Physicochemical Characterization of Some Fully Aromatic Polyamides*

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Synopsis

The characterization of eight fully aromatic polyamides are described with the procedures required to yield film- and fiber-forming materials. Solutions of these aromatic polyamides in dimethylacetamide were characterized by NMR and the effects of dissolved lithium chloride on these spectra investigated. The NMR resonances for specific protons in these polymers are assigned. The IR spectra of thin films and fibers of these polyamides are also reported, together with glass transition temperatures as measured by differential scanning calorimetry (DSC). The value of NMR and IR to identify specific polyamide homopolymers and copolymers is discussed.

INTRODUCTION

Although poly(1,3-phenyleneisophthalamide) has been commercially available since about 1962 under the name of Nomex (du Pont trademark), the uses of fully aromatic polyamides (aramids) until recently have been restricted to relatively low-volume specialty fiber applications. These applications depend on the inherent flame resistance and nonmelting characteristics of the fibers.[1] However, production of aramids is now rapidly approaching 10^7 lb p.a. with the recent or proposed[2] commercialization of the aramids Conex (Teijin), M3P (Monsanto), and Fenilon (Russia), and the introduction by du Pont of high-moduli aramids as reinforcing fibers, especially in vehicle tires. The latter are available under the trade names of Kevlar and Kevlar-49 (formerly Fiber B and PRD-49, respectively).

Various syntheses for aromatic polyamides are reported in the literature.[3,4,5] However, little has been published on the physicochemical properties of this class of increasingly important polymers. In particular, the infrared (IR) spectroscopy, nuclear magnetic resonance (NMR), and differential scanning calorimetry (DSC) have not been previously reported. In this paper, we present some IR, NMR, and DSC data for eight fully aromatic polyamides, as well as the synthetic procedures required to produce polymer samples of adequate molecular weight (film- and fiber-forming). The uses of IR and NMR spectroscopy to identify specific homopolymers and to estimate the composition of copolymers are also discussed.

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EXPERIMENTAL

Materials

The polymerization solvents N,N-dimethylacetamide (DMA) and hexamethylphosphoric triamide (HMPTA) (Eastman) were distilled prior to use at 3–5 torr from calcium hydride and transferred under N_2 into the baked-out polymerization flask. Isophthaloyl and terephthaloyl chlorides (Eastman) were each fractionated at 4 and 1 torr, respectively, through a 10-cm Vigreux column. The diamines (Eastman) were similarly distilled at 3–5 torr from calcium hydride into glass break-seal ampoules.

The m- and p-aminobenzoyl chloride hydrochlorides were prepared from each recrystallized aminobenzoic acid essentially as described by Pikl.[6] The acid was refluxed with thionyl chloride, the resulting solution diluted with redistilled 1,1,2-trichlorotrifluoroethane, and saturated with anhydrous hydrogen chloride to produce the acid chloride hydrochloride. This monomer was filtered under N_2 on a glass frit, washed repeatedly with the halogenated solvent, and vacuum dried.

Polymerizations

All poly(phenylenephthalamides), except poly(p-phenyleneterephthalamide), were prepared according to procedures adapted from the patent literature.[4,5] In one procedure, an accurately known weight of diamine sufficient to give a final polymer concentration of 10–20% was melted into the baked-out, N_2-purged polymerization flask from the (previously sealed) ampoule and then dissolved in DMA. The reaction flask was cooled to $-25 \pm 3°C$ and a precisely measured molecularly equivalent weight of diacid chloride was melted in from a break-seal ampoule over a period of ∼30 min with continuous, rapid stirring. In an alternate procedure, the diacid chloride was powdered and weighed out into a flask in an N_2 dry-box, and this monomer was then added in one batch to the chilled diamine solution. The polymerizations reached completion after ∼40 min at $-25°C$, when the temperature was raised to 25°C and the mixture stirred for an additional hour.

All polymerizations were terminated by the addition of benzoyl chloride (2% by weight of the diacid chloride) in order to cap any remaining amino endgroups. The products were neutralized by the addition of a sufficient quantity of lithium hydroxide to consume all of the liberated HCl. Finally, the reaction mixtures were heated to 50–60°C for 1 hr, filtered through a coarse glass frit, and precipitated into an ice-water slush in a high-speed blender. Repeated water and acetone washes followed by vacuum drying at 80°C ensured a lithium-, monomer-, and moisture-free material in a soluble form.

Poly(p-phenyleneterephthalamide) was prepared similarly, except that a mixed polymerization solvent, consisting of 35% DMA and 65% HMPTA saturated with dry LiCl (5%), was required to hold even a 2–3% final polymer concentration in solution. At lower LiCl concentrations, higher molec-

ular weights are possible, but the solutions gelled on standing or on rapid stirring.

The polybenzamides were prepared by the addition of the required aminobenzoyl chloride hydrochloride to slowly stirred DMA at $-25°C$ in the polymerization system described above. The monomer concentration was adjusted to give a 3–5% final concentration of polymer. Polymerization occurred over ~1 hr at $-25°C$, and the solution was stirred for an additional hour at $25°C$.

Portions of the all-para polymer solutions were not precipitated. Instead, film samples were cast directly from the neutralized solutions and the films subsequently freed from residual solvents and lithium by a water extraction. Once precipitated, these polymers could not be redissolved in DMA or HMPTA, only in sulfuric or chlorosulfonic acid.

IR Spectra

Transmission IR spectra of thin films were recorded with a Beckman IR 8 at 90 cm^{-1}min^{-1}. The transmission spectra of Nomex and Kevlar fibers were recorded on single-thickness coils wound between salt plates essentially as described by Sibilia.[7] The fiber spectra were recorded with a polarizer (Perkin-Elmer, gold-wire grid type) set either parallel to, or perpendicular to, the fiber axis. IR spectra of some commercial fabrics were recorded by attenuated total reflection (ATR) using a KRS-5 reflection element at 45°, as described previously.[8] Thin films for IR analysis were prepared from commercial Kevlar B, Kevlar 49, and Nomex II fiber samples by solution in chlorosulfonic acid and careful evaporation of the solvent.
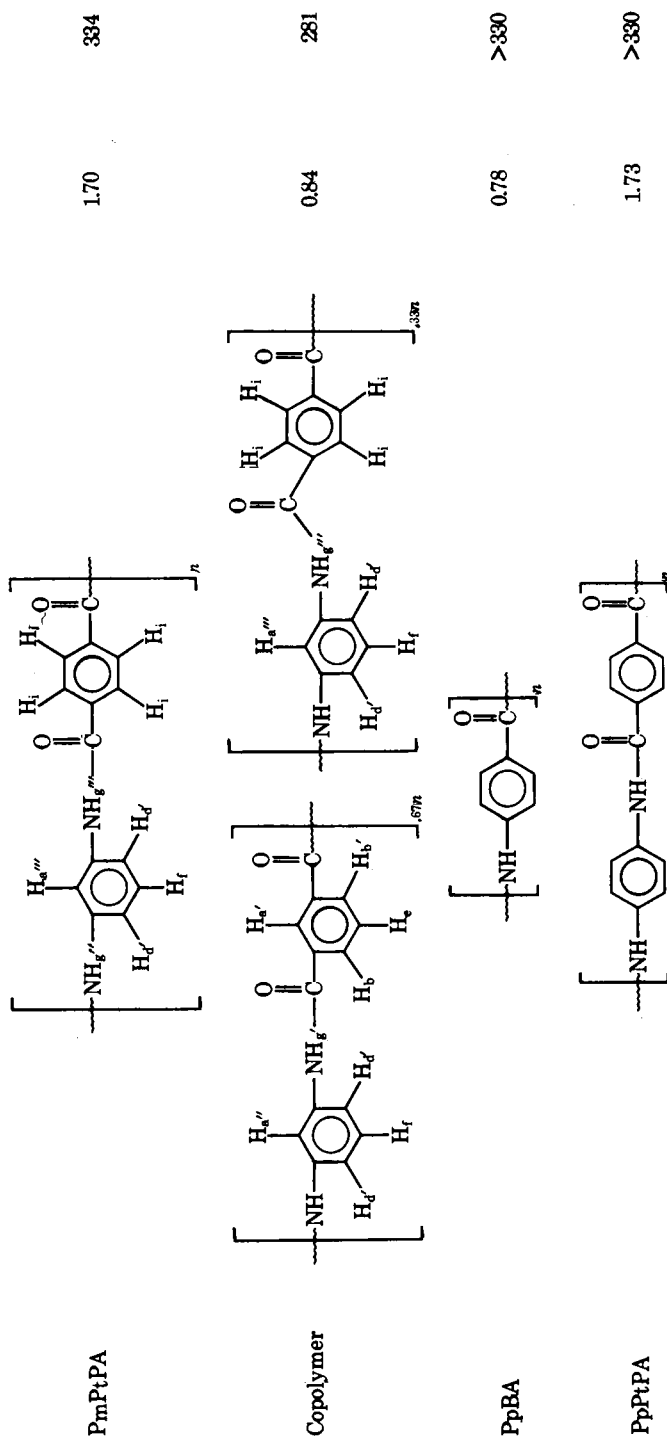
NMR Spectra

NMR spectra of polymer solutions were recorded on a Varian HA-100 spectrometer at $25°C$, using tetramethylsilane (TMS) as an internal standard. Where possible, the polymers were dissolved in DMA, but some of the para-substituted polymers required the addition of lithium chloride to achieve complete solution. The proton resonance of TMS was found to be unaffected by the presence of lithium chloride. Polymer solutions containing lithium chloride gave identical TMS proton resonances both when TMS was present in solution or when used as an external standard. The polymer proton chemical shifts were found to be independent of the polymer concentration in the DMA solutions within the experimental range examined (0.015–0.07 g/ml). However, the chemical shifts in the DMA–lithium chloride solutions were extremely dependent on the polymer–salt ratios.

DSC Measurements

Solid-state transitions were measured with a Perkin-Elmer differential scanning calorimeter (DSC-1B). The polymer powder samples (0.015 g) were purged with nitrogen before and during the measurements. Each transition temperature was estimated from the midpoint of the deflection of

TABLE I
Aromatic Polyamides: Structure, $[\eta]$, and Glass Transition Temperatures T_g

Polymer Abbreviation	Structure	$[\eta]$,ᵃ dl/g	T_g, °C
PmBA		1.26	265
PmPiPA		1.97	275
PMemPiPA		1.30	279
PpPiPA		1.84	306

334

1.70

281

0.84

>330

0.78

>330

1.73

PmPtPA

Copolymer

PpBA

PpPtPA

ᵃ Intrinsic viscosities of laboratory samples in sulfuric acid at 27.8°C.

the corrected temperature curve. The DSC cell temperature was cali-
brated at the scanning rate (10°C/min) with pure metals which melted in
the range of the polymer transitions detected.

RESULTS AND DISCUSSION

The polymerization procedures described yielded polymers which could
be cast into tough films ($\sim$15 μ thick) or could be drawn into fibers. The
abbreviated names and intrinsic viscosities ([η]) of these polymers are listed
in Table I. The synthesized PmPiPA had [η] of 1.97 dl/g, close to that of a
commercial Nomex (a fiber sample) at 1.70 dl/g and with a $\bar{M}_n$ of $\sim$39,000,
as determined previously by osmometry.[9] However, the laboratory-syn-
thesized sample of PpPtPA ([η] = 1.73 dl/g) had a molecular weight well
below that of the commercial material, for example, a Kevlar-49 fabric
with [η] = 5.3 dl/g.

NMR Characterization

The NMR spectra for a series of fully aromatic polyamides dissolved in
DMA or DMA + LiCl are shown in Figure 1. The proton chemical shifts
(τ) relative to TMS for these polymers are shown in Table II. The singlet
proton resonances at low field (τ −1.5 to −0.5) for all of the homopolymers
are due to the amide protons (H_g), the remaining resonances being due to
the ring protons.[10] Proton labelling is given in Table I.

The triplet at τ 2.57 in the NMR spectrum of PmBA in DMA (Fig. 1A)
must result from the proton H_c, and the singlet at τ 1.49 can only be as-
signed to H_a. The two doublets (τ 1.87 and 2.23) must result from H_b and
H_d but cannot be unambiguously assigned from this spectrum alone.

The singlet resonances at τ 2.07 and τ 1.46 in the NMR spectrum of
PpPiPA in DMA (Fig. 1B) have intensities in the ratio of 4:1. These
must then result from the four equivalent protons (H_b) on the p-phenylene
ring and the proton $H_{a'}$ on the isophthaloyl unit, respectively. The triplet
at τ 2.38 and the doublet at τ 1.84 have an intensity ratio of 1:2 and are
ascribed to the protons H_e and $H_{b'}$, respectively. Since proton $H_{b'}$ in
PpPiPA is in an almost identical magnetic environment to that of proton
H_b in PmBA, the doublets in the spectrum of PmBA can now be assigned
to H_b (τ 1.87) and H_d (τ 2.23).

The spectrum of PmPiPA in DMA (Fig. 1C) is more difficult to interpret
than those of the two previous polymers. The doublet at τ 1.86 probably
corresponds to proton $H_{b'}$, since the τ value is close to that for proton $H_{b'}$ of
PpPiPA (τ 1.84) and H_b of PmBA (τ 1.87). The triplet at τ 2.72 is prob-
ably due to H_f, since the triplet from H_e should have a chemical shift of
around τ 2.38, as indicated from the spectrum of PpPiPA [τ(H_e) 2.38].
The resonances in the τ 2.25–2.55 region result from an overlapping doublet
and a weak triplet. The triplet at τ $\sim$2.40 (estimated using the identical
triplet splittings of H_c for PmBA and H_e for PpPiPA) is due to the proton
H_e, since it has a chemical shift similar to that of the H_e of PpPiPA. The

TABLE II

NMR Proton Chemical Shifts τ for Some Aromatic Polyamides

Polymer[a]	Chemical shift τ[b]						
PmBA	H_a 1.49 (s)	H_c 2.57 (t)	H_d 2.23 (d)			H_g −0.58 (s)	
PpPiPA	$H_{a'}$ 1.46 (d)	$H_{b'}$ 1.84 (d)		H_e 2.38 (t)		$H_{g''}$ −0.54 (s)	H_h 2.07 (s)
PmPiPA	$H_{a'}$, $H_{a''}$ ~1.48 (s)	$H_{b'}$ 1.86 (d)	$H_{d'}$ 2.38 (d)	H_e ~2.40 (t)	H_f 2.72 (t)	$H_{g'}$ −0.58 (s)	
Copolymer	$H_{a'''}$, $H_{a'}$, $H_{a''}$ 1.42 1.48 (s)	$H_{b'}$ ~1.84	$H_{d'}$ ~2.32	H_e ~2.38	H_f 2.68	H_g, $H_{g'''}$ −0.56 −0.61	H_i ~1.84
PmPtPA[c]	$H_{a'''}$ 0.98 (s)		$H_{d'}$ 1.96 (d)		H_f 2.80 (t?)	$H_{g'''}$ −1.49 (s)	H_i 1.44 (s)

[a] Protons are labeled on structures in Table I. DMA solutions unless specified.
[b] Relative to TMS. Values ±0.03τ when clearly resolved. Terms in parentheses refer to multiplicities: singlet (s), doublet (d), or triplet (t).
[c] Measured in DMA/LiCl solution, polymer:LiCl ratio 1:1.44 by weight.
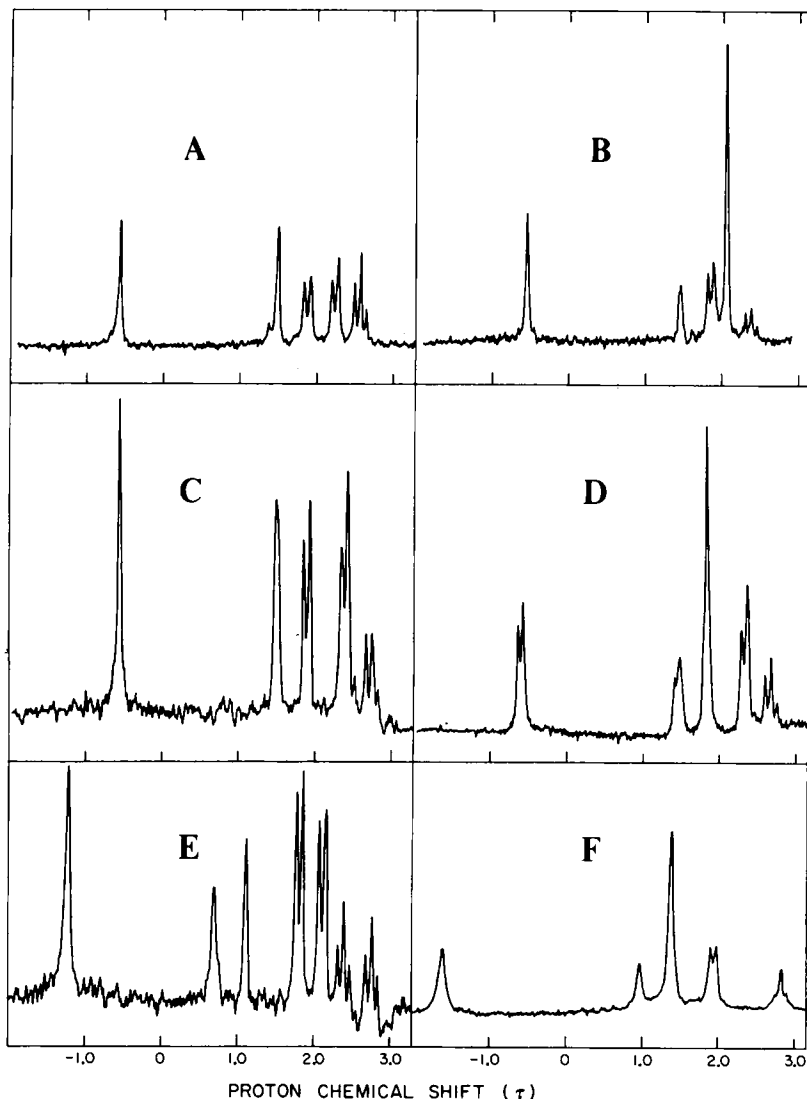
Fig. 1. NMR spectra of some fully aromatic polyamides. All in DMA solution, except for E and F, which were dissolved in DMA/LiCl (1:1.44); τ values relative to TMS: (A) PmBA; (B) PpPiPA; (C) PmPiPA; (D) copolymer (see Table I); (E) PmPiPA; (F) PmPtPA.

doublet at $\tau \sim 2.38$ must then result from $H_{d'}$ of PmPiPA. The singlet at $\tau \sim 1.48$ is due to the overlapping singlets from $H_{a'}$ and $H_{a''}$, since integration indicated that the overall intensity corresponded to that from two protons. A better resolved NMR spectrum of PmPiPA is obtained when the polymer is dissolved in DMA/LiCl (see below).

The NMR spectrum of PMemPiPA in DMA is quite complex (not shown). However, two distinct amide proton resonances were observed

at τ -0.48 and -0.11. A comparison with the τ values of the amide protons listed in Table II indicates that the higher field value is probably due to the proton of the amide group meta to the methyl ring substituent, the lower field resonance (τ -0.48) being closest to that of $H_{g'}$ in PmPiPA.

Figure 1D shows the NMR spectrum of a copolymer from the polymerization of m-phenylenediamine with isophthaloyl and terephthaloyl chlorides (in the ratio of 67:33). This spectrum should resemble the superimposition of the spectra of the homopolymers PmPiPA and PmPtPA. The copolymer shows two distinct amide proton resonances at τ -0.56 (for the meta-iso isomer) and at τ -0.61 (for the meta-para isomer). In addition, an extra resonance at τ 1.42 is visible close to the $H_{a'}$ and $H_{a''}$ absorptions (τ 1.48). This resonance probably results from $H_{a'''}$, of the m-phenyleneterephthalamide unit. The most striking difference in ring proton resonances between Figure 1C (for PmPiPA) and Figure 1D is the intense singlet at τ 1.84, which must result from the four equivalent protons H_i superimposed on the $H_{b'}$ doublets of the isophthaloyl group.

In all of the NMR spectra shown in Figure 1, only the ortho coupling constants ($J = 7$–$8\ Hz$) are visible.[11]

Effect of LiCl

When LiCl is dissolved in an aromatic polyamide–DMA solution, a marked change in the NMR spectrum is observed. Many of the proton resonances are shifted downfield, but the most significant shift is observed for the amide proton. For example, the amide proton of PmPiPA in a DMA solution with a polymer:LiCl ratio of 1:1.44 by weight ($0.12M$ in LiCl) is $0.65\ \tau$ further downfield (Fig. 1E) from the amide proton of the polymer in DMA alone (Fig. 1C). This extra shift increases with increasing LiCl concentration, reaching 1τ at a polymer:LiCl ratio of 1:6.72 by weight.

Many aliphatic amides have been shown to complex with LiCl, some amides forming stable adducts. For example, the crystalline adduct of LiCl and N-methylacetamide (NMA) has been isolated.[12,13] X-Ray crystallographic analysis[12] has shown that each Li^+ ion is coordinated to four molecules of NMA at the carbonyl oxygen and the amide hydrogens are hydrogen bonded to the chloride anions. Results from the NMR and IR[13] analysis of the interaction of LiCl with NMA are consistent with this interpretation. Thus, the downfield shift of the amide protons of PmPiPA (Fig. 1E) in the presence of LiCl is probably also caused by the interaction of Li^+ with the oxygen of the carbonyl group, leading to an increased acidity of the amide proton. This amide proton is probably hydrogen bonded to the chloride anion.

Since the addition of LiCl to the polymer solutions caused the NMR spectra to change markedly, essentially the salt is acting as a spectral-shift reagent. LiCl addition can then be used to advantage to separate complex overlapping NMR spectra (Fig. 1, cf C and E). In addition, some aromatic polyamides are soluble in DMA/LiCl but insoluble in DMA alone.

This is the case for PmPtPA; the NMR spectrum for this polymer in DMA/LiCl is shown in Figure 1F. The ratios of the peak intensities at τ -1.49 (singlet), 0.98 (singlet), 1.44 (singlet), 1.96 (doublet), and 2.80 (multiplet) are 2:1:4:2:1, corresponding to protons $H_{g'''}$, $H_{a'''}$, H_i, $H_{d'}$, and H_f, respectively. Curnuck and Jones[10] have recently shown that the four different amide protons of an aromatic poly(amide–sulfone–ether) copolymer can be resolved by the addition of LiCl, enabling the sequence distribution of these copolymers to be established.

Only broad, weak, featureless NMR resonances were observed with PpBA or PpPtPA in DMA/LiCl solutions. Broadening probably resulted from the extremely high viscosities of the very dilute solutions (limited by the low solubility of the all para polymers). Increasing the solution temperature to 80°C caused little improvement in spectral quality.

DSC Analysis

Sharp, reproducible endothermic baseline shifts were obtained for several of the aromatic polyamides. These endothermic shifts are shown in Figure 2, and the transition temperatures are listed in Table I. The transitions probably correspond to the glass transition temperature (T_g) of the polymers, since Black[14] has reported a T_g value of 273°C for PmPiPA from sonic modulus measurements, close to our DSC value (275°C). Butta and co-workers[15] have reported a T_g of 345°C for PpPtPA from DSC mea-
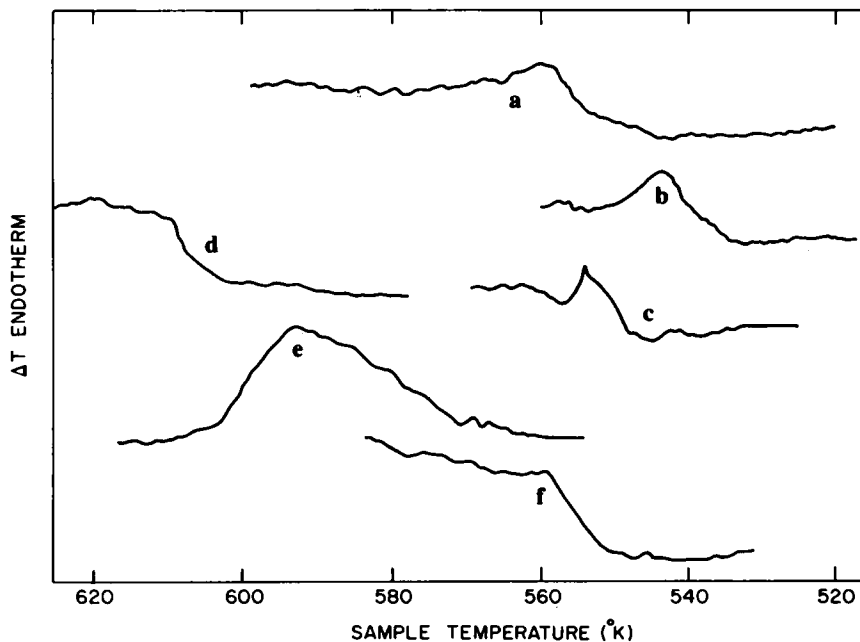

Fig. 2. T_g values for some aromatic polyamides; heating rate 10°C/min: (a) PMemPiPA; (b) PmBA; (c) PmPiPA; (d) PmPtPA; (e) PpPiPA; (f) copolymer (see Table I).

surements, and their sonic modulus data indicate T_g values of ∼280° for PmPiPA and ∼350°C for PpPtPA. T_g values in the range of 290–335°C have been reported by Preston[3] for several ordered aromatic copolyamides from DTA and penetrometer measurements.

The T_g values for the homopolymers (Table I) increase progressively with increasing para substitution, as can be expected from the corresponding increase in stiffness of the polymer backbone. The T_g for the copolymer is intermediate between that of PmPiPA and PmPtPA, a similar effect to that found for certain aliphatic–aromatic nylon copolymers.[16] T_g values for the all-para polymers could not be obtained, since only irreproducible endothermic shifts were observed, usually well above 330°C.

IR Characterization

Spectra of some aromatic polyamides have been previously published by Mark et al.,[17] although the observed absorptions in the 1200–600 cm^{-1} range were largely too weak to be useful. The transmission IR spectra of films of our eight laboratory-synthesized aromatic polyamides are shown in Figures 3 and 4. Although the 4000–2000 cm^{-1} region is relatively uninformative as to structure, H—CH stretching vibrations at 2860 and 2920 cm^{-1} are distinctive for the methyl substituent in poly(4-methyl-1,3-
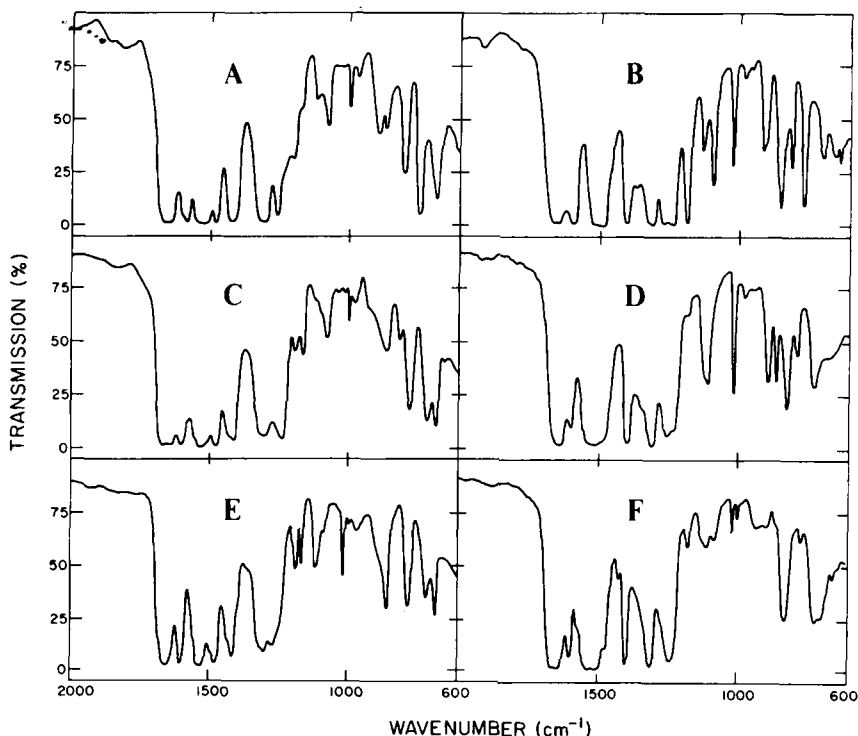

Fig. 3. Transition IR spectra of some aromatic polyamide films; film thickness 15 ± 5 μ; (A) PmBA; (B) PpBA; (C) PmPiPA; (D) PpPtPA; (E) PmPtPA; (F) PpPiPA.
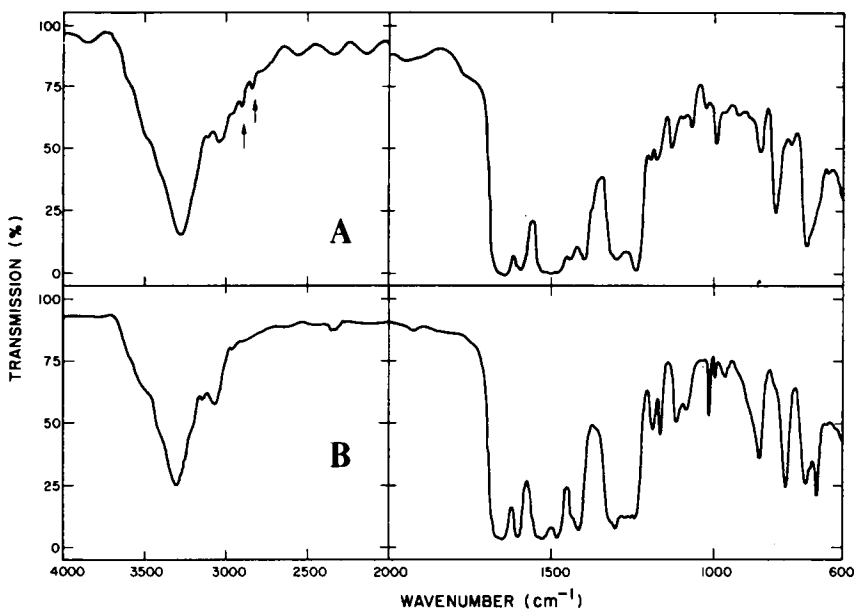
Fig. 4. Transition IR spectra of some aromatic polyamide films; film thickness 15 ± 5 μ: (A) PMemPiPA; (B) copolymer (see Table I).

phenyleneisophthalamide) (Fig. 4). The intensity of the amide NH absorption at 3300 cm^{-1} is markedly affected by the moisture content of the film.

The 2000–600 cm^{-1} region is distinctly different for each aromatic polyamide isomer and can be used to identify unknown compositions. The IR absorption bands in this region are extremely sensitive to the type of ring substitution, and it is difficult to assign them to specific groupings. However, based on the spectra shown in Figures 3 and 4, it is possible to make the following generalization. Only the absorptions at 1000 and 1016 cm^{-1} can be used unambiguously to identify the presence of meta and para monomer units, respectively. This generalization seems to hold for many m- and p-substituted aromatic compounds (di-halides, aminophenols, diesters, diacids).[18] However, the extinction coefficients (ϵ) of these absorptions appear to be very sensitive to the nature of the substituents. For example, ϵ_{1000} and ϵ_{1016} are small if only m- or p-amino groups, respectively, are present; and large if m- or p-carboxyl groups are present; all m-substituents have a smaller extinction coefficient than the equivalent p-isomers. From the IR spectra of the aligned commercial PmPiPA and PpPtPA fibers, it is apparent that the 1000 and 1016 cm^{-1} absorptions are also both affected by IR polarization, with dichroic ratios of $\sim$20 for the incident beam parallel to and perpendicular to the fiber axis. The polarization sensitivity of the 1016 cm^{-1} band in PpPA has been previously reported.[5]

From Figures 3 and 4 and published spectra of substituted aromatics,[18] an absorption at 1122 appears to be largely indicative of p-substituents in

many cases, and absorptions at 684 and 1080 cm^{-1} are indicative of m-substituents, although a few examples of polymers which absorb at these frequencies, but do not contain the required substituents, can be seen in Figures 3 and 4. Strong absorptions at 800 and 900 cm^{-1} do appear to result solely from aromatic rings bearing both —NH and —CO groups. Absorptions at 862 and 825 cm^{-1} frequently indicate the presence of m-NHC$_6$H$_4$NH— and p-NHC$_6$H$_4$NH—, respectively. The complexity of the spectra of aromatic polyamides means that the above tentative assignments may be used as preliminary guidelines but are not meant to be the sole basis of structural identification.

Aromatic Polyamide Structure Determination

If the aromatic polyamide can be dissolved in DMA or in DMA/LiCl, its composition can best be established from the features of its NMR spectrum and the chemical shift values given in Table II. In particular, the position of the high field triplet (from protons H$_e$, H$_f$, or H$_c$) is distinctive for two substituents both meta to this proton (i.e., a 1,3-ring substitution). In addition, an intense singlet in the region of τ 1.8–2.1 is a clear indication of a significant concentration of para-substituted units. All of the H$_a$ protons, ortho to a pair of amide groups (on the 1,3-substituted rings) are insensitive to the orientation of these amide groups (cf., the H$_a$ values for PmBA and PmPiPA). The use of LiCl/DMA as a spectral-shift reagent in solving unknown aromatic polyamide structures is limited by the dependence of the τ values for a specific proton on the strength of the polymer-LiCl interaction. For example, from a comparison of spectra E and F (Fig. 1), the resonances for H$_{d'}$ (τ 1.82 or 2.12) and H$_{a'}$ (τ 0.70 or 1.13) in PmPiPA are very different from H$_{d'}$ (τ 1.96) and H$_{a'''}$ (τ 0.98) of PmPtPA, both samples dissolved at the same polymer/LiCl ratio (1:1.44 by weight). The measurement of τ values at various polymer/LiCl ratios and extrapolation to zero LiCl concentration would allow comparison with the τ values in Table II but would be time consuming.

The IR spectra of thin films cast from a solution of an aromatic polyamide can give additional information on structure, although the complex dependence of absorption band positions in the 1200–600 cm^{-1} region (Figs. 3 and 4) on ring substitution makes unambiguous assignment of structures difficult. The presence of meta and para ring substituents can be identified, at least qualitatively, from the 1000 and 1016 cm^{-1} absorption, respectively. In addition, strong absorption at 800 and 900 cm^{-1} appear to be definitive for ⁓NH—ϕ—CO⁓ groups.

The NMR spectra of our synthesized PmPiPA and solutions of commercial Nomex aramid paper or fiber samples were identical. Similarly, fabric or fiber samples, or films prepared from fibrous substrates of commercial Nomex products, all gave IR spectra identical to that of PmPiPA (Fig. 3C). Para substituents (1016 cm^{-1} absorption) could not be detected in the commercial samples (probably below 5% impurity p-comonomer). The IR spectra of films prepared from our synthesized PpPtPA, from Kevlar 49

aramid fiber, Nomex II fabric, and Fiber B (Kevlar) tire cord were all identical to that shown in Figure 3D. Meta substituents (1000 cm^{-1} absorption) could not be detected in the commercial samples (probably below 5% m-comonomer). Good-quality IR spectra of Nomex and Fiber B fibers have recently been published by Hummel and co-workers,[19] using both ATR and KBr pellet techniques. Their Nomex spectrum was in complete agreement with our spectrum of PmPiPA (Fig. 3C), whereas their Fiber B spectrum matched our spectrum of PpPtPA (Fig. 3D), although guessed to be PpBA by Hummel et al.[19] As originally introduced in 1970, Fiber B was probably PpBA, but the higher-tenacity Fiber B available[20] since 1971 is PpPtPA from our IR data.

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