

Thin Films from 96% Quinoline

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SYNOPSIS

Films from 96% quinoline and from 96% quinoline with poly(1,4-cyclohexylene carbonate), mesoporphyrin IX dimethyl ester, and Pd(II) mesoporphyrin IX dimethyl ester have been cast via heating and subsequent evaporation. The films are approximately 3 μm thick, with a maximum variation normal to the surface of 0.10 μm in 2 mm of surface travel. The optical quality of the samples formed from 96% quinoline alone is excellent and variable from the 96% quinoline/solute combinations. The third-order nonlinear optical (NLO) properties of these materials have been examined. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polymers have been formed from quinoline in the presence of trimethyl boron¹ and ZnCl_2 and protonic acids² and via glow discharge.³ The formation of thin films by simple heating and evaporation of quinoline has apparently not been investigated. We present here a description of films formed by this method from 96% quinoline and 96% quinoline containing solutes.

EXPERIMENTAL

Surface profiles were obtained on a Tencor Alpha-Step 250 instrument. Infrared spectra were done on KBr pellets using a Perkin-Elmer 1800 FTIR machine. Proton NMR spectra were obtained on a JEOL FX90Q instrument at 90 MHz, in CDCl_3 unless otherwise stated and were referenced to internal TMS. Thermal analyses were done in N_2 on DuPont 951 TGA or 910 DSC machines, using the Thermal Analyst 2100 system. Elemental analyses were performed at E + R Microanalytical Laboratory, Corona, NY.

Material **2** was prepared by heating 5.5 mL of 96% quinoline in air in a 1.8×15 cm test tube at 200°C for 3 days. The resulting solution was evaporated on a glass slide at 65°C to give a homogeneous thin film of **2**.

Poly(1,4-cyclohexylene carbonate) (**3**) of approximate molecular weight 600 was obtained from Polysciences, Warrington, PA. Porphyrin diester **4a** was used as received from Aldrich Chemical Co., Milwaukee, WI.

The Pd(II) derivative of **4a**, **4b**, was made via the established method.^{4,5}

ANAL: Calcd for $\text{C}_{36}\text{H}_{40}\text{N}_4\text{O}_4\text{Pd}$: C, 61.85%; H, 5.77%; N, 8.01%; Cl, 0.00%. Found: C, 61.77%; H, 5.78%; N, 8.00%; Cl, 0.00%.

Materials **5a** and **5b** were prepared in the following manner. The polycarbonate (**3**, 5.5 mg) was placed in a 1.8×15 cm test tube with 1.0 mL of 96% quinoline and heated at 130°C in an oil bath for 1 min. Solid porphyrin diester (**4a**, 5.5 mg, 9.2×10^{-3} mmol) was added and the tube heated at 200°C for 2 days. A few drops of the resulting dark brown solution were evaporated on a commercial glass microscope slide at 65°C; the solvent evaporated in 4 h. Heating at 65°C for another 24 h yielded a thin film of **5a**. Material **5b** was made in the same way, from **3** and **4b**.

Third-order nonlinear optical susceptibilities were measured at 1.064 μm using degenerate four-wave mixing. The phase conjugate reflectivity of the polymer film **5a**, solutions of the precursor mate-

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rials, and the solvents were measured relative to CS_2 using apparatus and methods that were previously described.⁶

RESULTS AND DISCUSSION

When 96% quinoline (**1**, Fig. 1) is heated in air at 200°C for 3 d, it darkens appreciably. The resulting solution can be evaporated on a glass slide at 65°C to give a homogeneous thin film, **2**, of high optical quality. The infrared spectrum of **2** exhibits absorptions in the aliphatic C—H stretching region as well as the aromatic region. Aliphatic groups are present in the $^1\text{H-NMR}$ of the unheated 96% quinoline starting material. As the quinoline solvent evaporates from the slides, alkylated species remain if they are less volatile. The weight of material remaining after evaporation was 2.8% of the starting weight, roughly corresponding to the 4% of non-quinoline components originally present.

The peak at 1724 cm^{-1} and the broad absorption from 2500 to 3300 cm^{-1} for **2** suggests that carboxyl groups are present, possibly from oxidation of methyl groups. The possible intermediate in a methyl-to-carboxyl transformation, an aldehyde, is not present in the unheated starting material, as evidenced by the lack of peaks in the δ 11.0–11.5 region of the $^1\text{H-NMR}$.⁷

The $^1\text{H-NMR}$ of **2** in $\text{DMSO-}d_6$ exhibits the expected complex aromatic region from δ 7 to 9. In addition, a broad, low peak is visible between δ 2.25 and 2.40. This peak is not due to an impurity in the $\text{DMSO-}d_6$, as a solvent blank shows.

Thermogravimetric analysis indicates that **2** may contain some unsubstituted quinoline, with onset of weight loss at 153°C . Quinoline boils at 237°C . The DSC of **2** on the first pass exhibits a broad first-order endotherm at 119°C , followed by many sharp endotherms between 120 and 150°C . These features disappear on the second pass. In a melting-point capillary, this material forms a viscous black liquid gradually between 80 and 100°C . A melting endotherm was not evident in this range in either DSC pass. Material **2** is soluble in *N,N*-dimethylformamide, 96% quinoline, and dimethyl sulfoxide, suggesting that it is not cross-linked.

Quinoline is an excellent solvent for poly(1,4-cyclohexylene carbonate) (**3**) above its melting point of 50°C and for synthetic mesoporphyrin IX dimethyl ester (**4a**). The latter is a porphyrin with side chains containing only alkyl groups, plus two ester functionalities. When an approximately 1 : 1 molar solution of the polycarbonate and diester was heated in 96% quinoline at 200°C and subsequently evaporated at 65°C , a brown material resulted. This sample, **5a**, prepared on a microscope slide, was reflective, nontacky, and flat. It ranged in clarity from

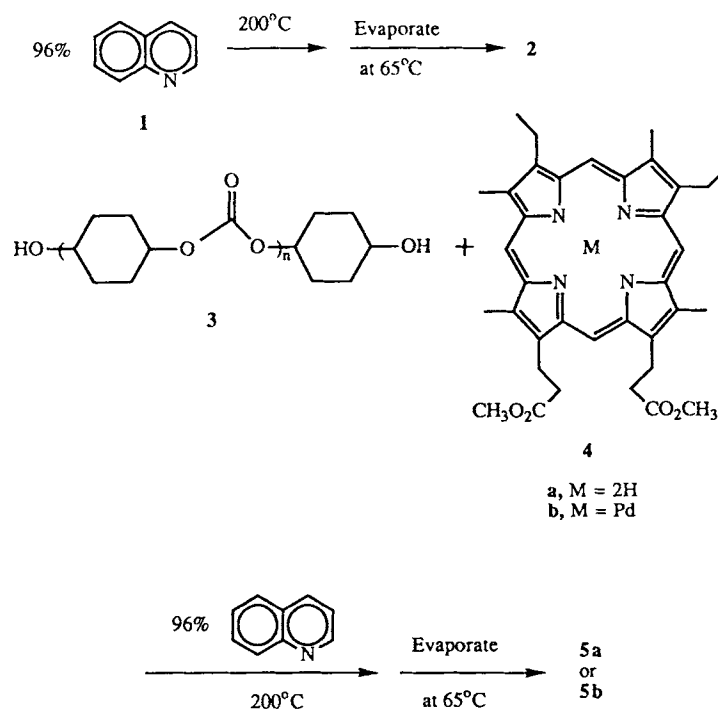


Figure 1 Preparation of materials **2**, **5a**, and **5b**.

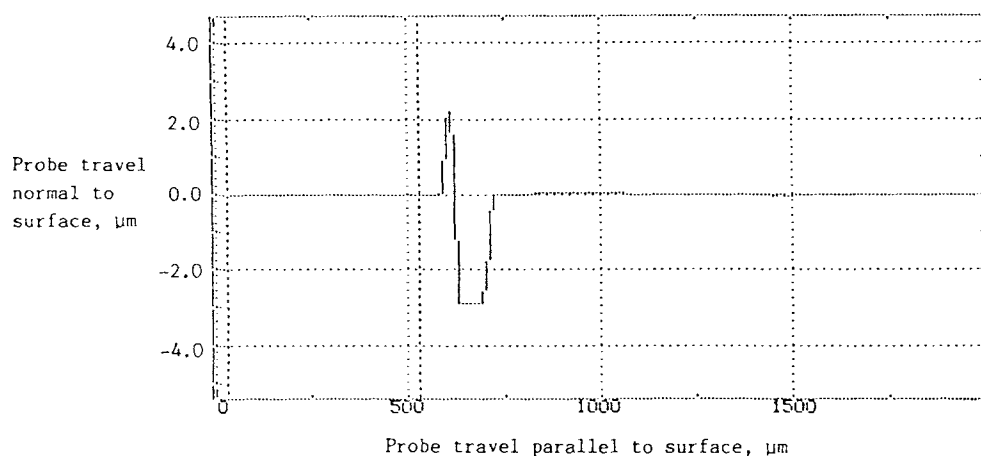


Figure 2 Surface profile of a **5a** thin film.

transparent at one end to cloudy in the middle to opaque at the other end.

The surface profile of a sample of **5a** is given in Figure 2. It provides information about the flatness and thickness of the film, attributes important for optical studies. The latter quantity cannot be determined from measurement at the edge of the film because the material has a thick lip wider than 2 mm, the maximum available horizontal probe travel. Instead, a scratch was made with a razor blade perpendicular to the direction of probe travel. The scratch extends down to the glass, and some of the material removed appears as a positive peak. The profile exhibits a maximum surface variation normal to the surface of $0.10\ \mu\text{m}$, with the probe traveling parallel to the surface a distance of 2 mm. The scratch reveals the flat glass of the substrate, a commercial microscope slide. In a separate experiment, the slide alone showed a maximum variation of $0.01\ \mu\text{m}$, and a scratch made in the same manner had a depth of $0.14\ \mu\text{m}$. Thus, the scratch in the material in Figure 2 represents primarily the thickness, $2.92\ \mu\text{m}$, of the organic film, determined at the point of laser impingement (see below).

The infrared spectrum of **5a**, taken in a KBr pellet, shows primarily peaks associated with the polycarbonate and the quinoline-derived material. In particular, the carbonyl frequencies (Table I) indicate that the major contributor is **2** or something similar.

The $^1\text{H-NMR}$ spectrum of material **5a** is most easily understood by comparison with the spectra of the starting materials. The most prominent feature of the spectrum of mesoporphyrin IX dimethyl ester, taken in chloroform-*d*, is in the methyl singlet region. Theoretically, there should be six singlets; in practice, four peaks and two shoulders appear,

entirely between 3.5 and 3.7 ppm. Poly(1,4-cyclohexylene carbonate) shows peaks between 0.9 and 2.0 ppm and between 3.4 and 4.1 ppm. The spectrum of **5a** in the same solvent shows the quinoline-derived material at 2.4 ppm and between 6 and 9 ppm and the polycarbonate between 1 and 4 ppm. The porphyrin methyls may contribute to the 3.4–3.7 ppm region. The entire spectrum is characterized by broad peaks except for the TMS and residual CHCl_3 peaks.

The appropriate thermal analysis studies were done. Thermogravimetric analysis of the porphyrin alone indicates remarkable stability, with no weight loss at 378°C . The onset of decomposition was at 411°C , with 54% of the weight remaining at 492°C . Loss of the eight groups around the porphyrin nucleus would give 50.8% residual weight.

Poly(1,4-cyclohexylene carbonate) shows a gradual decrease in weight after melting at 50°C . This is probably associated with polymerization and subsequent boiling of cyclohexanediol (bp 270°C)

Table I Carbonyl Stretching Frequencies^a

	$\nu_{\text{C=O}}$ (cm^{-1})
4a	1735
3	1739
1	^b
2	1724
5a	1724

^a All spectra taken in KBr pellets on a Perkin-Elmer 1800 FTIR. All intensities are strong unless otherwise noted.

^b Quinoline (96%) has very weak absorptions at 1718 and $1734\ \text{cm}^{-1}$.

Table II Nonlinear Optical Properties

	$\chi_{xxxx}^{(3)}$ (esu) ^a	α (cm ⁻¹) ^b	$\langle \gamma_{xxxx} \rangle$ (esu) ^c
4a ^d	3×10^{-14}		$< 3 \times 10^{-34}$
5a	6×10^{-12}	400	
96% quinoline	2×10^{-13}	< 1	

^a Third-order optical susceptibility with all polarizations parallel.

^b Absorption coefficient.

^c Third-order hyperpolarizability with all polarizations parallel.

^d 3×10^{-2} M solution in CHCl₃.

and boiling of remaining polycarbonate of MW 600 at 350°. The product material (**5a**) has a TGA that most closely resembles those of the polycarbonate and the quinoline-derived material. The steepest portion has an onset at 248°C, near the boiling point of quinoline and the melting point of the product material.

The DSC of **5a** on the first pass exhibits a broad endotherm centered at 61°C followed by a strong exotherm with an onset at 190°C. In a melting-point apparatus, some of the material melts at 225–230°C, forming a black solid in a black liquid. The second DSC pass is essentially featureless, suggesting that polymerization may have occurred during the first pass.

The yield in this reaction indicates that more than just the polycarbonate and porphyrin is present. The weight obtained, which is approximately 80 mg, represents more than seven times the initial weight of the polycarbonate and porphyrin. Experiments of a preliminary nature indicate that transesterification between **3** and **4a** does not occur under these conditions, but that self-condensation of **3** may.

The third-order nonlinear optical susceptibilities ($\chi^{(3)}$'s) of some of these materials have been measured at 1.064 μ m. The results are given in Table II. The $\chi^{(3)}$ for the polycarbonate–porphyrin–quinoline polymer film (**5a**) was substantially larger than that of any of the components. This response of this material is due primarily to the porphyrin or to some combination of it with the 96% quinoline-derived material. Material **2** alone underwent laser damage before a signal could be obtained, so unmodified **2** cannot be the source of the response of **5a**. Among the polymer precursor materials, the $\chi^{(3)}$ for 96% quinoline was surprisingly large. It was

about four times larger than that of the related molecule α -picoline⁸ and about half that of CS₂. The $\chi^{(3)}$ of the porphyrin, **4a**, in solution was indistinguishable from that of the solvent; only an upper limit for the molecular hyperpolarizability of this material was found.

CONCLUSIONS

New materials containing porphyrins and quinoline as the NLO-active moieties have been prepared. These materials range in optical quality from good to medium. The third-order nonlinear optical properties, thermal analysis, and spectroscopy of the films have been presented.

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