Thin-Film Processing and Optical Properties of Conjugated Rigid-Rod Polyquinolines for Nonlinear Optical Applications

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A structurally systematic series of 14 conjugated rigid-rod polyquinolines and polyanthrazolines of current interest as electronic and nonlinear optical materials have been prepared and solubilized in organic solvents by complexation and processed into thin films of high optical quality, and their optical properties characterized. The high molecular weight polyquinolines were solubilized in high concentrations by reversible complexation with either diaryl phosphates, dialkyl phosphates, or metal halide Lewis acids in organic solvents to produce viscous solutions processable to thin films, coatings, and fibers by conventional techniques. Thin film coatings on substrates and free standing films in frames suitable for the characterization of various solid-state properties were prepared from the soluble polyquinoline complexes. The optical properties, especially optical absorption spectra and refractive indexes, were characterized and related to the systematic variation in structure. The lowest energy absorption band maximum in the optical spectra of thin films of the polyquinolines was in the range 370–448 nm, and the corresponding optical bandgap was found to be in the range 2.5–3.0 eV. The phosphate and Lewis acid complexes of the polyquinolines II and III were found to exhibit greater degrees of π-electron delocalization than the pure polymers as evidenced by the larger λ_{max} of their lowest energy optical absorption band (389–547 nm). The intrinsic optical loss α of the conjugated polyquinolines was found to be of the order 1–10 cm^{-1} in the transparent region (800–1900 nm) of the materials. These results on the thin-film processing of the conjugated polyquinolines from their soluble complexes will make possible detailed investigation of their electronic, photoconductive, and nonlinear optical properties as well as their potential applications.

Introduction

Conjugated polymers have gained widespread interest as electronic and nonlinear optical materials.[1-3] Among the main current problems associated with conjugated polymers we wish to address two in one class of conjugated polymers, rigid-rod polyquinolines. One problem is the poor understanding of the structure–property relationships underlying the nonlinear optical properties of conjugated polymers, and the other is insolubility and the difficulty of processing the materials to thin films for the characterization of solid-state properties. One approach to the former problem is the molecular design and synthesis of a series of systematically varied polymer structure within one class of conjugated polymers. Conjugated rigid-rod polyquinolines[4-14] as a class, whose synthetic chemistry has been developed by Stille and co-workers in the past 2 decades, are an ideal candidate to pursue such an approach. Among the many features of rigid-rod polyquinolines are the following: The flexible synthetic approach to the polyquinolines developed by Stille and co-workers can be easily used to prepare conjugated polymers with diverse backbone structures.[4-14] The polyquinolines are thermally stable materials (up to 500–600 °C) that possess excellent mechanical properties.[5] The electronic properties[10,15] of the polyquinolines have been investigated, and electrical conductivities of chemically doped polymers as high as 10 S/cm have been reported. Highly conducting ion-implanted polyquinolines have also been reported.[16] The electronic structure, including bandgap and ionization potential of the parent polyquinoline, has been theoretically investigated.[17] However, to our knowledge, the op-

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tical, nonlinear optical, and photoconductive properties of conjugated polyquinolines have not been reported.

Conjugated rigid-rod polyquinolines are, in general, not soluble in organic solvents, and many of them are not even soluble in strong acids such as sulfuric, methanesulfonic, and trifluoromethanesulfonic acid.[4] Many synthetic approaches to the solubility of the polyquinolines have been explored by Stille and co-workers. Introduction of flexible linkages, such as $-CH_2-$, $-O-$, $-S-$, etc., can lead to organic solvent soluble but *nonconjugated* polyquinolines.[4] The solubility of rigid-rod polyquinolines could not be enhanced by attaching a long side group to the polymer chain.[6] The precursor route to a conjugated polyquinoline was very recently demonstrated.[7] However, this precursor approach to the polyquinolines is highly specific, and it places an enormous restriction on the flexibility of selecting diverse polymer structures and is thus not a viable general approach to solubility and processing of rigid-rod polyquinolines.

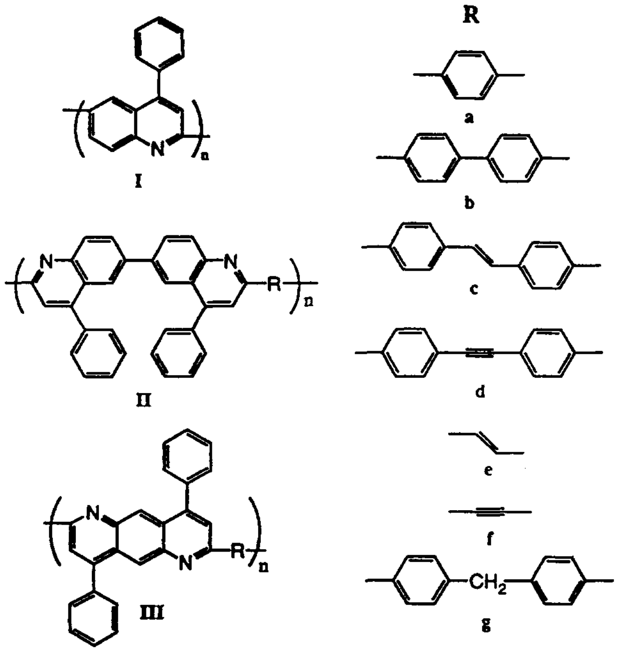
Rigid-rod polyquinolines, however, have been shown to be soluble to high concentrations in their polymerization medium consisting of di-*m*-cresyl phosphate (DCP) dissolved in *m*-cresol.[4,8] Although the polyquinolines can be processed into films and fibers from DCP/*m*-cresol solutions, there are inherent problems with this solvent system. First, DCP is not commercially available, and it is difficult to synthesize and purify. Second, the solutions of rigid-rod polyquinolines in DCP/*m*-cresol are highly viscous even at low concentrations (<0.5 wt %) and cannot be spin coated, and the solvent *m*-cresol is very difficult to remove, thereby making the processing of polyquinolines to high-quality, uniform, thin films extremely difficult. Furthermore, there is no convenient method for preparing high-optical-quality, uniform, freestanding films suitable for investigation of solid-state properties such as optical, nonlinear optical, and photoconductive properties.

In this paper, we report our studies of *complexation-mediated solubilization and thin-film processing* of a series of conjugated rigid-rod polyquinolines in common organic solvents. Soluble Lewis acid ($GaCl_3$, $AlCl_3$) complexes and alkyl phosphate or aryl phosphate complexes of the conjugated polyquinolines were prepared in organic solvents and shown to be processable by various techniques to yield high-optical-quality supported or freestanding films suitable for characterization of photoconductivity and optical and nonlinear optical properties. We also report the linear optical properties, i.e., optical absorption spectra, index of refraction, and optical loss, and effects of structures on these properties for a series of the polyquinolines shown in Chart I, i.e., I–III. The nonlinear optical properties[18a] and photoconductivity[18b] of the thin films of polyquinolines prepared from soluble complexes will be reported elsewhere.

Experimental Section

Polymers and Other Materials. The monomers were synthesized according to the methods reported in literature: 3,3′-dibenzoylbenzidine;[7,8] 2,5-dibenzoyl-1,4-phenylenediamine;[11] 5-acetyl-2-aminobenzophenone;[19] diacetylstilbene;[12] diacetylbiphenylacetylene;[13] hex-3-ene-2,4-dione;[20] hex-3-yne-2,4-dione.[21] Diacetylbiphenylene (methanol), diacetylbenzene (benzene), and diacetyldiphenylmethane (toluene) were obtained commercially and purified by crystallization. All other materials were used as obtained: dibenzyl phosphate (Aldrich); diethyl dithiophosphate (Aldrich); bis(2-ethylhexyl) hydrogen phosphate (Aldrich); diphenyl phosphate (Aldrich); triphenyl phosphate (Aldrich); $AlCl_3$ (Aldrich); $GaCl_3$ (Sigma); triethylamine (Baker).

Chart I



I = PPQ
IIa = PPPQ
IIb = PBPQ
IIc = PSPQ
IId = PBAPQ
IIe = PVPQ
IIf = PAPQ
IIg = PDMPQ
IIIa = PPDA
IIIb = PBDA
IIIc = PSDA
IIId = PBADA
IIIe = PVDA
IIIf = PADA
IIIg = PDMDA

A mixture of DCP/*m*-cresol was used as a polymerization medium and was synthesized as reported by Beever et al.[14] The various rigid-rod polyquinolines I–III were synthesized according to the established procedures developed by Stille and co-workers.[4,8] Equal moles of each bis(amino ketone) and bis(keto methylene) monomers were reacted in DCP/*m*-cresol at 140 °C under argon for 48 h. The resulting polymerization dope was precipitated in 10% triethylamine/ethanol mixture followed by extraction in it to obtain pure polymer, which was dried overnight at 80 °C under vacuum. All the polymers were obtained in high yield (>95%).

These polymers along with their intrinsic viscosities are as follows: PPQ, poly(2,6-(4-phenylquinoline)), $[\eta] = 0.95$ dL/g; PBPQ, poly(2,2′-(biphenylene)-6,6′-bis(4-phenylquinoline)), $[\eta] = 8.5$ dL/g; PSPQ, poly(2,2′-(*p*,*p*′-stilbene)-6,6′-bis(4-phenylquinoline)); $[\eta] = 31.3$ dL/g; PBAPQ, poly(2,2′-(*p*,*p*′-biphenylacetylene)-6,6′-bis(4-phenylquinoline)), $[\eta] = 8.9$ dL/g; PPPQ, poly(2,2′-(1,4-phenylene)-6,6′-bis(4-phenylquinoline)), $[\eta] = 18.5$ dL/g; PDMPQ, poly(2,2′-(4,4′-diphenylmethane)-6,6′-bis(4-phenylquinoline)), $[\eta] = 9.3$ dL/g; PBDA, poly(2,7-(*p*,*p*′-biphenylene)-4,9-diphenyl-1,6-anthrazoline), $[\eta] = 6.85$ dL/g; PSDA, poly(2,7-(*p*,*p*′-stilbene)-4,9-diphenyl-1,6-anthrazoline), $[\eta] = 30.3$ dL/g; PBADA, poly(2,7-(*p*,*p*′-biphenylacetylene)-4,9-diphenyl-1,6-anthrazoline), $[\eta] = 7.65$ dL/g; PPDA, poly(2,7-(1,4-phenylene)-4,9-diphenyl-1,6-anthrazoline), $[\eta] = 3.05$ dL/g; PDMDA, poly(2,7-(4,4′-diphenylmethane)-4,9-diphenyl-1,6-anthrazoline), $[\eta] = 0.87$ dL/g; random copolymer of PBPQ/PBAPQ (50:50), $[\eta] = 25$ dL/g; random copolymer of PSPQ/PBPQ (50:50), $[\eta] = 22.6$ dL/g; random copolymer of PSPQ/PBAPQ (50:50), $[\eta] = 14.3$ dL/g.

Solubilization Studies and Solution Preparation. *Solubility tests of polyquinolines in commercially available phosphates/m-cresol systems*: A 15–20 wt % solution of diaryl, triaryl, or dialkyl phosphate was made in *m*-cresol at or near room temperature (~40 °C) by stirring 0.3–0.4 g of phosphate in 2 g of

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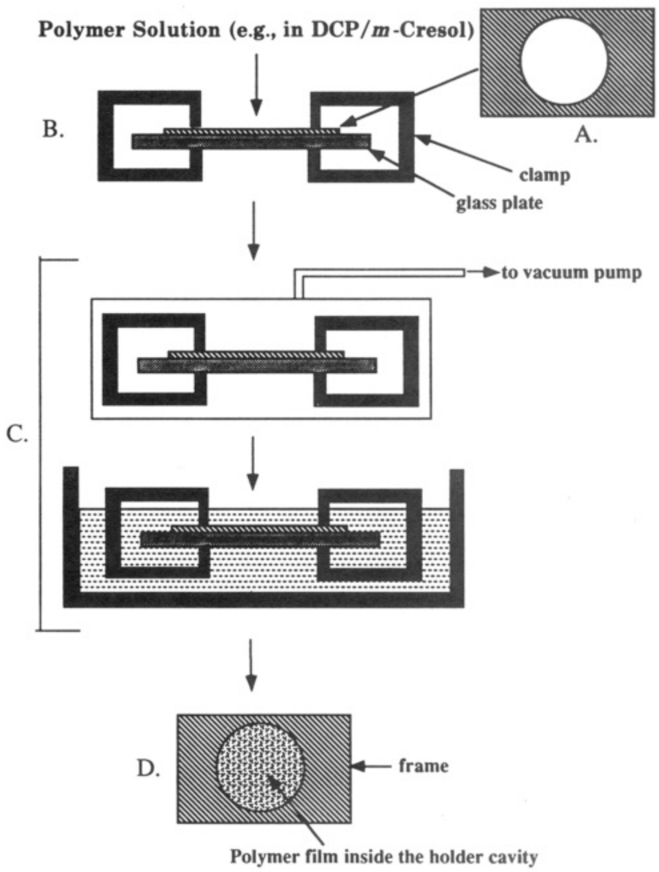
solution made in freshly distilled *m*-cresol in a 10-mL vial capped with a Teflon-lined cap. When a clear and transparent solution was obtained, 4–5 mg of polyquinoline was added, and the vial was purged with argon and capped. The mixture in the vial was then heated at 120–140 °C for 4–48 h (depending on the rate of dissolution of polymer in different phosphates/*m*-cresol systems) while the vial was shaken occasionally to ensure proper mixing. The mixtures were monitored for the signs of solubilization such as swelling, color change, viscosity change, etc.

Solubility test of polyquinolines in pure phosphates: An 8–10-mg sample of polyquinoline was added to 2 g of dialkyl or diaryl phosphate in a 10-mL vial, and the vial was purged with argon before capping it with a Teflon-lined cap (in the case of solid phosphates, the mixture was gently warmed to allow the phosphates to melt before the purging was carried out). The mixture in the vial was then heated at 120–140 °C for 4–48 h (depending on the different rate of dissolution in different phosphates) while the vial was shaken occassionally to ensure proper mixing and solubilization.

Solubility test of polymer–diphenyl phosphate (DPP) complexes in commercially available solvents: A 15–20-mg sample of 0.5–1.0 wt % solution of polyquinoline in DPP, prepared as described above, was added in 1 mL of the solvent under test. This mixture was stirred at room temperature until a true solution was obtained or the polymer was precipitated.

Solubility test of polyquinoline in Lewis acids/nitroalkane systems: Due to the moisture sensitivity of metal halide Lewis acids, the following solution preparations were done inside a glovebox filled with dry nitrogen. Our Vacuum Atmospheres Dri Lab glovebox was equipped with a Dri Train to remove residual water vapors or oxygen to below 5 ppm. Once prepared, the solutions were taken out of the glovebox if required for any processing. To 2 g of a 15 wt % solution of $GaCl_3$ or $AlCl_3$, prepared in nitromethane, 0.02 g of polyquinoline was added in a 10-mL vial. The mixture was stirred using a magnetic stir bar at 40 °C until a true solution was obtained.

Scheme I



Processing to Freestanding Films Supported on Frames. A round (or any other desirable shape) hole of 1-in. diameter was punched out in a sheet of material (~1–2 mm thick) to be used as a frame. We have successfully used Bakelite, copper, tin, steel, and poster paper sheets of various thicknesses as the frame material. Using a sharp edge blade, fine and deep (~1 mm) incisions were made all around the circumference of the hole (Scheme IA). A sufficiently high density of incisions are necessary for the holes made in metal and Bakelite sheets in order to properly attach the regenerated polymer films to the frame. Once a frame was prepared, it was cleaned using acetone and a high-pressure air jet. The frame was then placed on a clean flat glass plate of approximately the same dimensions and the two were tightly clamped together. The clamped assembly, with the circular cavity facing upward, was placed on a stand or a flat surface and was adjusted so as to level the glass plate in the horizontal plane. A 1–2 wt % solution of polyquinoline was poured into the cavity (Scheme IB). Using the edge of a knife or of a thin cover glass slide, the surface was smoothed out. Any air bubble pockets or other defects were removed by allowing the filled solution to stand for some time. This assembly, with the polymer solution in the cavity, was carefully placed into the vacuum oven and the more volatile component of the solution system was allowed to be slowly evaporated (Scheme IC). When a Lewis acid/nitroalkane solution was used, the cavity filling and the solvent evaporation were all carried out inside the glovebox to avoid premature regeneration of the polymer. The remaining highly viscous solution or film of the complex was precipitated by immersing the assembly in a glass container filled with a nonsolvent system (Scheme IC). The precipitation was completed by carrying out the extraction for 1–2 days at room temperature or 40–50 °C depending on the thickness of the film and the solvent system used. A 10% solution of triethylamine in ethanol was used for the precipitation of phosphate complexes while methanol followed by water was used in the case of Lewis acid complexes. The clamps were removed from the assembly, and the film along with the frame was carefully separated from the glass plate. This was washed again in fresh nonsolvent and dried overnight in a vacuum oven at 60 °C. A wrinkle-free, uniform, polyquinoline film held in the inside circumference of the hole was obtained as a result of the process (Scheme ID). Thicker (thinner) films of the polymer could be easily obtained by increasing (decreasing) the concentration of the polymer solution or by increasing (decreasing) the thickness of the frame or both.

Processing to Thin Films on Substrates by Spin Coating. *Attempted processing from diphenyl phosphate/m-cresol solutions*: A solution of 0.1–0.5 wt % polyquinoline was prepared in DPP/*m*-cresol (1:5) using the methods described above. The fused silica substrate of 5-cm diameter was first cleaned with soap and water followed by acetone and finally with tetrahydrofuran before drying in oven. The substrate was heated at 125 °C immediately before using it for spin coating. The solution was poured onto the heated substrate and immediately spun at 4000 rpm for 60 s. The substrate was then removed and heated in a vacuum at 95 °C to remove residual *m*-cresol to obtain a coating of DPP–polyquinoline complex. This coating was precipitated in 10% TEA/ethanol mixture to regenerate the polymer. Using this method, uniform and continuous films could not be obtained.

Processing from diphenyl phosphate solutions: A solution of 0.1–0.5 wt % polyquinoline was prepared in DPP using the method described above. A fused silica substrate of 5-cm diameter was cleaned and dried as described above. The substrate as well as the solution was heated in an oven at 125 °C. This allowed the otherwise highly viscous or solid DPP–polymer solution at room temperature to easily flow during the spinning process. The heated solution was poured onto the heated substrate and was immediately spun at 4350 rpm for 60 s. The coated substrate was removed and placed in a 10% TEA/ethanol mixture for regeneration to the pure polymer. The precipitation was completed by placing the coated film for 1–2 days in the nonsolvent mixture. The process can be expedited by replacing nonsolvents every 12 h and by gently stirring the mixture while heating it at ~40 °C. Uniform, transparent thin-film coatings were obtained and used for the study of optical properties.

Processing from DPP/nitromethane (NM), DPP/nitroethane (NE), DPP/dichloroethane (DCE), and DPP/dichloromethane (DCM) solutions: A solution of 0.1–0.2 wt % polyquinoline was prepared by stirring 1–2 mg of the polymer in 2 g of solution made in 15 wt % DPP in nitromethane at 40 °C. A fused silica substrate was cleaned and dried as described above. The solution was poured onto the substrate at room temperature and immediately spun at 1800–2500 rpm for 10–20 s. Nitromethane, being volatile, evaporated while the film was being spun, and a polymer–DPP complex was obtained as a result. The coated substrate was removed and precipitated in 10% TEA/ethanol mixture and worked up as above. The uniform, thin-film coatings thus obtained were dried in a vacuum at 60 °C and were used for optical measurements. Similar procedures were used to spin coat polyquinoline films from DPP/NE, DPP/DCE, and DPP/DCM solvent systems.

Processing from $GaCl_3$/nitromethane (NM) or $AlCl_3$/nitromethane solutions: A solution of 0.2–0.7 wt % polyquinoline was prepared in $GaCl_3$/NM as described above. A fused silica substrate of 5-cm diameter was cleaned using soap and water followed by acetone and was dried. The solution was poured onto the substrate and immediately spun at 2000 rpm for 5–10 s. To avoid premature precipitation of the polymers due to the contact with moisture in air, the exposure time of the solution to atmosphere before the spinning was minimized. The coating obtained was regenerated slowly by keeping it in atmosphere for 4–5 h. The regeneration was completed by placing the coatings in methanol for 1 h followed by in water overnight. The uniform films obtained, were dried in a vacuum at 60 °C. A similar procedure was used to spin coat the polyquinolines from $AlCl_3$/NM system.

Characterization and Measurement of Optical Properties. Intrinsic viscosities of the polyquinolines were measured in 0.1 mol % DCP/*m*-cresol solvent system at 25 °C. The thickness of the polymer films coated on the silica substrates was measured using Alfa step 200 (Tencor Instruments) with an accuracy of ±0.005 μm, and the thickness of the much thicker freestanding films, supported on the frames, was measured using an electronic micrometer with an accuracy of ±1 μm.

Optical absorption spectroscopy was performed on a Perkin-Elmer Model Lambda 9 UV/vis/NIR spectrophotometer. Solid-state spectra were taken on thin films of polyquinolines cast on silica substrates, while solution spectra were obtained in dilute solutions of polyquinolines in 0.1 mol % di-*m*-cresyl phosphate/*m*-cresol.

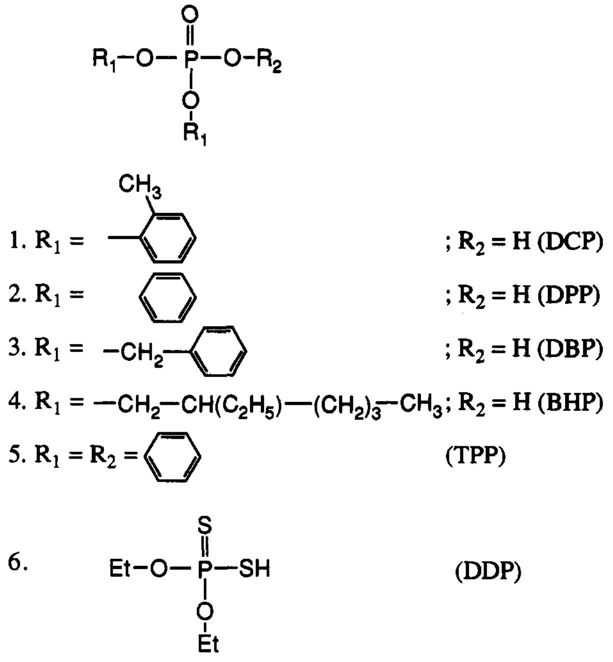
Optical losses were estimated using two different methods: (1) Extrapolation from solution optical losses: the polymer solutions of various concentrations (1–7 wt %) were prepared in 25 wt % DPP/*m*-cresol solvent system as described above. The absorption spectra were recorded for all the polymer concentrations by placing the highly viscous solutions between two optically flat silica substrates while maintaining a constant optical path length of 125 μm using standard spacers. Optical losses for the pure polymer were then estimated by extrapolating the linear plot of absorbance versus polymer concentration to 100 wt % polymer. (2) Direct measurement in solid state: Freestanding polymer films of various thicknesses were prepared according to the technique described above. The absorption spectra were recorded for 3–4 films of different thicknesses, and the optical losses were calculated from the slope of the straight line obtained by plotting absorption losses versus the thickness of the films.

Refractive indexes of the films of polyquinolines in the transparent region 500–3000 nm were obtained using the method developed by Swanepoel.[22]

Results and Discussion

(A) Solubilization Studies. Phosphate Complexes of Polyquinolines. Although, DCP/*m*-cresol solvent system is not suitable for thin-film processing of the polyquinolines, it has proven to be an excellent polymerization medium for obtaining high molecular weight and a good solvent for preparing solutions of high polymer concentrations. Therefore, our approach was to understand the mechanism of solubilization of the polyquinolines by DCP in *m*-cresol and with such an understanding to better design more suitable solvents for thin film processing. Since rigid-rod polyquinolines are not soluble in pure *m*-cresol, we thought that its role must be limited to that of a solvent for a DCP–polyquinoline complex. This hypothesis was also suggested by the fact that stable DCP–polyquinoline complexes, completely free of *m*-cresol, were obtained by casting DCP/*m*-cresol solutions of the polymers, followed by vacuum drying. Such phosphate–polyquinoline complexes are readily converted to the pure polymers by treatment with triethylamine (TEA)/ethanol solutions.

Chart II



Solubilization studies with several commercially available phosphates (**2**–**6**, Chart II) in *m*-cresol were done to confirm this picture of complexation-mediated solubilization of the polyquinolines. Polyquinolines were found to be soluble in *m*-cresol solutions of DPP, DDP, and DBP but not in BHP or TPP. Although low polymer concentrations in DPP/*m*-cresol, DDP/*m*-cresol, or DBP/*m*-cresol could be prepared at room temperature, high polymer concentrations required heating to 120–140 °C to effect complete dissolution. DPP/*m*-cresol was as effective as DCP/*m*-cresol in dissolving sufficiently high concentrations of polyquinolines to produce liquid-crystalline solutions ascertained by observations of thin layers under the cross polars of an optical microscope. In BHP/*m*-cresol in which the polymers did not show any sign of dissolution, the polymers changed colors similar to the case of other phosphates in which they dissolved. This suggests that an insoluble BHP–polyquinoline complex had formed. Insolubility of the BHP–polyquinoline complexes might be a result of incompatible intermolecular interactions between the long aliphatic groups of BHP and *m*-cresol as well as the aromatic polymer backbone. Thus, the structure of a phosphate affects the solubility of its complex with the polyquinolines. Triphenyl phosphate solutions in *m*-cresol did not dissolve any of the polyquinolines. Furthermore, there was no sign of any color change or swelling of the polymers in TPP/*m*-cresol, suggesting the absence of any form of interaction or complex formation between TPP and polyquinoline. These results and observations suggest the mechanism of complexation and solubilization shown in Scheme II. Disubstituted phosphates such as DCP, DPP, DDP, and DBP, which are proton donors, interact with a polyquinoline by protonation of the nitrogen atoms in the quinoline rings and subsequent binding of the phosphate anions to the qua-

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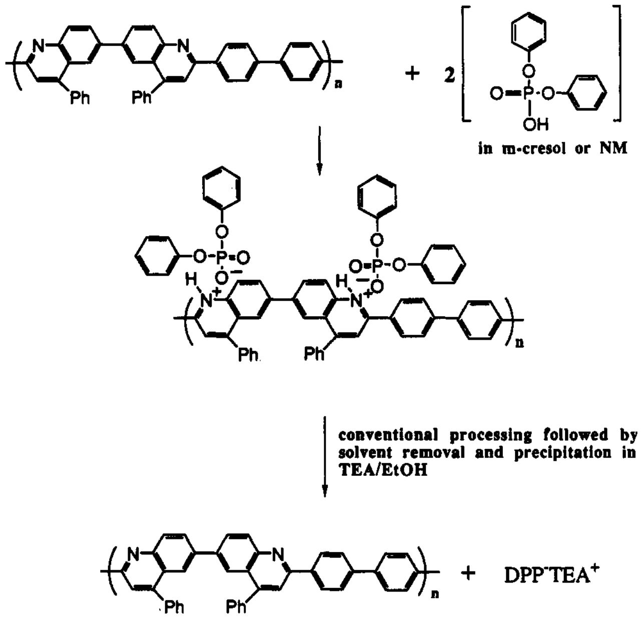
[22] Swanepoel, R. *J. Opt. Soc. Am. A* **1985**, *2*, 1339.

Scheme II

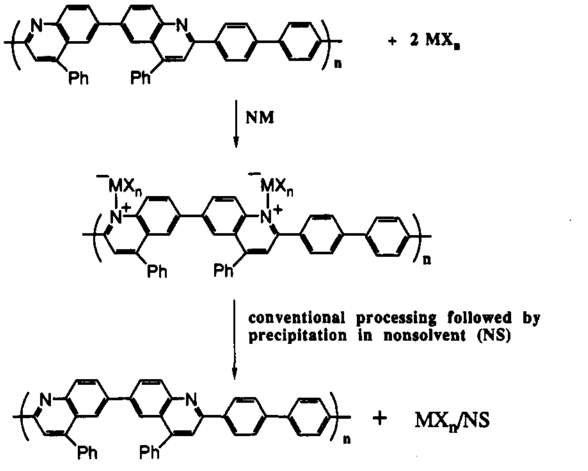


ternized nitrogen and charged sites. This is an essentially acid–base interaction leading to a disubstituted phosphate complex of the polyquinolines. Such a polymer–H$^+$(DPP$^-$) complex shown in Scheme II is easily soluble in *m*-cresol because it is a polyelectrolyte that can be more readily solvated, for example, through the anions. Triphenyl phosphate is thus not effective for solubilizing the polymers because it lacks the necessary acidic protons to participate in acid–base interactions.

If the proposed mechanism of complexation and solubilization of the polyquinolines in phosphate/*m*-cresol (Scheme II) is correct, then it should be possible to eliminate *m*-cresol as a solvent for the complex and find other more suitable solvents. We were able to dissolve the polymers to high concentrations in the pure phosphates *without m*-cresol. In this case, the excess phosphate acts as a solvent for the phosphate–polyquinoline complex. A number of common organic solvents were found to also solubilize the phosphate complexes of the polyquinolines. These were nitromethane (NM), nitroethane (NE), 1-nitropropane (NP), nitrobenzene (NB), dichloromethane (DCM), dichloroethane (DCE), acetophenone (AcPh), and phenol. NM, NE, NP, DCM, and DCE are relatively lower boiling point liquids than NB, AcPh, and phenol, and therefore solutions of the polymer complexes could be easily processed from them compared to the latter. However, they could not be heated to sufficiently high temperatures to aid in dissolving high concentrations of polyquinolines. For the purpose of spin-coating deposition of thin films of the polymers, dilute solutions of DPP–polyquinoline complexes in the low boiling point solvents were found very effective and were successfully used as described in section B. For the purpose of dissolving higher concentrations of polymers to produce liquid-crystalline solutions and for use as polymerization media, the higher boiling point solvents seem to be the better choice.

Lewis Acid Complexes of Polyquinolines. Recently,[23,24] we reported the preparation of Lewis acid complexes

Scheme III



of several conjugated polymers and their solubilization in organic solvents, including: poly(*p*-phenylene-2,6-benzobisthiazole) (PBZT), poly(*p*-phenylene-2,6-benzobisoxazole) (PBO), and benzimidazobenzophenanthroline ladder (BBL) and semiladder (BBB) polymers. We showed that in the case of the rigid-rod polymers such as PBZT, PBO, and BBL, liquid-crystalline solutions of their Lewis acid complexes in organic solvents can be obtained.[23c,24a] It was also suggested that since the basic mechanism of such a complexation-mediated solubilization of polymers involves Lewis acid–base interactions,[23,24] the approach should be general and applicable to polymers containing heteroatoms with nonbonding electrons that can function as Lewis base sites for complexation. We have therefore applied this approach to the polyquinolines since they contain imine nitrogen atoms in the backbone (see structures I–III).

Although many Lewis acids and organic solvents can be used for complexation-mediated solubilization of polymers,[23,24] we selected AlCl$_3$, GaCl$_3$, and nitromethane (NM) for the present studies of the polyquinolines. We found that all the polyquinolines readily dissolved at 1–2 wt % in AlCl$_3$/NM to form viscous solutions suitable for thin-film processing by spin coating. The Lewis acid (MX$_n$ = AlCl$_3$, GaCl$_3$) complexation and solubilization of a rigid-rod polyquinoline, PBPQ, is illustrated in Scheme III. The soluble AlCl$_3$ or GaCl$_3$ complexes of the polyquinolines were readily isolated by evaporation of nitromethane from solution cast films. The Lewis acid–polyquinoline complexes were readily converted to the pure polymers by treatment with water or methanol, which are stronger Lewis bases than the polymers.

(B) Solution Processing to Films and Coatings. Freestanding Films Supported on Frames. Although freestanding high molecular weight polymer films can generally be produced by peeling off films cast on substrate, it is difficult to prevent wrinkle or shrinkage of such films or to handle them in optical measurements or to use them as optical elements. The new technique illustrated in Scheme I provides a way to cast uniform freestanding films of desirable thickness and shape and supported on frames of various materials. The basic idea of this technique is to provide an anchor onto a frame for the polymer film as it is being solidified from the solution phase. The anchoring of the solid polymer film onto a frame such as Bakelite, aluminum, steel, or tin sheets comes about be-

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(23) (a) Jenekhe, S. A.; Johnson, P. O.; Agrawal, A. K. *Macromolecules* **1989**, *22*, 3216–3222. (b) Jenekhe, S. A.; Johnson, P. O.; Agrawal, A. K. *Polym. Mater. Sci. Eng.* **1989**, *60*, 404–409. (c) Jenekhe, S. A.; Johnson, P. O. *Macromolecules* **1990**, *23*, 4419–4429. (d) Roberts, M. F.; Jenekhe, S. A. *Chem. Mater.* **1990**, *2*, 629–631.

(24) (a) Roberts, M. F.; Jenekhe, S. A. *Polym. Commun.* **1990**, *31*, 215–217. (b) Roberts, M. F.; Jenekhe, S. A. *Macromolecules* **1991**, *24*, 3142–3146.

cause of the incisions made at the circumference of the hole. In other frame materials such as paper-based sheets, the anchor is through the intrinsic pore structure of the material. In both cases, the polymer solution flows into the incisions or narrow pores in which it is trapped after solidification by solvent evaporation or precipitation (Scheme II). This trapped polymer holds the rest of the freestanding cast film in the cavity of the frame (Scheme I).

Freestanding films of the polyquinolines prepared by this technique were uniform with thicknesses of the order 10–30 ± 1 μm. The different film thicknesses were obtained by varying the concentration of the polymer solution and the thickness of the frames used. These films of the polyquinolines, which are like slide pictures mounted on frames, were of high optical quality as judged by their transparency and subsequent measurements of optical loss. The films on frames could thus be easily handled, mounted, or stored without touching the film surface. We have found the films prepared by this technique to be ideal for use in optical experiments, for example, in degenerate four-wave mixing (DFWM), the Z-scan method, and in photoconductivity measurements. We have also found that films of other high molecular weight polymers can be similarly prepared on frames. For example, high-optical-quality films of PBZT supported on frames have been so prepared.

Thin-Film Coatings on Substrates. Thin films of polyquinolines can be obtained by solution casting of the viscous polymer solutions in DCP/*m*-cresol onto optically flat silica substrates, followed by solvent removal, regeneration by precipitation, and drying. However, this gives nonuniform films. All attempts of spin coating of the polyquinoline solutions in DCP/*m*-cresol were unsuccessful as the coatings shrunk and broke up as soon as the spinner was stopped.

Spin coating of solutions of polyquinolines in pure DPP avoided the problems associated with *m*-cresol. DPP, being a solid at room temperature, forms highly viscous solutions of the polymers at room temperature. The viscosity of these solutions could be sufficiently reduced to facilitate easy spin coating on heated substrates by preheating the solutions at 125 °C. As the solution spreads during spin coating, simultaneous cooling resulted in a highly viscous coating of the solution. It was necessary to run the spinner for about a minute to allow sufficient time for the solution to cool to near room temperature. These coatings were directly precipitated in triethylamine (TEA)/ethanol mixture, eliminating the step of evaporating *m*-cresol. One of the problems faced during precipitation was immediate separation of the films from the substrate on immersion. Incompatible contraction due to the different coefficients of thermal expansion of the film and of the silica substrate might be the cause of the poor adhesion between the two. Treating the clean silica substrate with tetrahydrofuran seems to modify the interface between the film and the substrate, thereby solving the problem of adhesion to a large extent. We were able to obtain high-quality uniform films using solutions of the polymers in pure DPP.

Polyquinolines could be spin coated in a much simpler and better way from their solutions in DPP/NM. Polyquinoline solutions in DPP/nitromethane were readily spin coated at room temperature and the solvent easily evaporated from the coatings during the spinning. A very uniform continuous coating of the DPP–polyquinoline complex, which did not shrink or separate from the substrate at any stage of the process, was obtained. These coatings of DPP–polymer complex were stable in ambient atmosphere and were easily regenerated in nonsolvent TEA/ethanol to give high-quality uniform films of the pure polymers.

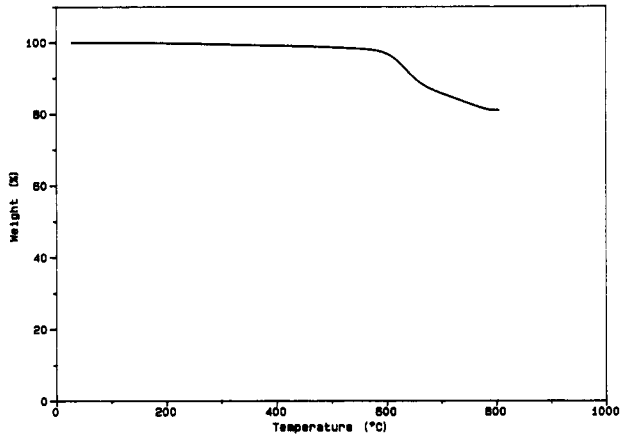


Figure 1. TGA thermogram of a rigid-rod polyquinoline (PBDA, IIIb) in flowing nitrogen at 10 °C/min.

Similarly, polyquinoline solutions in $AlCl_3$/NM and $GaCl_3$/NM were easily spin coated at room temperature on silica substrates. The resulting thin-film coatings of the Lewis acid–polyquinoline complexes were readily decomplexed by treating them with methanol or water, which is a stronger Lewis base than the pure polymers (Scheme III). Due to the moisture sensitivity of the Lewis acid complexes of the polyquinolines, the polymer solutions or spin-coated films of the complexes can regenerate in humid atmosphere if left for a sufficient time. Therefore, the polymer solutions were exposed to humid air for as little time as possible prior to spin coating which generally took 10–15 s. Once a coating of the complex was obtained, it was slowly regenerated in three stages as described in the Experimental Section to avoid separation of the films from the substrate in the nonsolvent.

The polyquinoline films or coatings obtained from their soluble diphosphate or Lewis acid complexes were shown by thermal analysis and spectroscopy to be the pure polymers. For example, Figure 1 shows the typical thermal stability in nitrogen revealed by thermogravimetric analysis (TGA) of a polyquinoline (PBDA) obtained from its soluble complex. Of particular effectiveness for the purpose of determining the complete regeneration or precipitation of polyquinoline from its complex is optical absorption spectroscopy. As will be discussed in section C, phosphate or Lewis acid complexes of the polyquinolines exhibit optical absorption spectra that are significantly red shifted from those of the corresponding pure polymers.

These results show that high-quality thin films or coating of the polyquinolines on substrates can be prepared by not only solution casting but especially the spin coating of their organic solvent soluble complexes. Such polyquinoline thin films were found to be of high optical quality and ideal for investigation of linear optical properties as well as for measurement of nonlinear optical properties by third harmonic generation.[18a]

(C) Optical Properties of Rigid-Rod Polyquinolines. Figure 2 shows the optical absorption spectrum of the thin film of the basic polyquinoline, PPQ. The lowest energy absorption band has a λ_{max} at 410 nm and a corresponding optical bandgap of 2.65 eV. This is in accord with the light yellow color of the polymer.

Figure 3 shows the optical absorption spectrum of the thin film of the most widely studied polyquinoline, PBPQ (IIb). The optical absorption maximum λ_{max} and bandgap

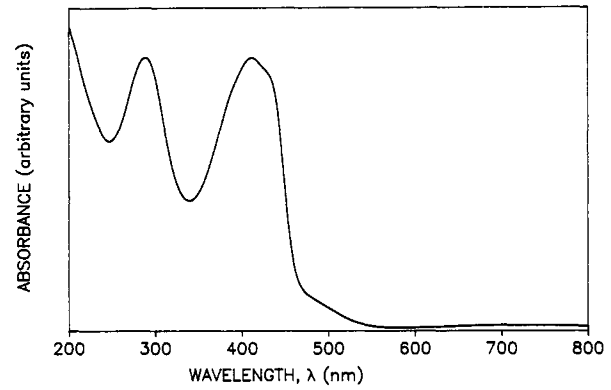


Figure 2. Optical absorption spectrum of a thin film of polyquinoline (PPQ).

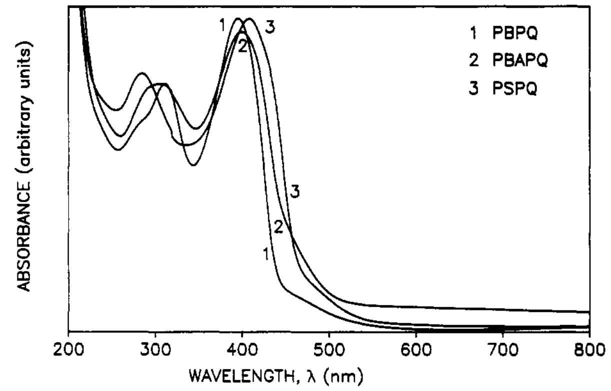
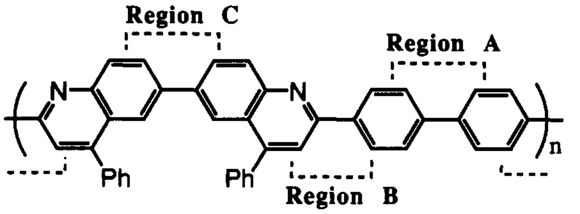


Figure 3. Optical absorption spectra of thin films of polyquinolines II (PBPQ, PBAPQ, and PSPQ).

are 394 nm and 2.81 eV, respectively. These results indicate a lower degree of π-electron delocalization along the backbone of the polymer chain compared to the parent polyquinoline (PPQ). Examination of the molecular structure of PBPQ indicates three regions (A,B,C) of steric hindrance:



In these regions, the ortho hydrogens to the bond linking the two adjacent aromatic rings forces the two rings to be noncoplanar and hence could limit the electron delocalization. This suggests that linear optical and possibly the nonlinear optical properties of the polyquinolines could be tuned if the structure can be systematically modified in these regions to vary the extent of effective π-electron delocalization along the polymer backbone. The various polymer structures designed and synthesized to explore these structure–property relationships were shown earlier as II and III. In the case of the series II, the R group was changed from the biphenyl linkage in PBPQ to phenyl in PPPQ (IIa), biphenylacetylene in PBAPQ (IId), and stilbene in PSPQ (IIc), respectively, to reduce the effects of adverse steric hindrance in region A. On the other hand, the diphenylmethane linkage in PDMPQ (IIg) was introduced to completely break the conjugation and consequently to determine the effect of π-conjugation beyond the repeating unit of the conjugated polyquinolines. From the optical absorption spectra of Figure 3 and the tabulated λ_{max} and optical bandgap (E_g), we found a progressive increase of π-electron delocalization in the series of polyquinolines II: PDMPQ < PBPQ < PPPQ < PBAPQ < PSPQ.

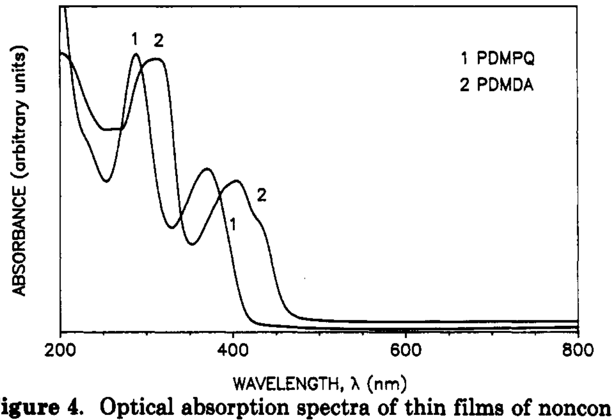


Figure 4. Optical absorption spectra of thin films of nonconjugated polyquinolines IIg (PDMPQ) and IIIg (PDMDA).

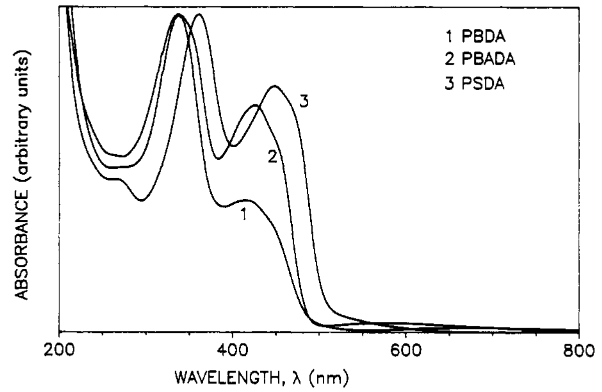


Figure 5. Optical absorption spectra of thin films of polyquinolines III (PBDA, PBADA, and PSDA).

The steric hindrance in region C was eliminated by fusing the two separate quinoline rings of polymer II into the fused three-ring anthrazoline structure in polymer III. All the polyanthrazolines (III) exhibited a higher λ_{max} and a smaller E_g compared to their respective polyquinoline (II) derivatives. The greater degree of π-electron delocalization in the polyanthrazolines compared to the polyquinolines can be clearly inferred by comparing the optical absorption spectra of the nonconjugated polymers PDMPQ and PDMDA in Figure 4. This effect can also be observed by comparing the optical absorption spectra of the polyanthrazoline series in Figure 5 to their corresponding polyquinoline series in Figure 3. Variation of the linkage group R within the polymer structure III leads to a progressive variation of the π-electron delocalization in the increasing order: PDMDA < PBDA < PBADA < PPDA < PSDA (Table I and Figure 5).

The steric hindrances in both regions A and B can also be addressed simultaneously by structural modification involving the R group; for example, by introduction of an acetylene or vinylene linkage. Such an R group substitution would result in poly(quinoline vinylene) or poly(anthrazoline vinylene) or their acetylene-linked derivatives. This was expected to further improve the degree of π-electron delocalization in the polymer series II and III. However, the corresponding polymers IIe, IIf, IIIe, and IIIf could not be successfully synthesized probably due to the instable nature of the diacetylacetylene and diacetylvinylene monomers at high temperatures and in the acidic environment of the polymerization medium.

Another approach to modifying optical properties is through copolymerization to give random, alternating, or

Table I. Optical Properties of Rigid-Rod Polyquinolines

polym	λ_{max}- (film), nm	E_g(film), eV	λ_{max}- (soln),[a] nm	log ϵ (soln)[a]
PPQ	410	2.65	389	4.16
PDMPQ	370	3.01	389	4.68
PBPQ	394	2.81	429	4.83
PBAPQ	399	2.72	436	4.86
PSPQ	408	2.65	467	4.88
PPPQ	398	2.78	405	4.63
PDMDA	404	2.70	431	4.62
PBDA	414	2.56	484	4.67
PBADA	426	2.57	490	4.65
PSDA	448	2.46	547	4.78
PPDA	443	2.47	442	4.49
PBPQ/PBAPQ	397	2.79	431	4.88
PBPQ/PSPQ	402	2.72	440	4.77
PSPQ/PBAPQ	404	2.72	445	4.81

[a] In 0.1 mol % DCP in *m*-cresol.

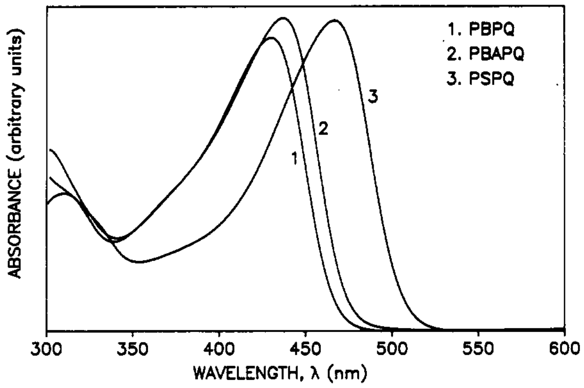


Figure 6. Solution optical absorption spectra of polyquinolines (PBPQ, PBAPQ, PSPQ) in 0.1 mol % DCP/*m*-cresol.

block copolymer structures. Our specific interest in synthesizing random copolymers was to study the effect of disorder in the polymer main chain on the nonlinear optical properties. It is also possible that random copolymerization could lead to more amorphous glassy materials than homopolymers and also provide a way to vary or blend optical properties. Three random copolymers with 50:50 molar composition were synthesized and investigated: PBAPQ/PSPQ; PBPQ/PSPQ; PBPQ/PBAPQ. As can be expected, the linear optical properties, ie., λ_{max} and optical bandgap, of the random copolymers were found to be an average of those of the constituent homopolymers (Table I).

The optical absorption spectra of all the polyquinolines were also obtained in 0.1 mol % DCP/*m*-cresol. Figure 6 shows the typical optical absorption spectra of the polyquinolines in solution. The solution λ_{max} and corresponding extinction coefficient for the lowest energy absorption band are shown in Table I. In solution, the polymers exhibit a substantial red shift in λ_{max} by about 20–100 nm compared to the solid-state spectra. These changes in the optical spectra of the polyquinolines II and III are due to protonation of the nitrogen on the quinoline rings and binding of the diaryl phosphate anions to the quaternary nitrogen sites which favor a more coplanar polymer conformation. Similar complexation-induced chromism in conjugated polymers have previously been reported in, for example, conjugated aromatic Schiff base polymers.[25] It is to be noted from Table I that the λ_{max} of the diaryl phosphate complexes of PPQ is less than that of the pure polymer. This suggests that the conformation of the pure PPQ is more planar and conducive to π-electron delocalization than its complexes. It is also noteworthy that the Lewis acid complexes of the polyquinolines II and III exhibited similar complexation-induced chromism and spectral red shift as the diaryl phosphate complexes.

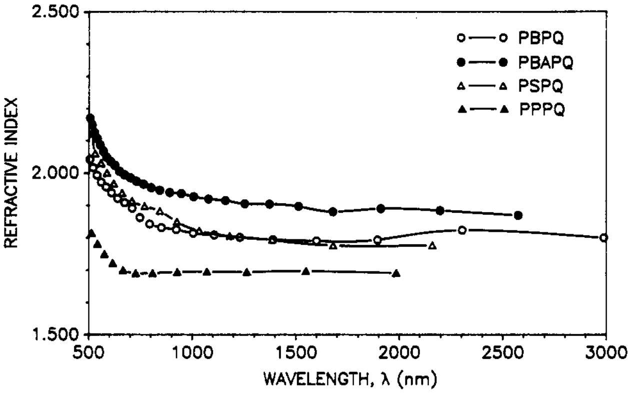


Figure 7. The dispersion of the refractive index of thin films of polyquinolines II (PBPQ, PBAPQ, PPPQ, and PSPQ).

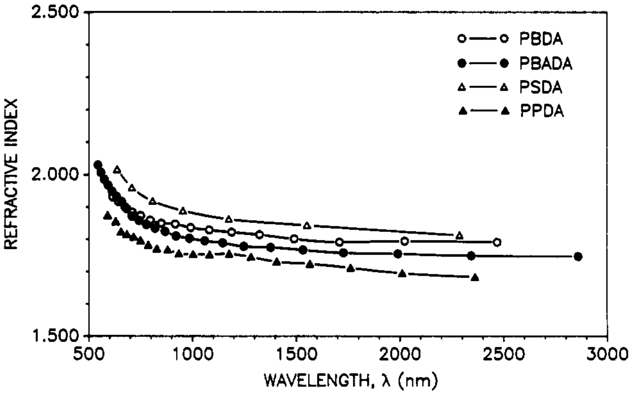


Figure 8. The dispersion of the refractive index of thin films of polyquinolines III (PBDA, PBADA, PPDA, and PSDA).

These results of the optical absorption spectra of the polyquinolines clearly show that we have been able to change the degree of steric hindrance and hence extent of π-electron delocalization through the backbone of this class of conjugated polymers by systematic structural modifications of the main chain. It remains to be seen to what extent these systematic structural changes are reflected in the third-order nonlinear optical properties of these polymers. The nonlinear optical properties of these polyquinolines are currently under investigation by using third harmonic generation spectroscopy to measure $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ and to explore the effects of structure. The results of these studies will be reported in a future paper.[26]

The linear refractive index, n_0, is an essential property of interest in optical materials in general and also a needed information for measuring or calculating the nonlinear optical properties of a material. Using the method described by Swanepoel,[22] we have measured the refractive index of the polyquinoline homopolymers in the transparent region of 500–3000 nm. The accuracy in the measured values of n_0 was ±5%. The refractive index spectra of representative members of the polyquinolines II and the polyanthrazolines III are shown in Figures 7 and

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Table II. Measured and Calculated Index of Refraction n_0 of Several Rigid-Rod Polyquinolines

	n_0			
polym	measd[a]	calcd[b]	calcd[c]	calcd[d]
PPQ		1.771	1.647	1.615
PPPQ	1.69	1.758	1.654	1.627
PBPQ	1.79	1.749	1.658	1.635
PBAPQ	1.87	1.763	1.666	1.641
PSPQ	1.78	1.744	1.659	1.636
PPDA	1.68	1.770	1.645	1.618
PBDA	1.79	1.758	1.651	1.629
PBADA	1.75	1.773	1.660	1.636
PSDA	1.83	1.752	1.652	1.631

[a] At wavelengths greater than 1500 nm. [b] Calculated using Vogel's semiempirical group correlation.[27] [c] Calculated using Gladstone–Dale empirical group correlation.[27] [d] Calculated using Lorentz-Lorenz theoretical model.[27]

8, respectively. As can be expected for highly polarizable conjugated polymers, the refractive indexes are quite high for organic polymers. Far away from the absorption edge, the index of refraction values are between 1.68 and 1.87 in the wavelength range 900–3,000 nm. However, due to dispersion, as the absorption edge at 500 nm is approached the n_0 values increase to greater than 2. These results also suggest that the polyquinolines can be used as waveguides on glass, silica, or related substrates which have lower index of refraction (~1.50–1.60).

In the absence of experimentally measured n_0 values, theoretical, semiempirical, and empirical correlations are usually used to estimate the refractive index of a given compound or polymer with known molecular structure.[27] Such correlations are based on the additivity of *molar refraction* of bonds and groups in a chemical compound. The correlations neglect the effects of wavelength dispersion on the index of refraction and in the case of Vogel's correlation, the solid polymer is assumed to be amorphous.[27] Table II shows the measured wavelength independent refractive index of several polyquinolines. The index of refraction of the polyquinolines and polyanthrazolines was in the range 1.69–1.87. Also shown in Table II are calculated n_0 values for the polyquinolines using three different correlations:[27] Vogel's empirical method for amorphous polymers; Gladstone–Dale semiempirical equation; Lorentz–Lorenz theoretical equation. Surprisingly, the calculated n_0 values using Vogel's empirical equation are very close to the data, within experimental errors (1–6%). However, the calculated refractive indexes using Gladstone–Dale and Lorentz–Lorenz correlations significantly underestimate the n_0 values of conjugated polyquinolines.

The use of these polymers as optical waveguides or as nonlinear optical materials for cubic nonlinear optics requires that optical loss α (cm^{-1}) from all sources, including intrinsic absorption and light scattering due to defects in morphology, be as small as possible. In the case of nonlinear optical materials, for example, a material figure of merit Re $\{\chi^{(3)}\}/\alpha$ is usually to be maximized, where Re $\{\chi^{(3)}\}$ is the real part of the third-order optical nonlinearity and α is the optical loss at the frequency of intended application of the materials.[18a,28] We have determined the intrinsic optical loss in several polyquinolines using two different methods. In the first method, optical losses obtained for different concentrations of polymer solutions in DPP/*m*-cresol were extrapolated to 100 wt % polymer solution (i.e., pure polymer). The values obtained varied from about 1 to 15.5 cm^{-1} in the transparent region of 0.8–1.9 μm, shown in Table III, and are orders of magnitude better than many other classes of conjugated polymers reported to date.[29] In the second method, polymer films of varying thicknesses were plotted against the absorbance values of those films. The intrinsic optical loss α (cm^{-1}) for the materials was then calculated from the slope of the straight line obtained from such a plot. This latter method avoids the influence of many physical phenomena such as surface reflections, surface dispersions, and multiple reflection, which are generally present in a single point measurement of the optical losses. The close agreement, found between the values from the two different methods described above, further substantiate the accuracy of the results. Therefore, the results obtained are a good estimation of the order of magnitude of the intrinsic optical losses in this class of conjugated polymers.

Table III. Intrinsic Optical Loss of Rigid-Rod Polyquinolines

	opt loss (α) at λ, cm^{-1}			
polym	800 nm	1200 nm	1500 nm	1900 nm
PPQ	15.5	9.8	6.0	9.2
PBPQ	2.5	2.8	4.5	6.4
PBAPQ	9.0	8.8	10.7	13.2
PSPQ	3.7	1.1	1.0	2.2
PBAPQ[a]	1.0	2.5	2.5	4.5

[a] Measured from thin films.

Conclusions

We have investigated the complexation-mediated solubilization of rigid-rod polyquinolines I–III in organic solvents with a view to enable easy processing of these polymers for electronic, photoconductive, and nonlinear optical applications. It was shown that phosphate or Lewis acid complexes of the polyquinolines were soluble in common organic solvents and processable to thin films and coatings. Of particular significance is the successful preparation of coatings of the polyquinolines on substrates by spin coating and the proposed novel technique for producing freestanding polymer films supported on frames.

The linear optical properties of a series of rigid-rod polyquinolines, designed for investigation of structure–property relationships, were investigated. It was shown that simple systematic variations in the backbone structure of conjugated polyquinolines can significantly and predictably modify the steric hindrance in the structure and hence the extent of π-electron delocalization. Significantly low intrinsic optical losses (α) of order 1–10 cm^{-1} were obtained for these polymers.

Acknowledgment. This research was supported by the New York State Science and Technology Foundation, the Amoco Foundation, and the National Science Foundation (Grant CHE881-0024).

Registry No. I (SRU), 59827-46-2; I (homopolymer), 59827-22-4; IIa (SRU), 75460-98-9; IIa (copolymer), 75454-66-9; IIb (SRU), 75460-97-8; IIb (copolymer), 75454-65-8; IIc (SRU), 94751-99-2; IIc (copolymer), 106500-72-5; IId (SRU), 135614-64-1; IId (copolymer), 135663-13-7; IIe (SRU), 137059-45-1; IIe (copolymer), 137059-48-4; IIf (SRU), 137059-46-2; IIf (copolymer), 137059-49-5; IIg (SRU), 137059-47-3; IIg (copolymer), 137059-50-8;

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IIIa (SRU), 137091-72-6; IIIa (copolymer), 57468-87-8; IIIb (SRU), 57468-80-1; IIIb (copolymer), 57469-13-3; IIIc (SRU), 137091-73-7; IIIc (copolymer), 137059-51-9; IIId (SRU), 137091-74-8; IIId (copolymer), 137059-52-0; IIIe (SRU), 137091-75-9; IIIe (copolymer), 137059-53-1; IIIf (SRU), 137091-76-0; IIIf (copolymer), 137059-54-2; IIIg (SRU), 137091-77-1; IIIg, 137059-55-3; DBP, 1623-08-1; DDP, 298-06-6; $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3; NEt_3, 838-85-7.

Transformation of Platinum Carbonyl Clusters on Graphite under Laser Irradiation and Their Scanning Tunneling Microscopy Observation

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Scanning tunneling microscopy (STM) images were obtained from an isolated aggregate of Pt carbonyl clusters $[NEt_4]_2[Pt_{12}(CO)_{24}]$, which were adsorbed from the tetrahydrofuran solution onto the surface of a freshly cleaved HOPG (highly oriented pyrolytic graphite) under the nitrogen atmosphere. The in situ STM images demonstrated the morphological changes of the surface-bound Pt_{12} carbonyl clusters under the pulse laser irradiation (532 nm; 2-3 mJ), resulting in the effective decarbonylation and fragmentation which was implied by the diffuse reflectance FTIR, coupled with mass. The Pt_{12} carbonyl clusters were converted by the successive pulse laser activation into a highly dispersed Pt microcrystalline (18 × 50 Å^2), which was imaged by STM.

Introduction

Grafting of molecular metal clusters on solid-surfaces has been a subject of recent interest in molecular approaches for preparation of the tailor-made metal catalysts having uniform distribution of particle sizes and metal compositions.[1] The composition and morphology of the grafted clusters is profoundly controlled by the nature of supports, temperature, and atmosphere;[2] absorption or diffraction spectroscopies are employed as tools to characterize the local structure of the clusters. In the extensive effort to directly observe the surface-grafted clusters, Iijima and Ichikawa succeeded in imaging individual Rh_6 clusters derived from $Rh_6(CO)_{16}$ attached on top of (111) oxide layer of alumina by the high-resolution electron micrograph,[3] however, some of the clusters grew larger due to electron irradiation during the TEM observation.

Scanning tunneling microscopy (STM)[4,5] is a powerful tool for the observation of solid surfaces and polymers.[6] In particular, the great advantage of STM in the study of catalysis is its applicability to imaging the surfaces under in situ conditions, e.g., under the reactant gas atmosphere. In some cases, the structural changes of electrode surfaces in solutions under operating conditions have been studied with STM.[7]

The photoactivation of transition-metal clusters is an important area of catalysis due to the potential usefulness of the activated species as catalyst precursors.[8] In addition, controlling the size of metal fine particles as small as nanometer-order is a recent topic to create highly functionalized materials.[9] As part of our continuing research on catalysis by grafted clusters,[10] it has been previously reported[11] that the STM images of the individual carbonyl clusters such as $Rh_4(CO)_{12}$ and $[NEt_4]_2[Pt_{12}(CO)_{24}]$ are observed on HOPG. There is considerable interest in the in situ observation of the metal complexes or clusters on solid surfaces activated by photon emission[12] or laser irradiation.[13] In this study we have conducted the photoactivation of $[NEt_4]_2[Pt_{12}(CO)_{24}]$ adsorbed on graphite by laser excitation and imaged the conversion of the Pt carbonyl clusters with an STM operating in situ. The diffuse reflectance FTIR, coupled mass spectroscopy is also performed on the Pt_{12} carbonyl clusters deposited on HOPG. We report here the morphological transformation of an aggregate of $[NEt_4]_2[Pt_{12}(CO)_{24}]$ on HOPG induced by the pulse laser irradiation to give a Pt microcrystalline in the size of ca. 18 × 50 Å^2.

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