charge/discharge cycles, but it may also reveal something about the relative homogeneity of these films. For example, the fact that the charge trapped during n- and p-doping is very similar in magnitude may suggest that this charge is trapped in the same region(s) of the film, suggesting the possibility of considerable heterogeneity within the film. Trapping via a homogeneous mechanism (e.g., trapping by isolation from the underlying electrode by the intervening polymer layer, which becomes insulating first during the undoping process[21] seems unlikely in this case, because it should depend on the film conductivities, which are known to be at least 2 orders of magnitude different for the n- and p-doped cases.[21,23] Also, careful ellipsometric studies of the mode of doping for poly(aniline), another (albeit, different) conducting polymer system, indicate uniform doping and undoping.[30] Thus, in the present case, trapping via a mechanism involving film heterogeneity seems more likely. We suggest that there are regions of these films that are in relatively poor physical contact with the bulk of the film and that the deswelling (caused by ion expulsion) that occurs during the undoping process causes the bulk of the film to draw away from these regions, thus degrading the quality of the electronic contact between them. On doping at the opposite potential extreme, reswelling (due to ionic insertion) occurs, reestablishing the electronic contact needed for efficient release of the trapped charge.

While this suggestion that charge trapping in such materials is caused by film heterogeneity is clearly of a speculative nature, it does suggest that microscopic investigations of such films are in order. Such studies are facilitated by the ability to make various types of spectroscopic measurements with relatively high spatial resolution, such as FTIR, Raman, fluorescence, etc., and may also be possible with very high resolution probes of electronic structure such as STM, at least at the film surface. We hope that this report will prompt such investigations.

Acknowledgment. We are grateful to the Office of Naval Research for the full support of this work.

Registry No. Bithiophene (homopolymer), 80029-99-8.

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Conjugated Aromatic Poly(azomethines). 1. Characterization of Structure, Electronic Spectra, and Processing of Thin Films from Soluble Complexes

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A series of conjugated aromatic poly(azomethines), poly(1,4-phenylenemethylidynenitrilo-1,4-phenylenenitrilomethylidyne) (PPI), poly(2-methyl-1,4-phenylenemethylidynenitrilo-1,4-phenylenenitrilomethylidyne) (PMPI), poly(1,4-phenylenemethylidynenitrilo-2,5-dimethoxy-1,4-phenylenenitrilomethylidyne) (PMOPI), poly(1,4-phenylenemethylidynenitrilo-2,5-dihydroxy-1,4-phenylenenitrilomethylidyne) (PHOPI), and copolymer PPI/PMPI, have been prepared and solubilized in organic solvents by reversible complexation with either gallium chloride or di-*m*-cresyl phosphate (DCP) and characterized. The molecular structure of the aromatic polyazomethines was characterized by ^{1}H NMR spectra of the polymers in $GaCl_3$/deuterated nitromethane. The conjugated aromatic poly(azomethines) were processed into optical-quality thin films from their soluble complexes in organic solvents and characterized. The solid-state electronic absorption spectra showed that the λ_{max} for π-π^* transition varies from 405 nm for PPI to 497 nm for PHOPI. The corresponding solid-state bandgap was in the range 2.07-2.50 eV. The relatively low bandgap of PHOPI (2.07 eV) compared to PMOPI (2.34 eV) and PPI (2.50 eV) is due to its intramolecular hydrogen-bonding-mediated coplanar structure. Intramolecular hydrogen bonding in PHOPI was further evidenced by FTIR spectra and the results of solubility and complexation studies. The solid-state electronic absorption spectra of complexes of these conjugated aromatic poly(azomethines) were found to exhibit greater electronic delocalization and smaller bandgaps (1.85-2.15 eV) than the pure polymers. Origin of this remarkable red shift of electronic spectra was attributed to complexation-induced change in polymer conformation. The preparation of soluble complexes of conjugated aromatic poly(azomethines) and their processing to optical-quality thin films has now opened up investigation of the solid-state properties of this class of liquid-crystalline conjugated polymers and high-temperature fiber-forming materials.

Introduction

Conjugated aromatic *p*-phenylene ring polymers occupy a central place in current efforts to elucidate the structure-property relationships of electronic, optical, and nonlinear optical polymers. Among the well-studied *p*-phenylene ring polymers are poly(*p*-phenylene) (PPP),[1,2] poly(*p*-phenylene sulfide) (PPS),[1,2] polyanilines[3-5] such as

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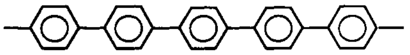
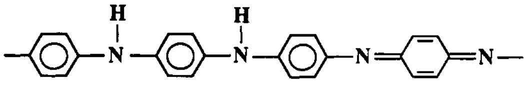
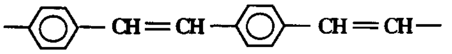
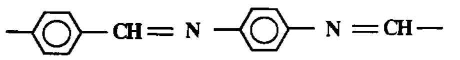
poly(emeraldine base) (PEMB), and poly(*p*-phenylenevinylene) (PPV).[6-8] The electronic,[1-4,6,7] electrochemical, linear optical,[1-8] or nonlinear optical properties[5,8,9] of these polymers and their derivatives have been widely investigated and reported on. For example, large third-order optical nonlinearities have recently been reported in thin films of PPV[8,9] and polyanilines.[5]


PPP


PEMB


PPV


PPI

A less well studied *p*-phenylene ring polymer, at least with respect to its electronic, optical, and nonlinear optical properties, is poly(1,4-phenylenemethylidynenitrilo-1,4-phenylenenitrilomethylidyne) (PPI). The conjugated aromatic poly(azomethine) or Schiff base polymer PPI is isoelectronic with PPV and intermediate between PPV and polyanilines in molecular structure. However, PPI has a reduced symmetry compared to PPV. Like the polyanilines and unlike PPV, the imine nitrogen of the PPI backbone introduces novel features and chemical flexibility. We have therefore decided to investigate the structure, processing, and solid-state properties of PPI and its derivatives.

The conjugated aromatic poly(azomethines), such as PPI and derivatives, have previously been synthesized, and aspects of their properties investigated for many years.[10,11] For example, their synthesis,[10,11] attractive thermal stability,[10,11] good mechanical strength and fiber-forming properties,[11] thermotropic liquid crystallinity,[11] lyotropic liquid crystallinity in sulfuric or methanesulfonic acid,[11,12] and semiconducting properties of long alkoxy derivatives[13] have been reported. However, a major obstacle to characterizing and developing the conjugated aromatic poly(azomethines) has been their insolubility and intractability. Although PPI and its derivatives have been known to dissolve in sulfuric acid, methanesulfonic acid, chlorosulfonic acid, and HF, forming lyotropic liquid-crystalline solutions at high concentrations, they rapidly degrade with time due to the acid-catalyzed hydrolysis of CH=N.[11]

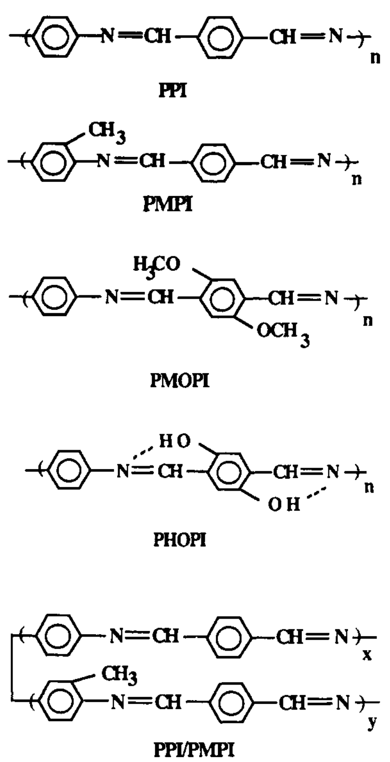


Figure 1. Structures of the conjugated aromatic poly(azomethines) investigated.

Recently, two research groups have reported the synthesis of new conjugated aromatic poly(azomethines) with long alkoxy side chains attached to the *p*-phenylene rings in attempts to improve the solubility of these polymers.[13,14] It was reported that introduction of a long alkoxy side chain ($C = 8-18$) yielded aromatic polyazomethines that were soluble in several organic solvents.[13] However, another study of high molecular weight aromatic polyazomethines with oxydecyl side chains ($C = 10$) showed that the polymer was not completely soluble in any organic solvents but was soluble only in acidic solvents.[14] Apart from the discrepancy in the reported extent of solubility of long alkoxy derivatives of aromatic poly(azomethines), presumably due to the difference in molecular weight of the polymers investigated by the two groups, the derivatization approach to solubility has the drawback that the problem of the solubility of the original nonderivatized polymers remains. Thus, while long alkyl or alkoxy derivatives of the conjugated aromatic poly(azomethines) are interesting materials in their own right, they are not solutions to the problem of solubilizing and investigating the nonderivatized polymers since the two types of polymers can be expected to exhibit dramatically different physical properties including glass transition temperature, morphology, and electronic structure.

A general approach to the solubility and processing of polymers containing lone-pair electron donors was recently introduced by our laboratory.[15-18] The approach is based

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on reversible Lewis acid–base complexation and has been used by us to dissolve and process otherwise insoluble rigid-chain, rigid-rod, ladder, or flexible-chain polymers in organic solvents.[15-19] In the case of aromatic poly(azomethines) of interest here, i.e., PPI and derivatives, the imine nitrogen on the backbone provides a Lewis base site for effecting reversible complexation, solubilization, and processing to thin films or fibers.

We have prepared and successfully dissolved the series of conjugated aromatic poly(azomethines) shown in Figure 1, including the basic polymer PPI, in organic solvents and prepared optical-quality thin films of all the materials. This has allowed us to investigate their molecular structure by ^{1}H NMR spectroscopy in solution and their electronic spectra and solid-state properties for the first time. This paper reports the characterization of structure, solution, and solid-state electronic absorption spectra, and thin-film processing of conjugated aromatic poly(azomethines) from soluble complexes in organic solvents. A detailed investigation of the structure and solid-state properties of the complexes[20] of these aromatic poly(azomethines) will be reported elsewhere as will be the third-order nonlinear optical properties[21] of thin films of all the polymers in Figure 1.

Experimental Section

Materials. All the monomers, purchased or synthesized, were rigorously purified before polymerization. 1,4-Phenylenediamine (99%, Aldrich) was recrystallized from benzene. 2-Methyl-1,4-phenylenediamine was purified by vacuum distillation in the presence of granular zinc after extracting the compound from the aqueous ammonium hydroxide solution of 2,5-diaminotoluene sulfate (97%, Aldrich) with ether. Terephthaldehyde (98%, Aldrich) was purified by vacuum sublimation at 100 °C. 2,5-Dimethoxyterephthaldehyde was prepared by a three-step reaction from 1,4-dimethoxybenzene (99%, Aldrich).[22-24] The product of each step in the monomer synthesis was characterized by its melting point and ^{1}H NMR spectrum. 2,5-Dihydroxyterephthaldehyde was prepared[25,26] by reaction of 2,5-dimethoxyterephthaldehyde with a mixture of acetic acid and hydrobromic acid followed by extraction overnight with benzene in a Soxhlet apparatus. The polymerization media, hexamethylenephosphoramide (HMPA, 99%, Aldrich) and 1-methyl-2-pyrrolidinone (NMP, 99+% anhydrous, Aldrich), and the water absorbing reagent, lithium chloride (99+%, Aldrich), were used as received. The complexing reagent, di-*m*-cresyl phosphate (DCP), was synthesized and purified by using literature methods.[27] Diphenyl phosphate (DPP, 99%, Aldrich) was used as received.

Preparation of Polymers. All the polymers were prepared by the solution polymerization of diamines and dialdehydes.

PPI and PMPI.[11] These polymers were prepared by using the literature method. Each polymer was precipitated out of the reaction medium (1:1 HMPA/NMP) after 20 h reaction by pouring into methanol. The product was washed several times with distilled water and methanol before further purification by overnight extraction with refluxing methanol in a Soxhlet apparatus. Both PPI and PMPI were obtained as yellow powders; ^{1}H NMR of PPI (in GaCl$_3$/deuterated nitromethane) 8.30, 8.70, and 9.86 ppm. ^{1}H NMR of PMPI 2.80, 8.10, 8.70, 9.66, and 9.80 ppm. The intrinsic viscosity values for PPI and PMPI at 30 °C were respectively 0.84 and 0.70 dL/g in 96% sulfuric acid and 1.38 and 1.35 dL/g in GaCl$_3$/nitromethane.

Copolymer PPI/PMPI. This copolymer was prepared by solution polymerization of 1.0677 g (8.74 mmol) of 2-methyl-1,4-phenylenediamine, 0.9453 g (8.74 mmol) of 1,4-phenylenediamine, and 2.3450 g (17.48 mmol) of terephthaldehyde in the presence of 1 g of LiCl in a 50-mL 1:1 HMPA/NMP solution at room temperature. After purification similar to PPI above and vacuum drying the yield was 3.647 g (98%); ^{1}H NMR of PPI/PMPI 2.80, 8.10, 8.30, 8.70, 9.70, and 9.83 ppm. The intrinsic viscosity at 30 °C in 96% sulfuric acid and in GaCl$_3$/nitromethane was 0.82 and 1.36 dL/g, respectively.

PMOPI. 1,4-Phenylenediamine (1.4339 g, 13.26 mmol) was reacted with 2.5724 g (13.26 mmol) of 2,5-dimethoxyterephthaldehyde in 40 mL of 1:1 HMPA/NMP and 0.8 g of LiCl under nitrogen purge at room temperature. After 48 h of polymerization time, the polymer was precipitated into methanol, washed repeatedly with water and methanol, and dried under vacuum to afford an orange powder (3.25 g, 92% yield); ^{1}H NMR of PMOPI 4.50, 8.20, and 9.60 ppm. The intrinsic viscosity at 30 °C in 96% sulfuric acid and in GaCl$_3$/nitromethane was 0.19 and 1.04 dL/g, respectively.

PHOPI.[22] 1,4-Phenylenediamine (0.3 g, 2.77 mmol) was reacted with 0.46 g (2.77 mmol) of 2,5-dihydroxyterephthaldehyde as in the other solution polymerizations. After 72 h of polymerization time, the polymer was precipitated into methanol and purified as in PPI above to afford a red powder (0.63 g, 95% yield); ^{1}H NMR of PHOPI 6.40, 8.20, 8.40, and 9.60 ppm. The intrinsic viscosity at 30 °C in 96% sulfuric acid and in GaCl$_3$/nitromethane was 0.34 and 1.14 dL/g, respectively.

Preparation of Complexes. Di-*m*-cresyl phosphate (DCP) complexes of the aromatic poly(azomethines) were prepared by dissolving known amounts of each polymer in a solution of DCP in *m*-cresol under vigorous stirring at room temperature. The molar ratio of DCP to the polymer repeat unit was varied between 1:2 and 2:1 depending on the desired DCP:CH=N ratio in the final complex. For the 1:1 (DCP:CH=N) complexes studied extensively, the molar ratio of DCP to polymer repeat unit was 2:1. The dissolution of the polymers in DCP/*m*-cresol was complete within 20 min. The solid complexes were obtained by evaporation of *m*-cresol from solution cast films on glass substrates in a vacuum at 100 °C. In this way DCP complexes of the polymers PPI, PMPI, PPI/PMPI, and PMOPI were prepared. DCP complexes of PHOPI at any molar ratio of DCP to PHOPI repeat unit could not be prepared because PHOPI is insoluble in DCP/*m*-cresol or in DCP with any organic solvent. The solid DCP complexes of the aromatic poly(azomethines) were completely soluble in *m*-cresol, *N*,*N*-dimethylformamide (DMF), NMP, and dimethyl sulfoxide (DMSO).

Lewis acid (GaCl$_3$) complexes of all the aromatic poly(azomethines), including PHOPI, were prepared in Lewis acid/nitromethane as previously described for other polymers.[15-19] Due to the moisture sensitivity of GaCl$_3$, the solution preparation and film casting to obtain solid complexes were done in a glovebox filled with nitrogen. The time required for complete dissolution of the polymers in GaCl$_3$/nitromethane at room temperature was 24 h.

Thin-Film Preparation. Thin films of PPI, PMPI, PPI, PMPI, and PMOPI were prepared from either their soluble DCP or GaCl$_3$ complexes. Thin films of PHOPI could be prepared only from its GaCl$_3$ complexes in nitromethane.

Thin films of PPI, PMPI, PPI/PMPI, and PMOPI prepared from DCP complexes in *m*-cresol were solution cast onto optically flat fused silica substrates (5 cm in diameter) or 2-in.^{2} glass by using 1.5 wt % (wt % polymer) solutions. The solution-cast films were dried in a vacuum oven at 100 °C for 6 h or overnight to

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remove *m*-cresol. The solid films of the complexes on substrates were then placed in a mixture of triethylamine (Et_3N) and ethanol overnight to regenerate a film of the pure polymer on the substrates. The respective colors of the pristine polymers were observed a few seconds after placing the films of DCP/polymer complexes in Et_3N/ethanol.

Thin films of PPI, PMPI, PPI/PMPI, PMOPI, and PHOPI were prepared from their $GaCl_3$ complexes in nitromethane solutions by either solution casting in a glovebox filled with nitrogen or spin coating. The solutions were typically 1 wt % polymer in solution with a $GaCl_3$:CH═N ratio of about 2:1. Spin coating was done at a speed of 1000 rpm for 30 s. Solution-cast or spin-coated thin films of the $GaCl_3$ complexes were dried in a vacuum oven at 50 °C for 1 h or overnight. Decomplexing of the $GaCl_3$/polymer films to obtain thin films of the pure polymers was done by immersing the films in methanol for 1–2 days.

Intrinsic Viscosity Measurement. Intrinsic viscosities, [η], of all the polymers in concentrated sulfuric acid and in $GaCl_3$/nitromethane were determined by using a Cannon-Ubbelohde capillary viscometer and a constant-temperature bath at 30 ± 0.1 °C. The $GaCl_3$:CN═N ratio in these solutions for intrinsic viscosity measurement was 2:1. The intrinsic viscosity values were obtained from the intersection of plots of the reduced viscosity (η_{sp}/c) and inherent viscosity ($\eta_{inh} = [\ln \eta_{rel}]/c$) versus concentration.

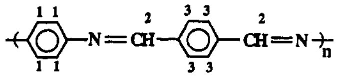
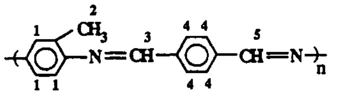
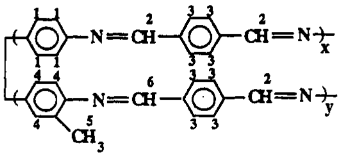
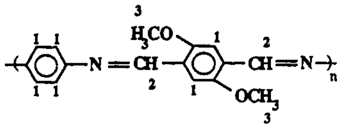
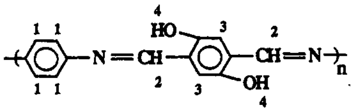
Instrumental Characterization. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were done using a Du Pont Model 2100 thermal analyst based on an IBM PS/2 Model 60 computer and equipped with a Model 951 TGA and a Model 910 DSC units. TGA data were obtained in flowing nitrogen at a heating rate of 10 °C/min. DSC thermograms were obtained in nitrogen at a heating rate of 20 °C/min.

FTIR spectra were taken at room temperature with a Nicolet Model 20 SXC Fourier transform infrared (FTIR) spectrometer under nitrogen purge. Samples were in the form of KBr pellets or films coated on NaCl disks. For example, FTIR spectra of pristine and regenerated PHOPI were obtained as KBr pellets, whereas the spectrum of PHOPI/$GaCl_3$ complex was obtained as a film cast on NaCl disk. The ^1H NMR spectra were taken at 300 MHz by using a General Electric Model QE 300 instrument. The samples for NMR spectra were solutions of the polymers in deuterated nitromethane (CD_3NO_2) containing $GaCl_3$. The $GaCl_3$:CH═N ratio in the solutions was about 1.5:1. For a 1.5 wt % polymer solution, this means about 1.5–1.9 wt % $GaCl_3$ in deuterated nitromethane.

Results and Discussion

Intrinsic Viscosity and Molecular Weight. The intrinsic viscosity values of the five aromatic polyazomethines in concentrated H_2SO_4 at 30 °C were in the range 0.19–0.84 dL/g. The solutions were prepared by stirring at room temperature (25 °C) for 2 h. Millaud and Strazielle[28] have studied the solution properties of PMPI in concentrated sulfuric acid and found the Mark–Houwink relation to be $[\eta] = 1.9 \times 10^{-3} M^{1.20}$, where [$\eta$] is in mL/g. The 0.70 dL/g intrinsic viscosity of our PMPI sample and the known Mark–Houwink relation suggest a molecular weight of 6390. However, it is well-known that poly(azomethines) undergo significant degradation in the presence of a strong protonic acid due to the hydrolysis of the azomethine linkage.[11,29] This degradation is exemplified by our observation of rapid decolorization of sulfuric acid cast films of the poly(azomethines) immersed in water. The estimated molecular weight value of 6390 for PMPI and intrinsic viscosity values of 0.19–0.84 dL/g in sulfuric acid are inconsistent with the excellent film-forming properties of the polymers. Therefore, the currently known Mark–Houwink relations for the aromatic poly(azomethines) that were obtained for sulfuric acid or other protonic acid solvents[28] must be treated with caution and cannot be expected to give reliable information about the true molecular weights of these polymers.

Table I. Chemical Shifts and Assignment of the ^1H NMR Spectra of Aromatic Poly(azomethines)

polymer	proton no.	chem shift, ppm
	1 2 3	8.30 9.86 8.70
	1 2 3 4 5	8.10 2.80 9.66 8.70 9.80
	1 2 3 4 5 6	8.30 9.83 8.70 8.10 2.80 9.70
	1 2 3	8.20 9.60 4.50
	1 2 3 4	8.20 9.60 8.40 6.40

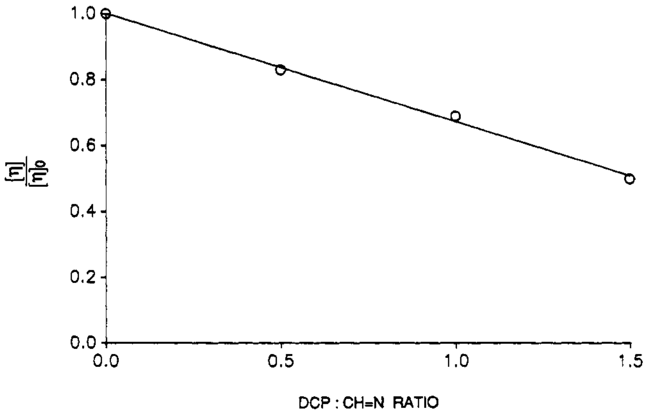


Figure 2. Degradation of PPI in DCP/*m*-cresol solution expressed as the relative intrinsic viscosity $[\eta]/[\eta]_0$ versus DCP:CH═N ratio.

The degradation of molecular weight caused by acid-catalyzed hydrolysis of CH═N was investigated in PPI with the relatively weak acid di-*m*-cresyl phosphate (DCP). Solutions of PPI in DCP/*m*-cresol were prepared by using a 20-min dissolution time and then the polymer was precipitated in triethylamine/ethanol. Figure 2 shows the relative intrinsic viscosity $[\eta]/[\eta]_0$ as a function of the molar ratio of DCP to CH═N group in *m*-cresol solutions. Since all other factors are approximately the same, including the dissolution time for preparing the H_2SO_4 solutions, the intrinsic viscosity measuring time, and the degradation in sulfuric acid, Figure 2 gives a direct measure of molecular weight change with extent of protonation of CH═N groups and interaction of the polymer with protonic acids in solution. Clearly, a linear decrease of intrinsic viscosity, and hence molecular weight, with amount of protonic acid is evidenced in Figure 2. For example, at a DCP:CH═N ratio of 1:1, a 30% decrease of molecular weight is observed. At a mole ratio of 1.5 DCP to each CH═N group, the loss in intrinsic viscosity is 50%. These

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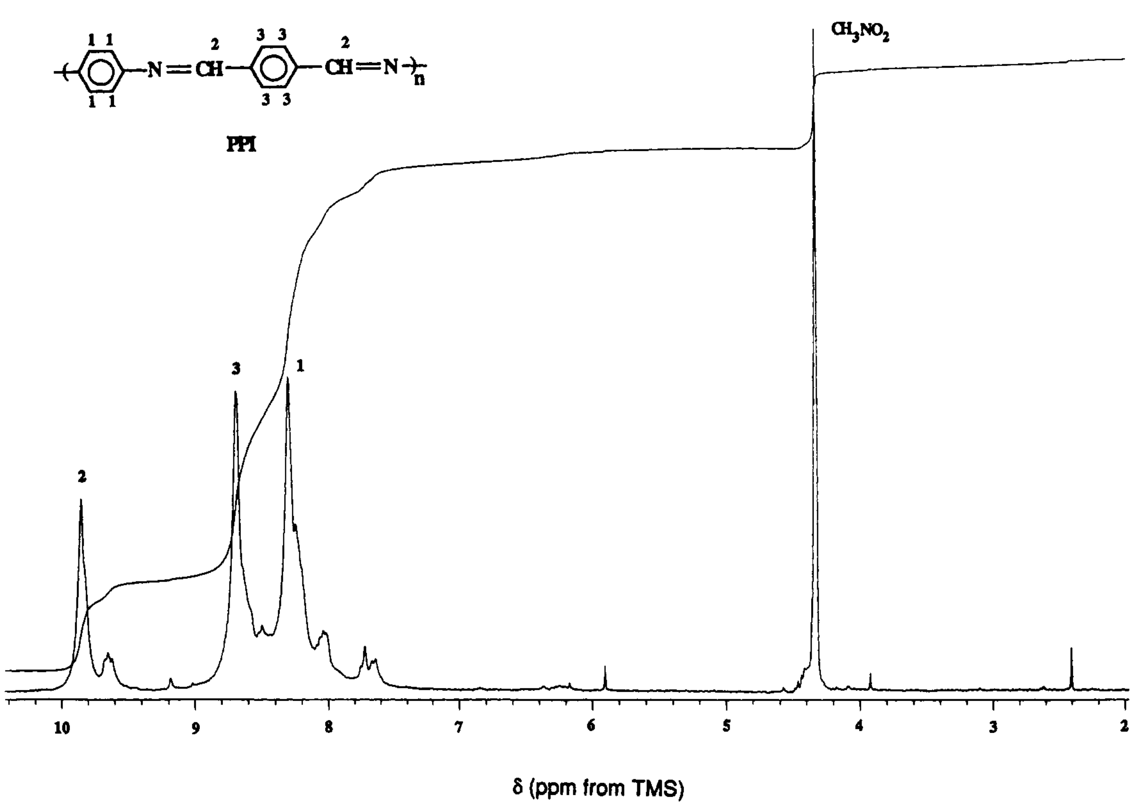


Figure 3. ^1H NMR spectrum of PPI in $CD_3NO_2/GaCl_3$ and its assignment.

results show that the protonated poly(azomethines) are relatively unstable in solution. In contrast, the protonated DCP/polymer complexes are very stable in the solid state, as will be discussed later.

The intrinsic viscosity of the aromatic poly(azomethines) in the aprotic organic solvent $GaCl_3$/nitromethane at 30 °C were in the range 1.04–1.38 dL/g and are considerably higher than in sulfuric acid (0.19–0.84 dL/g). However, light-scattering studies and Mark–Houwink correlations of molecular weight have not yet been done in this solvent system.

Soluble Complexes in Organic Solvents. Using our previously reported method of reversible Lewis acid–base complexation of polymers,[15–19] we have prepared soluble $GaCl_3$ complexes of all the aromatic polyazomethines in Figure 1 in nitromethane and other nitroalkanes. This has allowed us to investigate the molecular structure of PPI and derivatives by ^1H NMR for the first time as will be discussed in the next section.

Soluble acid–base complexes of PPI, PMPI, PMOPI, and PPI/PMPI were also prepared by reacting the polymers with DCP or DPP in *m*-cresol. In this case, DCP being a protonic acid, the complexation involves protonation of the imine nitrogen of the polymers. Particularly noteworthy is the inability to form soluble complexes of the dihydroxy polymer PHOPI in DCP/*m*-cresol. We attribute this to the intramolecular hydrogen bonding in PHOPI. This was further evidenced by the fact that $GaCl_3$ or $AlCl_3$ complexes of PHOPI that were soluble in nitromethane were readily prepared. Inability of the DCP to bind to PHOPI via protonation suggests that protonation is a comparable or less favorable process to the intramolecular hydrogen bonding at the imine nitrogen sites. However, in the competition between O–H hydrogen of the polymer and the Lewis acid ($MX_n = GaCl_3$) for the electron lone pair on the CH=N group, Lewis acid coordination to the nitrogen is favored because the Lewis acid is a stronger electron acceptor than O–H. Such preferential Lewis acid coordination compared to hydrogen bonding has also previously been observed in aliphatic and aromatic polyamides.[19]

Table II. Assignment of the FTIR Spectra of Aromatic Poly(azomethines)

	IR (cm^{-1})				
polymer	C=N str	out-of-plane C–H bend	methyl C–H str	C–O–C str	O–H str
PPI	1610	850			
PMPI	1615	830	2880		
PPI/PMPI	1615	845	2880		
PMOPI	1605	840	2910	1210	
PHOPI	1600	840–870			3380

Either solutions of the Lewis acid–base complexes in nitromethane or solutions of DCP complexes in *m*-cresol can be used to prepare optical-quality thin films by solution casting. However, because *m*-cresol is a relatively nonvolatile organic solvent, the solutions of the aromatic poly(azomethines) in this solvent could not be spin coated whereas the polymer solutions in nitromethane were used to produce thin films on substrates by spin coating.

Molecular Structure. The ^1H NMR spectra of PPI, PMPI, PPI/PMPI, PMOPI, and PHOPI were obtained in deuterated nitromethane containing $GaCl_3$ and their assignment fit the proposed structures. Figure 3 shows a typical ^1H NMR spectrum of PPI and the chemical shifts and their assignments are summarized in Table I. The number of protons corresponding to each resonance based on integration of the resonances of the NMR spectra were in good agreement with the proposed structures except in the case of the hydroxyl proton resonance ($\delta = 6.40$ ppm) in PHOPI. Integration of this O–H proton resonance gave a number less than the expected number of protons on the hydroxy groups. However, this is due to the fact that protons on heteroatoms such as oxygen can undergo rapid proton–deuterium exchange with water.

The anticipated consequence of complexation on the ^1H NMR spectra is a general shift of the chemical shifts downfield due to electron deshielding. Comparison of our ^1H NMR spectra was made with the ^1H NMR spectra (in

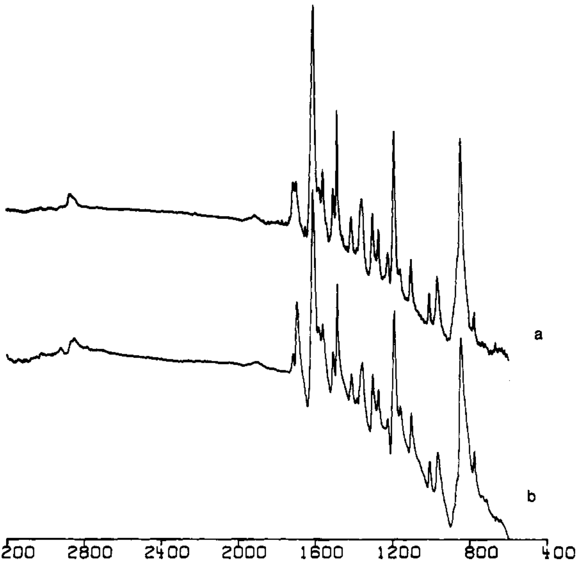
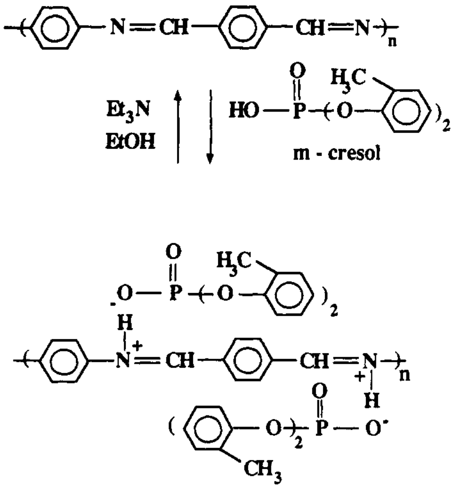


Figure 4. FTIR spectra of KBr pellets of pristine (a) and regenerated (b) PPI.

Scheme I



CDCl$_3$) of soluble aromatic poly(azomethines)[13] with long alkoxy side groups (-OC$_n$H$_{2n+1}$, n = 8, 12, 14, 16, 18). The latter give resonances of azomethine protons at 8.9 ppm and p-phenylene protons at 7.2–7.8 ppm. The resonances of azomethine and p-phenylene protons in deuterated nitromethane/GaCl$_3$ are shifted downfield by ~0.8 ppm. The NMR data spectra provide the first direct evidence for the molecular structures of the previously synthesized but insoluble aromatic poly(azomethines) of Figure 1.

The composition of the random copolymer PPI/PMPI was determined from its ^{1}H NMR spectrum by comparing the ratio of azomethine protons to the methyl protons. The mole fraction of PPI in the copolymer was found to be 0.52. Alternatively, comparison of the ratio of azomethine protons to p-phenylene protons gave the mole fraction of PPI of 0.54 in agreement with the first method. These results show that the actual composition of the random copolymer is very close to the starting 50/50 comonomer (reactants) composition which it must be for high conversion copolymerization.

FTIR spectra were obtained in order to (a) confirm the structures of the pristine, as-synthesized, polymers, (b) confirm the structures of pure polymers recovered from their soluble complexes, and (c) elucidate the intramolecular hydrogen bonding in PHOPI. Figure 4 shows a representative FTIR spectrum of KBr pellets of pristine PPI. Assignment of peaks to the characteristic vibrational bands in the proposed structures are collected in Table II. These results in conjunction with the ^{1}H NMR spectra clearly confirm the proposed structures of the aromatic poly(azomethines) in Figure 1.

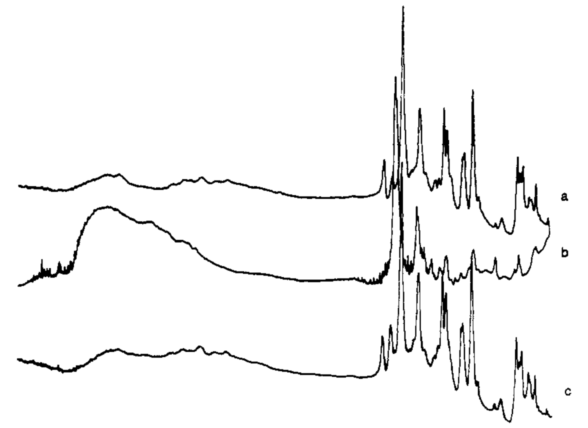
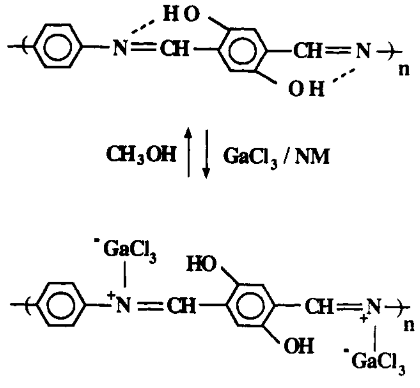


Figure 5. FTIR spectra of KBr pellets of pristine (a) and regenerated (c) PHOPI and film of PHOPI/GaCl$_3$ complex (b).

Scheme II



One of the important features of the acid–base complexes of the aromatic poly(azomethines) is the facile recovery of the pure polymers from their soluble complexes. As shown in Scheme I, DCP complexes of aromatic poly(azomethines) in solution or solid state are converted to the pure polymers by treatment with a base such as triethylamine (Et$_3$N)/ethanol. Figure 4 also shows the FTIR spectrum of PPI recovered from its DCP complexes by precipitation in Et$_3$N/ethanol as in Scheme I. The spectra of the regenerated polymers are identical with those of the pristine polymers in all respects, including absorption peak frequencies and their intensities. These results confirm the reversibility of the complexation of these polymers. Additional experimental evidence of complete regeneration of the pure polymers from their soluble complexes include TGA, DSC, and electronic spectra as will be discussed in other sections.

Figure 5 shows the FTIR spectra of KBr pellets of pristine PHOPI and PHOPI regenerated from its GaCl$_3$ complex. Also shown in Figure 5 is the FTIR spectrum of a film of PHOPI/GaCl$_3$ complex cast on NaCl disk. Since one of the primary reasons for obtaining these spectra of PHOPI and its GaCl$_3$ complex was to observe the O–H stretching region and any possible hydrogen bonding, extra care was taken to exclude moisture from the samples, including storing them overnight in a vacuum over at 100 °C. The GaCl$_3$ complexation of PHOPI and regeneration of the pure polymer from the PHOPI/GaCl$_3$

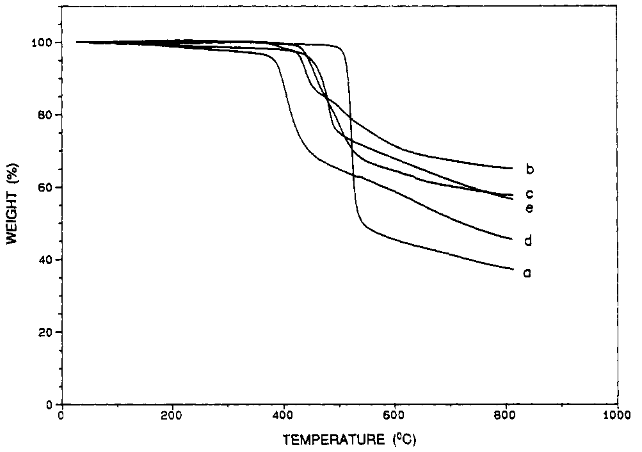


Figure 6. TGA thermograms of aromatic poly(azomethines) in flowing nitrogen at 10 °C/min: PPI (a), PMPI (b), PPI/PMPI (c), PMOPI (d), and PHOPI (e).

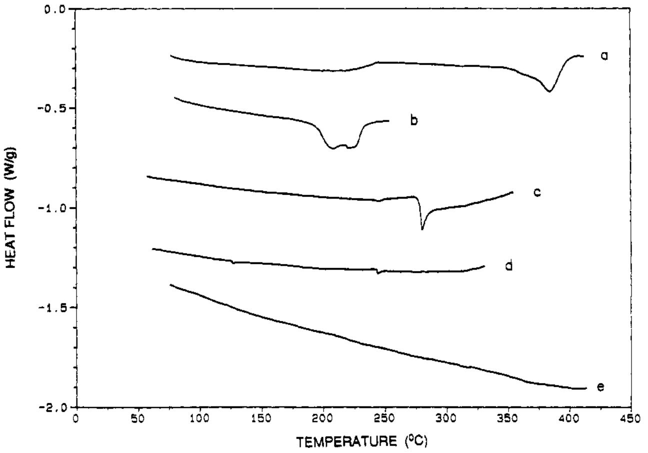


Figure 7. DSC thermograms of aromatic poly(azomethines) obtained at a heating rate of 20 °C/min: PPI (a), PMPI (b), PPI/PMPI (c), PMOPI (d), and PHOPI (e).

complex are shown in Scheme II. The FTIR spectra of the pristine and regenerated PHOPI samples were identical, confirming the recovery of the pure polymer from its complex. Similar results show that the other aromatic polyazomethines (PPI, PMPI, PPI/PMPI, PMOPI) are readily recovered from their soluble complexes according to Scheme II.

From Table II and Figure 5 it is seen that the C=N stretching frequency in PHOPI is 1600 cm^{-1} compared to 1610 cm^{-1} in PPI. This lower energy at which C=N stretching absorption occurs in PHOPI may be due to the effect of electron density withdrawal of hydrogen bonding at the imine nitrogen (CH=N). The O–H stretching absorption band in pristine and regenerated PHOPI in Figure 5 has a peak at ~3380 cm^{-1}. In the FTIR spectrum of the $GaCl_3$/PHOPI complex, also shown in Figure 5, the O–H stretching absorption band has a peak at 3450 cm^{-1}, which is more intense than the 3380-cm^{-1} peak in pure PHOPI. This suggests that the O–H in pure PHOPI is hydrogen bonded, whereas that in PHOPI/$GaCl_3$ complex is free. Additional evidence for intramolecular hydrogen bonding in PHOPI include insolubility of this polymer in DCP/*m*-cresol and the remarkable spectral red shift in the electronic absorption spectra of PHOPI compared to PMOPI. This latter result will be discussed in a subsequent section.

An interesting further result from the spectra of Figure 5 is revealed by a comparison of the C=N stretching frequency in pure PHOPI and in PHOPI/$GaCl_3$ complex. In PHOPI/$GaCl_3$ complex, the C=N stretching band is shifted to a higher energy, 1645 cm^{-1}, compared to 1600 cm^{-1} in the pure polymer. This can be explained in terms of the overcompensation for electron density withdrawal by the $GaCl_3$ coordination to the nitrogen atom and consequent electron density redistribution throughout the polymer backbone. If the azomethine group (CH=N) was in a nonconjugated environment, one might expect Lewis acid complexation at this site to result in electron density withdrawal from the C=N bond and a corresponding weakening of this bond. This is what is observed in polyamides, where Lewis acid complexation at the oxygen of amide group results in the weakening of C=O bond, a strengthening of N–H bond, and about the same C–N bond strength.[19] However, in the conjugated environment of the azomethine group in the present polymers, coordination of the Lewis acid to the imine nitrogen causes electron-density withdrawal from the nitrogen atom, but the π-system compensates, and in fact overcompensates, by redistributing electron density throughout the polymer backbone. Such a redistribution of electron density can be expected to represent a significant change in the electron structure and hence electronic spectra of the pure polymer.

Thermal Stability and Morphology. Figure 6 shows the TGA thermograms of the five aromatic poly(azomethines) investigated. The onset of thermal decomposition of PPI in flowing nitrogen is 504 °C. The thermal stability of the derivatives PMPI, PHOPI, and copolymer PPI/PMPI is reduced relative to PPI as evidenced by onset of thermal decomposition in the range 427–453 °C. The onset of thermal decomposition of PMOPI was significantly less than others at 386 °C.

The morphology of the aromatic polyazomethines as revealed by DSC is shown in the DSC thermograms of Figure 7. PPI exhibited a crystalline melting peak at 385 °C, whereas PMPI had two endothermic peaks at 208 and 222 °C. The copolymer PPI/PMPI had a melting peak at 281 °C, which is intermediate between those of the component homopolymers. No crystalline melting or glass transition temperature was observed for PMOPI and PHOPI before reaching decomposition. A T_g value of 336 °C has been reported for a PHOPI sample with intrinsic viscosity of 0.2 dL/g in concentrated H_2SO_4.[22] The observed multiple transitions for PMPI are similar to prior observations on this polymer[11] and were interpreted as due to one crystalline form that is present in a sample with a distribution of crystallite size or degrees of crystal perfection.[11] Another possible explanation of this result is thermotropic liquid crystallinity. The lower endotherm in this case would be associated with a crystal to liquid crystalline (LC) phase transition (T_{CN}) and the higher endotherm would be due to LC to isotropic phase transition (T_{NI}).

Film Processing from Soluble Complexes. Thin films of all the conjugated aromatic poly(azomethines) investigated were prepared readily from viscous solutions of DCP or $GaCl_3$ complexes. Thin films of PPI, PMPI, PPI/PMPI, and PMOPI with good optical quality were prepared by solution casting from their DCP complexes in *m*-cresol. The key step in preparing thin films of the polymers from their soluble DCP complexes is decomplexation or regeneration of the pure polymers by using Et_3N/ethanol as the precipitating nonsolvent according to Scheme I.

Optical-quality thin films of PPI, PMPI, PPI/PMPI, PMOPI, and PHOPI were prepared from their $GaCl_3$ complexes in nitromethane by either solution casting or spin coating. The decomplexation step in this case (see

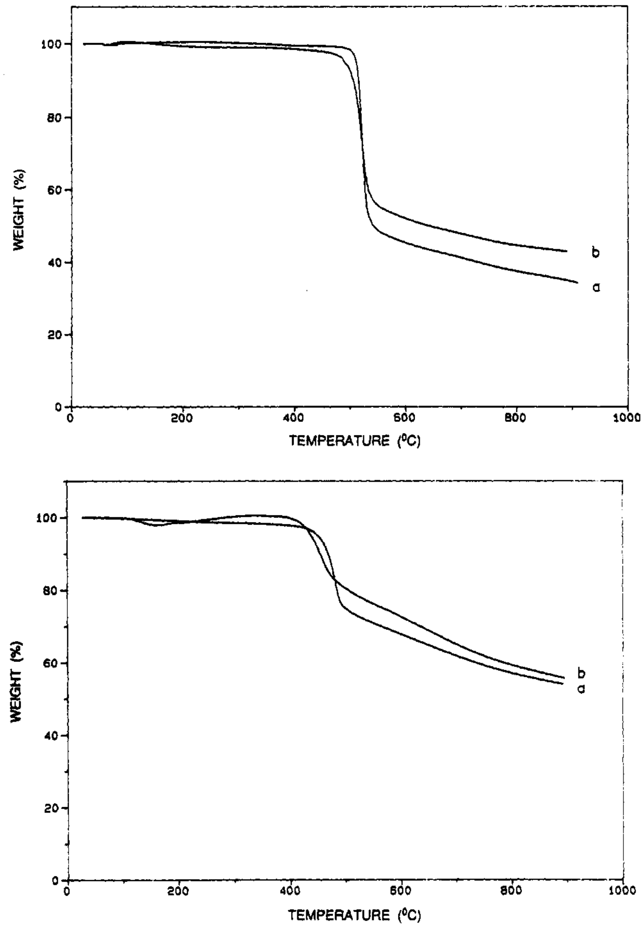


Figure 8. Top: TGA thermograms of pristine (a) and regenerated (b) PPI obtained in flowing nitrogen at 10 °C/min. Bottom: TGA thermograms of pristine (a) and regenerated (b) PHOPI obtained in flowing nitrogen at 10 °C/min.

Scheme II) involves precipitation in a Lewis base solvent such as water, methanol, ethanol, or DMF. It was found that the precipitating solvent used influenced adhesion of the film of the pure polymer to the silica or glass substrates; methanol or ethanol gave films with better adhesion than water. The films were considered to have good optical quality if they were transparent and nonscattering as well as suitable for optical measurements.

Spectroscopic techniques (FTIR and electronic absorption spectra) and thermal analysis (TGA and DSC) were used to confirm the complete recovery of the pure polymers from their soluble DCP or $GaCl_3$ complexes. As already discussed under molecular structure, comparison of the FTIR spectra of the pristine and regenerated polymers showed that they were identical (see Figures 4 and 5) and hence that the pure polymers were completely recovered during the decomplexation step. As will be discussed in the next section, the pure polymers and their complexes exhibit dramatically different electronic absorption spectra. Thus, the electronic absorption spectrum can also be used to assess the recovery of the pure polymers from their complexes. It was found according to this criterion that the pure polymers were completely regenerated from the complexes.

Thermal analysis, especially the TGA, provides a quick method for assessing the decomplexation process. Figure 8, top, shows the TGA thermograms of pristine PPI and pure PPI regenerated from its DCP complex by using Et_3N/ethanol as the precipitating nonsolvent. The two TGA thermograms are essentially the same with onset of thermal decomposition in both samples at about 500 °C.

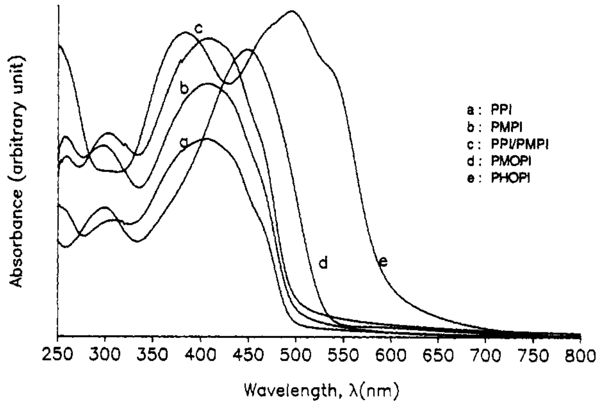


Figure 9. Electronic absorption spectra of thin films of conjugated aromatic poly(azomethines).

Table III. Electronic Absorption Maxima, Absorption Edge, and Solid-State Bandgap of Conjugated Aromatic Poly(azomethines)

polymer	λ_{max}, nm	abs edge, nm	E_g, eV
PPI	405	496	2.50
PMPI	406	497	2.49
PPI/PMPI	407	497	2.49
PMOPI	447	529	2.34
PHOPI	494	600	2.07
PPV	~405[a]	512	2.43
DMOPPV	~500[a]	~600[a]	2.07

[a] Value from the spectra in the cited literature.[32,33]

Similar TGA results were obtained for PMPI, PPI/PMPI, and PMOPI recovered from their DCP complexes. Figure 8, bottom, shows the TGA thermograms of pristine PHOPI and a PHOPI sample recovered from its $GaCl_3$ complex. The two PHOPI samples exhibit essentially the same thermal stability. The results of a DSC study of regenerated samples of the aromatic poly(azomethines) compared to the pristine polymers essentially confirmed the recovery of the pure polymers from their complexes but revealed some changes in morphology. In the case of PMOPI and PHOPI, no discernible difference between the pristine and regenerated samples was observed. Identical melting peak temperatures were observed in the DSC thermograms of pristine and regenerated PPI and PMPI. However, regenerated PPI and PMPI had a lower degree of crystallinity as judged from their lower heats of fusion compared to the pristine samples. In the case of the copolymer PPI/PMPI the regenerated sample was amorphous with no observable endotherms prior to decomposition. These results suggest that the decomplexation process affects the morphology of thin films of the polymers prepared from their soluble complexes, which may play an important role in the applications of this class of conjugated high-temperature polymers.

Electronic Absorption Spectra of Thin Films. Figure 9 shows the electronic absorption spectra of thin films of conjugated aromatic polyazomethines. All the polymers strongly absorb visible light. The lowest energy absorption maximum λ_{max}, the optical absorption edge, and the corresponding solid-state bandgaps of these polymers are collected in Table III. The λ_{max} of PPI is 405 nm and its optical bandgap is 2.50 eV, a consequence of the poor electron delocalization in the polymer due to the lack of

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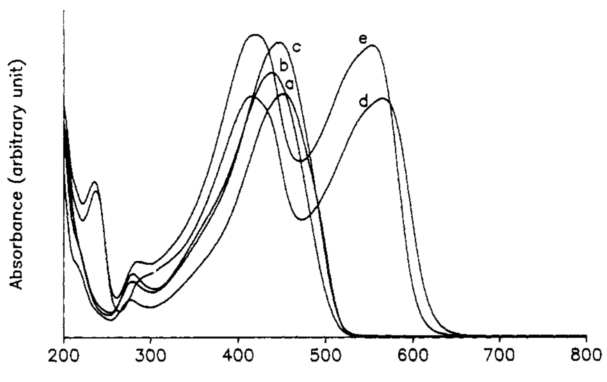


Figure 10. Solution electronic absorption spectra of aromatic poly(azomethines) in concentrated H_2SO_4: PPI (a), PMPI (b), PPI/PMPI (c), PMOPI (d), and PHOPI (e).

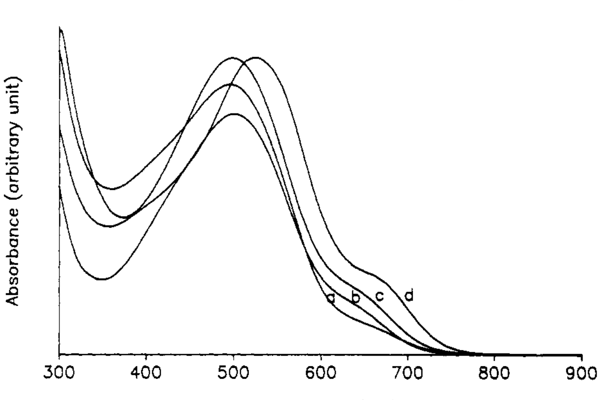


Figure 11. Solution electronic absorption spectra of aromatic poly(azomethines) in DCP/*m*-cresol with DCP:CH=N ratio of 1:1: PPI (a), PMPI (b), PPI/PMPI (c), and PMOPI (d).

coplanarity of the *p*-phenylene rings with the azomethine (CH=N) units. The X-ray diffraction results on benzylidene aniline show that it has a nonplanar conformation in which the *N*-phenyl ring is twisted 55° from the CH=N plane, and the benzylidene ring is twisted 10° from the CH=N plane in the opposite direction.[30,31] Such a nonplanar structure can be expected to be maintained in the polymers and to result in a decrease in the efficiency of π-electron delocalization along the polymer backbone.

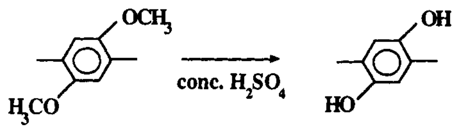
The effects of methyl, dimethoxy, or dihydroxy substitution on one of the *p*-phenylene rings of PPI on the electronic structure and bandgap are discernible from Figure 9 and Table III. PMPI and PPI/PMPI with methyl substitution have electronic structures that are virtually identical with that of PPI. However, stronger electron-donating substituents have significant effects on the electronic structure and bandgap. Dimethoxy substitution reduces the bandgap from 2.50 to 2.34 eV in PMOPI. A similar dihydroxy substitution significantly reduces the bandgap from 2.50 to 2.07 eV in PHOPI. On the basis of the inductive effect of substituents on the π-electron system of the polymer backbone, dimethoxy and dihydroxy substitution might be expected to be comparable. However, as discussed previously, dihydroxy substitution gives rise to intramolecular hydrogen bonding that forces the *p*-phenylene rings and CH=N groups in PHOPI into a coplanar conformation.[30b] Thus, intramolecular hydrogen bonding explains the remarkably small bandgap of PHOPI compared to PPI and PMOPI.

It is also of interest to compare the electronic structure of PPI and derivatives to related polymers. The bandgap of PPI (2.50 eV) is slightly larger than that of PPV (2.43 eV), which is isoelectronic with PPI and is an alternating copolymer of *p*-phenylene and vinylene (CH=CH).[6,7,32,33] Its bandgap is intermediate between those of poly(*p*-phenylene) (PPP, 2.80 eV)[34] and *trans*-polyacetylene (1.5 eV).[7] Although the experimental bandgap of poly(methineimine) (PMI, $(CH=N)_n$) is not known, its calculated bandgap is 5.4 eV.[35] This very large bandgap was attributed to the very large overlap between the σ nitrogen lone-pair and the π band.[35] The observed bandgap of PPI does not fall in between those of PMI and PPP but is smaller.

Also listed in Table III is the bandgap of poly(2,5-dimethoxy-*p*-phenylenevinylene) (DMOPPV, 2.07 eV) to be compared to the bandgap of PMOPI (2.34 eV). The difference in the bandgaps of these two polymers may be due in large part to the fact that 2,5-dimethoxy substitution occurs only on every other *p*-phenylene ring in PMOPI whereas every ring in DMOPPV is substituted. It is to be noted that the bandgap of PHOPI is identical with that of DMOPPV (2.07 eV).

In the light of the present results on the solid-state electronic spectra and structure of the aromatic poly(azomethines) and their similarity to those of PPV and derivatives, it can be anticipated that this class of conjugated polymers will have large nonlinear optical properties[21] and, in doped forms, high electrical conductivity.

Electronic Absorption Spectra of Solutions and Complexes. The electronic absorption spectra of the polymers in concentrated H_2SO_4 are shown in Figure 10. The λ_{max}[log ϵ] of the lowest energy π–π^* transition in the solution spectra of PPI, PMPI, and PPI/PMPI was 453 nm [4.24], 438 nm [4.22], and 448 nm [4.23], respectively. The solution electronic spectra of PMOPI and PHOPI in sulfuric acid had two-band structures in the visible with λ_{max}[log ϵ] of 415 nm [3.98] and 565 nm [3.98] and 420 nm [4.30] and 554 nm [4.30], respectively. The solution absorption spectrum of PMOPI in sulfuric acid is identical with that of PHOPI because of the acid-catalyzed hydrolysis of the 2,5-dimethoxy groups of PMOPI, essentially converting PMOPI to PHOPI:



In fact, this reaction of PMOPI in sulfuric acid is similar to that described in the experimental section for preparing 2,5-dihydroxyterephthaldehyde from 2,5-dimethoxyterephthaldehyde.

One notable aspect of the electronic spectra of the aromatic polyazomethines in sulfuric acid is their significant red shift compared to the solid-state spectra. For example, the λ_{max} of PPI in sulfuric acid is 453 nm compared to 405 nm in the solid state.

The solution electronic absorption spectra of 1:1 (DCP:CH=N) complexes of PPI, PMPI, PPI/PMPI, and PMOPI in *m*-cresol are shown in Figure 11. The corresponding λ_{max} of these spectra are 502, 496, 499, and 523 nm, respectively. Thus, these spectra show even larger red shifts from the solid-state spectra of the pure polymers and are broader than those of the concentrated H_2SO_4 solu-

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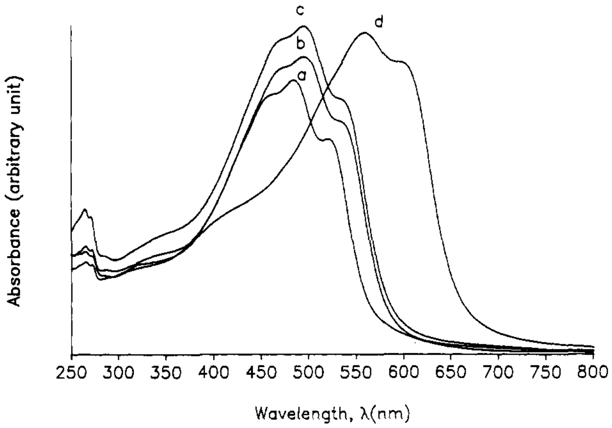

Figure 12. Electronic absorption spectra of thin films of 1:1 (DCP:CH=N) complexes of PPI (a), PMPI (b) PPI/PMPI (c), and PMOPI (d).

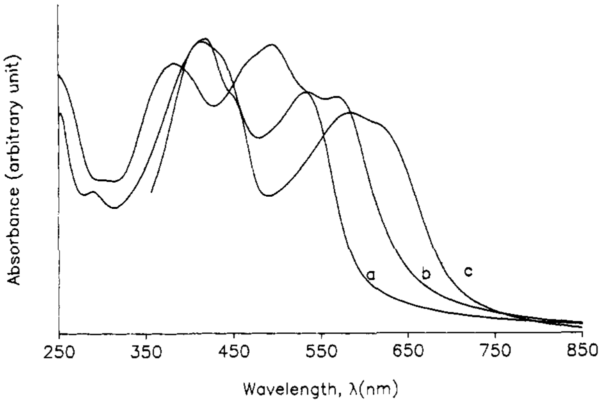

Figure 13. Electronic spectra of thin films of PHOPI (a) and PHOPI/GaCl$_3$ complex (b) and PHOPI/GaCl$_3$ in nitromethane (c).

tions. The DCP complexes of PPI, PMPI, and PPI/PMPI are red in color, whereas those of PMOPI are purple. Figure 12 shows the optical absorption spectra of thin films of the 1:1 DCP complexes of PPI, PMPI, PPI/PMPI, and PMOPI. A comparison of these solid-state spectra of the polymer/DCP complexes to those of the corresponding pure polymers shows that the λ_{max} of the complexes are red shifted by about 90 nm, and in the case of PMOPI the red shift is even larger, being 110 nm. The solid-state bandgap of the polymer/DCP complexes is 2.15, 2.12, 2.11, and 1.85 eV for the 1:1 (DCP:CH=N) complexes of PPI, PMPI, PPI/PMPI, and PMOPI, respectively.

These results of the electronic absorption spectra of the di-*m*-cresyl phosphate complexes of the conjugated aromatic poly(azomethines), either in solution or solid state, show that the complexes have a more delocalized electronic structure compared to the pure conjugated polymers. The reason for this remarkable change in electronic structure on complexation is most likely due in large part to a significant modification of the polymer chain conformation by interaction with DCP, forcing the geometric structure of the π-electron system of the polymer to become more coplanar. Future studies to confirm this will include complexation and X-ray diffraction studies on benzylidene aniline and related model compounds and polymers. In fact, a similar red shift of electronic spectra on protonation of Schiff base compounds has been reported.[36] These authors also explained the structural origin of observed spectral red shift in terms of conformational changes.

The electronic absorption spectrum of PHOPI was also significantly modified on GaCl$_3$ complexation as shown in the electronic spectra of Figure 13. The red shift in the λ_{max} of the GaCl$_3$/PHOPI complex in solution or solid state was ~80–90 nm relative to the pure polymer. This further supports our view that the observed changes in electronic structure of the aromatic poly(azomethines) are not due merely to protonation[37] in sulfuric acid or by DCP. Prior observations on electronic spectra of structures protonated by strong acids showed broadening of bands with no significant red shifts.[37]

Conclusions

The solubilization of a series of five conjugated aromatic poly(azomethines) in organic solvents by complexation with either Lewis acids (GaCl$_3$) or di-*m*-cresyl phosphate (DCP) has allowed us to (1) elucidate the molecular structures of these polymers by ^{1}H NMR for the first time; (2) prepare optical-quality thin films for investigation of electronic structure and solid state properties; and (3) characterize their solid-state electronic absorption spectra and optical bandgaps.

The solid-state electronic spectra of the aromatic polyazomethines were found to exhibit λ_{max} in the range 405–497 nm and optical bandgaps in the range 2.07–2.50 eV. Electron-releasing substituents such as methoxy and hydroxy thus significantly reduced the bandgap of the basic aromatic poly(azomethine) PPI (2.50 eV). The polymer with the smallest bandgap in the series, PHOPI, was found to have a favorable intramolecular hydrogen bonding that enforces a coplanar structure in the backbone and hence a more efficient electronic delocalization. These results suggest that conjugated aromatic poly(azomethines) are very similar in electronic structure to poly(*p*-phenylenevinylene) and derivatives and hence can be expected to exhibit similar electrical and nonlinear optical properties.

The solution and solid-state electronic absorption spectra of complexes of these conjugated aromatic poly(azomethines) were found to exhibit greater electronic delocalization and smaller optical bandgaps than the pure polymers. The origin of this remarkable red shift of electronic spectra is due to complexation-induced change in polymer chain conformation. Since the solid-state complexes are quite stable in air, their electronic spectra showing no changes during storage in air for months, these complexes themselves might have interesting nonlinear optical properties.

Now that the conjugated aromatic polyazomethines have been shown to be readily processable into thin films from their soluble complexes, it is clear that further investigation of their solid-state properties would be necessary to assess their potential for applications as fibers,[11] high-temperature materials,[10,11] liquid-crystalline materials,[11,12] or electronic[13,38] and photonic materials.[21]

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