

It is not surprising that the relative reduction for the two properties is different. The conductivity, while being sensitive to the intrachain interactions (i.e., the electron delocalization), is also sensitive to interchain interactions (i.e., electron hopping between chains), which depend on the polymer molecular weight and degree of alignment, as well as other factors such as dopant species and concentration. The optical nonlinearity is also sensitive to intrachain interactions but has different interchain physics. Also, although 2-methyl substitution on the ring reduces the  $\chi^{(3)}$  of polyaniline, other ring substituents such as the highly polarizable sulfonate or strong electron donors/acceptors might have a beneficial effect.

The effect of the oxidation state,  $1 - y$ , on the  $\chi^{(3)}$  of polyanilines appears to be large, although it is yet to be fully investigated. The fully reduced base ( $1 - y = 0$ ) is expected to have a small  $\chi^{(3)}$  because the  $sp^3$ -hybridized nitrogen prevents electron delocalization. Thus, the bond additivity model is expected to work well, and the  $\chi^{(3)}$  is expected to be close to any substituted benzene because the second hyperpolarizability would be dominated by the benzene ring. So, even though the polyleucoemeraldine base has not yet been measured due to its ready oxidation in air, its  $\chi^{(3)}$  can be estimated to be about that of aniline, which has a  $\chi^{(3)} = 1.7 \times 10^{-13}$  esu ( $\gamma = 5.7 \times 10^{-36}$  esu).<sup>19</sup> This apparent 2 orders of magnitude increase in  $\chi^{(3)}$  in going from zero to intermediate oxidation state ( $1 - y \approx 0.44$ ) is understandable considering the increase in electronic delocalization and the greater polarizability of the quinoid rings in PEMB compared to the all-benzenoid rings in polyleucoemeraldine base. In fact, similar effects of oxidation on the  $\chi^{(3)}$  of poly(thiophene methylene) and poly(thiophene methine) system have been observed.<sup>6</sup> Hence, it can be expected that further oxidation of polyaniline to the fully oxidized ( $1 - y = 1$ ) polypernigraniline<sup>9d</sup> will result in enhanced  $\chi^{(3)}$ .

The measured nonresonant  $\chi^{(3)}$  values of PEMB and POTB are large and compare favorably to the reported  $\chi^{(3)}$  values, determined by third harmonic generation at similar wavelength, of other conjugated polymers. Films of poly(*p*-phenylene vinylene) (PPV) and its methoxy derivative have a  $\chi^{(3)}$  of  $7.8 \times 10^{-12}$  and  $5.4 \times 10^{-11}$  esu, respectively, at  $1.85 \mu\text{m}$ .<sup>4a,c</sup> However, highly oriented PPV films have a  $\chi^{(3)}$  of  $1.5 \times 10^{-10}$  esu at  $1.85 \mu\text{m}$ .<sup>4b</sup> The  $\chi^{(3)}$  value of amorphous spin-coated thin films of 3,4-dialkylpolythiophene is  $4.4 \times 10^{-11}$  esu at  $2.4 \mu\text{m}$ ,<sup>5a</sup> and that of polythiophene vinylene is  $3.2 \times 10^{-11}$  esu at  $1.85 \mu\text{m}$ .<sup>4d</sup> Isotropic thin films of the rigid-rod poly(*p*-phenylenebenzobisthiazole) have a  $\chi^{(3)}$  of  $1.4 \times 10^{-11}$  esu,<sup>7,8</sup> whereas polyacetylene has a  $\chi^{(3)}$  of  $5 \times 10^{-10}$  esu.<sup>3a</sup>

In summary, we have investigated the third-order nonlinear optical properties of polyanilines and poly(*o*-toluidine) in their emeraldine base forms by picosecond third harmonic generation at  $2.4\text{-}\mu\text{m}$  wavelength. The  $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$  was found to be  $2.6 \times 10^{-11}$  esu for polyemeraldine base (PEMB) and  $1.07 \times 10^{-11}$  esu for poly(*o*-toluidine). The results suggest a strong dependence of  $\chi^{(3)}$  on the oxidation state and on derivatization of the phenylene rings of polyanilines. It is suggested that the fully oxidized polypernigraniline will be found to exhibit the largest  $\chi^{(3)}$  among the family of polyanilines. Our ongoing work is investigating the effects of oxidation states ( $0 \leq 1 - y \leq 1$ ) and dispersion on the  $\chi^{(3)}$  of polyanilines.

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## $\mathbf{M}_2(\mathbf{OR})_6$ Compounds ( $\mathbf{M} = \mathbf{Al, Mo, W}$ ; $\mathbf{R} = t\text{-Bu, cy-Hex}$ ) as Single-Source Precursors. Studies of Thermolysis under He Flow

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The term "single-source precursor" is one that has gained popular recognition with the development of the molecular precursor strategy for the synthesis of solid-state materials. Particularly fruitful have been the syntheses of group III:V materials such as GaAs from molecules containing covalent Ga-As bonds.<sup>1</sup> The advantages that a single-source precursor may offer include the lack of a need for the intimate mixing of reagents, control of stoichiometry, and lower reaction temperatures. The success of the single-source precursor strategy is, however, mostly fortuitous at the present time since very little is known of the detailed chemical pathways leading from molecules to materials. Knowledge of the latter should be useful in the selection and design of molecular precursors leading ultimately to higher purity, milder reaction conditions, and even kinetic control in product formation.

Metal alkoxides are commonly used as molecular precursors to metal oxides<sup>2</sup> by either hydrolytic (sol-gel) or organometallic chemical vapor deposition (OMCVD) techniques, but little is known of their thermolytic decomposition pathways.<sup>3,4</sup> We report here on some preliminary studies on the thermal decomposition of  $\mathbf{M}_2(\mathbf{OR})_6$  compounds,<sup>5</sup> where the metal M is one of the oxophilic elements Al, Mo, or W.

The thermolytic studies have been carried out by a coupled TGA-MS system under a purified helium flow.<sup>6</sup> The balance of the TGA system has been installed inside a Vacuum Atmospheres Dri-Box equipped with a drying

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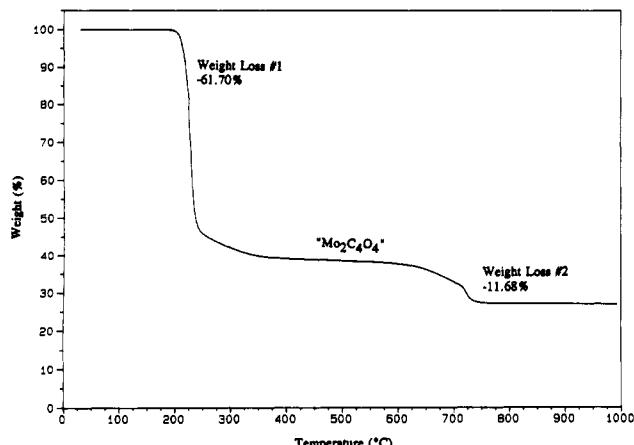
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**Figure 1.** Thermogram of  $\text{Mo}_2(\text{O-cy-C}_6\text{H}_{11})_6$  under He flow (50 mL/min) showing the weight loss versus temperature profile with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ .

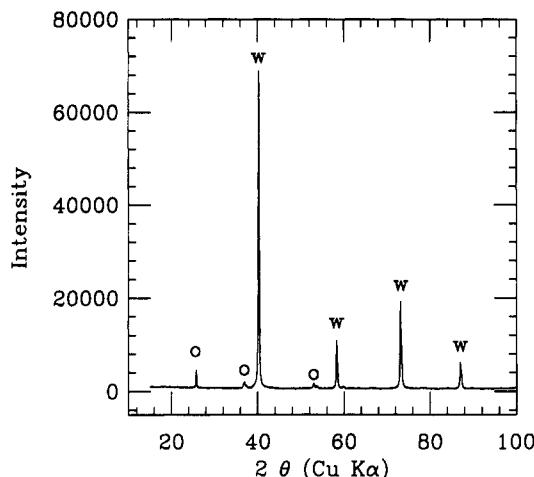
train and oxygen analyzer. The atmosphere in the box was chosen to be He (less than 1 ppm  $\text{O}_2$ ) so as to eliminate the problems arising from static electricity. Under these rigorous conditions  $\text{Al}_2(\text{O-}t\text{-Bu})_6$  sublimes without decomposition at ca.  $200\text{--}220\text{ }^\circ\text{C}$ , 1 atm. However, in the presence of trace amounts of moisture or oxygen, i.e., when the He carrier gas is not purified or when the TGA-MS is performed "outside" of the drybox using a glovebag and  $\text{N}_2$  purge for sample preparation, the  $\text{M}_2(\text{O-}t\text{-Bu})_6$  compounds where  $\text{M} = \text{Al}$  and Mo decompose in the temperature range  $190\text{--}230\text{ }^\circ\text{C}$  to give  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{MoO}_2$ , respectively. The volatile components were  $t\text{-BuOH}$ ,  $\text{Me}_2\text{C}=\text{CH}_2$ , and  $t\text{-BuH}$ . Under the more rigorous conditions,  $\text{Mo}_2(\text{O-}t\text{-Bu})_6$  undergoes competitive sublimation and decomposition to yield  $\text{MoO}_2$  at ca.  $200\text{ }^\circ\text{C}$ .

By contrast  $\text{Mo}_2(\text{O-cy-C}_6\text{H}_{11})_6$  undergoes thermolysis in two distinct stages as shown in Figure 1. At around  $210\text{ }^\circ\text{C}$  there is elimination of cyclohexane, cyclohexene, cyclohexanone, and cyclohexanol to give a material of composition  $\text{Mo}_2\text{C}_4\text{O}_4$  that is stable to  $550\text{ }^\circ\text{C}$ . This material shows a diffuse X-ray diffraction pattern that is consistent with very fine grains (on the order of  $20\text{ \AA}$ ) of  $\gamma\text{-MoC}$  suspended in an amorphous matrix. When this is heated to  $660\text{--}706\text{ }^\circ\text{C}$ , carbon dioxide and carbon monoxide are evolved according to the stoichiometry  $\text{Mo}_2\text{C}_4\text{O}_4 \rightarrow \gamma\text{-Mo}_2\text{C} + \text{CO}_2 + 2\text{CO}$ . The carbide  $\gamma\text{-Mo}_2\text{C}$  was identified by elemental composition and X-ray diffraction (XRD).

It is known from previous work that  $\text{W}_2(\text{OR})_6$  compounds are less thermally stable than their molybdenum analogues.<sup>7</sup> None are known to sublime without decomposition. We find that  $\text{W}_2(\text{O-}t\text{-Bu})_6$  is cleanly converted to  $\text{WO}_2$  (elemental composition, XRD) at  $120\text{--}200\text{ }^\circ\text{C}$  even under the most rigorously pure He atmosphere. The cyclohexoxide  $\text{W}_2(\text{O-cy-C}_6\text{H}_{11})_6$  undergoes a decomposition that is superficially similar to its molybdenum analogue. When this is heated to  $200\text{--}250\text{ }^\circ\text{C}$ , cyclohexane, cyclohexene, cyclohexanone, and cyclohexanol are evolved with the formation of a material of composition  $\text{W}_2\text{C}_4\text{O}_4$  that is thermally stable to  $750\text{ }^\circ\text{C}$ . However, at ca.  $800\text{ }^\circ\text{C}$ , this material evolves carbon monoxide, yielding tungsten metal (XRD) with only trace detectable quantities of  $\text{WO}_2$  (XRD) as shown in Figure 2.

The following points are worthy of note:

Trace quantities of  $\text{H}_2\text{O}$  (or  $\text{O}_2$ ) may facilitate an autocatalytic decomposition as seen here for  $\text{Mo}_2(\text{O-}t\text{-Bu})_6$  and  $\text{Al}_2(\text{O-}t\text{-Bu})_6$ . This type of autocatalytic decomposition was



**Figure 2.** X-ray diffraction pattern on the ultimate product formed in the thermal decomposition of  $\text{W}_2(\text{O-cy-C}_6\text{H}_{11})_6$  after heating to  $1000\text{ }^\circ\text{C}$  under a He flow. The identifiable species are  $\text{W}(\text{m})$  and  $\text{WO}_2$  as shown by W and O in the figure.

first seen by Bradley and Factor<sup>3b</sup> in their pioneering studies of the thermal decomposition of  $\text{Zr}(\text{O-}t\text{-amyl})_4$ .

The stoichiometry of the oxide  $\text{M}_2\text{O}_3$  ( $\text{M} = \text{Al}$ ) or  $\text{MO}_2$  ( $\text{M} = \text{Mo}$  and  $\text{W}$ ) reflects the influence of the metal in achieving a thermodynamically stable oxide. There is no known oxide of formula  $\text{W}_2\text{O}_3$ , and only recently has  $\text{Mo}_2\text{O}_3$  been mentioned in the literature.<sup>8</sup>

The partitioning of products between  $\text{MO}_2$  and  $\text{Mo}_2\text{C}$  or  $\text{W}(\text{m})$  as a function of  $\text{R} = t\text{-Bu}$  versus cy-Hex indicates the potential versatility of metal alkoxides as single source precursors and that much needs to be learned before product formation is predictable.

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## Kinetic Studies of the Chemical Vapor Deposition of Platinum

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The organometallic chemical vapor deposition (CVD) of metallic platinum films has potential applications in microelectronics and in wear protection and has been the subject of several recent studies.<sup>1-3</sup> Qualitative observa-

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