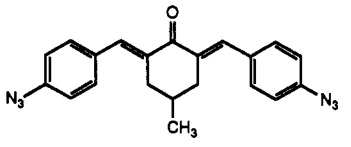
sensitivity. The face of a NaCl plate (IR transparent) was coated with a film of CPI containing varying amounts of the bisazide and then irradiated with 254-nm light. Photolysis was monitored by FTIR at 2120 cm^{-1} (azide absorption). When this was complete ($\sim$1 min), the plate was developed by 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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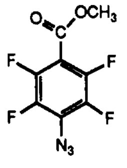

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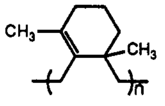
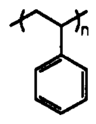
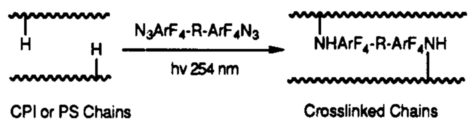


CPI



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$_6$H$_4$O)$_2$]$_n$ 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$_2$N)$_2$Ge, R$_2$Sn, 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$_6$H$_4$O)$_2$]$_n$.[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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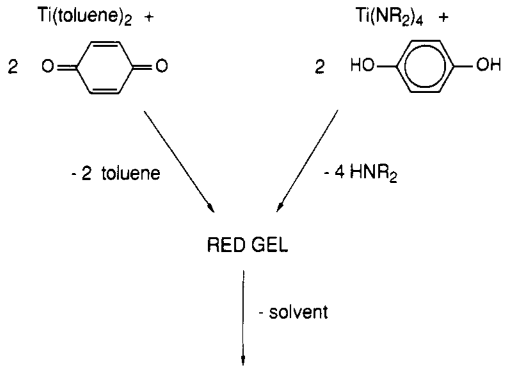
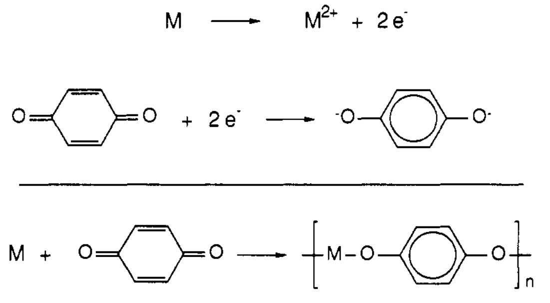


Figure 1. Synthesis of the network polymer $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$ by an oxidation–reduction pathway or by a condensation polymerization.

Scheme I



formed by condensation of tetravalent $\mathrm{Ti}[\mathrm{N}(\mathrm{CH}_3)_2]_4$ with 2 equiv of hydroquinone (Figure 1). Qualitatively, the condensation route gives a less stable gel than the redox method of preparing $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$, although both routes give $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$ quantitatively.

$[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$ is insoluble in common organic solvents, suggesting a highly cross-linked structure. Elemental analysis, infrared spectroscopy, and solid-state $^{13}\mathrm{C}$ NMR spectroscopy are all consistent with the formulation $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$.[5] Additionally, wide-angle X-ray analysis shows that the network structure is amorphous. $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O}_2]_n$ is air stable but hydrolyzes in the presence of large amounts of water. The solid dissolves in organic solvents such as $\mathrm{CH}_2\mathrm{Cl}_2$ containing large excesses of phenol, ethanol, or hydroquinone to give the $\mathrm{Ti}(\mathrm{OR})_4$ starting material, showing the reversibility of the polymerization. $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$ has a high surface area, up to 250 m^2/g with a broad pore size distribution (N_2 absorption, BET method), although the relationship between preparative details and surface area is unclear. These surface areas are comparable to that of alumina. Infrared spectroscopic studies show physisorbed water is present, anhydrous product being obtained by heating to 180 °C. Thermal gravimetric analysis of the hydrated samples shows an endothermic loss of water at about 180 °C with loss of 23% of the mass, followed by a gradual loss of an additional 50% of the sample weight up to 800 °C. The pyrolysis of $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$ at 1065 °C in air leaves 25.5% of the sample weight as the rutile phase of TiO_2, by X-ray analysis (carbon content = 0.14%, by microanalysis).

Thin films of $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$ on quartz slides were prepared by alternately dipping the slide into solutions of $\mathrm{Ti}[\mathrm{N}(\mathrm{CH}_3)_2]_4$ and hydroquinone, thickness depending on the number of dipping cycles. These films have a broad UV absorption maximum at 350 nm which tails into the visible region. The absorption maximum is red-shifted by about 15 nm from that of $\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_5)_4$. Electrochemical studies of thin films on electrode surfaces showed no evidence for reduction of the polymer, but an oxidation wave was observed for oxidation of the organic ligand.[6] The oxidation dissolved the film from the electrode, presumably depolymerizing the solid by reversing the benzoquinone reduction shown in Scheme I.

Treatment of a pentane slurry of $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$ with AlEt_3 and 20 atm of ethylene at 80 °C yielded polyethylene, although the polymerization was slow compared to $\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_5)_4$ treated identically with AlEt_3 and ethylene in pentane. Nevertheless these results show that $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$ is an air-stable catalyst precursor for ethylene polymerization.

These synthetic methods are general and apply to a wide range of metals and quinones or hydroquinones. $\mathrm{Ti}(\mathrm{OR})_4$ can be used interchangeably with $\mathrm{Ti}(\mathrm{NR}_2)_4$ in the condensation reaction with 1,4-hydroquinone. Reaction of $\mathrm{Zr}(\mathrm{NEt}_2)_4$ with 1,4-hydroquinone gives a white powder of formulation $[\mathrm{Zr}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$. $\mathrm{Cr}(\mathrm{benzene})_2$ reacts with *p*-benzoquinone (> 3 equiv.) to yield a dark yellow powder, but no gel forms. The infrared spectrum of this solid shows the presence of $-\mathrm{OC}_6\mathrm{H}_4\mathrm{O}-$ groups, although the exact composition is unclear. Its pyrolysis gives $\mathrm{Cr}_2\mathrm{O}_3$ with a small amount of some unidentified phase.

Other quinones used in the redox reaction with $\mathrm{Ti}(\mathrm{tol})_2$ include 1,4-anthraquinone and 2,5-dihydroxy-1,4-benzoquinone. The 2,5-dihydroxy-1,4-benzoquinone-derived polymer is stable to water, presumably because the titanium is of higher coordination number, thereby blocking hydrolysis. Reaction of $\mathrm{Ti}(\mathrm{NMe}_2)_4$ with 4,4′-isopropylidenediphenol and with 4,4′-biphenol gives yellow solids with an infrared spectrum consistent with the formulation $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{C}(\mathrm{CH}_3)_2\mathrm{C}_6\mathrm{H}_4\mathrm{O})_2]_n$ and $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{C}_6\mathrm{H}_4\mathrm{O})_2]_n$, respectively. Reaction of 1,4-hydroquinone with cosolutions of $\mathrm{Ti}(\mathrm{NMe}_2)_4$ and $\mathrm{Zr}(\mathrm{NEt}_2)_4$ gives the copolymer of the two metal oxide fragments.

Nitrogen analogues of the hybrid metal oxide/organic polymers were prepared by condensation of $\mathrm{Ti}(\mathrm{NR}_2)_4$ with 1,4-phenylendiamine.[7] This reaction is much slower and yields a more stable gel than the hydroquinone. The product can be isolated by removal of solvent, but the product is extremely air sensitive, decomposing to a brown residue within seconds in open air. The air sensitivity of this material has precluded characterization. We are presently attempting to stabilize gels from the benzoquinone and hydroquinone polymers with the aim of preparing aerogels, xerogels, and interpenetrating networks. Finally we note that network polymers based on coordination complexes of $\mathrm{C}(\mathrm{C}_6\mathrm{H}_4\mathrm{CN})_4$ with metal ions form crystals with a porous structure.[8] Also, hybrid organic–inorganic network polymers based on silica gel have been described.[9–12]

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(5) Elemental anal. Found: 52.84, 52.92% C; 3.88, 3.93% H (Microanalysis, Inc.). Calcd for $\mathrm{C}_{12}\mathrm{H}_8\mathrm{O}_4\mathrm{Ti}$: 54.55% C, 3.03% H. Infrared spectrum (KBr pellet): 3386 (s), 1595 (w), 1480 (s), 1210 (s), 830 (s), 810 (s) cm^{-1}. The infrared spectra were identical for the samples for the two methods of preparation. Solid-state $^{13}\mathrm{C}$ NMR spectra for $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$ was also identical for the two methods of preparation: 160.0 and 117.9 ppm in intensity ratio 1:2. Scanning electron microscopy showed that the $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$ particles were irregular in size and shape.

(6) $[\mathrm{Ti}(\mathrm{OC}_6\mathrm{H}_4\mathrm{O})_2]_n$ was coated on indium–tin oxide electrodes by dipping alternately in $\mathrm{Ti}(\mathrm{NR}_2)_4$ solutions and hydroquinone solutions for 10 dipping cycles. No electrochemical activity was observed for negative potentials in acetonitrile. On cycling to positive potentials, anodic current was observed at +0.8 V (vs SCE) which peaked at +1.6 V. This process removed the film from the electrodes; consequently, no current was observed on the next scan.

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Supplementary Material Available: Detailed preparation of $[\mathrm{Ti(OC_6H_4O)_2}]_n$, TGA curve of $[\mathrm{Ti(OC_6H_4O)_2}]_n$, and infrared spectral data on products from reaction of $\mathrm{Ti(NMe_2)_4}$ with 4,4′-isopropylidenediphenol and with 4,4′-diphenol, from reaction of $\mathrm{Cr(benzene)_2}$ with *p*-benzoquinone, from reaction of $\mathrm{Zr(NEt_2)_4}$ with 1,4-hydroquinone, and from reaction of $\mathrm{Ti(tol)_2}$ with 1,4-anthraquinone and with 2,5-dihydroxy-1,4-benzoquinone (3 pages). Ordering information is given on any current masthead page.

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AM1 Study of Hydrogen-Bonded Mixed Dimers of Substituted Benzoic Acids

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Crystals of stoichiometric 1:1 mixtures of compounds that can complex with each other have been shown to form preferentially, rather than pure crystals of the individual components. In some cases these crystals have potential nonlinear optical properties. An interesting example is the 1:1 mixture of *p*-aminobenzoic acid and *m*,*m*-dinitrobenzoic acid.[1] A view of the crystal structure is shown in Figure 1. Examination of this figure leads one to the hypotheses that the preference for the mixed crystal may be due to either (a) a more stable H-bonded interaction between the different benzoic acids in the heterodimer than in the homodimer or (b) the ability of the mixed crystal (heterodimers) to H bond between their amino and nitro groups. It is likely that both of these factors play a role in the stability of the crystal structure. Calculational modeling can aid in determining the importance of these factors.

To determine whether molecular orbital methods could be used to predict and explain preferences for cocrystallization analogous to that discussed above, we present AM1 calculations on the dimerization energies of variously substituted benzoic acids.

Methods

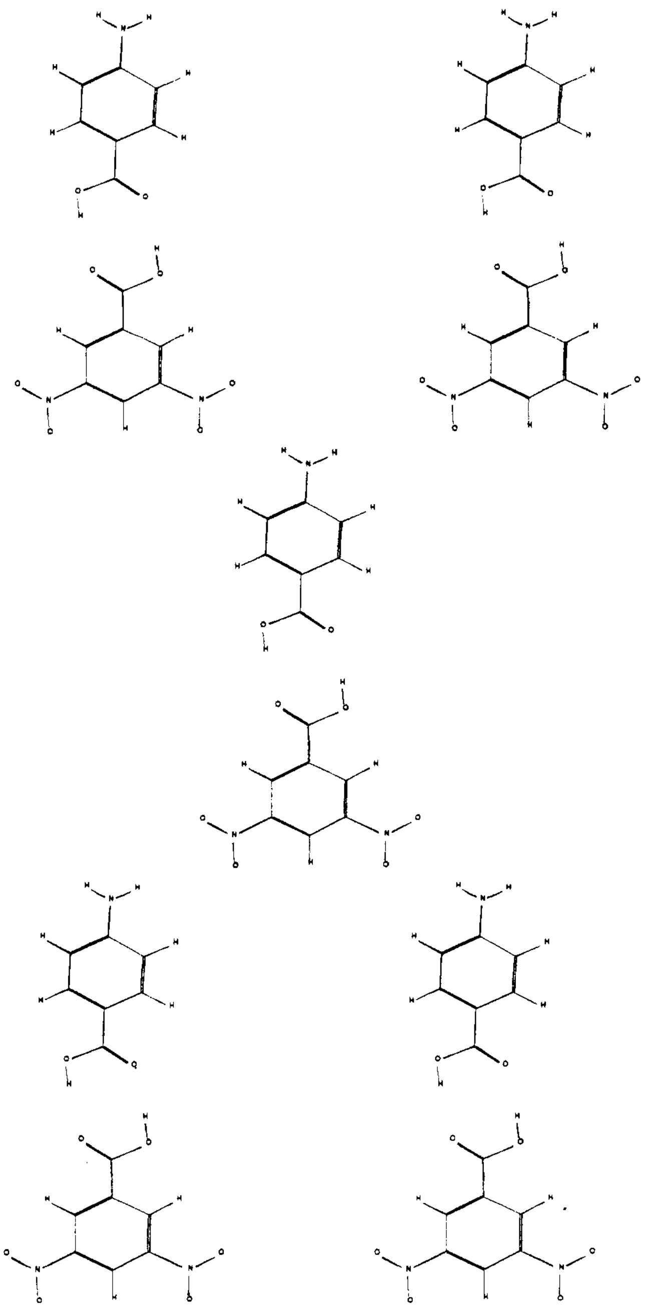

Figure 1. H-bonded aggregate of the crystal of the 1:1 complex of *p*-aminobenzoic acid and 3,5-dinitrobenzoic acid.

The AM1[2] approximation to molecular orbital theory has been used for these studies. This method overcomes the problems that previous semiempirical methods (notably, MNDO[3]) have in describing hydrogen bonds. It has been used with success in several hydrogen-bonding studies,[4] including modeling of the H bonding between molecules of various nitroanilines in the crystalline state.[5] Ab initio studies of H-bonding systems are very sensitive to basis set and correction for electron correlation, as exemplified in studies of the water dimer.[4b,6] Calculations of sufficient accuracy on molecular complexes of the size to be considered here are not practicable using such costly methods.

All geometrical parameters for each monomer and dimer were individually optimized.

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