Synthesis and Photolithography of Polymers and Copolymers Based on Poly(3-(2-(methacryloyloxy)ethyl)thiophene)

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ABSTRACT: Electronically conducting polythiophenes functionalized with methacrylate side chains have been synthesized and characterized. Irradiation with UV–visible light leads to photochemical cross-linking and insolubilization of the polymer films. The minimum gel dose required to leave an insoluble residue for poly[3-(2-(methacryloyloxy)ethyl)thiophene-*co*-3-hexylthiophene] was 2.6 mJ cm^{-2} and the dose required to obtain 50% insolubilization was 24 mJ cm^{-2}. Films of the homopolymer, poly(3-(2-(methacryloyloxy)ethyl)thiophene), were lithographically more sensitive than the copolymer as indicated by the lower gel dose (1.2 mJ cm^{-2}) and lower dose required for 50% insolubilization (13.4 mJ cm^{-2}). Polymer films were imaged by conventional semiconductor photolithography. Patterned images were obtained having film thicknesses of 75 nm and a resolution of 3 μm. Films doped with gold trichloride achieved conductivities up to 12 S cm^{-1}.

Introduction

Novel electonic and microelectronic applications are emerging which utilize the unique electrical and optical properties of π-conjugated polymers. These include devices based on nonlinear optical activity,[1–4] Schottky barrier devices,[5–10] electroluminescent displays,[11–13] field effect transistors,[14–18] waveguides, and integrated circuit technologies.[19] To integrate organic components into electronic and optical devices, spatial control of deposition of the organic material is becoming increasingly important. In pursuing this, the researcher is often faced with the task of devising strategies for producing micron-sized polymer channels in a controlled, defined, and reproducible fashion.

Several reports of forming π-conjugated polymer patterns have emerged. A number employ "wet" photochemical or photoelectrochemical methods which are incompatible with present integrated circuit technologies.[20,21] Others use multistep procedures using conventional photoresists[20,22] or laser irradiation of insulating precursor polymers or appropriate composites.[23] Recently, lithographic patterning of polythiophene has been accomplished by direct deposition of polythiophene into SiO_2 trenches and by an oxygen plasma etch.[24] The patterning methods mentioned above require multistep techniques since polythiophene is insoluble and not readily processible. A simple and clean chemical system for depositing polymer wires which is compatible with conventional semiconductor photolithography has yet to be established.

Our studies in this field were initiated with a photochemical investigation of poly(3-hexylthiophene) in which we showed that thin films of soluble poly(3-hexylthiophene) undergo photoinduced cross-linking and insolubilization upon exposure to UV–visible light.[25] The irradiated regions are insoluble, and thus patterns of micron resolution can be achieved by dissolution of unexposed regions. Using this concept, π-conjugated polythiophenes have been imaged as illustrated in Figure 1.

The gel dose required for 50% gel formation was found to be 61 mJ cm^{-2} using He–Cd laser irradiation.[19] The photoimaging process occurs via a photooxidation process photoinitiated by residual transition metal impurities in the presence of oxygen and terminated by coupling of polymer-bound radicals. Photoinduced cross-linking thus requires generation of a critical, and large, concentration of free radicals.[26] Laser sources and intense UV lamps are sufficient to generate such a large concentration of radicals. However, the photoinduced cross-linking process is inherently inefficient, and we have been unsuccessful in imaging polymers using conventional semiconductor photolithographic apparatus where irradiation intensities are substantially lower than laser light or focused steady-state sources.

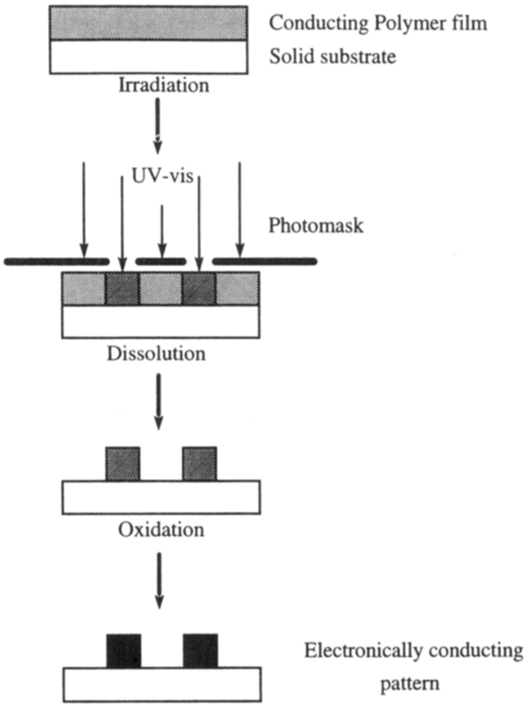

Figure 1. Photolithography of conducting polymers.

The vinyl functionality attached to the 3-position of the thienyl ring should be an excellent candidate for radical-induced cross-linking of these systems since polythiophenes are relatively inert to free radicals.[26] Zinger et al. have reported the polymerization of 3-(2-(acryloyloxy)ethyl)thiophene electrochemically and chemi-

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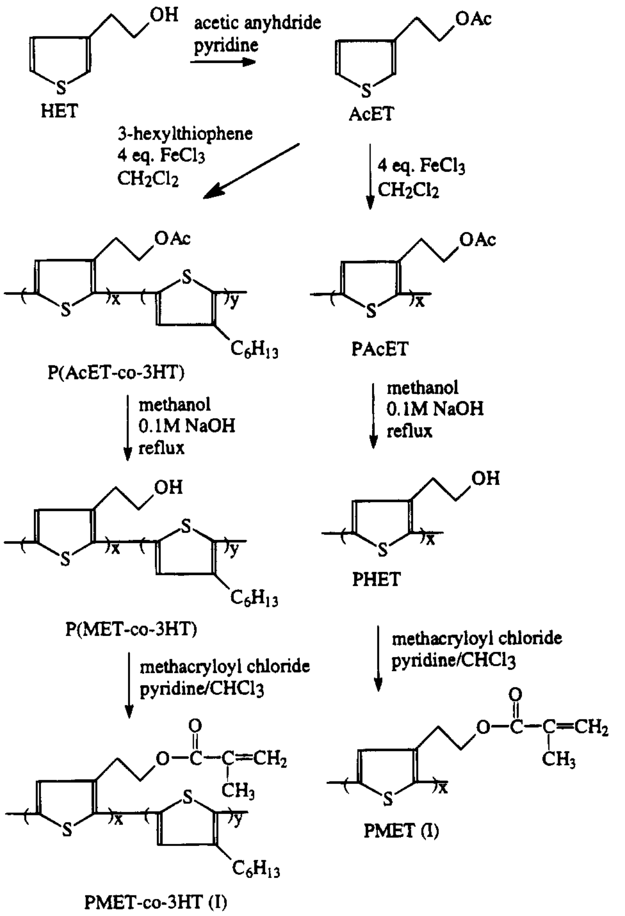
Scheme 1. Method I: Oxidative Coupling of Protected Monomers



cally with ferric chloride.[27] In a previous study, poly(3-(2-(acryloyloxy)ethyl)thiophene) was subjected to electron beam radiation, and cyclic voltammetry was employed to show that cross-linking had occurred.[28] Punkka et al. have studied the thermal stability of conductivity in electron beam irradiated blends of ferric chloride doped poly(3-octylthiophene) and ethylene-vinyl acetate.[29] However, no studies of photoimaging of poly(3-(2-(acryloyloxy)ethyl)thiophene) or related polymers have been reported.

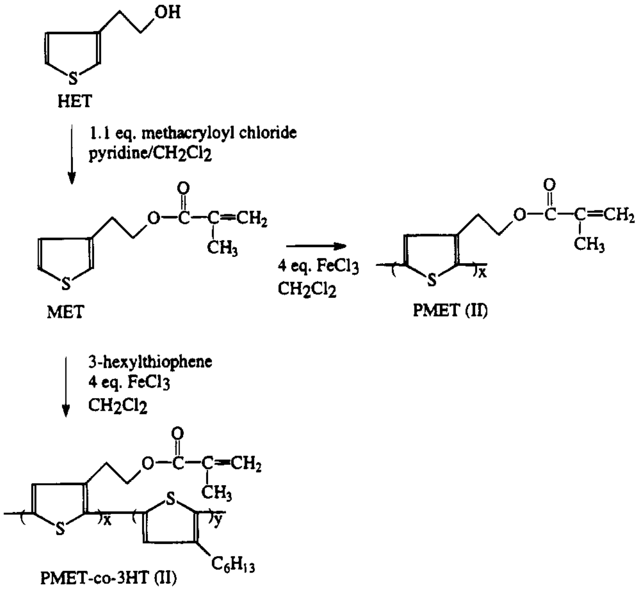
In the present paper, the synthesis, photochemistry, and photoimaging of π-conjugated polymers and copolymers based on poly(3-(2-(methacryloyloxy)ethyl)thiophene) are described. Two different synthetic routes were used to achieve the target polymers. One of the routes leads to polymers which adhere very strongly to polar substrates. Films of homopolymers and copolymers are rendered insoluble when subjected to low-intensity UV–visible irradiation, and the photolithographic parameters have been evaluated. As anticipated, cross-linking occurs via the methacrylate functionality.

Experimental Section

Chemicals. 3-(2-Hydroxyethyl)thiophene (Aldrich), acetic anhydride, $CHCl_3$ (spectroscopic grade) (Caledon), anhydrous ferric chloride, and sodium hydroxide (BDH) were all used as received. $CHCl_3$ was dried over CaH_2 and distilled under N_2 before use. Methacryloyl chloride (Aldrich) was distilled and stored under N_2. Pyridine (Caledon) was dried with sodium hydroxide, distilled, and stored under N_2 with molecular sieves.

Synthesis of Poly(3-(2-(methacryloyloxy)ethyl)thiophene) and Copolymers. Poly(3-(2-(methacryloyloxy)ethyl)thiophene) (PMET) and copolymers with 3-hexylthiophene (3HT) were synthesized by two methods: (I) oxidative coupling of 3-(2-acetoxyethyl)thiophene, followed by deprotection and esterification (Scheme 1); (II) direct oxidative coupling of 3-(2-(methacryloyloxy)ethyl)thiophene (Scheme 2).

Scheme 2. Method II: Oxidative Coupling of Methacrylate-Functionalized Monomers



3-Hexylthiophene was synthesized according to the procedure outlined by Kumada et al.[30] 3-(2-Acetoxyethyl)thiophene (AcET) was prepared by reacting 3-(2-hydroxyethyl)thiophene (HET) (1.32 g, 10.3 mmol), acetic anhydride (1.26 mL, 13.4 mmol), and pyridine (5 mL) by refluxing for 5 h (Scheme 1). The solution was then acidified and extracted with ether. The ether extract (150 mL) was washed with deionized water (3 × 50 mL), treated with $MgSO_4$, and filtered, and the ether was flash evaporated to give 1.57 g (9.22 mmol, 90% yield) of the monomer (AcET). IR (neat) 3104, 2959, 1740, 1537, 1433, 1383, 1242, 1036, 978, 943, 899, 858, 777 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (1H, dd, $J_{4,5} = 5$ Hz, $J_{2,5} = 3$ Hz, H_5), 7.02 (1H, dd, $J_{2,5} = 3$ Hz, $J_{2,4} =$ 1Hz, H_2), 6.98 (1H, dd, $J_{4,5} = 5$ Hz, $J_{2,4} = 1$ Hz, H_4), 4.28 (2H, t, $J = 8$ Hz, $CH_2\mathit{CH_2}$), 2.96 (2H, t, $J = 8$ Hz, $\mathit{CH_2}CH_2$), 2.05 (3H, s, $\mathit{CH_3}$). Anal. Calcd for $C_8H_{10}SO_2$: C, 56.44; H, 5.92. Found: C, 56.35; H, 5.97.

3-(2-(Methacryloyloxy)ethyl)thiophene (MET) was prepared by stirring 3-(2-hydroxyethyl)thiophene (8.92 mmol) with pyridine (2.4 mL), CH_2Cl_2, and methacryloyl chloride (35.4 mmol) at 0 °C for 5 h. The workup was the same as for AcET, giving a yield of 60–70%. IR (neat) 3106, 3023, 2961, 2930, 1784, 1721, 1638, 1537, 1452, 1321, 1169, 1051, 943, 876, 816, 758 cm^{-1}; ^1H NMR δ 7.28 (1H, t, $J_{4,5} = 5$ Hz, $J_{2,5} = 3$ Hz, H_5), 7.03 (1H, t, $J_{2,5} = 1$ Hz, $J_{2,4} = 1$ Hz, H_2), 6.98 (t, 1H, $J_{4,5} = 5$ Hz, $J_{2,4} = 1$ Hz, H_4), 6.08 (1H, H_{gem}), 5.63 (1H, H_{gem}), 4.37 (2H, t, $J = 6.9$ Hz, $CH_2\mathit{CH_2}$), 3.01 (2H, t, $J = 6.9$ Hz, $\mathit{CH_2}CH_2$), 1.96 (3H, s, CH_3,). Anal. Calcd for $C_{10}H_{12}SO_2$: C, 61.12; H, 6.16. Found: C, 61.16; H, 6.16.

Method I: Oxidative Coupling of Acetyl-Protected Thiophenes. The monomer, AcET, was polymerized by chemical oxidative coupling using ferric chloride following the method of Sugimoto et al.[31] The mixture was stirred for 4 h, precipitated in methanol, filtered, and washed successively with NH_4OH (28%), water, and acidified methanol. The crude polymer was dissolved in dichloromethane, filtered to remove insolubles, and precipitated in methanol to provide 50–60% yield of poly(3-(2-acetoxyethyl)thiophene) (PAcET). A copolymer was obtained by reacting 3-(2-acetoxyethyl)thiophene (2.58 mmol) with 3-hexylthiophene (3HT) (4.08 mmol). The mole ratio of 3-hexylthiophene in the feed is 62%. The polymer, poly[3-(2-acetoxyethyl)thiophene-*co*-3-hexylthiophene] (PAcET-*co*-3HT), was purified as described above to give 78% yield.

The acetate protecting group on both the homopolymer and copolymer was removed by refluxing the polymer (0.5 g) in 25 mL of a methanol solution of NaOH (0.1 M) for 24 h.[32] The product was filtered and washed with methanol to provide the polymers poly(3-(2-hydroxyethyl)thiophene) (PHET) and poly-[3-(2-hydroxyethyl)thiophene-*co*-3-hexylthiophene] (PHET-*co*-3HT) in near-quantitative yields.

PHET and PHET-*co*-3HT were functionalized with the methacrylate group by the following procedure. Distilled $CHCl_3$ (15 mL) and pyridine (20 mL) were combined with the polymer (0.32 g). The mixture was cooled with an ice/salt bath, and excess methacryloyl chloride (0.8 mL, 8.3 mmol) was added dropwise under N_2. The reaction was continued for 72 and 24 h for the homopolymer and the copolymer, respectively. The polymers were precipitated in methanol, filtered dissolved in $CHCl_3$, and reprecipitated in methanol. Poly(3-(2-(methacryloyloxy)ethyl)thiophene) (PMET) (I)) and poly[3-(2-(methacryloyloxy)ethyl)thiophene-*co*-3-hexylthiophene] (PMET-*co*-3HT (I)) were obtained in 65–70% yields. Characterization of the polymers is discussed in the Results and Discussion.

Method II: Oxidative Coupling of Methacryloyl-Substituted Thiophenes. Poly(3-(2-(methacryloyloxy)ethyl)-thiophene) (PMET (II)) was synthesized by reacting 3-(2-(methacryloyloxy)ethyl)thiophene (8.4 mmol) with 4 equiv of $FeCl_3$ (33.7 mmol) for 2 h. The resultant polymer was precipitated in methanol and collected by filtration, giving a yield of 30%. Using the same procedure, a copolymer of MET (2.1 mmol) and 3HT (4.7 mmol) was synthesized. The yield of PMET-*co*-3HT (II) was 48%.

Characterization. ^1H NMR spectra were recorded on a 400 MHz Bruker AMX400 in $CDCl_3$. Molecular weight distribution curves of polymers were determined by gel permeation chromatography (GPC) using 10^5, 10^4, and 10^3 Å μ-Styragel columns at 25 °C. Polymers were eluted with tetrahydrofuran (BDH, HPLC grade) and detected using a UV–visible spectrophotometer (Spectra-Physics, Model SP8000) and a refractive index detector (Waters, Model R400). Data were acquired, stored, and analyzed using an IBM personal computer and custom-written software. Polystyrene (PS) standards (Polymer Laboratories Inc.) of molecular weights ranging from 233 000 to 750 were used for calibrating GPC columns for hydrodynamic volume versus elution volume. The PS calibration curve was converted to a poly(3-hexylthiophene) (P3HT) based calibration using the following Mark–Houwink constants: for P3HT, $K = 2.28 \times 10^{-3}$ cm^3/g and $a = 0.96$; for PS, $K = 1.29 \times 10^{-2}$ cm^3/g and $a = 0.713$.[33–34] Infrared spectra were recorded on a Bomem Michelson FTIR (120 series). UV–visible absorption spectra were recorded on a Perkin-Elmer Lambda 3A UV–visible spectrophotometer at 25 °C.

For measurements of conductivity, thin films of polymer were cast on quartz slides from dilute solutions of polymer in chloroform. The polymers were oxidized to their electronically conductive form by submersion of the polymer/substrate into an anhydrous 0.1 M solution of gold trichloride in acetonitrile.[35] Electronic conductivities were measured using the four-point probe technique.

Photolithography. Polymer films were spin-cast from chloroform solution on quartz slides or silicon substrates. The optical density of the films at λ_{max} was 0.5–0.8. The illumination source was a 200 W high-pressure mercury lamp (Illumination Industries Ltd.). The wavelength of incident light was selected with the use of a 300 nm cut-off filter and selected 10 nm band-pass interference filters. The light was focused to a diameter of 4 cm. Gel dose measurements of the polymers were determined by measuring the residual film as a function of the exposure dose received by the film. The optical density was monitored at λ_{max}. For polymer images, films were irradiated through a photomask. The relief image was obtained upon dissolution of the unexposed polymer in chloroform. All experiments were performed with front-face irradiation of films in ambient air at 25 °C. The light intensity was measured using a photodetector (International Light). The thicknesses of several poly(3-hexylthiophene) films were measured using a stylus profilometer (Tencor Instruments, Alpha-step 200).[36] The measured thicknesses were linearly correlated to the absorbance of the polymer films at λ_{max}.

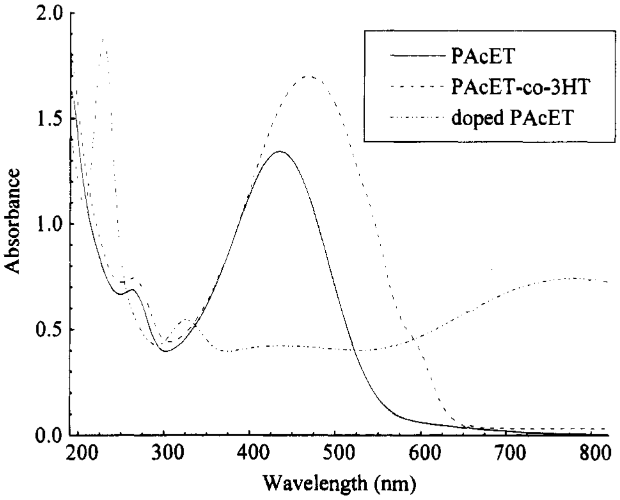


Figure 2. UV–visible spectra of poly(3-(2-acetoxyethyl)-thiophene) (PAcET), (PAcET-*co*-3HT), and doped PAcET films.

Table 1. Physical and Optical Properties of Polymers

	λ_{max} (nm)					σ
polymer	solution	film	M_w	M_n	MWD	(S cm^{-1})
PAcET-*co*-3HT	432	468	63 000	26 200	2.4	9–12
PHET-*co*-3HT	430	468	51 200	18 100	2.8	9–12
PMET-*co*-3HT (I)	434	464	45 800	19 200	2.4	9–12
PAcET	414	438	61 800	25 900	2.4	4
PMET (I)	414	438	19 500	12 700	1.5	2–3
PMET-*co*-3HT (II)	426	458	16 000	8 200	1.95	2–3
PMET (II)	422	434	28 800	10 500	2.7	1

Results and Discussion

Spectroscopic Analysis. The polymers exhibited a broad UV–visible absorption spectrum with a maximum wavelength of absorption, λ_{max}, indicative of extensive π-electron delocalization. Spectra of the films exhibited a red shift in λ_{max} compared to polymer solutions, indicating increased coplanarity and conjugation in the solid state. Figure 2 shows the UV–visible spectra of PAcET, PAcET-*co*-3HT, and PAcET oxidized with $AuCl_3$. The ligand-to-metal charge transfer bands of $AuCl_4^-$ appear at 232 and 324 nm in the "doped" polymer. In addition, the absorption band at 438 nm due to the π–π^* transition decreased due to the formation of the conducting bipolaronic state (λ = 794 nm). UV–visible absorption data are presented in Table 1 together with molecular weights and electrical conductivity data.

PHET was insoluble; therefore solution spectroscopy and molecular weight analysis could not be performed. Esterification of PHET with methacryloyl chloride yielded a soluble product. However, the reaction did not go to completion, and as a result, lower molecular weight chains were solubilized preferentially over long chains, causing the molecular weight of PMET (I) to be lower than that of the parent PAcET, and the molecular weight distribution, narrower. In the analogous case involving the copolymer, PHET-*co*-3HT, the presence of pendant hexyl groups was sufficient to increase its solubility. Molecular weights and UV–visible absorption spectra for this polymer are similar to those of its parent polymers.

In addition to the desired polymer, we obtained polymer gels as a side product from the esterification reaction with methacryloyl chloride via method I. The weight percentage of gels formed was in the range of 10–20% of the final polymer yield. During filtration of PMET (I) and PMET-*co*-3HT (I) in $CHCl_3$ solutions, it was observed that the gels were yellow whereas the

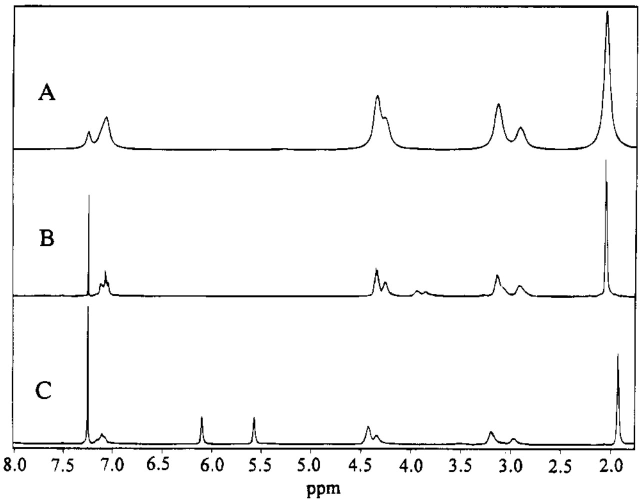


Figure 3. 400 MHz ^1H NMR of (A) poly(3-(2-acetoxyethyl)thiophene) (PAcET); (B) poly(3-(2-hydroxyethyl)thiophene) (PHET), 25% deacetylation of PAcET; and (C) poly(3-(2-(methacryloyloxy)ethyl)thiophene) (PMET (I)). No peaks were observed below 1.9 ppm.

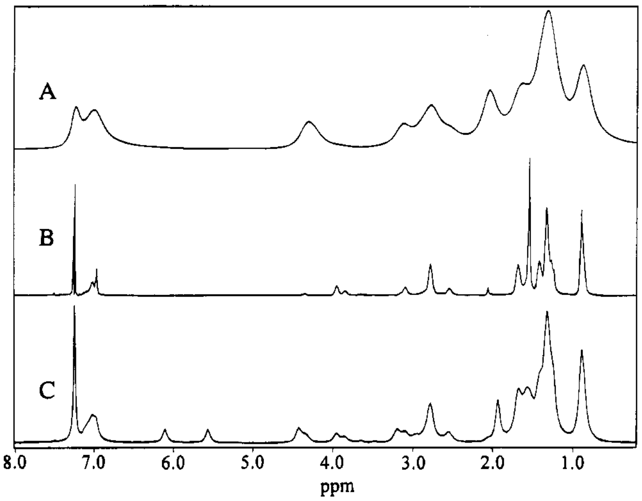


Figure 4. 400 MHz ^1H NMR of (A) poly[3-(2-acetoxyethyl)thiophene-*co*-3-hexylthiophene] (PTAc-*co*-3HT), (B) poly[3-(2-hydroxyethyl)thiophene-*co*-3-hexylthiophene] (PHET-*co*-3HT), and (C) poly[3-(2-(methacryloyloxy)ethyl)thiophene-*co*-3-hexylthiophene] (PMET-*co*-3HT (I)). The peak at 1.55 ppm is due to H_2O.

soluble polymer was orange. Cross-linked poly(3-alkylthiophenes) are known to expand/swell when heated or treated with chloroform to provide yellow gels.[37-39] Thus methacrylate-based gels should display the same thermochromic and solvatochromic properties as the poly(3-alkylthiophene)-based gels investigated by Yoshino et al.[37-39] In addition, the reversible volume changes of the poly(3-(2-(methacryloyloxy)ethyl)thiophene) gels upon changing temperature or solvent composition make them excellent candidates for mechanical actuators or shape memory polymers.[37,40]

^1H NMR and FTIR Spectroscopy. ^1H NMR spectroscopy is a powerful technique for determining configurational preferences in polymers and copolymers. This is particularly true in the case of polythiophenes, for which it is known that the presence of head-to-head configurations leads to a larger degree of twisting between adjacent thienyl rings because of resulting steric interactions.[41] Figures 3 and 4 show ^1H NMR spectra for poly(3-(2-(methacryloyloxy)ethyl)thiophene) (PMET (I)), poly[3-(2-(methacryloyloxy)ethyl)thiophene-*co*-3-hexylthiophene] (PMET-*co*-3HT (I)), and their corresponding intermediate polymers. It is well documented that in the ^1H NMR spectra of poly(3-alkylthiophenes) the proton signals associated with the α-methylenes are split because polymerization results in diads which are either head-to-tail (HT) or head-to-head (HH) in configuration.[42,43] These proton signals are downfield and upfield, respectively. Similar splitting patterns were observed for the α-methylene of the thienyl ring of PAcET. Integration of the signals at 3.17 and 2.92 ppm, corresponding to HT and HH diads, respectively, indicates a HT:HH ratio of 62:38 (Table 2). This ratio is within the range of HT coupling values (i.e., 50–80%) observed for polymerization of 3-alkylthiophenes by electrochemical methods or oxidative coupling.[41-47]

Table 2. Percent Composition of Thiophene Polymers and Copolymers

polymer	CH_2CH_2O HT	CH_2CH_2O HH[a]	$CH_2(C_5H_{11})$ HT	$CH_2(C_5H_{11})$ HH[a]	% of functional monomer[b]
PAcET-*co*-3HT	60	40	75	25	35
PHET-*co*-3HT	60	40	78	22	31
PMET-*co*-3HT (I)	64	36	75	25	27
PMET-*co*-3HT (II)	66	34	76	34	49
PAcET	62	38			100
PMET (I)	65	35			88
PMET (II)	60	40			90

[a] α-Methylene. [b] Overall percent composition of 3-(2-X-ethyl)thiophene groups (X = acetoxy, hydroxy, or methacryloyloxy) in polymer.

The ^1H NMR spectra of the corresponding copolymers, PAcET-*co*-3HT, PHET-*co*-3HT, and PMET-*co*-3HT, exhibit signals that correspond to the spectra of P3HT superimposed with PAcET, PHET, and PMET, respectively. For example, PAcET-*co*-3HT exhibited α-CH_2 signals of 2.79 and 2.55 ppm and 3.14 and 2.87 ppm corresponding to HT and HH couplings of the 3-hexylthiophene and 3-(2-acetoxyethyl)thiophene units, respectively (Figure 4). From their integrals, the HT:HH ratio was determined to be 75:25 based on the α-CH_2 signals of 3HT and 60:40 based on the methylene signal of the AcET group. From this, it is apparent that AcET confers a higher degree of steric hindrance in the transition state of the polymerization reaction. It is not certain, however, whether the polymer is a random or block copolymer since it is not known if the chemical shift of an α-CH_2 associated with an AcET unit, for example, is affected by an adjacent thienyl group possessing a hexyl group any more than it is affected by one possessing an adjacent ethyl acetate. It appears that the chemical shift of α-CH_2 groups is determined largely by electronic effects of substituents directly attached to the ring and by the regiochemistry of adjacent units, irrespective of the side chain attached to the adjacent unit, but this requires clarification. The ratio of the integral of the α-methylene signal at 3.14 and 2.87 ppm for AcET to the α-methylene signal of 3HT at 2.79 and 2.55 ppm gives the percent composition of the copolymers. The HH integral of AcET at 2.87 ppm units overlaps with the HT signal of 3HT at 2.79 ppm, yielding an uncertainty of ±5%. Nevertheless, the composition of the copolymer was estimated to be 35% AcET and 65% 3HT.

The efficiency of the reaction steps leading toward methacrylate-substituted polymers can be followed by NMR. Partial deacetylation of PAcET and PAcET-*co*-3HT yields an upfield shift of the methylene signal from 4.36 to 3.96 ppm (Figures 3B and 4B). Coupling of methacryloyl chloride to PHET and PHET-*co*-3HT yields

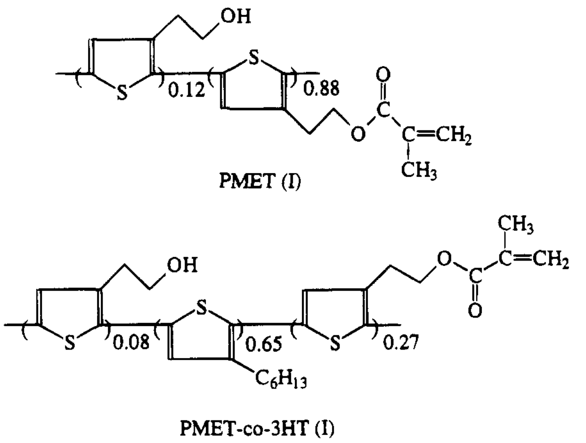


Figure 5. True compositions of PMET (I) and PMET-*co*-3HT (I).

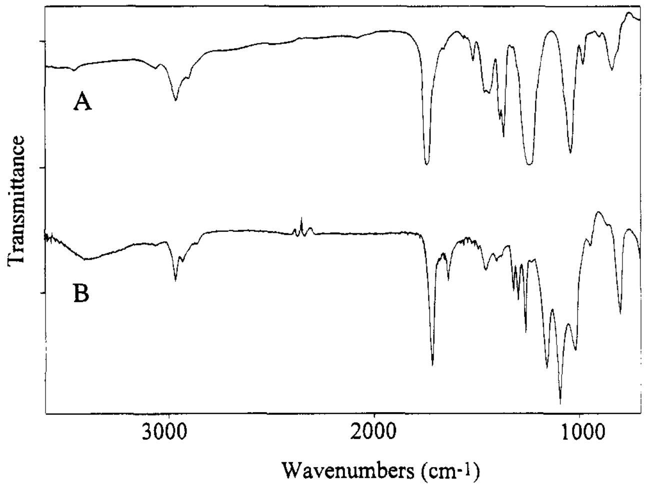


Figure 6. FTIR of (A) poly(3-(2-acetoxyethyl)thiophene) (PAcET) and (B) poly(3-(2-(methacryloyloxy)ethyl)thiophene) (PMET (I)).

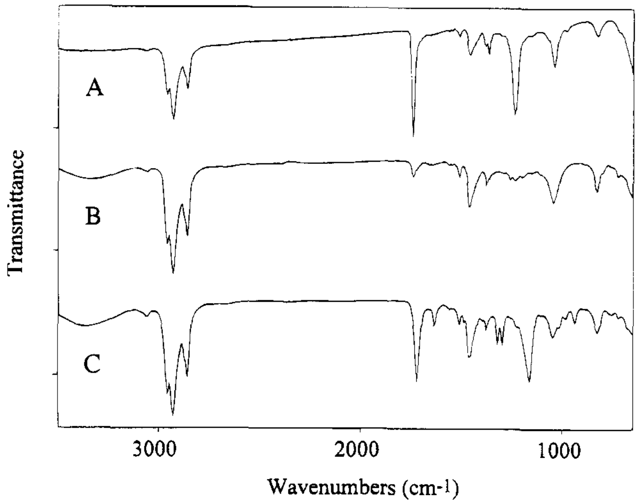
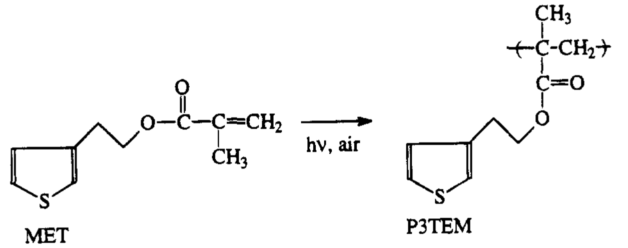


Figure 7. FTIR of (A) poly[3-(2-acetoxyethyl)thiophene-*co*-3-hexylthiophene] (PAcET-*co*-3HT); (B) poly[3-(2-hydroxyethyl)-thiophene-*co*-3-hexylthiophene] (PHET-*co*-3HT), 89% deacetylation of PAcET-*co*-3HT; and (C) poly[3-(2-(methacryloyloxy)-ethyl)thiophene-*co*-3-hexylthiophene] (PMET-*co*-3HT (I)).

Scheme 3. UV–Initiated Radical Polymerization of MET Monomer



singlets associated with vinylidene protons at 6.11 and 5.58 ppm for both polymers (Figures 3C and 4C). However, residual NMR signals at 3.97 and 3.86 ppm (Figure 4C) indicate incomplete reaction between the hydroxyls and methacryloyl chloride. Thus NMR indicates that the composition of the starting polymer, PAcET-*co*-3HT, possessed 35% thienyl ethyl acetate (AcET) units, of which 77% were converted to 3-(2-(methacryloyloxy)ethyl)thiophene (MET) groups based on the integration of the β-methylene signal of MET and 3-(2-hydroxyethyl)thiophene (HET) groups. Integration of the vinylidene and aromatic proton signals for PMET-*co*-3HT (I) yields a final composition of the polymer being comprised of 27% MET units, 8% HET units, and 65% 3HT units (Figure 5). Thus the homopolymer, PMET (I), does not possess a methacrylate unit on every ring because of incomplete deacetylation and coupling reactions. Similarly, the composition of PMET (I) was 88% MET units and 12% HET units (Figure 5).

FTIR spectroscopy (Figures 6 and 7) was used to support NMR data in regard to the composition of the polymers during each reaction step. The procedure used for deacetylation of PAcET and PAcET-*co*-3HT was adopted from Sato et al. for converting poly(vinyl acetate) to poly(vinyl alcohol).[32] With this reported procedure ~1% of acetate groups still remain in the final polymer. Loss of the carbonyl stretch at 1738 cm^{-1} for the acetyl group can be observed in Figure 7 with formation of a hydroxyl stretch at 3341 cm^{-1}. Formation of the methacrylate ester yields a carbonyl stretch at 1720 cm^{-1} and a vinylidene stretch at 1638 cm^{-1} (Figures 6B and 7C). These absorption bands can be compared to the respective stretches for 2-hydroxyethyl methacrylate, which were observed at 1718 (ν_{CO}) and 1636 cm^{-1} ($\nu_{C=C}$).[48]

The ^{1}H NMR and FTIR spectra of polymers prepared via method II are similar to those of their respective polymers synthesized by method I. The composition of the directly synthesized copolymer, PMET-*co*-3HT (II), was ~50% MET units and ~50% 3HT units based on integration of the aromatic and alkene NMR signals. Integration of the aromatic to alkene protons for PMET (II) indicates 90% of the methacrylate units remain intact after polymerization. The other 10% might have undergone polymerization with a thiophene ring since it is known that Lewis acids can facilitate reaction of double bonds with aromatic molecules.[49] Alternatively, some methacrylate groups may have undergone vinyl polymerization. Recently, Gumbs has shown that certain vinyl monomers undergo copolymerization with 3-methylthiophene initiated by ferric chloride.[50] No residual thienyl ethanol units were present since they were completely converted prior to polymerization.

Photochemistry and Photolithography. The methacrylate functionality attached to the thienyl group is light sensitive. The literature provides ample evidence of methacrylate polymerizations initiated by ultraviolet radiation, e.g., methyl methacrylate[51] and octadecyl methacrylate.[52] Exposure of the monomer, MET, to ambient lighting produced a gumlike polymer, poly[(3-thienyl)ethyl methacrylate], (P3TEM) (Scheme 3). The UV–visible spectrum of the solution exhibited

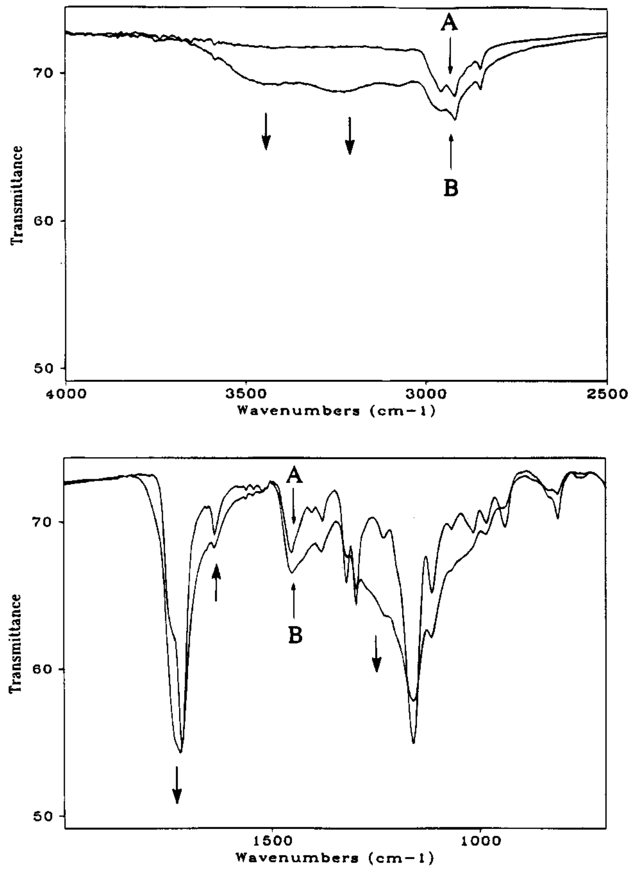


Figure 8. FTIR of photolyzed PMET (II): (A) pristine film; (B) film photolyzed for 12.6 h at 313 nm (I_0 = 0.22 mW cm^{-2}). Arrows show the growth and decrease of peak intensities.

a λ_{max} at 250 nm and a shoulder at 304 nm. The monomer, MET, possessed a single absorption peak at 250 nm. ^{1}H NMR confirmed the loss of vinylidene protons (6.08 and 5.63 ppm), while FTIR also confirmed the loss of the vinylidene stretch (1638 cm^{-1}). A carbonyl stretch for P3TEM was observed at 1726 cm^{-1}, which is consistent with the work of Khanna et al. on the radical polymerization of 2-((methacryloyloxy)-methyl)thiophene.[53]

Similarly, the methacrylate group underwent photochemical coupling when attached to polythiophenes. Figure 8 shows the FTIR spectrum of the photolyzed film of PMET (II). The ~80 nm thick film was irradiated with the 313 nm band interference filter. A decrease in the vinylidene stretch at 1638 cm^{-1} was observed in conjunction with a shift in the carbonyl stretch toward higher frequency. The latter can be explained by a decrease in α,β conjugation associated with the carbonyl and the double bond in the methacrylate side chain.[54] Photolyses were performed in air, which meant that the reaction products of photosensitized singlet oxygen are also observed since thiophene oligomers and polymers are known to be efficient singlet oxygen photosensitizers.[26,55-58] These include the growth of FTIR peaks from 3600 to 3080 cm^{-1} due to hydroxyls and hydroperoxides which are formed as a result of sensitization and reaction of singlet oxygen.[24,59,60] Increases in the peak intensity in the region of 1300−1160 cm^{-1} indicate the formation of sulfine residuals resulting from $^1O_2$ attack on the thienyl ring.[26]

Methacrylate-functionalized thiophenes are rendered insoluble upon irradiation. FTIR indicates that this is most likely the result of cross-linking via free-radical induced coupling of the methacrylate groups. There are two possible sources of free-radical initiators that could lead to cross-linked films: residual Fe(III) salts in the polymer which generate free radicals upon irradiation;[26] attack of singlet oxygen on the methacrylate double bond to yield hydroperoxide and its subsequent dissociation into free radicals.[59] The relative efficiencies of these competing processes requires further investigation.

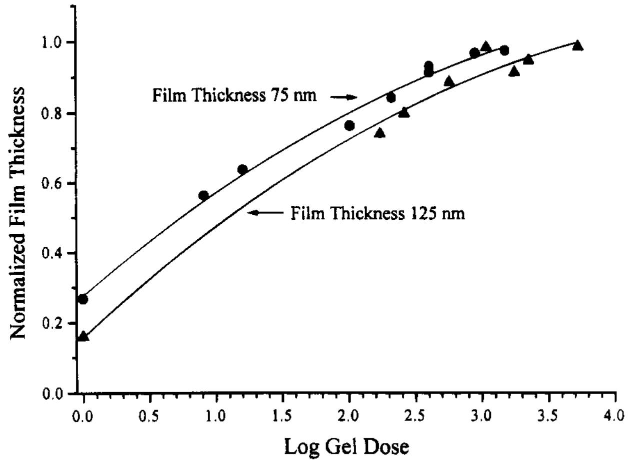


Figure 9. Gel dose curves of PMET-*co*-3HT (I) for two film thicknesses.

Lithographic data were determined from gel dose curves made by plotting the residual thickness of the polymer image after solvent development as a function of energy absorbed by the polymer.[61] Figure 9 shows the gel dose curve for PMET-*co*-3HT (I) irradiated through a 435 nm band interference filter. Prior to irradiation, redissolution of films of PMET-*co*-3HT (I) and PMET (I) cast on polar substrates, such as glass, quartz, and silicon, left a residual film (~20 nm thick). This is indicated in Figure 8 at zero irradiation dose. This adhesion layer is accounted for by the presence of free hydroxyls in the polymer side chain which adsorb strongly to the polar surface. A hydroxyl stretch is observed at 3340 cm^{-1} in the FTIR of the polymers, PMET (I) and PMET-*co*-3HT (I) (Figures 5 and 6). In contrast, PMET (II) and PMET-*co*-3HT (II) synthesized by method II were able to dissolve *completely* prior to irradiation since by this method hydroxyl groups were completely converted to methacrylate units prior to polymerization as indicated by FTIR.

Gel dose curves for PMET (II) and P3HT versus PMET-*co*-3HT (II) are shown in Figures 10 and 11. The light intensity at 313 nm was 0.22 mW cm^{-2}. The minimum dose required to leave an insoluble residue, D_g^{i}, for PMET (II) was 1.2 mJ cm^{-2} and the incident dose required for 50% gel formation, $D_g^{0.5}$, was 13.4 mJ cm^{-2}. The rate at which gel forms is determined by the slope of the gel dose curve. This value is the contrast, γ, which was found to be 0.5. D_g^{i} was 2.6 mJ cm^{-2} for PMET-*co*-3HT (II), and $D_g^{0.5}$ was 24 mJ cm^{-2} with a contrast of 0.6. Under the same photolysis conditions, we observe negligible cross-linking of films of P3HT prepared by oxidative coupling with ferric chloride (M_n of 8500, MWD of 3.4, HT:HH ratio ~ 60:40, λ_{max} = 435 nm) due to the low intensity of irradiation. This plot clearly shows that PMET-*co*-3HT (II) can be cross-linked with greater efficiency than P3HT due to the presence of the methacrylate side chain.

As an indication of the sensitivity of these resists, it is worth comparing their efficiency with classical photoresists. For example, copolymers based on 4-(ac-

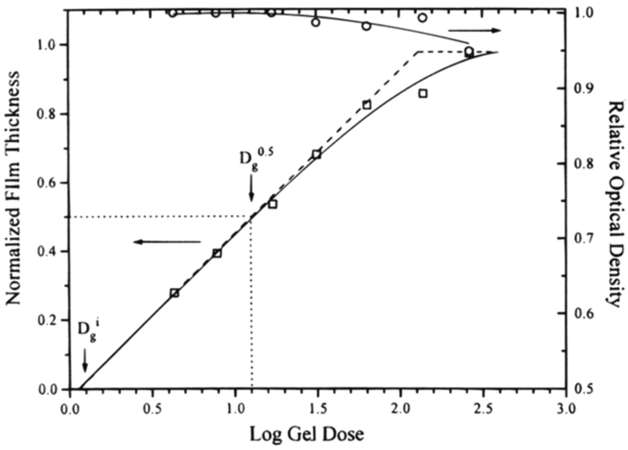


Figure 10. Gel dose curve of PMET (II) and the relative optical density at λ_{max} (434 nm) as a function of exposure dose. The optical density of the films is 0.5.

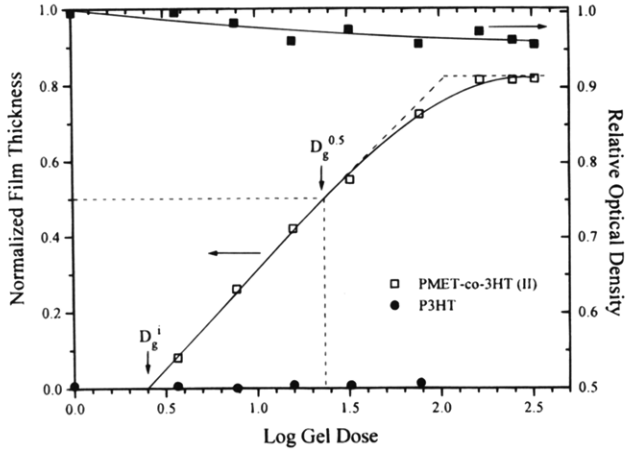


Figure 11. Gel dose curve of P3HT versus PMET-*co*-3HT (II). The optical density of the films is 0.5. Also shown is a plot of the relative optical density for PMET-*co*-3HT (II) ($\lambda_{max} = 458$ nm) versus the exposure dose.

etoxymethyl)styrene) and 4-hydroxystyrene, which cross-link via electrophilic aromatic substitution when irradiated with triarylsulfonium salts, exhibit gel doses in the range of 1–2 mJ cm^{-2} and contrasts greater than 2.[62] Thus the gel dose sensitivity of polymers containing ((methacryloyloxy)ethyl)thiophene is comparable to the state-of-the-art photoresists; however, their rate of insolubilization as indicated by the contrast value is lower.

The optical density of the polymer film at λ_{max} is representative of the π-conjugation present in the polymer chains. Photobleaching of P3HT is known to occur by the photosensitization and reaction of singlet oxygen, and this leads to a decrease in optical density and a loss of π-conjugation.[26] Figures 10 and 11 show the change in optical density (at λ_{max}) for the polymer films as a function of irradiation dose. Only short irradiation times are required to totally cross-link the film, during which time only small losses in the optical density are observed. From this we infer that high conductivities should be obtained upon oxidative doping because π-conjugation is retained during imaging.

Polymer images were obtained by irradiating spin-cast films on glass slides or silicon wafers through patterned masks. Films were irradiated for 2 min with the 313 nm interference filter ($I_0 = 26.2$ mJ cm^{-1}). The light intensity was 0.22 mW cm^{-2} and the films had an optical density of 0.5. Development of the relief image was achieved by immersion into chloroform for 2 min, to leave an insoluble orange pattern, followed by a chloroform rinse (Figure 12). The highest resolution obtained for the features was 3 μm for films of ~75 nm thickness. Exposure times of >3 min (>40 mJ cm^{-1}) resulted in films with poor resolution due to cross-linking of unexposed polymer regions caused by free radicals which propagate beyond the boundary of the exposed film pattern (Figure 13).

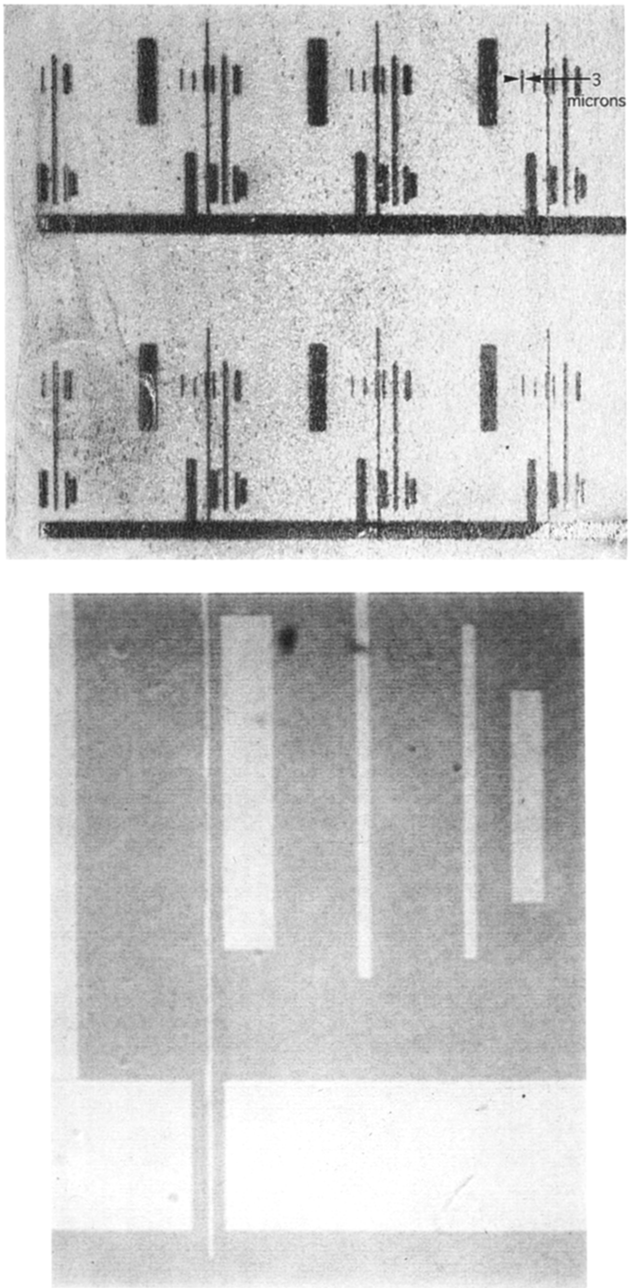


Figure 12. (Top) Photolithography of PMET-*co*-3HT (II) on a silicon wafer. The polymer thickness is ~75 nm, and the narrowest line width = 3 μm. (Bottom) Picture of enlarged area showing fine features. The narrowest line width = 5 μm.

Electronic Conductivities. Polymer films were cast from solution onto glass slides and oxidized with 0.1 M acetonitrile solutions of gold trichloride, and the conductivity was measured by the four-point probe technique (Table 1). The trend in conductivity indicates that higher conductivities are achieved with increasing 3HT content. In comparison, P3HT doped with $AuCl_3$ showed a conductivity of 15 S cm^{-1}.[35] This is interpreted on the basis that a greater degree of steric

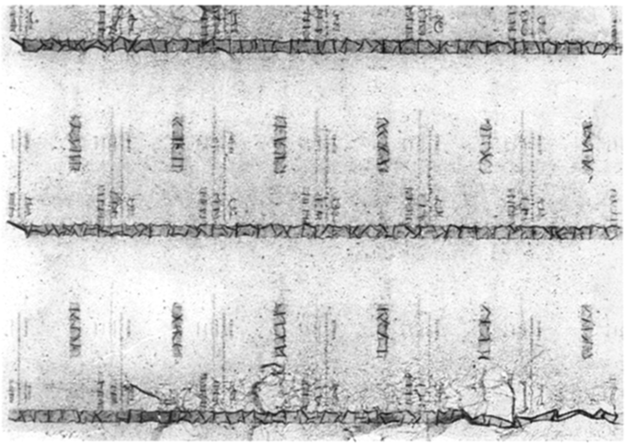


Figure 13. Photolithography using high irradiation dose: Overexposure of films leads to poor resolution. The dark gray areas are cross-linked polymer regions that were unexposed during irradiation.

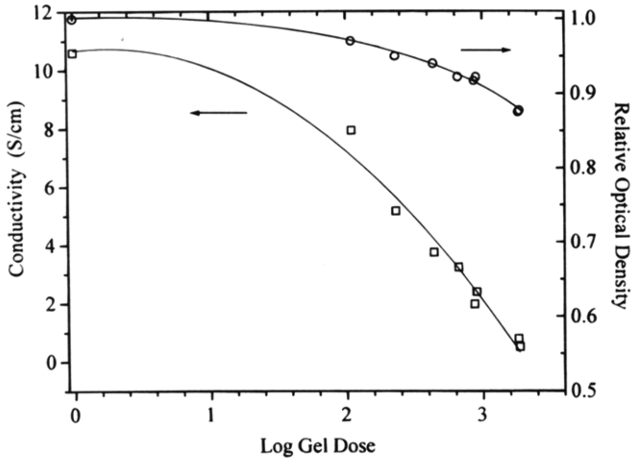


Figure 14. Effect of irradiation dose on the relative optical density (λ_{max}) and on the conductivity of oxidized films following irradiation of PMET-*co*-3HT (I).

interaction associated with MET units confers a greater degree of "twisting" of the individual chains, and hence a shorter conjugation length. In addition, polymers with higher 3HT content yield a corresponding increase in λ_{max}, indicating a more coplanar backbone.

To determine the effect of irradiation on the conductivity of the polymer, spin-coated films of PMET-*co*-3HT (I) were irradiated for different times. The light intensity was 2.8 mW cm^{-2} and the wavelength was controlled by an interference filter at 435 nm. Following photolysis, the films were oxidized with gold trichloride solution in acetonitrile, and the conductivities were measured by the four-point probe technique. Figure 14 shows a plot of conductivity versus irradiation dose and the change in optical density of the polymer. Although the plot shows a large decrease for both σ and optical density upon prolonged exposure, small dosages are required for insolubility. Thus the σ of imaged polymers remains very high and similar to that of the doped pristine polymer. This correlates well with the small loss in optical density (Figure 14).

Conclusions

Electronically conducting polymers containing 3-(2-(methacryloyloxy)ethyl)thiophene can function as negative photoresists. They are photolabile and require relatively small gel doses. Photolithographic patterns of micron resolution can be achieved. Only small losses in π-conjugation are observed; thus the electronic conductivity of "doped" imaged polymers is similar to that of doped pristine polymers. These findings should serve to facilitate fabrication of π-conjugated structures with micron dimensionality for photonic and microelectronic devices.

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