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High Index Resist for 193 nm Immersion Lithography

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ABSTRACT: Leading edge semiconductor products are made by immersion lithography at 193 nm using water as a fluid medium. This imaging process enables production of 45 nm features. Extending immersion lithography to 32 nm or below requires increases in the refractive indices of the lens material, the immersion fluid, and the resist material. Future generations of resist materials require a refractive index approaching 1.9 at 193 nm. It is known that incorporation of sulfur atoms increases the refractive index of polymers. However, increasing the refractive index is normally linked to a corresponding increase in the absorbance. In attempt to design resist polymers with a high refractive index and low absorbance, we studied several new sulfur-containing monomers and polymers and found functionality that can increase the refractive index without increasing the absorbance at 193 nm. New thioester and sulfone structures are particularly useful in that regard. These new monomers have been used produce imageable polymers with a refractive index of 1.8 at 193 nm and an absorbance less than 1.4 μm^{-1}.

Introduction

Immersion lithography offers promise for extending the resolution limits of optical lithography. The lower resolution limit of projection optics systems is described by the Rayleigh equation:

$$R = k_1 \frac{\lambda}{n \sin \theta} \tag{1}$$

where R is the feature size, λ the wavelength, n the refractive index, and $\sin \theta$ the incident angle. In this equation, the denominator is the limiting numerical aperture of the lens, which is the product of the index of refraction of the medium through which the image is propagated and the sine of the capture angle. Clearly, increasing the index of refraction of the medium enables printing of smaller features. Until very recently, the medium in the gap between the final lens element and photoresist was air. In the past several years, advances in engineering have enabled the use of water in this medium. With the currently available lens materials and resists, water enables production of 45 nm features. Smaller feature sizes could be obtained by increasing the numerical aperture further,[1] but that requires corresponding increases in the refractive indices of the lens material, the immersion fluid, and the resist material.

Lutetium aluminum garnet (LuAG), which has a refractive index of 2.14[2] at 193 nm, has been identified as a promising candidate for the high index lens material. Immersion fluids for the next generations of lenses are required to have a refractive index of 1.65 and 1.8 at 193 nm. The refractive index of water at that wavelength is 1.43. Certain cycloalkanes such as decalin have refractive indices near 1.65 and acceptable transparency,[3] but no candidate has yet been identified with a refractive index of 1.8. Research directed toward finding such a fluid is actively being pursued.

In order to realize the full potential of the higher numerical apertures enabled by high index lens materials and fluids, a resist with corresponding index is required. Typical 193 nm resists in use today have a refractive index of ~1.75. Next generation immersion lithography requires the development of resists with a target refractive index of 1.9.[4–7] Such a resist has not yet been demonstrated. This is still a challenging issue.

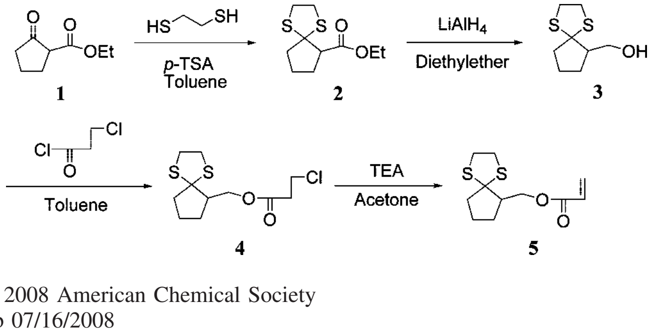
Whittaker et al. designed sulfur-containing polymers which have high refractive indices.[8–10] The highest index polymer that they imaged is reported to have a refractive index of 1.8, but its absorbance value ($>7\ \mu m^{-1}$) is much higher than acceptable. The absorbance target is $<3\ \mu m^{-1}$.[11]

We have studied the tradeoff between high refractive index and low absorbance in materials in some detail and concluded as did Whittaker that sulfur-containing polymers have the potential to increase refractive index without increasing absorbance at 193 nm because of the location and intensity of their absorbance bands that are just to the blue of 193 nm. This effect derives at least in part from the phenomenon of anomalous dispersion.

Results and Discussion

Synthesis of Monomers. Monomer **5** was synthesized by thioacetalization of the ketone **1** followed by reduction and acrylation (Scheme 1). Monomer **10** was synthesized in a similar manner from ketone **7**, which was synthesized via a Michael reaction with enone **6** (Scheme 2). The sulfone monomer was obtained by oxidation of compound **4** by using H_2O_2 (Scheme 3). Monomers **17** and **18** were synthesized by a corresponding Michael reaction followed by reduction and acrylation (Scheme

Scheme 1. Synthesis of Acrylate Monomer 5 Bearing a Thioacetal Group



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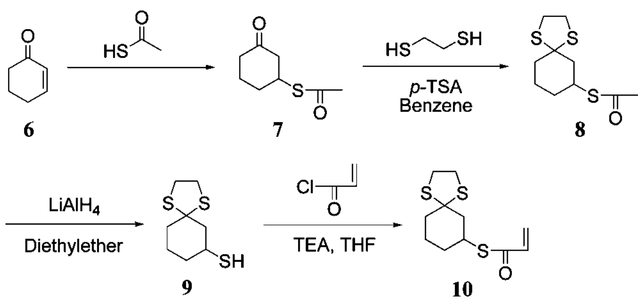
Scheme 2. Synthesis of Acrylate Monomer 10 Incorporating Both Thioacetal and Thioester Groups



4). Monomer **23** was synthesized by thioesterification followed by oxidation, hydrolysis, and methacrylation (Scheme 5).

Synthesis of Polymers. All of the polymers were synthesized by free-radical polymerization using AIBN as an initiator. Homopolymers of **12**, **17**, **18**, and **23** were not studied because of their poor solubility. The feed ratio of the copolymers was 1:1, and the copolymer ratios of resulting copolymers were determined to be similar to the feed ratios by ^{1}H NMR.

Solubility Switching. Chemically amplified positive tone resists have a photoinduced solubility switch. Upon exposure and baking, the polymers should become soluble in the industry standard developer, 2.38 wt % tetramethylammonium hydroxide (TMAH). We therefore prepared copolymers of the new monomers and 2-methyl-2-adamantyl acrylate or the corresponding methacrylate. These base-insoluble esters are known to undergo acid-catalyzed thermolysis to produce carboxylic acids, which render the materials soluble in TMAH.[12] These adamantyl esters were developed by Fujitsu[12,13] and are now well-known and widely used in commercial resist formulations.

Sulfur-Containing High Index Polymers. The cycloalkanes have relatively high refractive indices and good transparency at 193 nm. Adamantane has the highest density and should have the highest refractive index of the common cycloalkanes, but the typical adamantyl ester copolymers in use today have a refractive index of only ~1.7.

In an attempt to find comonomers that would significantly increase the index of refraction of the adamantyl ester copolymers, we auditioned thioacetal and thioester structures because they can be easily incorporated in acrylate-containing monomers. As expected, polymers with thioester (**P3**) or thioacetal structure (**P4**) showed higher refractive indices than poly(cycloalkyl acrylate) (**P1**, **P2**) (Table 1). The absorption spectra of **P1**−**P5** are shown in Figure 1. The absorbance spectrum of the thioester polymer (**P3**) shows peaks at 240 and 185 nm. The absorption spectrum of the thioacetal (**P4**) shows no peak in the 240 nm region, but a shoulder at about 200 nm. Interestingly, **P4** and **P3** have similar refractive indices. The trough in the absorbance spectrum of the thioester (**P3**) at around 210 nm is fortuitous and contributes to the relatively low absorption of that polymer at 193 nm. The polymer that has both the thioester and the thioacetal structure (**P5**) has a very high refractive index, 1.94, but its absorbance is also very high. The absorption spectrum of **P5** looks like a simple summation of the spectra of the thioacetal polymer (**P4**) and thioester polymer (**P3**).

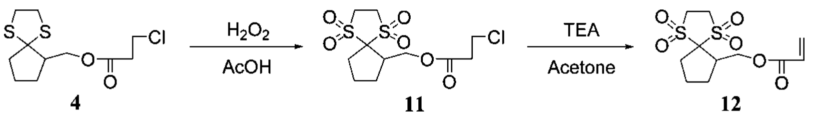
A series of experiments were conducted on liquid alkane samples directed toward development of a high index immersion liquid. Some of these data are provided in Figure 2, which shows the relationship between ionization energy (IE) and absorbance for a series of normal alkanes and cycloalkanes. The absorbance was measured on a Acton Research Corp. CAMS-507 VUV spectrophotometer,[14] and the IE data were obtained from the NIST Chemistry Webbook.[16] There is a nearly linear relationship between IE and the wavelength at which the absorbance reaches 2 cm^{-1} (absorbance edge) for both sets of analogous compounds. Clearly, we need materials with a high IE to achieve low absorbance. Sulfones have a relatively high IE[16] (for example, the IE of diethylsulfone is 9.96 eV[15]). Therefore, we explored the utility of the sulfone functional group as a candidate for the design of high index resist materials. Figure 3 shows the UV spectra of a model thioacetal and a model sulfone. Obviously, the sulfone is more transparent than the thioacetal. Copolymer **P7** was synthesized as a sulfone-containing polymer because of the poor solubility of its corresponding homopolymer. **P7** is more transparent at 193 nm than **P3** or **P4** (Figure 4) and has a higher refractive index than poly(cycloalkane acrylate)s (**P1, P2**) but lower than that of **P3** and **P4**. The indices of **P6** and **P7** are nearly the same, but the sulfone (**P7**) has a much lower absorbance, further proving that sulfone structures lower the absorbance without significantly affecting the index. In summary, the thioester functional group contributes effectively to increase the refractive index, and the sulfone structure has relatively high refractive index and excellent transparency at 193 nm. The thioester has an absorption trough around 210 nm, and its absorbance at 193 nm is relatively low. We therefore designed polymers that incorporate both thioester and sulfone functionalities in their structure. To that end, the new monomers **17**, **18**, and **23** were prepared, and their homopolymers were prepared. Unfortunately, these materials were insoluble in common casting solvents and could not be fully characterized. However, imaging demands inclusion of a solubility switch, so we prepared the 1:1 copolymers **P8** and **P9**, which are freely soluble in common casting solvents.

P8 has a refractive index of 1.82 and an absorbance of 1.25 μm^{-1}. The refractive index of **P8** is higher than that of **P6**, and the absorbance of **P6** is a bit lower. The inclusion of a methylene linkage (**P9**) or an ethylene linkage (**P8**) between the sulfone and the thioester does not produce any significant shift in the absorption bands (Figure 5). Each of the groups studied—thioacetals, thioesters, and sulfones—contributes to the refractive index and the absorbance by the rules of mixing, simply by a weighted sum of their spectra as homopolymers. As can be seen in Figure 6, the refractive index has a peak at 10−15 nm longer wavelength than that of the absorption peak, which is explained by anomalous dispersion. Thus, the ideal structure would have a deeper absorption trough at 193 nm and higher absorption around 180 nm. That should induce a high refractive index at 193 nm due to anomalous dispersion. We are continuing to explore alternative combinations of sulfur-containing acrylates and methacrylates for this application, but the copolymers **P8** and **P9** have by far the best combination of spectral characteristics we have seen to date.

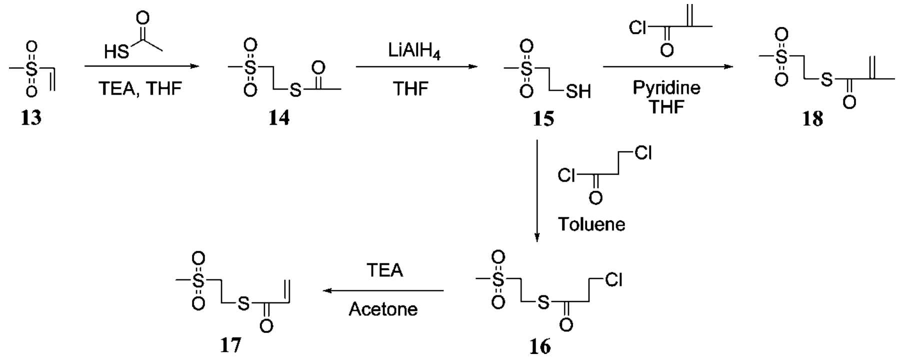
Resist Copolymers. The copolymers **P8** and **P9** have grass transition temperatures (T_gs) of 84 and 141 °C, respectively. Photoresist applications demand polymers with high enough T_gs to allow thermolysis in the glassy state, which suppresses blurring due to acid diffusion. We have, therefore, prepared the polymethacrylates **P10** and **P11** (Figure 7), which have T_gs of 130 and 153 °C, respectively. The refractive index and the absorbance at 193 nm of **P11** (n = 1.78, abs = 1.15) were almost the same as those of **P8** and **P9**. We selected **P11** as the copolymer for imaging tests.

Imaging Test. The resist was formulated from 0.85 g of **P11**, 0.026 g of triphenylsulfonium nonafluorobutanesulfonate, 0.0026 g of trioctylamine, and 21 g of cyclohexanone and spin-coated on 8 in. wafers over 90 nm of ARC29C antireflection coating from Nissan Chemical Corp. at 1500 rpm and then baked at 205 °C for 60 s to give a film thickness of 77 nm. The wafers were exposed on a Nikon S305B (NA = 0.68, 3/4 annular with phase shift mask), applied post exposure bake at 130 °C for

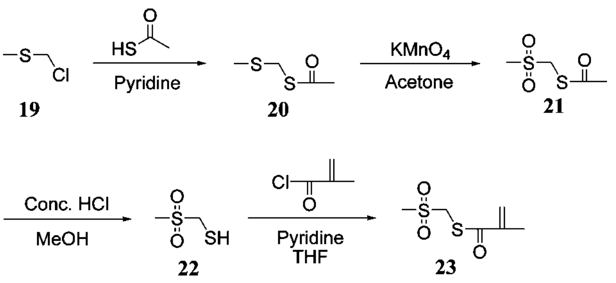
Scheme 3. Synthesis of Acrylate Monomer 12 Incorporating a Sulfone Group



Scheme 4. Synthesis of Acrylate and Methacrylate Monomers 17 and 18 Having Both Thioester and Sulfone Groups



Scheme 5. Synthesis of Methacrylate Monomer 23 Having Both Thioester and Sulfone Groups



90 s, and developed for 60 s in 2.38 wt % TMAH to give very satisfactory images considering that no process or formulation optimization at all was done. Scanning electron micrographs of 110 nm line and space in the high index resist are shown in Figure 8. The pictures show that **P11** has good resolution and that the *k* factor is 0.39. Further optimization will be achieved by the formulation of photoacid generators and quenchers.

Conclusion

We have studied the tradeoff between high refractive index and low absorbance in polymers. Sulfur-containing polymers with different functionalities including thioacetal, thioester, and sulfone were synthesized, and their properties were measured. The thioester functional group contributes effectively to increase the refractive index and has an absorption trough around 210 nm such that its absorbance at 193 nm is suppressed. The sulfone functional group has relatively high refractive index and excellent transparency at 193 nm. Preparing polymers that have both thioester and sulfone functionalities provided materials with refractive index of about 1.8 and absorbance less than 1.4 μm^{-1}. Preliminary imaging tests were performed using such polymers, and 110 nm line and space pattern were successfully demonstrated.

Experimental Section

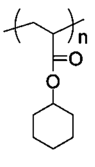
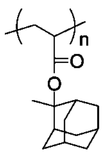
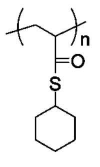
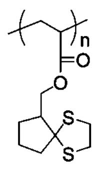
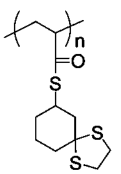
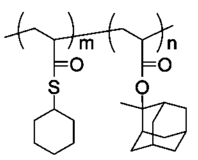
General Methods and Materials. All solvents and reagents were used without further purification except where noted. Dry triethylamine was obtained by distillation over CaH_2. 3-Chloropropionyl chloride was distilled prior to use. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Plus 300 MHz instrument. All chemical shifts are reported in ppm downfield from TMS using the residual protonated solvent as an internal standard ($CDCl_3$, ^1H 7.29 ppm and ^{13}C 77.0 ppm). HRMS (CI) was obtained on a VG analytical ZAB2-E instrument, and IR data were recorded on a Nicolet Avatar 360 FT-IR. Refractive index measurements were performed on a J.A. Woollam VUV variable angle spectroscopic ellipsometer. Absorbance measurements were performed on an Acton Research Corp. CAMS-507 spectrophotometer.

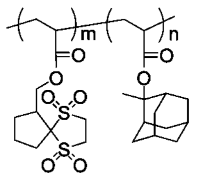
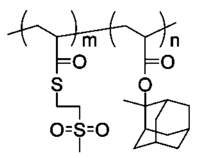
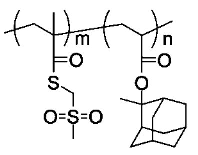
1,4-Dithiaspiro[4.4]nonane-6-carboxylic Acid Ethyl Ester (2). To a solution of ethyl 2-oxocyclopentanecarboxylate (**1**) (3.12 g, 20 mmol) in toluene (20 mL) were added 1,2-ethanedithiol (2.07 g, 22 mmol) and *p*-toluenesulfonic acid (0.38 g, 2 mmol) under nitrogen. The reaction mixture was azeotropically distilled for 3 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, washed with 3 wt % $NaHCO_3$ solution and water, and then dried over $MgSO_4$. Removal of the solvent in vacuo gave **2** (3.68 g, 79%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.24 (t, $J = 7.2$ Hz, 3H), 1.67−2.20 (m, 5H), 2.38−2.49 (m, 1H), 3.12 (dd, $J = 7.2$, 6.6 Hz, 1H), 3.25−3.30 (m, 4H), 4.13 (q, $J = 7.2$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.19, 23.78, 28.49, 39.09, 39.66, 43.30, 58.36, 60.42, 72.90, 173.16. IR (NaCl, cm^{-1}): 1338, 1443 (−S−), 1723 (ester). HRMS *m/z* calcd for $C_{10}H_{17}O_2S_2$ [M + H^+]: 233.0670; found: 233.0673.

1,4-Dithiaspiro[4.4]nonane-6-methanol (3). To a stirred solution of $LiAlH_4$ (0.41 g, 10 mmol) in dry ether (27 mL) was added dropwise **2** (2.0 g, 8.6 mmol) in dry ether (19 mL) at 0 °C under nitrogen. The mixture was stirred at room temperature for 1 h. To the reaction mixture was added dropwise water at 0 °C. The mixture was washed with 1 N HCl solution and water, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc/DCM = 1/3) to yield **3** (1.47 g, 90%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.35−1.48 (m, 1H), 1.64−1.76 (m, 2H), 1.85−1.97 (m, 1H), 2.10−2.25 (m, 2H), 2.32−2.42 (m, 1H), 2.60−2.66 (m, 1H), 3.25−3.32 (m, 4H), 3.66−3.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.21, 27.29, 38.54, 39.03, 45.89, 51.34, 64.25, 73.41. IR (NaCl, cm^{-1}): 1276, 1420 (−S−), 3395 (−OH). HRMS *m/z* calcd for $C_8H_{15}OS_2$ [M + H^+]: 191.0564; found: 191.0564.

3-Chloropropionic Acid 1,4-Dithiaspiro[4.4]non-6-ylmethyl Ester (4). A solution of **3** (0.91 g, 4.8 mmol) and 3-chloropropionyl chloride (0.91 g, 7.2 mmol) in toluene (5 mL) was stirred at 60 °C overnight under nitrogen. The mixture was washed with 3 wt % $NaHCO_3$ solution and water and dried over $MgSO_4$. Removal of the solvent in vacuo gave **4** (1.30 g, 97%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.40−1.53 (m, 1H), 1.66−1.76 (m, 2H), 1.93−2.05 (m, 1H), 2.14−2.22 (m, 2H), 2.39−2.49 (m, 1H), 2.76 (t, $J = 6.6$ Hz, 2H), 3.22−3.26 (m, 4H), 3.73 (t, $J = 6.6$ Hz, 2H), 4.15−4.43 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.80, 28.33, 37.40, 38.87,

Table 1. Refractive Indices and Absorbances of Polymers P1−P9

	 **P1**	 **P2**	 **P3**	 **P4**	 **P5**	 **P6**
n_{193}	1.66	1.73	1.84	1.84	1.94	1.78
Abs_{193} (mm^{-1})	0.08	0.13	3.15	3.28	5.29	1.19
S (wt%)	0	0	18.8	26.2	36.9	8.2

	 **P7**	 **P8**	 **P9**
n_{193}	1.74	1.82	1.81
Abs_{193} (mm^{-1})	0.17	1.25	1.32
S (wt%)	12.1	15.5	15.5

39.00, 39.37, 45.84, 48.87, 66.61, 72.69, 170.02. IR (NaCl, cm^{-1}): 1361, 1422 (−S−), 1737 (ester). HRMS *m/z* calcd for $C_{11}H_{17}ClO_2S_2$ [M$^+$]: 280.0359; found: 280.0359.

Acrylic Acid 1,4-Dithiaspiro[4.4]non-6-ylmethyl Ester (5). To a stirred solution of **4** (1.12 g, 4.0 mmol) in acetone (8 mL) was added dropwise triethylamine (0.84 mL, 6.0 mmol) at room temperature, and the mixture was stirred at 40 °C for 3 h under nitrogen. The mixture was poured into water, extracted with dichloromethane (DCM), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (DCM) to yield **5** (0.93 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40−1.55 (m, 1H), 1.65−1.78 (m, 2H), 1.95−2.07 (m, 1H), 2.15−2.25 (m, 2H), 2.40−2.52 (m, 1H), 3.22 (s, 4H), 4.15−4.46 (m, 2H), 5.78 (dd, J = 10.2, 1.5 Hz, 1H), 6.08 (dd, J = 17.4, 10.5 Hz, 1H), 6.37 (dd, J = 17.4, 1.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.95, 28.53, 39.10, 39.50, 45.91, 49.23, 66.36, 72.86, 128.44, 130.50, 166.08. IR (NaCl, cm^{-1}): 1271, 1406 (−S−), 1718 (ester). HRMS *m/z* calcd for $C_{11}H_{17}O_2S_2$ [M + H$^+$]: 245.0670; found: 245.0672.

Thioacetic Acid *S*-(3-Oxocyclohexyl) Ester (7). A mixture of 2-cyclohexen-1-one (**6**) (1.92 g, 20 mmol) and thioacetic acid (2.23 mL, 30 mmol) was stirred at 100 °C for 1 h under nitrogen. After the reaction, remaining starting materials were removed in vacuo to yield **7** (3.44 g, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61−1.80 (m, 2H), 1.85−2.10 (m, 2H), 2.12−2.35 (m, 6H), 2.54−2.65 (m, 1H), 3.66−3.78 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.10, 30.49, 30.76, 40.56, 41.37, 46.91, 194.20, 207.77. IR (NaCl, cm^{-1}): 1692, 1720 (ester). HRMS *m/z* calcd for $C_8H_{13}O_2S$ [M + H$^+$]: 173.0636; found: 173.0639.

Thioacetic Acid *S*-(1,4-Dithiaspiro[4.5]dec-7-yl) Ester (8). To a solution of **7** (1.05 g, 6.1 mmol) in benzene (10 mL) were added 1,2-ethanedithiol (0.63 g, 6.7 mmol) and *p*-toluenesulfonic acid (0.12 g, 0.6 mmol) under nitrogen. The reaction mixture was azeotropically distilled for 3 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, washed with 3 wt % $NaHCO_3$ solution, water, and then dried over $MgSO_4$. Removal of the solvent in vacuo gave **8** (1.50 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (qd, J = 12.6, 4.2 Hz, 1H), 1.61−1.72 (m, 1H), 1.75−1.98 (m, 4H), 2.04−2.14 (m, 1H), 2.25 (s, 3H), 2.31−2.37 (m, 1H), 3.27 (s, 4H), 3.61 (tt, J = 12.3, 3.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.85, 30.57, 31.46, 38.10, 38.86, 41.13, 48.09, 67.80, 194.85. IR (NaCl, cm^{-1}): 1353, 1429 (−S−), 1686 (ester).

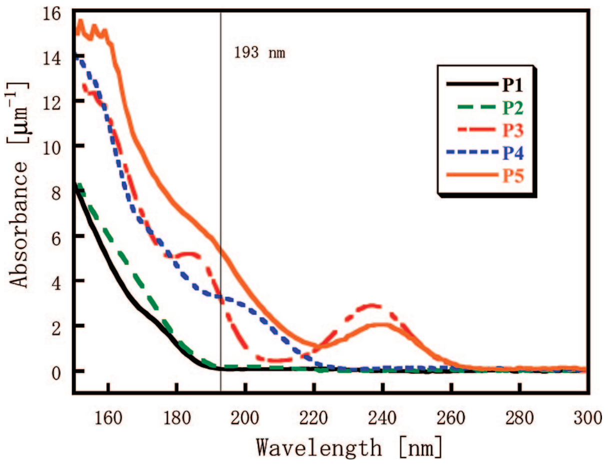


Figure 1. Absorption spectra of **P1**−**P5**.

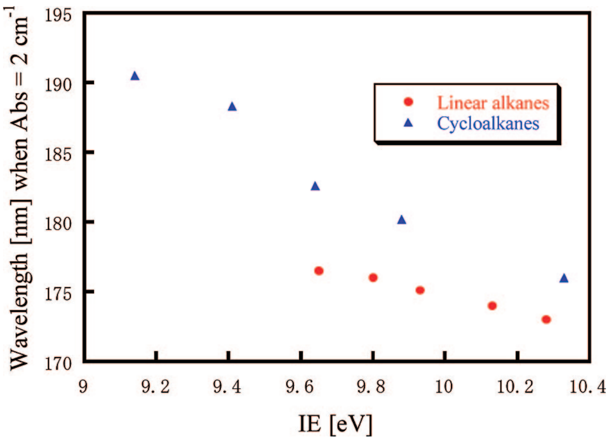


Figure 2. Relationship between ionization energy (IE) and absorbance.

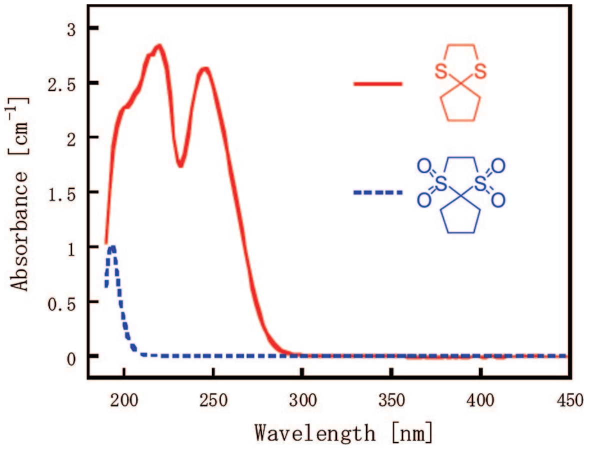


Figure 3. UV spectra of model compounds (0.01 M acetonitrile solution).

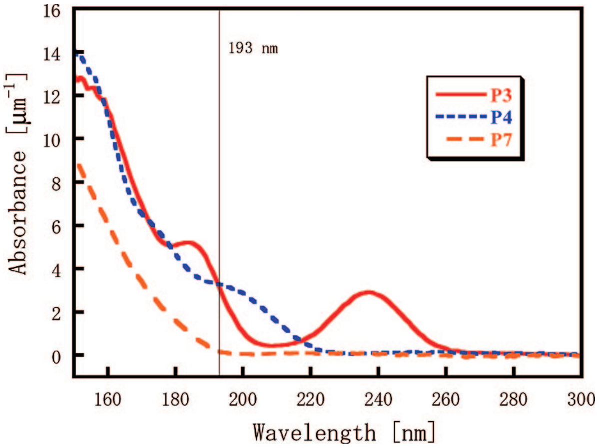


Figure 4. Absorption spectra of **P3**, **P4**, and **P7**.

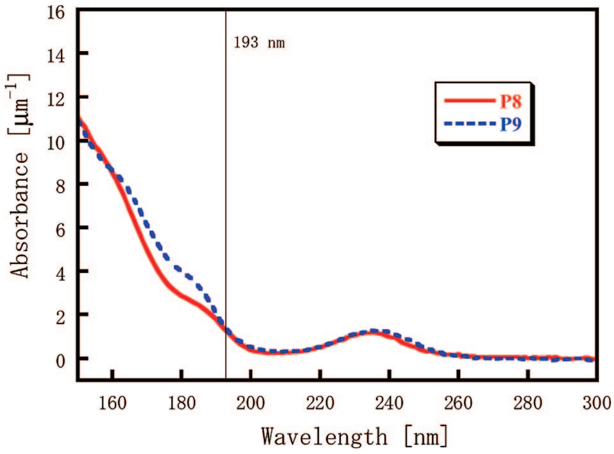


Figure 5. Absorption spectra of **P8** and **P9**.

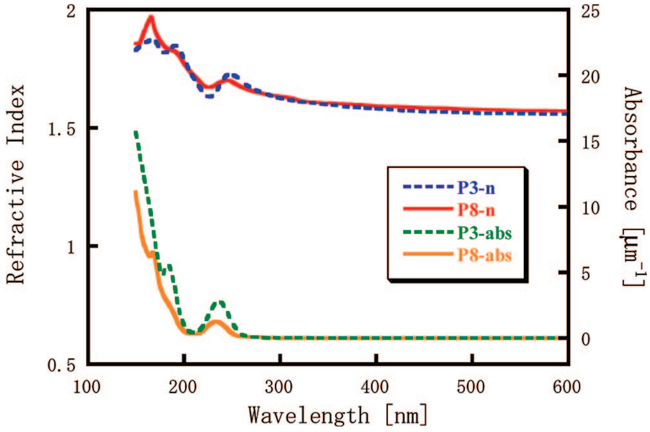
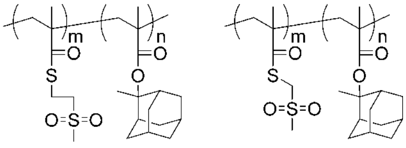


Figure 6. Refractive index and absorbance spectra of **P3** and **P8**.



P10 **P11**

Figure 7. Structures of **P10** and **P11**.

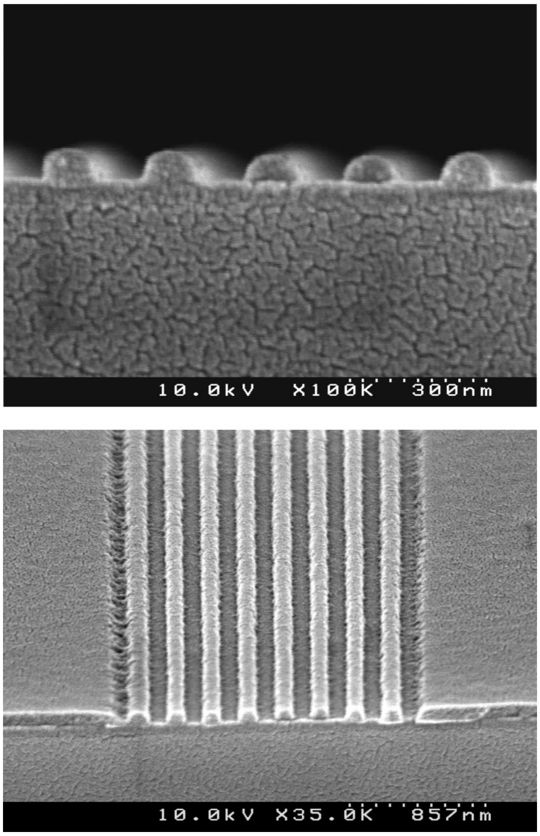


Figure 8. Imaging results for **P11**. Images show 110 nm line and space.

HRMS *m*/*z* calcd for $C_{10}H_{17}OS_3$ [M + H$^+$]: 249.0442; found: 249.0438.

1,4-Dithiaspiro[4.5]decane-7-thiol (9). To a stirred solution of $LiAlH_4$ (0.29 g, 7.2 mmol) in dry ether (20 mL) was added dropwise **8** (1.50 g, 6.0 mmol) in dry ether (14 mL) at 0 °C under nitrogen. The mixture was stirred at room temperature for 6 h. To the reaction mixture was added dropwise water at 0 °C. The mixture was washed with 1 N HCl solution and water, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (DCM/hexane = 3/1) to yield **9** (1.20 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (qd, J = 12.9, 3.6 Hz, 1H), 1.48−1.65 (m, 2H), 1.73−1.94 (m, 3H), 1.97−2.11 (m, 2H), 2.39−2.48 (m, 1H), 2.85−2.98 (m, 1H), 3.21−3.31 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.26, 36.41, 37.10, 38.01, 39.00, 41.06, 53.51, 68.01. IR (NaCl, cm^{-1}): 2921 (−SH). HRMS *m*/*z* calcd for $C_8H_{15}S_3$ [M + H$^+$]: 207.0336; found: 207.0333.

Thioacrylic Acid *S*-(1,4-Dithiaspiro[4.5]dec-7-yl) Ester (10). A solution of **9** (1.0 g, 4.8 mmol) in triethylamine (2.45 mL) and THF (2 mL) was added dropwise to a stirred solution of acryloyl chloride (1.32 g, 14.5 mmol) in THF (6 mL) at −30 °C under nitrogen. The mixture was stirred at −30 °C for 3 h. The mixture was diluted with ethyl acetate, washed with water, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (DCM/hexane = 2/1) to yield **10** (0.94 g, 74%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.28 (qd, J = 12.6, 3.9 Hz, 1H), 1.60−2.15 (m, 6H), 2.34−2.41 (m, 1H), 3.26 (s, 4H), 3.71 (tt, J = 12.3, 3.9 Hz, 1H), 5.60 (dd, J = 8.4, 0.6 Hz, 1H), 6.22−6.30 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.95, 31.41, 38.16, 38.93, 40.95, 41.18, 48.27, 67.84, 126.19, 134.94, 189.38. IR (NaCl, cm^{-1}): 1394, 1444 (−S−), 1670 (ester). HRMS *m/z* calcd for $C_{11}H_{17}OS_3$ [M + H^+]: 261.0442; found: 261.0444.

3-Chloropropionic Acid 1,1,4,4-Tetraoxodithiaspiro[4.4]non-6-ylmethyl Ester (11). To a stirred solution of **4** (0.82 g, 2.9 mmol) in glacial acetic acid (4.8 mL) was added dropwise H_2O_2 (2.11 mL) at room temperature. The reaction mixture was stirred at 80 °C for 3 h. After cooling to room temperature, the reaction mixture was poured into ice-cold water. The precipitate was filtered, washed with water, and then dried in vacuo to yield **11** (0.59 g, 59%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.79−1.92 (m, 2H), 1.95−2.18 (m, 2H), 2.45−2.62 (m, 2H), 2.80 (td, J = 6.9, 0.9 Hz, 2H), 3.08−3.18 (m, 1H), 3.48−3.83 (m, 6H), 4.52 (qd, J = 11.4, 6.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.61, 29.42, 33.30, 37.43, 38.79, 44.60, 48.36, 50.61, 62.82, 82.00, 169.76. IR (NaCl, cm^{-1}): 1125, 1321 (−SO_2−), 1739 (ester). HRMS *m/z* calcd for $C_{11}H_{18}ClO_6S_2$ [M + H^+]: 345.0233; found: 345.0230.

Acrylic Acid 1,1,4,4-Tetraoxodithiaspiro[4.4]non-6-ylmethyl Ester (12). A mixture of **11** (1.03 g, 3.0 mmol), triethylamine (0.63 mL, 4.5 mmol), and acetone (9 mL) was stirred at 50 °C overnight under nitrogen. The mixture was poured into water, extracted with ethyl acetate, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (DCM/ethyl acetate = 3/1) to yield **12** (0.82 g, 89%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.80−2.20 (m, 4H), 2.45−2.62 (m, 2H), 3.08−3.20 (m, 1H), 3.50−3.85 (m, 4H), 4.45−4.60 (m, 2H), 5.83 (dd, J = 10.5, 1.5 Hz, 1H), 6.09 (dd, J = 17.1, 10.5 Hz, 1H), 6.40 (dd, J = 17.1, 1.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.47, 29.36, 32.96, 44.57, 48.36, 50.57, 62.42, 81.97, 127.89, 131.35, 165.48. IR (NaCl, cm^{-1}): 1126, 1337 (−SO_2−), 1719 (ester). HRMS *m/z* calcd for $C_{11}H_{17}O_6S_2$ [M + H^+]: 309.0467; found: 309.0467.

***S*-2-(Methylsulfonyl)ethyl Ethanethioate (14).** To a stirred solution of methyl vinyl sulfone (**13**) (1.59 g, 15 mmol) and thiolacetic acid (1.28 mL, 18 mmol) in THF (22 mL) was added dropwise triethylamine (2.53 mL, 18 mmol) at room temperature and continued stirring for 3 h. After the reaction, 1 N HCl solution was added to the reaction mixture. The mixture was extracted with DCM, dried over $MgSO_4$, and concentrated in vacuo to yield **14** (2.68 g, 98%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.97 (s, 3H), 3.22 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.06, 30.49, 40.82, 54.30, 194.85. IR (NaCl, cm^{-1}): 1132, 1306 (−SO_2−), 1684 (ester). HRMS *m/z* calcd for $C_5H_{11}O_3S_2$ [M + H^+]: 183.0150; found: 183.0151.

2-(Methylsulfonyl)ethanethiol (15). To a stirred solution of $LiAlH_4$ (0.24 g, 6.0 mmol) in dry THF (10 mL) was added dropwise **14** (0.91 g, 5.0 mmol) in dry THF (15 mL) at 0 °C under nitrogen. The mixture was stirred at room temperature for 2 h. To the reaction mixture was added dropwise water at 0 °C and then 1 N HCl solution. The mixture was extracted with DCM, washed with water, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 3/1) to yield **15** (0.62 g, 89%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.78 (t, J = 8.4 Hz, 1H), 2.93−3.00 (m, 5H), 3.28 (dd, J = 8.1, 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.91, 41.22, 57.72. IR (NaCl, cm^{-1}): 1120, 2565 (−SO_2−), 2565 (−SH). HRMS *m/z* calcd for $C_3H_9O_2S_2$ [M + H^+]: 141.0044; found: 141.0041.

***S*-2-(Methylsulfonyl)ethyl 3-Chloropropanethioate (16).** A solution of **15** (0.59 g, 4.2 mmol) and 3-chloropropionyl chloride (0.80 g, 6.3 mmol) in toluene (5 mL) was stirred at 60 °C overnight under nitrogen. The mixture was diluted with ethyl acetate, washed with 3 wt % $NaHCO_3$ solution and water, and dried over $MgSO_4$. Removal of the solvent in vacuo gave **16** (0.93 g, 96%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.98 (s, 3H), 3.03 (t, J = 6.6 Hz, 2H), 3.24−3.30 (m, 4H), 3.76 (t, J = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.85, 38.40, 40.84, 45.85, 53.96, 195.27. IR (NaCl, cm^{-1}): 1120, 1312 (−SO_2−), 1684 (ester). HRMS *m/z* calcd for $C_6H_{12}ClO_3S_2$ [M + H^+]: 230.9916; found: 230.9917.

***S*-2-(Methylsulfonyl)ethyl Prop-2-enethioate (17).** To a stirred solution of **16** (0.93 g, 4.0 mmol) in acetone (8 mL) was added dropwise triethylamine (0.84 mL, 6.0 mmol) at room temperature, and the mixture was stirred at 50 °C overnight under nitrogen. The mixture was poured into water, extracted with DCM, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 3/1) to yield **17** (0.62 g, 80%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.98 (s, 3H), 3.20−3.35 (m, 4H), 5.77 (dd, J = 8.4, 0.6 Hz, 1H), 6.30−6.38 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.69, 40.89, 54.25, 127.94, 134.28, 189.35. IR (NaCl, cm^{-1}): 1120, 1313 (−SO_2−), 1670 (ester). HRMS *m/z* calcd for $C_6H_{11}O_3S_2$ [M + H^+]: 195.0150; found: 195.0152.

***S*-2-(Methylsulfonyl)ethyl 2-Methylprop-2-enethioate (18).** To a stirred solution of **15** (1.46 g, 10 mmol) and methacryloyl chloride (1.24 g, 11 mmol) in THF (14 mL) was added dropwise pyridine (0.94 mL, 11 mmol) at −30 °C under nitrogen. The mixture was stirred at −30 °C for 3 h. The mixture was poured into water, extracted with DCM, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 3/1) to yield **18** (1.28 g, 59%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.96 (t, J = 7.2 Hz, 3H), 3.00 (s, 3H), 3.26 (s, 4H), 5.67 (s, 1H), 6.08 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.78, 21.73, 40.75, 54.23, 124.39, 142.99, 192.27. IR (NaCl, cm^{-1}): 1120, 1313 (−SO_2−), 1664 (ester). HRMS *m/z* calcd for $C_7H_{13}O_3S_2$ [M + H^+]: 209.0306; found: 209.0303.

***S*-Methylthiomethyl Ethanethioate (20).** **20** was synthesized by a reported method.[17]

***S*-Methylsulfonylmethyl Ethanethioate (21).** To a stirred solution of **20** (4.08 g, 30 mmol) in acetone (140 mL) was added potassium permanganate (9.46 g, 60 mmol) in small portions. The reaction mixture was stirred at room temperature for 19 h. The mixture was filtered, and filtrate was concentrated in vacuo. DCM was added, and the mixture was dried over $MgSO_4$ and concentrated in vacuo to yield **21** (3.00 g, 60%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.46 (s, 3H), 2.87 (s, 3H), 4.33 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.03, 38.84, 50.33, 191.28. IR (NaCl, cm^{-1}): 1112, 1302 (−SO_2−), 1700 (ester). HRMS *m/z* calcd for $C_4H_9O_3S_2$ [M + H^+]: 168.9993; found: 168.9993.

Methylsulfonylmethanethiol (22). A mixture of **21** (1.22 g, 7.3 mmol) and concentrated HCl solution (1 mL) in methanol (50 mL) was refluxed overnight. After cooling to room temperature, the reaction mixture was poured into water, extracted with DCM, dried over $MgSO_4$, and concentrated in vacuo to yield **22** (0.67 g, 73%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.40 (t, J = 9.3 Hz, 1H), 3.02 (s, 3H), 3.82 (d, J = 9.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.43, 47.40. IR (NaCl, cm^{-1}): 1114, 1299 (−SO_2−), 2562 (−SH). HRMS *m/z* calcd for $C_2H_7O_2S_2$ [M + H^+]: 126.9887; found: 126.9891.

***S*-Methylsulfonylmethyl 2-Methylprop-2-enethioate (23).** To a stirred solution of **22** (0.46 g, 3.6 mmol) and methacryloyl chloride (0.42 g, 4.0 mmol) in THF (6 mL) was added dropwise pyridine (0.33 mL, 4.0 mmol) at −30 °C under nitrogen. The mixture was stirred at −30 °C for 3 h. The mixture was poured into water, extracted with DCM, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 3/1) to yield **23** (0.59 g, 83%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.99 (s, 3H), 2.86 (s, 3H), 4.39 (s, 2H), 5.79 (s, 1H), 6.19 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.67, 38.71, 50.05, 125.94, 142.14, 188.31. IR (NaCl, cm^{-1}): 1117, 1309 (−SO_2−), 1680 (ester). HRMS *m/z* calcd for $C_6H_{11}O_3S_2$ [M + H^+]: 195.0150; found: 195.0153.

1,4-Dithiaspiro[4.4]nonane. To a solution of cyclopentanone (3.37 g, 40 mmol) in toluene (40 mL) were added 1,2-ethanedithiol (3.77 g, 40 mmol) and *p*-toluenesulfonic acid (0.76 g, 4 mmol) under nitrogen. The reaction mixture was azeotropically distilled for 3 h. After cooling to room temperature, the mixture was diluted with ethyl acetate, washed with 3 wt % $NaHCO_3$ solution, water, and then dried over $MgSO_4$. Removal of the solvent in vacuo gave 1,4-dithiaspiro[4.4]nonane (5.51 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.70−1.75 (m, 4H), 2.08−2.13 (m, 4H), 3.28 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.41, 39.32, 43.84, 70.78. IR (NaCl, cm^{-1}): 1275, 1436 (−S−). HRMS *m/z* calcd for $C_7H_{13}S_2$ [M + H$^+$]: 161.0459; found: 161.0458.

1,1,4,4-Tetraoxodithiaspiro[4.4]nonane. To a stirred solution of 1,4-dithiaspiro[4.4]nonane (0.96 g, 6 mmol) in glacial acetic acid (9.8 mL) was added dropwise H_2O_2 (4.3 mL) at room temperature. The reaction mixture was stirred at 80 °C for 3 h. After cooling to room temperature, the reaction mixture was poured into ice-cold water. The precipitate was filtered, washed with water, and then dried in vacuo to yield 1,1,4,4-tetraoxodithiaspiro[4.5]nonane (1.03 g, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.84−1.89 (m, 4H), 2.41−2.46 (m, 4H), 3.61 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.02, 31.36, 48.80, 81.58. IR (NaCl, cm^{-1}): 1124, 1315 ($-SO_2-$). HRMS *m/z* calcd for $C_7H_{13}O_4S_2$ [M + H$^+$]: 225.0256; found: 225.0252.

Synthesis of Polymers. All of the polymers were prepared by free radical initiated polymerization using AIBN (1 mol %). Polymerizations were performed in methylethyl ketone (**P1**−**P3**), dioxane (**P4**−**P6**), DMSO (**P7**), and cyclohexanone (**P8**−**P11**) at a concentration of 30 wt %. The feed ratio of comonomers was 1:1. The ratio of monomers in the resulting copolymers was determined by ^{1}H NMR and is almost the same as the feed ratio even at low conversion. There was no evidence for large differences in reactivity ratios.

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References and Notes

(1) French, R. H.; Liberman, V.; Tran, H. V.; Feldman, J.; Adelman, D. J.; Wheland, R. C.; Qiu, W.; McLain, S. J.; Nagao, O.; Kaku, M.; Mocella, M.; Yang, M. K.; Lemon, M. F.; Brubaker, L.; Shoe, A. L.; Fones, B.; Fischell, B. E.; Krohn, K.; Hardy, D.; Chen, C. Y. *Proc. SPIE—Opt. Microlithogr.* **2007**, *6520*, 65201O/1–O/12.

(2) Parthier, L.; Wehrhan, G.; Keutel, D.; Knapp, K. *SEMATECH High Index Materials Critical Review*, Kyoto, 2006.

(3) López-Gejo, J.; Kunjappu, J. T.; Zhou, J.; Smith, B. W.; Zimmerman, P.; Conley, W.; Turro, N. J. *Chem. Mater.* **2007**, *19*, 3641–3647.

(4) Kusumoto, S.; Shima, M.; Wang, Y.; Shimokawa, T.; Sato, H.; Hieda, K. *Poly. Adv. Technol.* **2006**, *17*, 122–130.

(5) Conley, W.; Warrick, S.; Garza, C.; Goirand, P.-J.; Gemmink, J.-W.; Van Steenwinckel, D. *3rd Int. Symp. on Immersion Lithography*, Kyoto, 2006.

(6) Smith, B. W.; Zhou, J. *Proc. SPIE—Opt. Microlithogr.* **2007**, *6520*, 65200A/1–A/10.

(7) Costner, E.; Taylor, J. C.; Caporale, S.; Wojtczak, W.; Dewulf, D.; Conley, W.; Willson, C. G. *Proc. SPIE—Opt. Microlithogr.* **2006**, *6153*, 61530B/1–B/11.

(8) Whittaker, A. K.; Blakey, I.; Liu, H.; Hill, D. J. T.; George, G. A.; Conley, W.; Zimmerman, P. *Proc. SPIE—Opt. Microlithogr.* **2005**, *5753*, 827–835.

(9) Blakey, I.; Conley, W.; George, G. A.; Hill, D. J. T.; Liu, H.; Rasoul, F.; Whittaker, A. K. *Proc. SPIE—Opt. Microlithogr.* **2006**, *6153*, 61530H/1–H/10.

(10) Blakey, I.; Chen, L.; Dargaville, B.; Liu, H.; Whittaker, A. K.; Conley, W.; Piscani, E.; Rich, G.; Williams, A.; Zimmerman, P. *Proc. SPIE—Opt. Microlithogr.* **2007**, *6519*, 651909/1–651909/9.

(11) Zimmerman, P.; Peski, C.; Rice, B.; Byers, J.; Turro, N. J.; Lei, X.; López-Gejo, J.; Liberman, V.; Palmacci, S.; Rothschild, M.; Whittaker, A.; Blakey, I.; Chen, L.; Dargaville, B.; Liu, H. *J. Photopolym. Sci. Technol.* **2007**, *20*, 643–650.

(12) Takechi, S.; Takahashi, M.; Kotachi, A.; Nozaki, K.; Yano, E.; Hanyu, I. *J. Photopolym. Sci. Technol.* **1996**, *9*, 475–487.

(13) Nozaki, K.; Watanabe, K.; Yano, E. *J. Photopolym. Sci. Technol.* **1996**, *9*, 509–522.

(14) Costner, E. A.; Matsumoto, K.; Long, B. K.; Taylor, J. C.; Wojtczak, W.; Willson, C. G. *Proc SPIE—Opt. Microlithogr.* **2008**, *6923*, 000. in press.

(15) Block, E.; Corey, E. R.; Penn, R. E.; Renken, T. L.; Sherwin, P. F.; Bock, H.; Hirabayashi, T.; Mohmand, S.; Solouki, B. *J. Am. Chem. Soc.* **1982**, *104*, 3119–3130.

(16) NIST database, http://webbook.nist.gov/chemistry/.

(17) Ahern, T. P.; Haley, M. F.; Langler, R. F.; Trenholm, J. E. *Can. J. Chem.* **1984**, *62*, 610–614.

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