annealed for short times. The increased intensities at lower angles are indicative of the formation of larger structures. Therefore, the occurrence of trans-amorphous conformations in tie molecules is inferred.

The effect of the increased trans-amorphous content on the presently reported fold structure is now considered. Since the species cannot be spectroscopically distinguished from the crystalline trans conformation, the calculated number of crystalline stem segments is overestimated (eq 5). The total gauche will not be affected by the presence of trans conformers in the amorphous phase. It follows that the calculated number of gauche units in the chain fold is too low. This accounts for the small observed decrease in the number of gauche units in the fold of annealed samples. We therefore conclude that the annealing of solution-crystallized PET as a function of time and temperature does not significantly affect the fold structure. Note that this conclusion is not applicable to annealing temperatures which approach the melting point of the crystalline regions where the number of fold gauche units drops to one.

Conclusions

The relative trans content as measured by least-squares curve-fitting of digitized FTIR spectra increases asymptotically as the temperature of crystallization in dilute solution approaches the dissolution temperature. The trans content increases in a similar manner when dry samples are annealed close to the melt. Concurrent with the trans increases are asymptotic rises in the lamellar thickness as measured by SAXD. Linear changes in the trans content and the lamellar thickness are observed as a function of time of anneal. Correlation of FTIR and SAXD data establishes a fold structure of between two and three gauche units in solution-crystallized PET. At high temperatures of anneal, the number of gauche units is reduced to one. Time of anneal has no effect on the fold structure.

Acknowledgment. We express our appreciation to C. Heffelfinger for the poly(ethylene terephthalate) glass, to Dr. J. S. Lin of Oak Ridge National Laboratory for assistance with SAXD measurements, to R. A. Chivers for suggestions concerning the paper, and to the Polymer Section of the National Science Foundation for financial support under Grant DMR80-20245.

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Photoacoustic Infrared Spectroscopy of Doped and Undoped Poly(*p*-phenylene)

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ABSTRACT: The Fourier transform infrared photoacoustic spectra of poly(*p*-phenylene) (PPP) prepared by different means, perdeuterated PPP, and heavily doped PPP are examined. Upon doping, new spectral features appear similar to those observed in doped oligomers. The effect of dopant on polymer chain length is discussed. Also examined is PPP coordinatively doped by metal carbonyls.

Introduction

Its remarkable thermostable properties, in addition to access to electroconductivity, make poly(*p*-phenylene) (PPP), a unique polymer. Like many other extended π polymers, PPP may be oxidized or reduced with a concomitant increase in electroconductivity of over 12 orders of magnitude.[1] Also like other extended π polymers, PPP and its derivatives present a plethora of interesting experimental challenges due to insolubility, infusibility, opacity, varying and uncertain morphologies, and, in the

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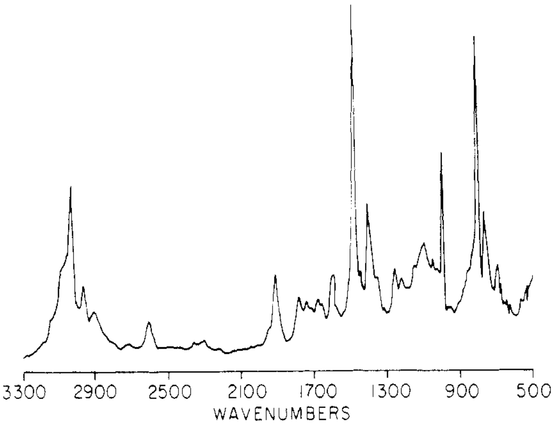

Figure 1. FT-IR/PA spectrum of undoped Kovacic PPP.

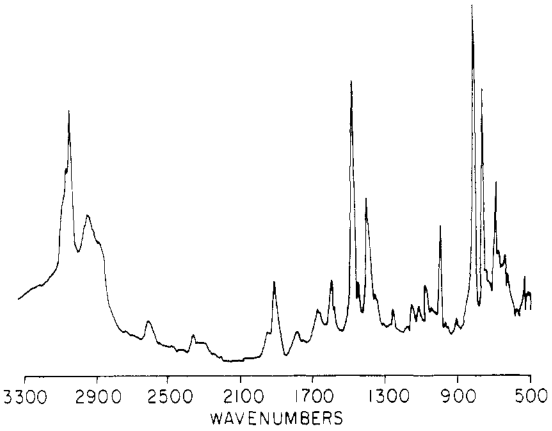

Figure 2. FT-IR/PA spectrum of undoped Yamamoto PPP.

case of the electroconductive derivatives, oxygen and/or water sensitivity.

Fourier transform infrared photoacoustic (FT-IR/PA) spectroscopy can be a useful technique in the acquisition of structural information from such systems.[2-4] The above-mentioned difficulties present no additional problems, since photoacoustic techniques require little (if any) sample preparation and similar polymers of varying morphologies yield similar spectra.[5] Additionally, since absorption is measured directly, opacity and scattering do not interfere with the measurement. The large surface areas[6] (ca. 50 m^2/g) give large photoacoustic signals, allowing a measurement time of less than 1 h. One major advantage of FT-IR/PA over transmission spectroscopy is that the materials examined are of the same morphology as actually used in electrochemical applications.[4] One may, then, examine materials *as used*, with no further complications from differences in crystallinity, doping homogeneity, Christiansen effect, and scattering between free-standing polymers and ultrathin microcrystalline samples.

The data presented below offer insight into some ill-defined properties of PPP such as the dependence of conjugation length on the preparative method employed, chain extension upon doping, the effects of metal carbonyl coordination, and the effect of deuteration of the polymer.

Experimental Section

Two methods of preparation of PPP were employed. The first, due to Kovacic et al.,[7] involves a cationic polymerization of benzene by a $CuCl_2/AlCl_3$ Friedel–Crafts system. This reaction, after workup with HCl and water, yields a brown powder with a conductivity $\sigma < 10^{-8}$ S cm^{-1} (our measurement limit).

The second method, that of Yamamoto et al.,[8] involves the coupling of *p*-aryl Grignard with *p*-dibromobenzene, using $NiCl_2(bpy)$ as a catalyst. The resulting yellow powder also has conductivity below 10^{-8} S cm^{-1}.

Perdeuterated PPP was prepared by the Kovacic method, using benzene-d_6 as a monomer at a reaction temperature of 34 °C. This yields an insulating light tan powder.

Reduction of the polymer with potassium or sodium was accomplished by stirring the polyphenylene powder in a THF solution of the alkali metal naphthalide, a strong electron donor. Oxidation was carried out by exposure of the polymer to gas-phase SbF_5.

Coordinatively modified PPP was prepared by refluxing the polymer in dry hexane under nitrogen with $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo) for several hours.

FT-IR/PA spectra were taken on a modified Nicolet 7199A FT-IR spectrometer, using a cell and interface of local design.[9] Resolution was 2 cm^{-1}. Spectra were normalized against the output of a DTGS detector, modified[4] to take into account the dependence of the photoacoustic signal on the source modulation frequency.

All manipulations were done under vacuum or an inert atmosphere in a Vacuum Atmospheres Dri-Lab glovebox with a MO-40-2H Dri-Train. ESCA and magic-angle ^{13}C NMR were used to monitor the integrity of the polymers.

Results and Discussion

A. Undoped PPP. Figure 1 shows the FT-IR/PA spectrum of PPP prepared by the Kovacic method. Sample preparation consisted of placing ca. 30 mg of PPP into the sample cell in an argon-filled drybox.

A very useful diagnostic feature in PPP is the set of absorbances in the 800-cm^{-1} region, characteristic of a C–H out-of-plane bend. A purely para product should exhibit only one band in this region. However, in the actual polymers, two other absorbances are seen at about 765 and 695 cm^{-1}, characteristic of monosubstituted phenyls. Thus, the relative intensities of the para band and the monosubstituted bands provide a probe of chain length in PPP.

Upon heating (400 °C in vacuo), the monosubstituted bands diminish in intensity. Simultaneously, the 800-cm^{-1} band shifts downward slightly in frequency from 809 to 803 cm^{-1}. After about 2 h of heating, no further change in the spectrum was observed. It has been suggested that this annealing process causes chain extension with loss of chlorine contamination from the polymerization catalyst.[7] Similar downward shifts in the C–H para absorbance with increasing chain length have been observed in transmission infrared studies.[7]

Another common method for the preparation of PPP is that of Yamamoto. Greater structural regularity for PPP prepared by this method has been claimed.[10] A shorter chain length for Yamamoto PPP may be inferred from our spectrum (Figure 2) by the relative band intensities and the position of the para C–H out-of-plane band (812 cm^{-1}). Upon annealing, spectra show an extension of chain length, but to a smaller degree than that which occurs in Kovacic PPP, supporting the notion that annealing is a function of catalyst impurities present in the polymer. At the point where further annealing causes no spectral changes, the chain length appears to be less than that of the Kovacic polymer before annealing.

Recently, the properties of perdeuterated PPP (PDP) were examined by Kovacic et al.[11] Figure 3 is the FT-IR/PA spectrum of PDP. This is qualitatively similar to the PPP spectrum. The para C–D out-of-plane band appears at about 670 cm^{-1}. As with Kovacic PPP, this absorbance shifts downward after annealing. However, this process occurs somewhat more slowly in PDP, requiring about 3 h of heating for complete annealing. Whether this is because of deuteration or peculiarities in the morphology of our sample is open to question.

B. Doped PPP. As with polyacetylene, the doping of PPP causes an increase in conductivity, along with major

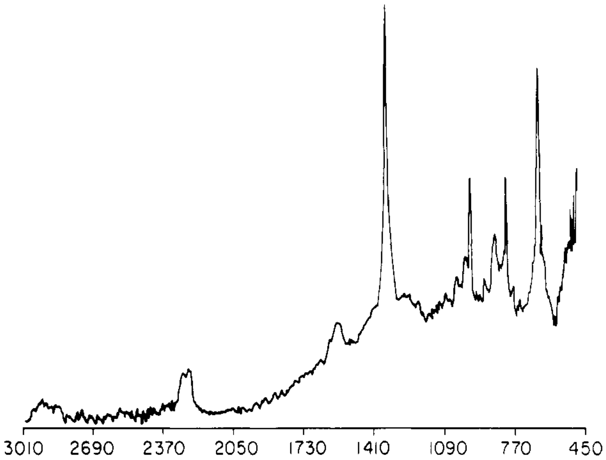

Figure 3. FT-IR/PA spectrum of undoped Kovacic PDP.

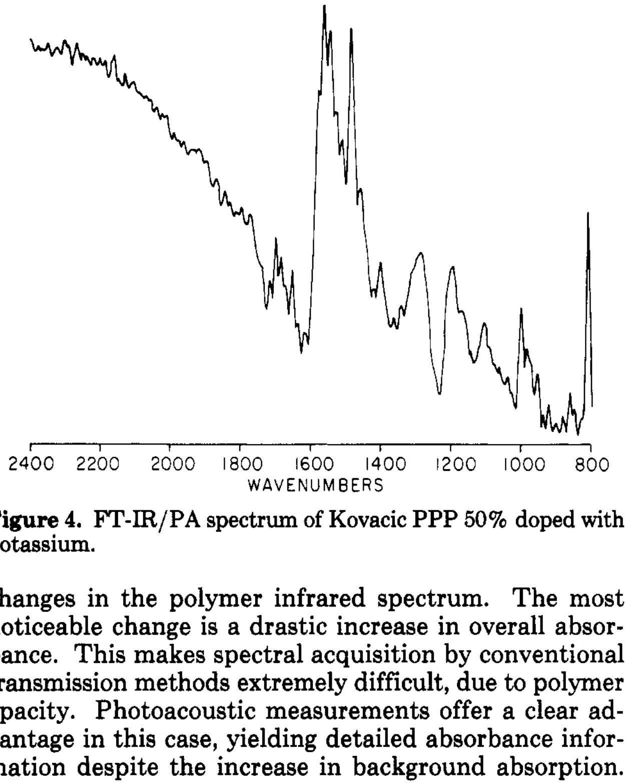

Figure 4. FT-IR/PA spectrum of Kovacic PPP 50% doped with potassium.

changes in the polymer infrared spectrum. The most noticeable change is a drastic increase in overall absorbance. This makes spectral acquisition by conventional transmission methods extremely difficult, due to polymer opacity. Photoacoustic measurements offer a clear advantage in this case, yielding detailed absorbance information despite the increase in background absorption.

Earlier infrared data on doped PPP were obtained by transmission through microcrystalline thin films of oligomers exposed to AsF_5. Compensation, followed by annealing, allowed Shacklette et al.[12] to observe polymerization of oligomers by this procedure. However, this was not observed in the AsF_5-treated oligomers directly, since the diagnostic regions were obscured, despite the thinness of their crystals. Thus, their data did not exclude the possibility of chain extension from the compensation reaction and/or the annealing process. Additionally, evidence for chain extension in the polymer upon doping is incomplete.

Shown in Figure 4 is the FT-IR/PA spectrum of heavily (50%) n-doped PPP. Additional absorbances are seen at 1560, 1280, 1170, and 980 cm^{-1}, corresponding to the new bands present in AsF_5-doped oligomers.[12] Since the dopant (K^+) would not be expected to exhibit infrared structure, these absorbances may be attributed to the polymer anion. In the case of oligomers oxidized by AsF_5, results of elemental analysis did not exclude the possibility of polymer fluorination.[12] That a similar set of absorbances is seen here confirms that these bands do not arise from such a side reaction. PPP is an alternant π hydrocarbon; thus, it is not surprising that these new bands have the same position and width in the cationic and anionic polymer.

Table I
Band Positions for σ_{C-H} (para)

PPP	σ_{C-H}, cm^{-1}
Kovacic, unannealed	809
Kovacic, annealed	803
Yamamoto, unannealed	812
Yamamoto, annealed	810
Kovacic, K^+ or Na^+ doped	809
Kovacic, SbF_5 doped	805
Kovacic, annealed, SbF_5 doped	802

In the n-doped polymer, the C–H out-of-plane bend does not shift downward in frequency. This also is in accord with results obtained on n-doped oligomers.[12] With strong p-type dopants, such as SbF_5, we observe a red shift in this band, both in the annealed and unannealed polymer. The amount of shift is greater in the unannealed polymer. However, the annealed polymer yields the lowest frequency absorbance upon doping. Table I summarizes these results.

These data are strongly indicative of polymer chain extension upon p-doping but not upon n-doping. Chain extension is seen to occur during the doping step, rather than during compensation. It seems likely that the positive charge created on the polymer chain from doping causes an electrophilic attack on neighboring chain ends, not dissimilar to the reaction proposed by Shacklette in the case of crystalline *p*-terphenyl oxidized by AsF_5.[12] In the latter case, a *c*-axis reaction was postulated. This is probably not the case for the less crystalline PPP polymer. Interestingly, no evidence in our spectra was found for increased cross-linking. Further study of the reaction mode in PPP is under way.

Recent Raman results[13] on undoped PPP show vibrations at ca. 1598, 1276, and 1216 cm^{-1}. It is possible that the new infrared-active modes observed in doped PPP may correspond to the Raman-active vibrations in the undoped polymer, due to symmetry breaking from the charge induced on the polymer chain in the doping process.

If a quinoidal defect is induced by the doping process, the 1216-cm^{-1} Raman mode would be expected to increase in frequency, since it involves motions along the C–C bonds which experience an increase in bond order when going from benzoidal to quinoidal PPP; hence this mode might correspond to the 1280-cm^{-1} infrared band in doped PPP. The 1598-cm^{-1} Raman mode would then correlate with the 1560-cm^{-1} infrared band in the doped polymer. In the absence of a complete molecular model, these assignments are tentative but consistent with preliminary FT-IR results on doped PDP and doped poly(*p*-phenylenexylene).[14]

C. Carbonyl Complexes of PPP. The change in reactivity of arenes by complexation with transition metals is well-known. For example, the susceptibility to nucleophilic attack of arenes is enhanced by coordination with group 6B metal carbonyls. These complexes also exhibit catalytic activity.[15]

Generally, arene complexes are prepared in solution. This does not exclude the possibility of a heterogeneous reaction, however. We have found that PPP reacts readily with $M(CO)_3(CH_3CN)_3$ (M = Cr, Mo) in boiling hexane and with $M(CO)_6$ in boiling dibutyl ether.

Figure 5 shows the FT-IR/PA spectrum of PPP reacted with $Mo(CO)_3(CH_3CN)_3$ in hexane. Elemental analysis by ESCA shows a composition $(C_6H_4[M(CO)_3]_{0.25})_x$. Two sets of features that do not appear in the spectrum of pristine PPP are seen here. The most striking change is the appearance of bands in the 1800–2000-cm^{-1} region, attrib-

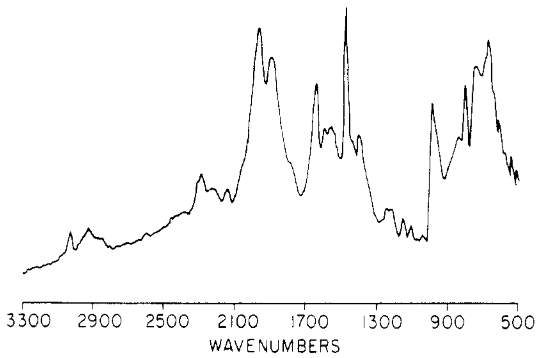

Figure 5. FT-IR/PA spectrum of Kovacic PPP modified by coordination with molybdenum tricarbonyl.

Table II
M-C-O Absorbances (cm^{-1})

	$(C_6H_4[Cr(CO)_3]_{0.25})_x$	(η^6-4,4′-dimethylbiphenyl)-$(CO)_3Cr^0$
$\nu_{C\equiv O}$	1903	1909
	1968	1976
ν_{M-C}	485	482
	541	536
	619	626
	661	667

utable to $\nu_{C\equiv O}$ in the coordinated metal carbonyl. In the uncoordinated $M(CO)_6$, these absorbances appear at and above 2000 cm^{-1}. Upon reaction with PPP, the bands shift downward in frequency to 1965 and 1895 cm^{-1} due to increasing occupancy of the π^* C–O orbital, reflecting a transfer of electron density from the polymer to the metal.

This electron transfer is probably a good deal less than one electron per coordinated metal. Despite this, new absorbances appear at the same positions as the absorbances characteristic of doping, although at reduced intensity relative to the ionically reacted polymer. We attribute this to planarization of the polymer in the region of the coordinated metal, similar to the dopant-induced planarization believed to occur in doped PPP. Consistent with this observation of partial doping of the polymer is the increase in conductivity to about 10^{-4} S cm^{-1}, accompanied by a darkening in color of the polymer to a very dark brown. Magic-angle ^{13}C NMR shows line broadening quite similar to that which occurs in SbF_5-doped PPP.[16]

A similar reaction occurs between PPP and either chromium hexacarbonyl in boiling dibutyl ether or chromium tricarbonyl tris(acetonitrile) in boiling hexane. The resulting modified polymer does not darken in color nor exhibit any increase in conductivity. Likewise, infrared features characteristic of the doped polymer do not appear. However, some charge transfer from the polymer to the metal does occur, since the carbonyl stretching bands appear in nearly the same positions as those of the molybdenum–PPP complex. Hence, we conclude that planarization of the phenyls does not occur in the chromium complex.

The spectra of the metal complexes in the carbonyl stretch region are shown in Figure 6. The molybdenum complex shows infrared structure which is qualitatively quite different from that of the chromium complex. Perhaps the planarization of the polymer that seems to occur introduces a greater randomness in the site symmetry of the molybdenum, or the electroconductivity of the polymer might perturb the carbonyls is a nonuniform manner. Liebman has suggested that the differences in the two products might be accounted for by the fact that the molybdenum carbonyl is a softer acid than the chromium carbonyl.[17]

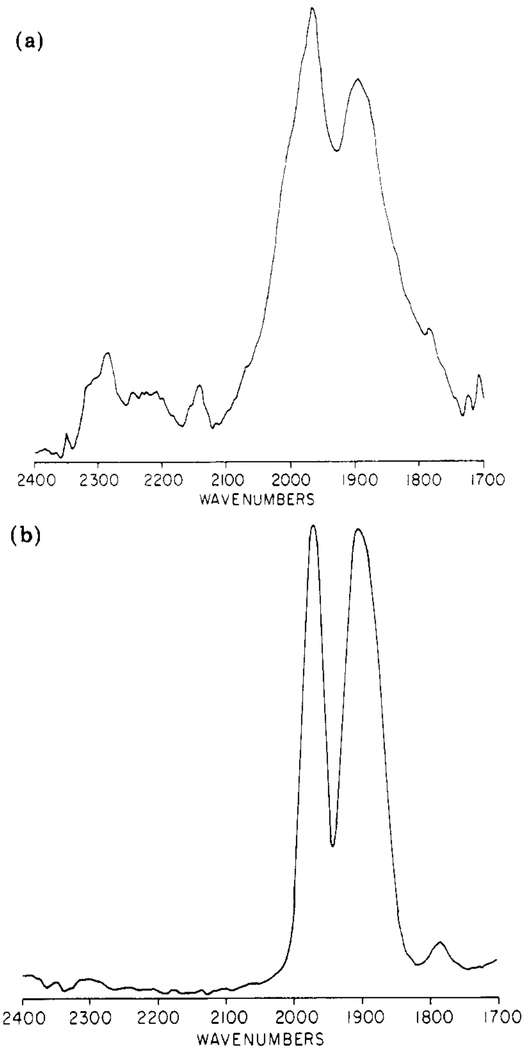

Figure 6. (a) Carbonyl stretch region in molybdenum carbonyl modified PPP. (b) Carbonyl stretch region in chromium carbonyl modified PPP.

Table II compares the positions of the C≡O stretching and metal–carbonyl stretching frequencies of the chromium–PPP complex with the known complex (η^6-4,4′-dimethylbiphenyl)tricarbonylchromium(0). The excellent correlation here lends credence to our assignment of a η^6 structure to the polymer complex.

Conclusions

We have shown that doped PPP exhibits distinctive structure in the infrared. The polymer exhibits a dramatic increase in overall absorption, along with the appearance of new bands at 1560, 1280, 1170, and 980 cm^{-1}, similar to those seen in doped oligomers. Irreversible polymer chain length extension is seen to occur upon doping with strong electron acceptors and prior to compensation and annealing. Molybdenum and chromium tricarbonyl complexes of undoped PPP may be prepared. The molybdenum complex shows greater conductivity ($\sim 10^{-4}$ S cm^{-1}) than the chromium complex and has infrared structure indicative of partial doping. This conductivity is believed to arise from increased planarization of the polymer upon coordination of the molybdenum tricarbonyl.

Acknowledgment. We thank J. A. Gladysz, T. Cymbaluk, and J. F. Liebman for valuable discussions concerning metal carbonyl chemistry and W. Woolfenden for providing NMR data. We gratefully acknowledge financial support from the Department of Energy (Office of Basic Energy Sciences).

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Molecular Order in Condensed States of Semiflexible Poly(amic acid) and Polyimide

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ABSTRACT: The molecular order in condensed states of the aromatic poly(amic acid) (PAA) poly(4,4′-oxydiphenylenepyromellitamic acid) and the resulting polyimide (PI) poly(4,4′-oxydiphenylenepyromellitimide) obtained by heating PAA films was determined from wide-angle X-ray diffraction studies. PAA chains in films containing solvents of ~30% by weight exhibit parallel alignment and correlated (smectic-like) lateral packing of highly extended chain segments, as shown by the appearance of a diffraction peak due to the intramolecular periodicity of ~14 Å. Upon imidization and removal of solvents by heating at 200 °C, this molecular order is preserved and slightly improved in the resulting PI films. Further improvement in order occurs upon annealing PI films at temperatures above ca. 300 °C, with the details of changes depending strongly on the initial orientation. In all PI samples, however, the high-angle diffraction patterns in the region of the scattering vector s $(=(2 \sin \theta)/\lambda) > 0.35$ Å^{-1} are matched very closely by the theoretical curve calculated for a single repeat unit, thereby indicating the absence of any appreciable long-range crystalline order in the thermally imidized PI films. The ramifications of such molecular order in condensed states of PAA (which cannot crystallize due to the meta–para isomers in the pyromellitamic acid unit) and PI are discussed in light of recent theoretical developments in the statistical thermodynamics of semiflexible polymers as well as some unique characteristics exhibited by this polyimide.

Introduction

The polymers comprising planar rigid groups interconnected to each other with fixed bond angles (i.e., aromatic polyimides, polysulfones, polycarbonates, etc.) normally exhibit a combination of high softening temperatures, thermal stability, and tough mechanical properties and thus are highly desirable for various demanding technological applications. On the molecular level, inclusion of such long rigid groups in the polymer backbone reduces the chain "flexibility", as demonstrated by detailed investigations[1,2] of their unperturbed chain configurations in dilute solutions devoid of excluded volume effect. For polymers with sufficient flexibility, the *unperturbed random coil* configuration is directly applicable to the chains in concentrated solutions and in the bulk.[3] However, this relationship cannot hold for polymers with limited flexibility as shown by theoretical considerations of semiflexible polymers in condensed states.[4–7] These considerations lead to the prediction that, for polymers with insufficient flexibility, an ordered state exhibiting both orientational and conformational order can be more stable than the isotropic state of random chains. Furthermore, the degree of order in conformation and orientation in the ordered state depends strongly on the chain model. Hence, the decreased chain flexibility due to the presence of planar cyclic groups of considerable length in the chain backbone poses a rather important question concerning the chain configurations, or molecular order, of these polymers in condensed states.

In this paper, we examine the molecular order of the aromatic poly(amic acid) (PAA) poly(4,4′-oxydiphenylenepyromellitamic acid) and the corresponding polyimide (PI) poly(4,4′-oxydiphenylenepyromellitimide) obtained by thermal imidization of PAA films,[8] shown schematically in Figure 1. The PAA chain comprises rigid groups of ca. 18 and 9 Å in length for the para and meta linkages of the pyromellitamic unit,[2], respectively, distributed randomly along the chain[9] and due to this structural irregularity cannot crystallize. The PI chain comprises rigid groups of ca. 18 Å in length[2] and is known to exhibit crystallinity upon heating the highly drawn fibers or films.[10–12] The structure of PAA films has received very little attention. While the structure in PI films or fibers has been the subject of a rather large number of studies,[10–14] most of the attention has been focused on the issues of crystallinity, crystal structure, and crystalline aggregates, etc. The structures or molecular order in

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