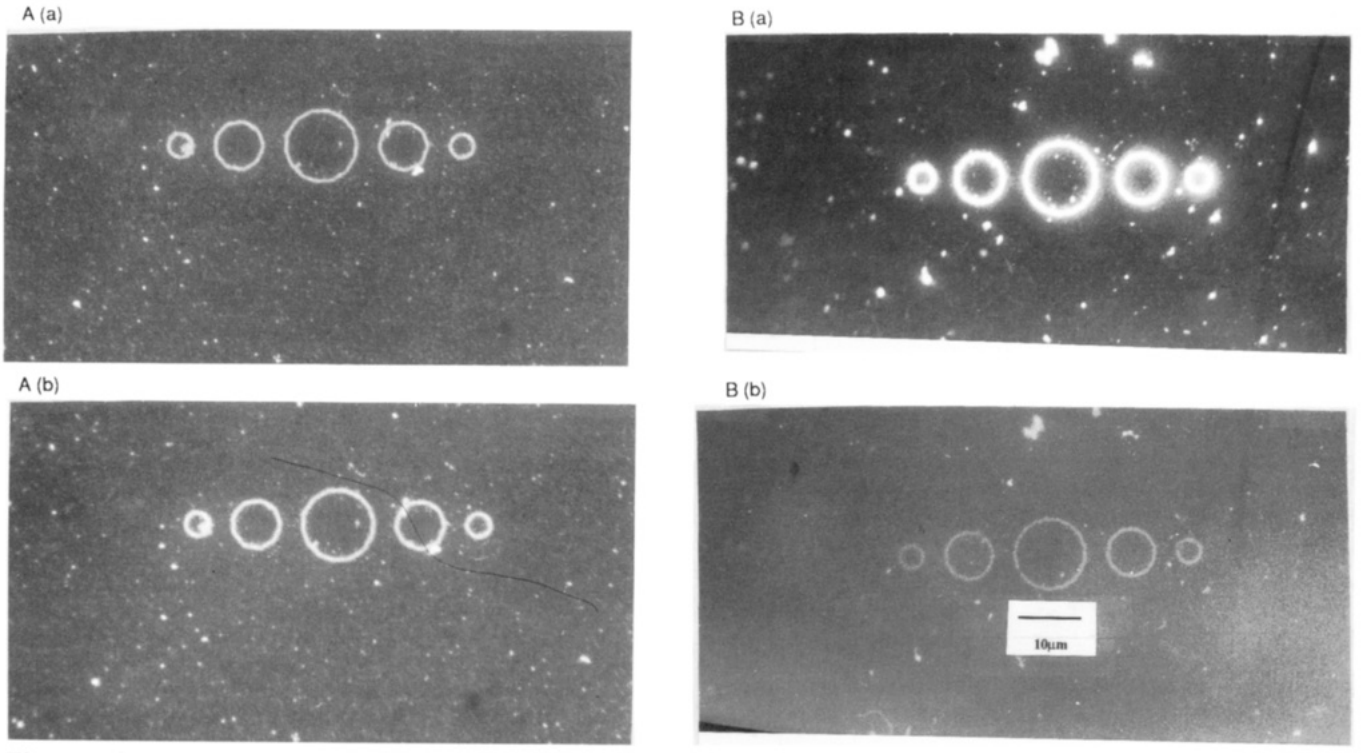

Figure 4. Micrographs taken under a fluorescence microscope (A, left) showing the patterns produced from poly(3-octylthiophene) containing 7 wt % of **1** by electron beam lithography and after treatment with amino fluorescein **7**: (a) with a rhodamine filter set, (b) with a fluorescein filter set; (B, right) showing the patterns produced from poly(3-octylthiophene) by electron beam lithography and after treatment with amino fluorescein **7**: (a) with a rhodamine filter set, (b) with a fluorescein filter set. The drawn line thickness for the circles are 0.5 μm and doses are (A) 20 $\mu C/cm^2$ and (B) 30 $\mu C/cm^2$.

ester **1** in 0.8 mL of xylene was spin coated, dried, photolyzed, developed to give film **9**, and treated with amine **3** under similar conditions as that of PS. The IR spectrum of the resulting film **10** showed a moderately strong absorption at 2121 cm^{-1} for the azide group (Figure 2). In the control experiment, a solution of 23.2 mg of P3OT in 0.8 mL of xylene was processed under identical conditions. No azide absorption was observed in the IR spectrum.

Procedure for the Electron-Beam Lithography of Polystyrene Film Containing NHS-Active Ester 1 and the Subsequent Reaction with Amino Fluorescein 7. A solution of 50.2 mg of PS and 4.0 mg of NHS ester **1** in 1.0 mL of xylene was spin coated on a silicon wafer. The film was baked for 35 min at 90 °C and exposed by an electron beam in a modified SEM.[23] The exposed sample was developed by dipping in xylene for 35 s, rinsing in isopropyl alcohol for 10 s, and drying with a stream of nitrogen, giving film **2**. The developed sample was photographed using an optical microscope (Figure 3a). The sample was then immersed in a solution of 2.5 mg of amino fluorescein **7** and 8.3 mg of Et_3N in 1.5 mL of EtOH for 4 h. It was washed by EtOH, immersed in EtOH for 2 h, rinsed by EtOH and air dried, giving film **8**. The sample was then observed under a fluorescence microscope with a fluorescein filter set, and the fluorescence pattern was photographed (Figure 3b). A PS film was exposed and developed under identical conditions and photographed using an optical microscope. The sample was then treated with amino fluorescein **7** as described above, and the sample was observed under the fluorescence microscope. No fluorescence pattern was observed.

Procedure for the Electron-Beam Lithography of Poly(3-octylthiophene) Film Containing NHS-Active Ester 1 and the Subsequent Reaction with Amino Fluorescein 7. A solution of 25.7 mg of P3OT and 1.8 mg of NHS ester **1** in 0.6 mL of xylene was spin coated and baked at 60 °C for 30 min and exposed by electron beam. It was developed by dipping in xylene for 10 s, rinsing in isopropyl alcohol for 10 s, and drying with a stream of nitrogen, giving film **9**. The sample was immersed in a solution of 1.5 mg of amino fluorescein **7** and 8 mg of Et_3N in 1 mL of EtOH for 4 h. It was washed by EtOH, immersed in EtOH for 1 h, washed by EtOH, and air dried, giving film **11**. The sample was observed and photographed under the fluorescence microscope using a rhodamine filter set and then a fluorescein filter set (Figure 4A). A P3OT film was exposed and developed and then treated with **7** as described above. The sample was observed and photographed under the fluorescence microscope using the rhodamine filter set and then the fluorescein filter set (Figure 4B).

Acknowledgment. This work was supported by a grant from Oregon Resource Technology Development Corp. and by NIH Grant GM 27137. We thank Dr. Karen Hedberg for her help in obtaining the fluorescent micrographs and the reviewers for their comments and suggestions.

Registry No. **3**, 126695-61-2; **5**, 142039-21-2; **6**, 142039-22-3; 4-aminotetrafluorobenzoic acid, 944-43-4; *N*-hydroxysuccinimide, 6066-82-6.