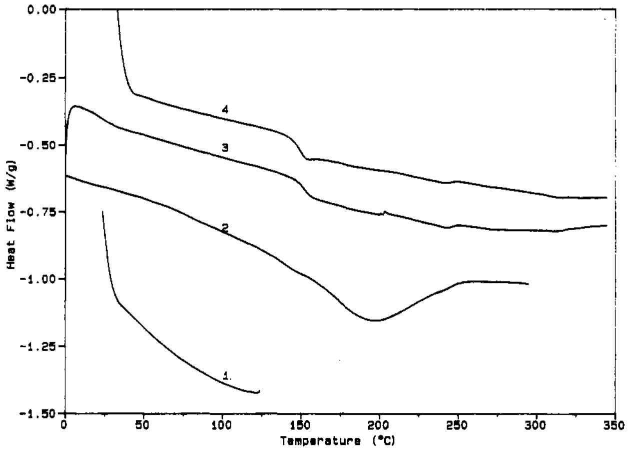

Figure 2. DSC thermograms of the 1:1 PBZT/PTMHT composite heated at 20 °C/min. The first (1), second (2), third (3), and fourth (4) heating indicated.

PTMHT composites did not exhibit any T_g. However, as Figure 2 shows, after first and second heating to 300 °C, cooling, and reheating, the 1:1 PBZT/PTMHT composite showed a sharp T_g at 153 °C, which is identical with the T_g of the pure PTMHT. In the case of PBZT/nylon 66 composites, the DSC results revealed a broad endothermic transition with peak at 247 °C on first heating to 300 °C. Cooling and twice reheating the same sample to 300 °C resulted in a sharp endotherm with peak at 247 °C, which we interpret as the melting point of the nylon 66 phase in the phase-separated composite. These DSC results show that thermally induced phase separation had occurred due to heating of both rod/coil composites.

Direct visualization of the morphology and thermally induced phase separation of the PBZT/PTMHT and PBZT/nylon 66 composites was made by optical microscopy. A homogeneous featureless morphology was observed on the scale of 100 nm in the as-prepared molecular composites. However, when the same films were heated to 300 °C and cooled, a heterogeneous morphology containing a dispersed phase feature with a diameter of about 1–2 μm was observed. A similar observation of the morphology and thermally induced phase separation in the PBZT/nylon 66 composite system has previously been reported by others.[5]

The nonresonant third-order NLO coefficient, $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$, of the molecular composites was investigated by picosecond third harmonic generation (THG) experiments whose details will be reported elsewhere.[11] The THG measurements on thin films with thicknesses in the range 120–640 nm were done at a fundamental wavelength of 1.9 μm and were accurate to ±20%. Each data point was obtained from the averages of several samples. Table II shows the $\chi^{(3)}$ values for the pure PBZT and four rod/coil molecular composites. The composition dependence of the $\chi^{(3)}$ of PBZT/nylon 66 composites shows the expected linear decrease with decreasing mole fraction of the NLO component, PBZT. However, the measured $\chi^{(3)}$ for the PBZT/PTMHT molecular composites shows significantly enhanced values compared to what is predicted from a linear mixing rule. The mechanism for this enhancement of the third-order NLO properties of PBZT/PTMHT molecular composites is yet to be elucidated.

In summary, thin films of molecular composites of the nonlinear optical rigid-rod polymer PBZT in the matrix of two flexible-coil polyamides, nylon 66 and PTMHT, have been prepared from ternary solutions of the Lewis acid complexes of the polymers in organic solvents. The measured nonlinear optical properties of the molecular composites showed a linear dependence with composition in the case of PBZT/nylon 66 composites and more enhanced optical nonlinearities than expected from a linear mixing rule in the case of PBZT/PTMHT composites. These results demonstrate that thin-film nonlinear optical composite materials with enhanced optical properties can be prepared from soluble complexes of the component polymers. The results also demonstrate that nonlinear optical techniques, such as third harmonic generation, constitute a promising sensitive probe of the solid-state structure of polymer molecular composites.

Table II. Composition Dependence of the Third-Order Nonlinear Optical Properties of Molecular Composites

sample	mol % PBZT	$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$,[a] 10^{-11} esu
PBZT	100	1.37
1:1 PBZT/nylon 66	50	0.70
1:2 PBZT/nylon 66	33	0.39
1:1 PBZT/PTMHT	50	1.07
1:2 PBZT/PTMHT	33	0.62

[a] All $\chi^{(3)}$ data accurate to ±20%.

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Registry No. PBZT (SRU), 69794-31-6; PTMHT (copolymer), 53834-90-5; PTMHT (SRU), 61991-47-7; $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3; nylon 66, 32131-17-2.

Bis(perfluorophenyl) Azides: Efficient Cross-Linking Agents for Deep-UV and Electron Beam Lithography

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The miniaturization of integrated circuits in the microelectronics industry[1] has spearheaded the development of alternatives to conventional photolithography.[2–4] Deep-UV,[5] electron beam (EB),[6] and X-ray lithography[7] techniques have thus emerged using resists with submicron resolution. However, these resists are not without limitation.

Deep-UV-initiated cross-linking of polymers such as poly(*p*-vinylphenol)[8] and novolac (polycresol–form-

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[†] Department of Chemistry.

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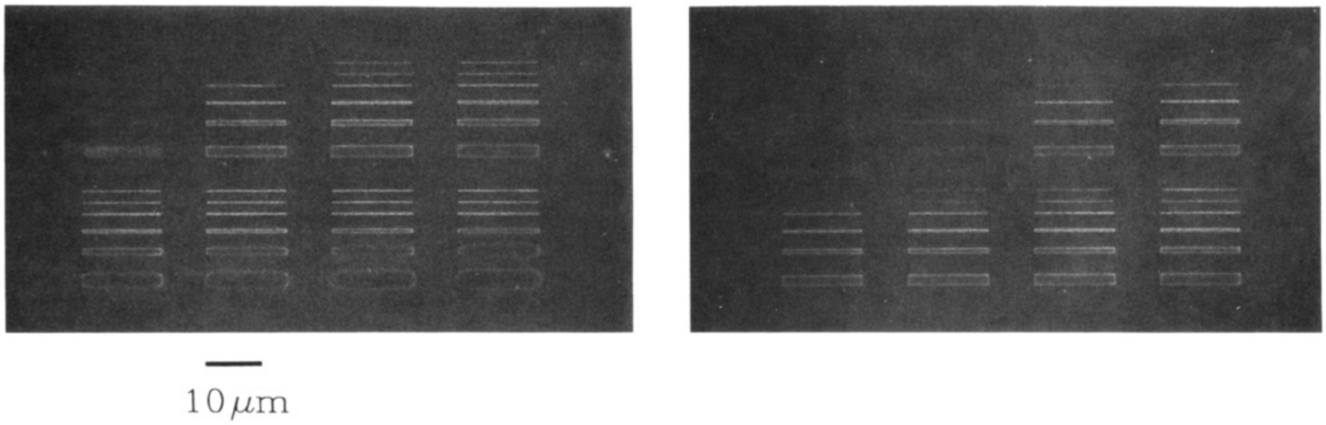
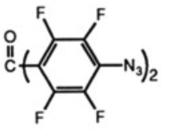


Figure 1. Micrographs comparing the sensitivities of PS resists containing **2** (left) and **6** (right). Each micrograph consists of eight six-line patterns. Within each pattern, the drawn line thicknesses are 0.1 (top), 0.1, 0.2, 0.5, 1.0, and 2.0 μm. EB doses increased from left to right: top rows, 5, 10, 15, and 20 $\mu C/cm^2$; bottom rows, 25, 30, 35, and 40 $\mu C/cm^2$.

aldehyde) resin[9] by bisazides such as bis(3-azidophenyl) sulfone gives negative resists. However, owing to poor cross-linking efficiency, a high percentage (20 wt %) of the bisazide is required, which renders a resist film of 1-μm thickness virtually opaque to 200–300-nm light. Consequently, undercut profiles are typically observed after development, requiring careful control of processing conditions to maintain line width and reproducibility.

We have recently reported the synthesis of functionalized perfluorophenyl azides (PFPAs) as photolabeling agents showing improved CH insertion efficiency over nonfluorinated analogues.[10-12] Since the overall cross-linking efficiency of a bisazide depends on the square of the efficiency of the individual azide groups,[13] we reasoned that bis-PFPAs should be efficient cross-linkers in resist chemistry. Herein, we describe a convenient synthesis of bis-PFPAs **1** and **2** and demonstrate their improved performance in relation to deep-UV and EB lithography.



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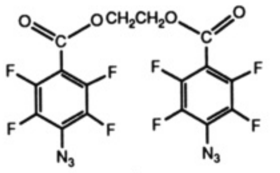

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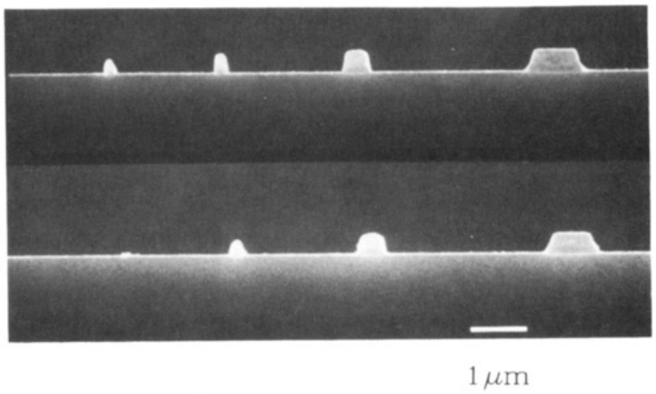
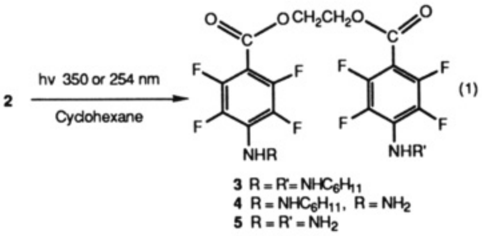


Figure 2. Micrographs comparing the cross sections of lines drawn in PS resists containing **2** (top; dose, 15 $\mu C/cm^2$) and **6** (bottom; dose, 30 $\mu C/cm^2$). The drawn line thicknesses are 0.1, 0.2, 0.5, and 1.0 μm.

Bis-PFPA **1**[14] (96%, mp 134–135 °C, $\lambda_{max} = 249$ and 293 nm, log $\epsilon = 4.1$ and 4.6, respectively) was prepared by the reaction of decafluorobenzophenone (Aldrich Co.) with NaN_3.[10,15] Acylation of ethylene glycol with 2 equiv of 4-azidotetrafluorobenzoyl chloride[10] in ether containing 2 equiv of Et_3N gave bis-PFPA **2**[14] (98%, mp 75–76 °C, $\lambda_{max} = 264$ nm, log $\epsilon = 4.6$, log $\epsilon_{254} = 4.5$). Photolysis[16] of **2** in cyclohexane gave a remarkable 45% yield of bis-CH insertion product **3**[14] ($\lambda_{max} = 292$ nm, log ϵ 4.6, log $\epsilon_{254} = 3.6$) along with mono-CH insertion product **4**[14] (21%, $\lambda_{max} = 285$ nm, log $\epsilon = 4.3$, log $\epsilon_{254} = 3.8$) and bisaniline **5**[14] (5%, eq 1). The longer λ_{max} and the smaller ϵ_{254} values of major products **3** and **4** compared to those of **2** indicate that **2** is partially bleachable at 254 nm. Photolysis of the popular cross-linking agent 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone (**6**) under conditions used for **2** gave only a red tar that is possibly a poly(1,2-azepine).[17]



The next series of experiments compares operationally the cross-linking abilities of **1**, **2**, and nonfluorinated bisazide **6** toward cyclized poly(isoprene) (CPI)[18] and polystyrene (PS). PS is used as a negative deep-UV[19] and high-resolution EB[20,21] resist, but its limitation is low

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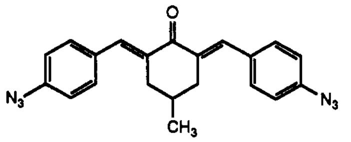
sensitivity. The face of a NaCl plate (IR transparent) was coated with a film of CPI containing varying amounts of the bisazide and then irradiated with 254-nm light. Photolysis was monitored by FTIR at 2120 cm^{-1} (azide absorption). When this was complete ($\sim$1 min), the plate was developed by dipping in xylene for 1 min followed by an isopropyl alcohol rinse. The relative intensity of the C–H stretching band at 2900–3000 cm^{-1} in the FTIR spectrum was used to estimate the amount of CPI rendered insoluble through cross-linking. A control experiment consisting of CPI without cross-linking agent showed no C–H absorption after development, confirming that only cross-linked CPI remained on the plate. To achieve 80% retention of the film, the presence of 1.0 wt % of **2** was required compared to 4.8 wt % of **6**. With PS, 5.8 wt % of **1** gave 80% retention whereas 5.9 wt % of the mono-PFPA, methyl 4-azidotetrafluorobenzoate (**7**),[10] and 23.1 wt % of **6** both gave <10% retention. These data support the notion that efficient cross-linking of polymer chains occurs with bis-PFPAs **1** and **2**. The cross-linking process may involve bis-C–H insertion reactions (eq 2) analogous to that observed in the solution photolysis of **2** in cyclohexane (eq 1). With CPI, the cross-linking process can also involve a reaction between the nitrene intermediate and a carbon–carbon double bond with formation of an aziridine.



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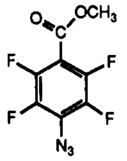

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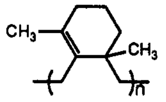
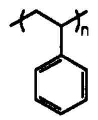
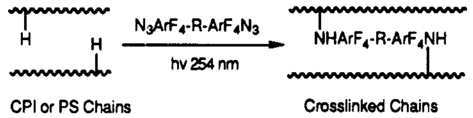


CPI



PS



(2)

Comparative EB lithography on films of **2** and **6** in PS utilized a scanning electron microscope (SEM) controlled by a pattern generator to provide accurate exposure conditions.[22] The resists were spin coated (0.4-μm thickness) on silicon wafers and prebaked for 35 min at 90 °C. A pattern consisting of a group of horizontal lines was reproduced many times, each time with a different electron dose but a constant accelerating voltage of 15 kV. The EB-exposed films were developed by dipping in xylene for 25 s and then rinsing in isopropyl alcohol for 10 s.

The SEM was used to observe the developed patterns after coating with 20 nm of gold (Figure 1). The sensitivity of each resist was estimated from the lowest electron dose that produced the 0.1-μm lines. The lines designed to be 0.1 μm were found to be almost 0.2 μm after exposure and processing (Figure 2). This implies that 0.2 μm is the resolution limit for the conditions used. We find that 6.6 wt % of **2** in PS increased the sensitivity of PS about 7-fold, while **6** at the same molar concentration gave only a 3-fold sensitivity increase. Control experiments showed that PS containing mono-PFPA **7** ([**7**] = 2[**2**]) performed only marginally better than PS itself in EB lithography.

We conclude that bis-PFPAs **1** and **2** are efficient cross-linkers for deep-UV and EB lithography. Bisazide **2** also shows a higher sensitivity in EB lithography than the nonfluorinated analogue, bisazide **6**.

Acknowledgment. This work was supported by NIH Grant GM-23137. We thank Tektronix, Inc., for supporting the scanning electron microscope used in this work.

Registry No. 1, 129835-90-1; 2, 129835-91-2; CPI, 9003-31-0; PS, 9003-53-6.

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Oxidation–Reduction Reactions for Preparation of $[Ti(OC_6H_4O)_2]_n$ and Related Metalloquinone Polymers: Hybrid Inorganic–Organic Metal Oxides

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We have explored the preparation of inorganic and transition-metal-containing polymers using common, high-yield reactions in inorganic chemistry. In this way two approaches were found to novel polymeric solids that are hybrids of metal oxides and organic spacer groups. One approach couples a two-electron oxidation of zero- or low-valent metals with reduction of difunctional organic molecules, such as benzoquinone. For oxophilic metals, this redox process results in polymer formation as outlined in Scheme I. This polymerization was demonstrated by reaction of a variety of divalent main-group metal complexes, such as $(R_2N)_2Ge$, R_2Sn, and Sn(β-ketoenolate)$_2$, with *p*-benzoquinone, giving linear polymers of general formulation $\{L_nM(OC_6H_4O)\}_n$.[1,2] The second approach is a condensation reaction of selected organometallic reagents with difunctional organic molecules.[3] In the present work we combine the two approaches, showing that the redox reaction applied to a zerovalent transition-metal complex gives a polymeric solid and that essentially the same solid is obtained through the condensation of a high-valent transition-metal complex with hydroquinones.

A novel solid is obtained by reaction of $Ti(tol)_2$ (tol = toluene) with 2 equiv of 1,4-benzoquinone. Reaction of a solution of the zero-valent titanium complex $Ti(tol)_2$ with a solution of *p*-benzoquinone gives a red gel nearly within the time of mixing. The gel slowly converts to a red powder in the THF polymerization solvent. The red powder retains about 5 times its weight in solvent. Final removal of solvent requires 72 h under vacuum to give a product formulated as a three-dimensional network structure of $[Ti(OC_6H_4O)_2]_n$.[4] The same product is also

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† Contribution no. 5553.

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(4) Toluene (1.25 equiv) was detected by GC in the supernatant solution. The remaining toluene presumably is trapped in the network structure, released only after prolonged times in dynamic vacuum.

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