**Figure 5.** Schematic diagram (not drawn to scale) of the proposed mode of transfer of reversed-micelle-entrapped silver particles to a solid support.

critical for good deposition of one layer of reversed micelles. STM images of reversed-micelle-coated HOPG substrates were taken subsequent to drying in air for 1 h.

STM images revealed the presence of silver islands on atomically smooth HOPG (Figure 3). Concentrations of reversed micelles affected the interisland separation distance. In undiluted ($1.0 \times 10^{-2}$ M AOT) samples, the substrate was fairly completely covered by interconnected silver islands (not shown). Ten-fold dilution of the silver-particle-containing reversed micelles by heptane (prior to transfer) appeared to be optimal for assessing interisland distances (Figure 3). At further dilutions, it became increasingly difficult to find images. Most significantly, heights of silver islands were consistently the same ($4.0 \pm 0.5$ nm; see $z$–$x$ plots in Figure 3a,c), thus indicating the effective transfer of only one layer of reversed micelles on HOPG. A similar behavior was observed for the transfer of silver particles, in situ generated in reversed micelles, prepared from 1 (Figure 4). Hydrophobic interactions between HOPG and the surfactant tails appear to be stronger than the reversed micelle–reversed micelle interactions. Interisland distances (5.5–6.5 nm for $w = 10$ and 4.5–5.5 nm for $w = 20$) were, however, smaller than the hydrodynamic diameter of the reversed micelles. Apparently, the hydrocarbon tails of the micelles are well intercalated. The proposed mode of transfer is illustrated in Figure 5.

The convenient preparation of ultrathin metal-island films, described in the present report, opens the door to a new approach for solid-state device construction. Additionally, STM images of particles generated in the cavities of reversed micelles could provide important information on the structure of the surfactant–aqueous interface. This is particularly important for the characterization of the complex surfactant systems used in the lubricant industry.

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# Third-Order Nonlinear Optical Properties of Thin Films of Polyanilines and Poly(o-toluidines)

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Organic nonlinear optical (NLO) materials with large third-order electronic susceptibility $\chi^{(3)}$ are currently of interest for diverse applications in photonic switching devices.[1-8] The third-order nonlinear optical properties of some of the well-known conjugated polymers have thus been investigated, including polyacetylene,[3] polydiacetylenes,[3e] polythiophenes,[5,6] poly(p-phenylene vinylenes),[4] poly(thiophene vinylene),[4d] conjugated rigid-rod and ladder polymers,[7,8] and their derivatives and composites.[7,8a] Although polyanilines[9-13] represent a versatile family of

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**Table I. Intrinsic Viscosity of Polyanilines in Various Solvents at 40 °C**

| polym | $[\eta]$, dL/g | | | |
|---|---|---|---|---|
| | $H_2SO_4{}^a$ | $MSA^b$ | $GaCl_3/NM^c$ | $AlCl_3/NM^c$ |
| PEMB | 0.74 | 1.63 | 2.40 | 2.10 |
| PEMS | 0.53 | 1.17 | 2.03 | 2.03 |
| POTB | 0.22 | 0.72 | 0.46 | 0.44 |
| POTS | 0.20 | 0.56 | 0.47 | 0.46 |

$^a$ 96%. $^b$ Methanesulfonic acid (99%). $^c$ NM = nitromethane.

polymers with interesting electronic, linear optical, and electrochemical properties that can be varied by addition or removal of electrons or protons on the polymer backbone, their NLO properties have so far been investigated only by photoinduced absorption spectroscopy.[10] The $\chi^{(3)}$ of any member of the polyanilines has not been reported.

As third-order nonlinear optical materials, polyanilines offer the potential for investigation of structure–$\chi^{(3)}$ relationships. The oxidation state, $1-y$, can be varied continuously from the fully reduced $(1 - y = 0)$ polyleucoemeraldine base to the fully oxidized $(1 - y = 1)$ polypernigraniline base shown in I.[9-13] Protonation of the par-
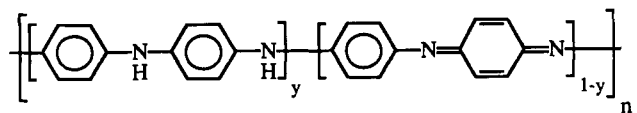
I
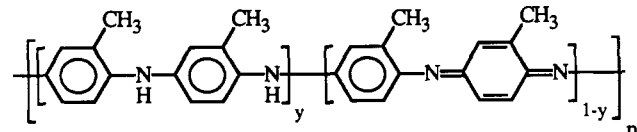
II

tially oxidized polyanilines could also provide a way for investigating the role of protonation and the conducting state on electronic $\chi^{(3)}$ of polyanilines. The $p$-phenylene rings that alternate with nitrogens in polyanilines' backbone can be derivatized to get corresponding poly($o$-toluidines) in the case of 2-methyl substitution as shown in II. Furthermore, to obtain a better understanding of structure–$\chi^{(3)}$ relationships in polymers, the measured NLO properties of polyanilines can be compared to or contrasted with the known NLO properties of other $p$-phenylene ring polymers such as poly($p$-phenylene vinylenes)[4] and those of other quinoid ring heterocyclic polymers.[6]

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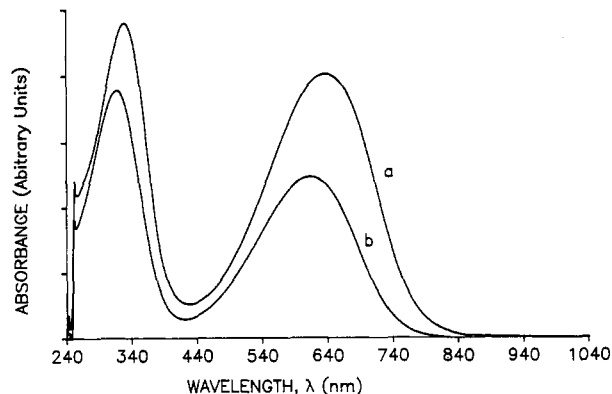
**Figure 1.** Dilute solution electronic absorption spectra of polyemeraldine base (a) and poly($o$-toluidine) base (b) in $N$-methylpyrrolidone.
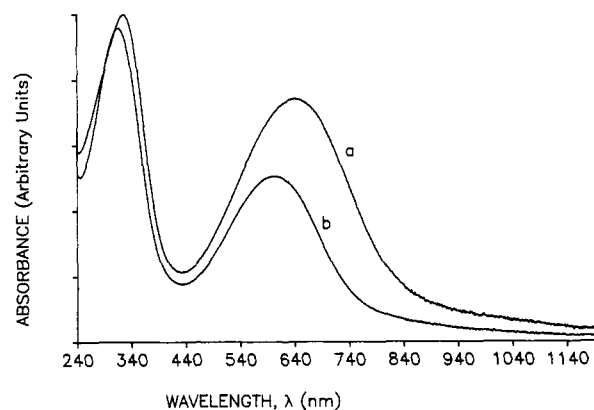
**Figure 2.** Electronic absorption spectra of spin-coated thin films of polyemeraldine base (a) and poly($o$-toluidine) base (b) used for third harmonic generation measurements.

In this communication, we report our picosecond third harmonic generation (THG) measurement of the $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of spin-coated thin films of polyaniline and poly($o$-toluidine) in their intermediate oxidation state (emeraldine, $1 - y \approx 0.5$), i.e., polyemeraldine base (PEMB) and poly($o$-toluidine) base (POTB).

Polyemeraldine salt (hydrochloride; PEMS) was prepared by the chemical oxidation of aniline with ammonium persulfate in 1 M HCl in air by using the literature method[12a,12b] and was subsequently converted to polyemeraldine base (PEMB) by stirring it in aqueous 0.1 M $NH_4OH$ solution for 15 h.[12a] Poly($o$-toluidine) salt (hydrochloride; POTS) was similarly prepared by chemical oxidation of $o$-toluidine with ammonium persulfate and subsequently converted to the emeraldine base form (POTB).[12c] The intrinsic viscosity $[\eta]$ of the four polymers in different solvents are shown in Table I. The solution electronic absorption spectra of PEMB and POTB in $N$-methylpyrrolidone (NMP) are shown in Figure 1, indicating a blue shift of the two absorption bands in POTB relative to PEMB in accord with previous observations.[13d,e] The ratio of the intensity of the infrared absorption bands at $\sim$1600 (quinoid) and $\sim$1500 cm$^{-1}$ (benzenoid) in polyaniline can be used to estimate the oxidation state of polyemeraldine base.[13c,d] Using this approach we have estimated $1 - y$ in the PEMB and POTB thin films to be $\sim$0.44 and $\sim$0.42, respectively.

Thin films of PEMB (27 nm) and POTB (58 nm) for third harmonic generation (THG) experiments were prepared by spin coating of NMP solutions onto optically flat fused silica substrates (5-cm diameter). About 0.5 g of POTB was dissolved in 25 mL of NMP by stirring. The

POTB solution was centrifuged and filtered, but no insoluble material was found. However, following the same approach, it was observed that 0.5 g of PEMB did not completely dissolve in 25 mL of NMP in agreement with the observed partial solubility of PEMB in NMP by others.[12d-h,13b] The residue of PEMB obtained after filtration could be further dissolved in fresh NMP, with only about 10% of the original material being insoluble. This shows that the 25 mL NMP solution was saturated with PEMB at room temperature, which after filtration gives a dark blue solution suitable for spin-coating deposition of thin films. Solutions of PEMB and POTB were typically spin coated at 3000 rpm for 60 s followed by vacuum drying at 60 °C for 3–4 h. The electronic absorption spectra of typical spin-coated thin films of PEMB and POTB used for THG measurements are shown in Figure 2. The thin films were of good optical quality.

Separate experiments were done to further characterize the solubility of PEMB in NMP and the nature of the soluble and insoluble fractions. PEMB (0.5 g) was stirred in NMP and filtered, and the residue dried under vacuum at 70 °C for 48 h. From the weights of the residue and the starting material we determined that about 65 ± 5% of the bulk PEMB dissolved in NMP to give 1.25 wt/wt % solution. Infrared spectra of the NMP-soluble and -insoluble fractions of PEMB were identical as were their dilute solution electronic spectra in NMP. This suggests that the insoluble PEMB fraction is the higher molecular weight fraction. To confirm this point, the soluble fraction of PEMB was precipitated from NMP and dried under vacuum at 60 °C for 48 h. The intrinsic viscosity of the NMP-soluble fraction of PEMB was found to be 0.71 dL/g in methanesulfonic acid (MSA) at 40 °C compared to 1.63 dL/g for the bulk polymer (Table I). The insoluble fraction of PEMB did not completely dissolve in either MSA or sulfuric acid after sitrring at 50 °C for 1 week. This insolubility in acid solvents of the NMP-insoluble fraction of PEMB has been observed previously and attributed to an increased degree of crystallinity or cross-linking.[12h,13b] It is also noteworthy that the molecular weight of the soluble fraction of PEMB in NMP has been estimated to be 335 000 by using gel permeation chromatography (GPC) and polystyrene standards.[12f] However, after correction of the GPC data with a model compound of PEMB the molecular weight of the soluble PEMB in NMP was found to be ca. 200 000.[12g] We note that our chemical polymerization conditions for PEMB are similar to those of these authors.[12f,g]

THG experiments were performed with a picosecond laser system, continuously tunable in the range 0.6–4 μm. This versatile source, which has been described in detail elsewhere,[14] can be operated at either low (10 Hz) or high (MHz) repetition rate with the possibility to independently select the pulse width out of two ranges (typically 3–5 and 30–50 ps), regardless of the choice of wavelength. The average output power is in the milliwatt range for all modes of operation. For this work, the repetition rate was set at 10 Hz, and the long pulse width range was selected since THG probes only the electronic contribution to $\chi^{(3)}$. The pulse-to-pulse instability, which is typically 5%, was decreased to 1% by monitoring the pulse energy of a small fraction of the output beam and by rejecting all laser shots that fall outside a predetermined window. The main output beam (attenuated to 100 μJ/pulse) was divided into two optical paths: a reference path and a sample path. In the reference path the THG signal from 0.5-μm film of

poly(benzimidazobenzophenanthroline) semi-ladder polymer (BBB) on a 1-mm fused silica disk was measured with a setup identical with that in the sample path. The BBB film thickness was chosen to be smaller than the coherence length to avoid Maker fringes in the THG signal, yet is thick enough to give a THG signal that is 2 orders of magnitude larger than that from the substrate (to avoid interference). The use of BBB as opposed to fused silica in the reference arm greatly improves the reproducibility of the measurements. The effect of fluctuations in both power and pulse width of the input beam are effectively eliminated by taking the ratio of the THG signals in the two arms shot after shot. Finally, the standard deviation of this ratio typically is 0.5% by averaging the ratio of the THG signals over some 250 laser shots. The sample is located on a computer-controlled rotation stage for obtaining the Maker fringes of the THG signal.

The third-order susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of the sample is obtained relative to fused silica in the following way: First, the Maker fringe pattern of the sample (thin film on a fused silica substrate) is compared to the Maker fringe pattern of a blank substrate also placed in the sample path. Following the procedure outlined in ref 15, a value of $\chi^{(3)}$ of the thin film is inferred. This $\chi^{(3)}$ value is then used as a starting value for an exact determination of $\chi^{(3)}$ by a theoretical fit of the Maker fringe pattern of the sample,[16] using an optical transfer matrix technique.[17] In addition to being exact, our method has the advantage of requiring a minimal set of fitting parameters ($\chi^{(3)}$ for fused silica, the film and substrate thicknesses, and indexes of refraction), thereby eliminating all other experimental calibration factors such as transmission of filters, beam-splitter ratios, and analog/digital gain factors in the computerized data acquisition system.

THG measurements were performed at a fundamental wavelength of 2.4 μm. At this wavelength, one-, two- or three-photon resonance effects are presumably weak. The reported $\chi^{(3)}$ values are average values, corrected for absorption at the third harmonic wavelength, and are obtained relative to $\chi^{(3)}$ for fused silica. For the latter we used $\chi^{(3)} = 2.8 \times 10^{-14}$ esu at 1.9 μm.[18] The error for $\chi^{(3)}$ of the films, typically ±20%, reflect mostly the error in film thickness mesurements since the repeatability of individual results for each material is ±5%.

The measured nonresonant $\chi^{(3)}$ of PEMB and POTB thin films was $2.6 \times 10^{-11}$ esu and $1.07 \times 10^{-11}$ esu, respectively. Thus, the effect of the 2-methyl substitution on the *p*-phenylene rings of polyemeraldine base is a factor of 2.4 reduction of $\chi^{(3)}$. For comparison, the reported electrical conductivities of PEMS and POTS are ~5[12a,b] and 0.1 S/cm,[12c] respectively. This ~50-fold reduction in the conductivity was attributed to the decrease in electron delocalization arising from the increase in the torsional angle between adjacent phenylene rings.[12] Presumably this same effect is responsible for the observed decrease in the optical nonlinearity. The electronic spectra presented in Figures 1 and 2 support this interpretation, since a reduction in electron delocalization would cause a blue shift in the absorption peak, as observed. It must be emphasized that part of the reduction in $\chi^{(3)}$ for POTB is due to the blue shift of its absorption peak, which effectively makes the 2.4-μm light further off resonance. So a slight decrease in $\chi^{(3)}$ is expected purely from dispersive effects.

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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 elelctron 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 sp³-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).[19] 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.[6] Hence, it can be expected that further oxidation of polyaniline to the fully oxidized ($1 - y = 1$) polypernigraniline[9d] 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 × 10⁻¹² and 5.4 × 10⁻¹¹ esu, respectively, at 1.85 μm.[4a,c] However, highly oriented PPV films have a $\chi^{(3)}$ of 1.5 × 10⁻¹⁰ esu at 1.85 μm.[4b] The $\chi^{(3)}$ value of amorphous spin-coated thin films of 3,4-dialkylpolythiophene is 4.4 × 10⁻¹¹ esu at 2.4 μm,[5a] and that of polythiophene vinylene is 3.2 × 10⁻¹¹ esu at 1.85 μm.[4d] Isotropic thin films of the rigid-rod poly(p-phenylenebenzobisthiazole) have a $\chi^{(3)}$ of 1.4 × 10⁻¹¹ esu,[7,8] whereas polyacetylene has a $\chi^{(3)}$ of 5 × 10⁻¹⁰ esu.[3a]

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-μm wavelength. The $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ was found to be 2.6 × 10⁻¹¹ esu for polyemeraldine base (PEMB) and 1.07 × 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.

## M₂(OR)₆ Compounds (M = Al, Mo, W; R = t-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.[1] 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[2] by either hydrolytic (sol–gel) or organometallic chemical vapor deposition (OMCVD) techniques, but little is known of their thermolytic decomposition pathways.[3,4] We report here on some preliminary studies on the thermal decomposition of M₂(OR)₆ compounds,[5] 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.[6] The balance of the TGA system has been installed inside a Vacuum Atmospheres Dri-Box equipped with a drying

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(6) TGA experiments were run on a Du Pont Instrument 951 thermogravimetric analyzer using a heating rate of 1–10 °C/min and a 50 mL/min He flow. Data were collected on a Du Pont Instrument thermal analyst 2100, and mass spectra were recorded on a VG Micromass PC quadrupole mass spectrometer.

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