# A Solid-State NMR Study of Aromatic Polyimides Based on 4,4′-Diaminotriphenylmethane

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**ABSTRACT:** The effect of different synthesis routes on the chemical and molecular order of polyimides based on 4,4′-diaminotripenylmethane (DA-TPM) and various aromatic dianhydrides (PI-TPM) was studied by solid-state carbon-13 nuclear magnetic resonance ($^{13}$C-NMR). Polyimides were prepared by three different methods including a two-step procedure with either thermal or chemical imidization of precursor poly(amic acid)s (PAA) and one-step high-temperature polycondensation in phenolic solvents. Model compounds were also obtained and used in the assignment of the NMR signals. The NMR spectra for PI-TPMs obtained by one-step high-temperature polycondensation and—to a lesser extent—by thermal imidization of PAA, show sharper lines than those observed in the spectra of polymers prepared from PAA via chemical imidization. These differences are due mainly to the lower degree of ordering of the latter polyimides. WAXD patterns of polyimide films also indicated a less-ordered structure of the polymers resulting from the chemical imidization of PAA. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1053–1064, 1998

**Key words:** high-resolution solid-state $^{13}$C-nuclear magnetic resonance; polyimides, 4,4′-diaminotriphenylmethane

## INTRODUCTION

The monomer 4,4′-diaminotriphenylmethane (DA-TPM) was tried for the first time in the synthesis of aromatic polyimides in 1980. A low-temperature condensation with both pyromellitic or 3,3′,4,4′-oxydiphthalic anhydrides yielded high molecular weight poly(amic acid)s, but further thermal imidization in the condensed state resulted in fragile and insoluble polyimides.[1]

In a recent article,[2] it was shown that these drawbacks can be overcome if thermal imidization is replaced by a chemically induced process at room temperature. The obtained polymers (PI-TPM) possessed a good solubility in organic solvents. This fact led to a successful attempt of applying the one-step high-temperature polycondensation in phenolic solvents for the synthesis of polyimides based on DA-TPM and various aromatic dianhydrides.[3] This convenient method gave high molecular weight PI-TPM with well-defined glass transition temperatures in the range from 270 to 350°C depending on the structure of the dianhydride moiety. A fairly high level of mechanical and thermal properties along with availability of the monomers permit one to consider some of these polyimides as promising candidates for various practical applications.

Because PI-TPMs can be prepared by the three most common techniques including thermal or chemical imidization of precursor poly(amic acid)s (PAAs) or one-step high-temperature poly-

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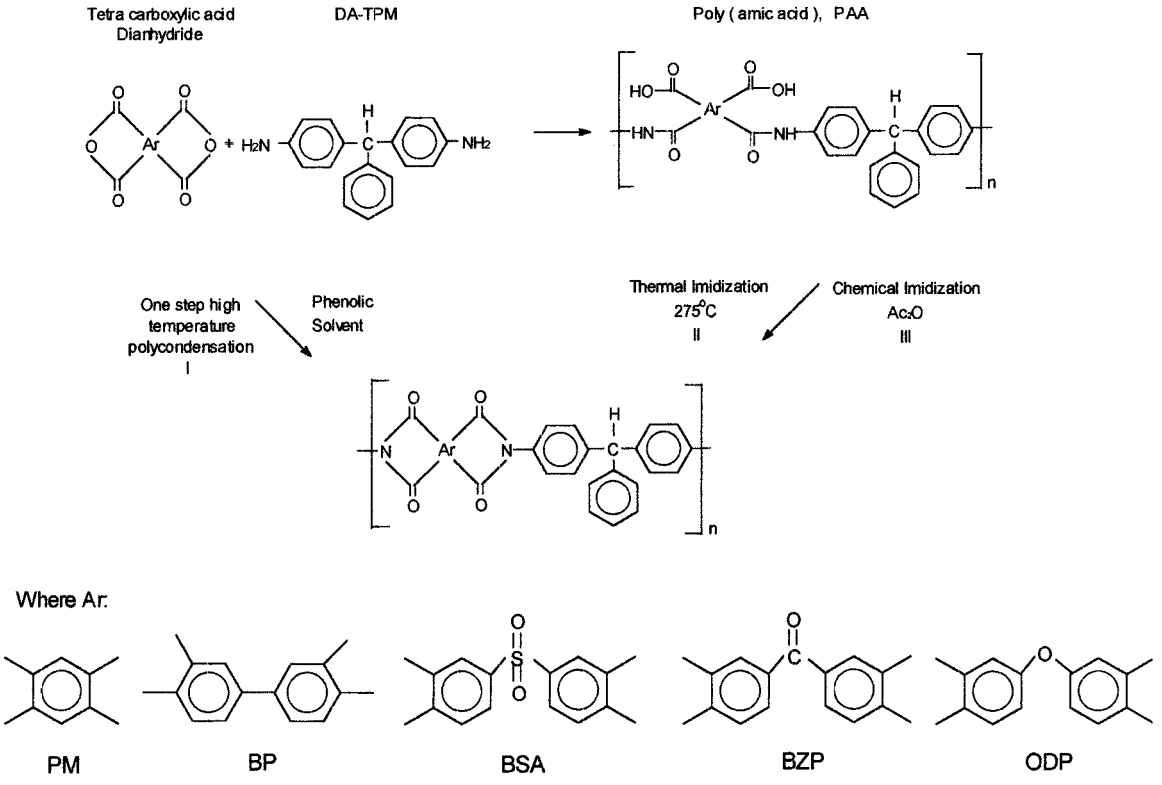



**Scheme 1**

condensation (see Scheme 1), it is possible to use this system as a model in the study of the effects of the different synthetic routes on the chemical structure and morphology.

Solution and solid-state nuclear magnetic resonance (NMR) techniques have been widely used for the elucidation of structure of polyimides.[4–9] This technique has also made possible the identification of different reactions pathways that can occur during the imidization process.[8] The CP-MAS $^{13}$C-NMR spectra of the described aromatic polyimides based on 4,4′-diaminotriphenylmethane as well as the model compounds of these PI-TPMs are presented here for the first time and further analyzed. Comparative studies of the final polymers produced under different imidization routes and reaction conditions were also undertaken. Our results provide clear insight about the effects of the route and reaction conditions on both the structure and morphology of the PI-TPMs. CP-MAS $^{13}$C-NMR analysis was also performed on poly[*N,N*′-bis(phenoxyphenyl)pyromellitimide] prepared by the thermal imidization of the corresponding PAA and commercial polyimide film (Kapton-NH).

## EXPERIMENTAL

### Materials

Aromatic dianhydrides including pyromellitic dianhydride (PMDA), 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (s-BPDA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), 3,3′,4,4′-diphenylsulfone tetracarboxylic dianhydride (DSDA), and 4,4′-oxydiphthalic anhydride (ODPA), all from Chriskev Co, Kansas City, were purified by sublimation under a vacuum prior to use. The monomer 4,4-diaminotriphenylmethane (DA-TPM) was prepared by the reaction of aniline with benzaldehyde at 140°C under a nitrogen flow.[2,3,10,11] Polymer-grade DA-TPM (mp 126°C) was obtained by repeating the recrystallization of the crude product from benzene followed by sublimation at 110°C and $10^{-4}$ mmHg.

ANAL: Calcd C, 83.17%; H, 6.61%; N, 10.21%. Found: C, 83.15%; H, 6.47%; N, 10.17%.

The other reagents and solvents were obtained from Aldrich Chemical Co, Milwaukee, WI. The structures of the polyimides studied here are de-

picted in Scheme 2, along with the designated abbreviations.

### *Synthesis of Model Compounds*

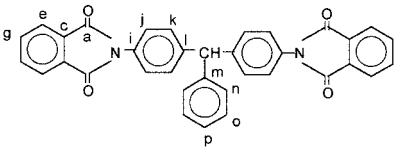
The model compounds **I** and **II** were obtained by condensation of phthalic or pyromellitic anhydrides with DA-TPM or aniline, respectively. Stoichiometric amounts of reagents were dissolved in *N*-methyl-2-pyrrolidone (NMP) and stirred at room temperature for 3 h. The solutions were heated at 150°C for 4 h with nitrogen bubbling through it and then poured into water. Precipitates were filtered out, washed with a mixture of ethanol/ethyl ester, and dried in vacuum at room temperature.

### *Synthesis of Polyimides*

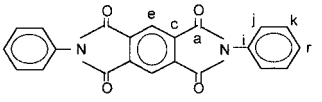
The polyimide films of PI-TPM were prepared via polycondensation of DA-TPM with the aromatic dianhydrides mentioned above. Three different methods were used for the synthesis including two-step polycondensation with either thermal (1) or chemical (2) imidization of the precursor PAA or one-step high-temperature reaction in nitrobenzene (3).

The precursor PAAs used in the two-step route were synthesized by reacting stoichiometric amounts of DA-TPM with a dianhydride in the NMP solution at room temperature for 5 h. The reaction solutions were cast onto glass plates, and polymer films (about 25 $\mu$m) were obtained by evaporating the solvent under a vacuum at 50°C for 4 h. The precursor films were converted to the final polyimides by heating at 275°C for 30 min (thermal imidization) or by treatment with a mixture (50/50 by volume) of acetic anhydride and *N,N,N′,N′*-tetramethylethylenediamine at room temperature for 20 h (chemical imidization) followed by annealing at 230°C for 6 h to remove residual solvents. One-step high-temperature polycondensation was carried out by stirring stoichiometric amounts of the monomers in nitrobenzene at 180°C for 5 h under a nitrogen atmosphere. Films were obtained by casting these solutions onto glass plates and drying first at 230°C and $10^{-6}$ mmHg for 15 h and then at 275°C for 30 min to remove the residual solvent.[2,3]

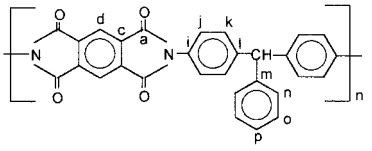
Poly[*N,N′*-bis(phenoxyphenyl)pyromellitimide] (PM-ODA) was obtained by the acylation of 4,4′-oxydianiline with PMDA in NMP at room temperature for 4 h followed by thermal imidization of the resulting PAA in a condensed state (as a film) at 300°C for 30 min. The used nomenclature of the PI-TPMs is based on the dianhydride moiety as PM-TPM, BSA-TPM, ODP-TPM, BZP-TPM,



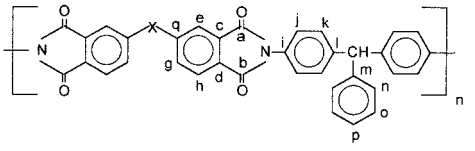
**MODEL COMPOUND I**



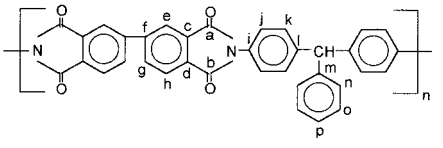
**MODEL COMPOUND II**



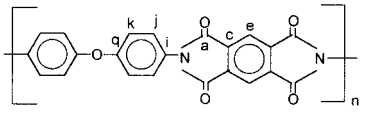
**PM-TPM**



**X = -$SO_2$- BSA**
**X = -O- ODP**
**X = -C- BZP**
**O**



**BP-TPM**



**KAPTON**

**Scheme 2**

**Table I $^{13}$C-NMR Chemical Shifts in the Solid State at 298 K for Various Polyimides**

| Compound | Imide Carbonyl *a*,*b* | Substituted Aromatic Carbons *c*, *l*, *m*, and *q* | Protonated Aromatic and Carbons *d* and *i* | Methine | Other |
|---|---|---|---|---|---|
| Model compound I | 167.8 (sh)<br>166.0 | 146.6<br>144.2<br>141.1<br>135.0 (*c*) | 132.6<br>130.5<br>126.9<br>123.3 | 57.2 | |
| Model compound II | 171.8 (sh)<br>164.7 | 137.6 (*c*) | 127.5<br>121.6<br>115.1 | | |
| PM-TPM (chemical imidization)<br>Poly condensation | 166.0 | 143.0<br>141 (sh)<br>137.3 (*c*) | 129.9<br>121.3 | 57.0 | |
| PM-TPM (one-step imidization) | 165.3 | 143.5<br>140.4 (sh)<br>137.2 (*c*) | 129.3<br>119.8<br>119.3 | 56.4 | |
| BSA-TPM | 166.0 | 145.1 | 128.7 | 56.2 | |
| ODP-TPM | 166.1<br>159.7 (sh) | 143.1 | 116.4<br>130.0 | 56.2 | |
| BP-TPM | 166.0<br>159.0 (sh) | 143.5<br>142.2 | 129.8<br>124.1 | 56.8 | |
| BZP-TPM (chemical) | 166.1 | | 129.6 | 57.6 | 192.1 (carbonyl) |
| BZP-TPM (one-step) | 166.4 | 142.8 | 129.9 | 56.4 | 193.6 (carbonyl) |
| Pyromellitimide PM-ODA (Kapton) | 166.2 | 155.8 (*q*)<br>137.0 (*c*) | 130.9 (*i*)<br>127.6 (*j*, *k*)<br>119.7 (*e*)<br>114.8 | | |
| Pyromellitimide PM-ODA (this work) | 165.6 | 158.1 (*q*)<br>155.1<br>137.1 (*c*) | 127.4 (*j*, *k*)<br>119.4 (*e*) | | |

and BP-TPM. The structures of the model compounds and the polyimides studied here are depicted in Scheme 2, along with the designated abbreviations.

### Measurements

The inherent viscosity, $\eta_{inh}$, of the polyimides was determined using an Ubbelohde viscometer in 0.5 g/dL DMF solutions at 25°C. FTIR spectra were recorded in a Nicolet 510P spectrophotometer. Thermogravimetric analysis (TGA) was conducted using a DuPont TG analyzer 2950 at a heating rate of 5°C/min under nitrogen. Wide-angle X-ray diffractometry (WAXD) was performed on a Siemen's D-500 diffractometer, with a CuK$\alpha_1$ radiation of 1.5406 Å using stacks of PM-TPM films.

Solid-state NMR spectra were recorded under proton decoupling on a Varian Unity Plus 300 NMR spectrometer operating at 75.47 MHz for $^{13}$C. Approximately 300 mg of the sample in a film form or as a powder was packed into a 7-mm-diameter silicon nitride rotors with Kel-F packs. The spectra were obtained under Hartmann–Hann matching conditions with a contact time of 1 ms, a repetition time of 4 s, and a spinning rate of 4.5–5 kHz. The measurements were made using a spin-lock power in radio-frequency units of 60 kHz and 1028 transients per spectrum were typically recorded for each sample. Elimination of spinning side bands was accomplished by the TOSS sequence. Chemical shifts for solid-state spectra were obtained using the right peak of

adamantane at 29.5 ppm as an external reference (see Table I).

## RESULTS AND DISCUSSION

The carbon-13 chemical shifts for the various polyimides and model compounds studied here are given in Table I. The observed chemical shifts were assigned based upon the results of the solution $^{13}C$ spectra of model compounds and soluble polyimides, as well as from reported data,[4,7] and substituent additivity rules.

Both solid-state and solution (in $CDCl_3$) spectra of model compound **I** are shown in Figure 1. It can be observed that some resonance lines present in the solution spectrum are split in the CP-MAS spectrum. In the solid spectrum, an imide carbonyl asymmetric doublet, at 167.8 and 166 ppm, can be observed, and three signals at 146.6, 144.2, and 141.1 ppm can be clearly distinguished in the substituted aromatic region. Splitting of the carbonyl signals was also observed in the solid-state spectrum of *N,N′*-diphenylpyromellitimide, **II** (see Fig. 2), and has been reported for other crystalline polyimide model compounds.[4,5,12]

The observation of splitting for substituted aromatic carbons has been explained by the existence of an asymmetric environment around certain carbons due to conformation and chain packing in the solid state. Splitting of the imide carbonyl carbon is caused mainly by the residual dipolar coupling between $^{13}C$ and $^{14}N$, which is

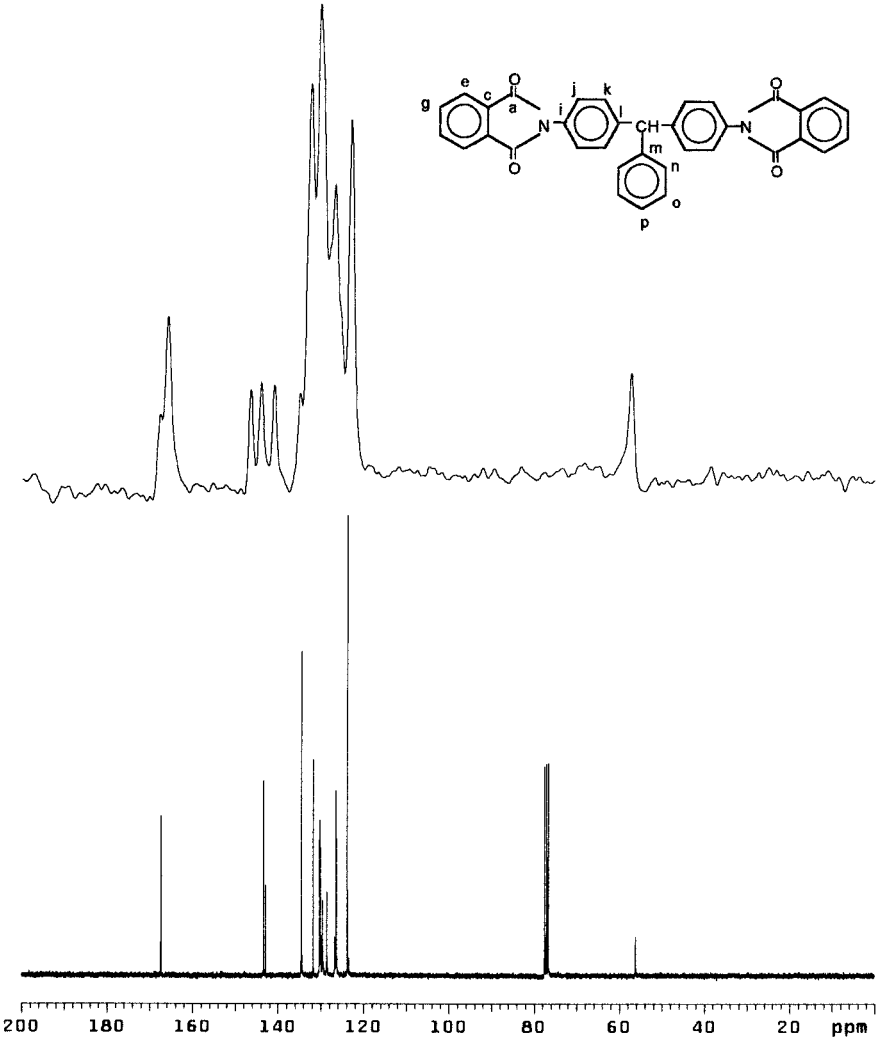



**Figure 1** High-resolution (top) CP-MAS and (in $CDCl_3$, bottom) solution $^{13}C$-NMR spectra of model compound **I.**

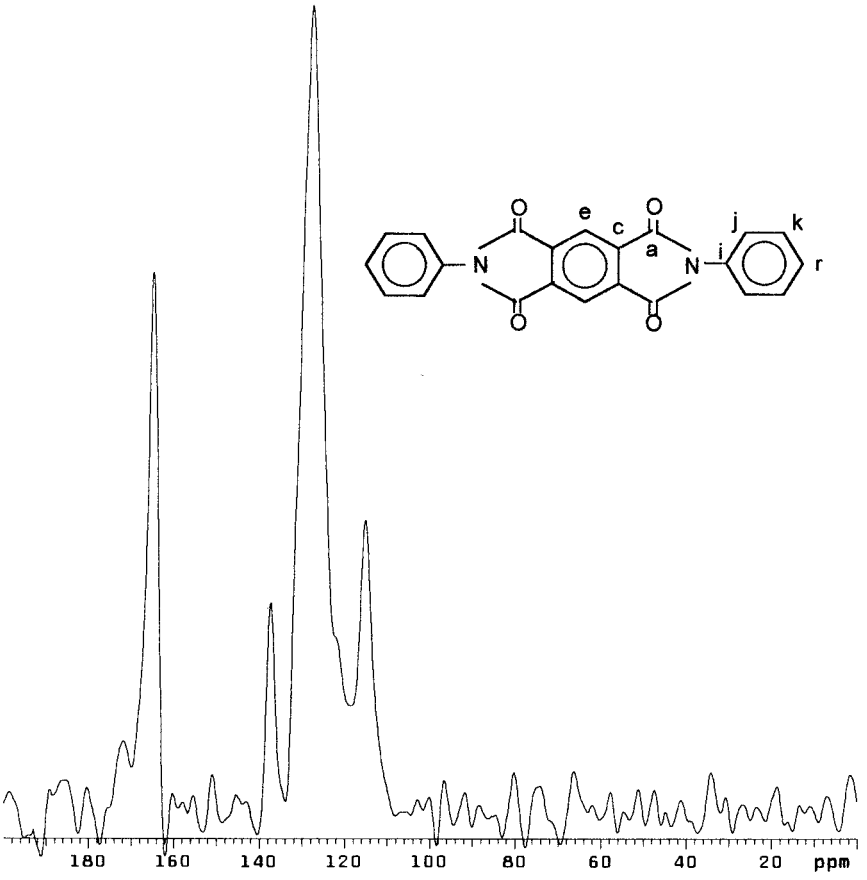



**Figure 2** High-resolution CP-MAS $^{13}$C-NMR spectrum of model compound **II.**

not fully removed by magic angle spinning, and it is not due to crystallographic inequivalence.[4,13]

It is important to state that the splitting of carbonyl signals is also observed in the infrared spectra of model pyromellitimides,[14,15] in substituted *N*-phenylphthalimides,[16] and in the model compounds studied in the present work.[17] Multiple peaks are observed in the FTIR spectra in the region 1700–1800 $cm^{-1}$, where only peaks for the symmetric and asymmetric imide carbonyls stretching modes are expected. Splitting of the carbonyl signals in the FTIR spectra of these compounds has been attributed by some authors to intermolecular dipole–dipole coupling enhanced as the neighboring carbonyl groups pack closer in the crystalline state.[14,15] However, it was demonstrated that the splitting of both in- and out-of-phase carbonyl stretching modes at 1780 and 1710 $cm^{-1}$ in the spectra of the substituted *N*-phenylphthalimides results from Fermi resonance of $\nu$(C═O) with the overtone $2\nu$ of the Ph—CO mode around 885 $cm^{-1}$.[17,18] This explanation is supported by the fact that a split remains in the infrared spectra in the solution of *N*-phenylphthalimides and the model compound **I** studied in the present work.[17]

For PI-TPMs obtained from the chemical imidization of PAA or from the one-step high-temperature polycondensation, the inherent viscosity ranged from 0.4 to 1.4 dL/g depending on the structure of the anhydride moiety.[2,3] The molecular weight of PMDA–ODA was characterized by measuring the inherent viscosity of the corresponding precursor PAA (0.5 g/dL DMF solutions at 25°C). The obtained $\eta_{inh}$ was 2.5 dL/g.

The imidization degree of all studied polyimides was calculated by infrared spectroscopy, and for all samples, the imidization reactions were carried out up to completion. The removal of the residual solvents from the films resulting from the chemical imidization of PAA or from the one-step polycondensation was confirmed by TGA. The content of volatile compounds was below 2 wt % for all the polymers studied.

The $^{13}$C-CP/MAS spectra of PM-TPM obtained by the chemical imidization of the precursor PAA

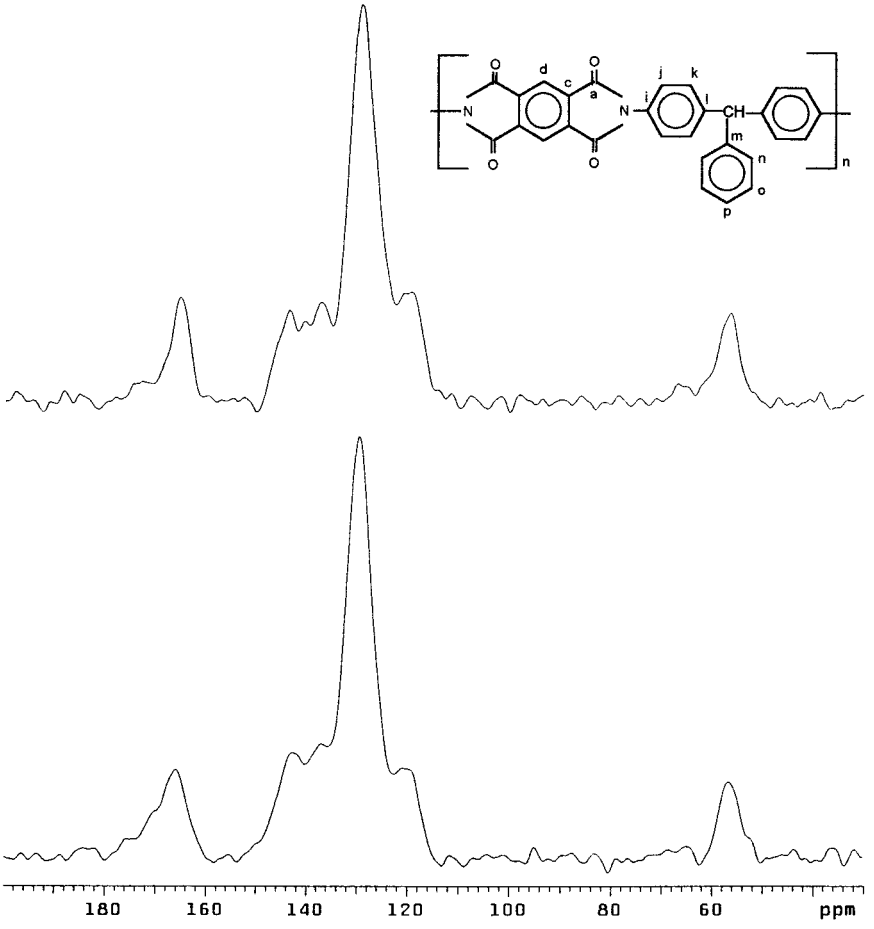



**Figure 3** High-resolution CP-MAS $^{13}$C-NMR spectra of PM-TPM obtained by (top) one-step high-temperature polycondensation and (bottom) chemical imidization of the precursor PAA.

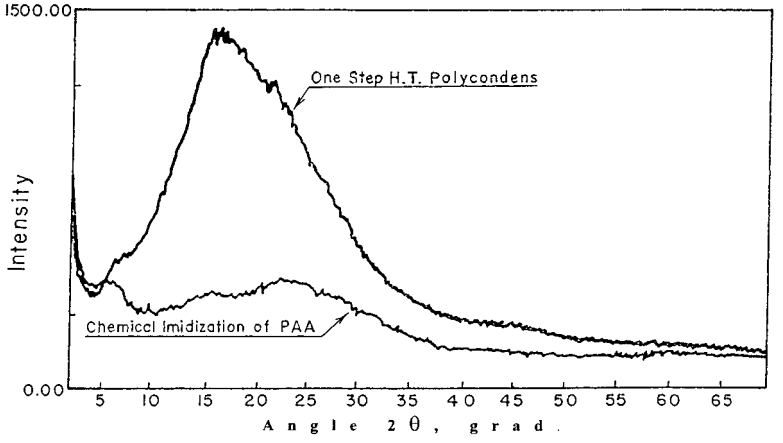



**Figure 4** WAXD pattern of PM-TPM films obtained by chemical imidization and one-step high-temperature polycondensation in nitrobenzene.

and by the one-step high-temperature polycondensation are shown in Figure 3. The latter spectrum resembles that for the same polymer resulting from the thermal imidization of PAA. PM-TPMs have similar molecular weights: Inherent viscosities in DMF at 25°C were 1.4 and 1.1 dL/g for the PM-TPMs obtained by the one-step high-temperature polycondensation and via the chemical imidization of PAA, respectively.

At least six peaks can be distinguished in the spectra of the PM-TPMs: the imide carbonyl peak around 166 ppm, aromatic peaks in the region between 146 and 119 ppm, and a methine signal at 56.0–57.5 ppm. Differences in the peak positions (see Table I) and line shapes between the spectra of PM-TPMs suggest important differences in the short-range order of PM-TPM.[19] Chemical-shift positions of the polyimide obtained by chemical imidization are displaced to lower fields, and the carbonyl, some aromatic, and methine signals are notably broader. In particular, the carbonyl peak position is shifted 0.7 ppm and the methine peak 0.6 ppm downfield with respect to that observed for the polyimide obtained by the one-step high-temperature polycondensation (and to a lesser extent by the thermal imidization of PAA).

The WAXD pattern obtained from the stacks of films with similar total thicknesses of about 100 $\mu$m (see Fig. 4) also evidences remarkable differences in the morphology between the PM-TPMs. Diffraction patterns indicate that an amorphous structure is present in both polyimides, with a significant lower intermolecular packing order for the polymer obtained by chemical imidization of PAA. This feature can be the consequence of dif-

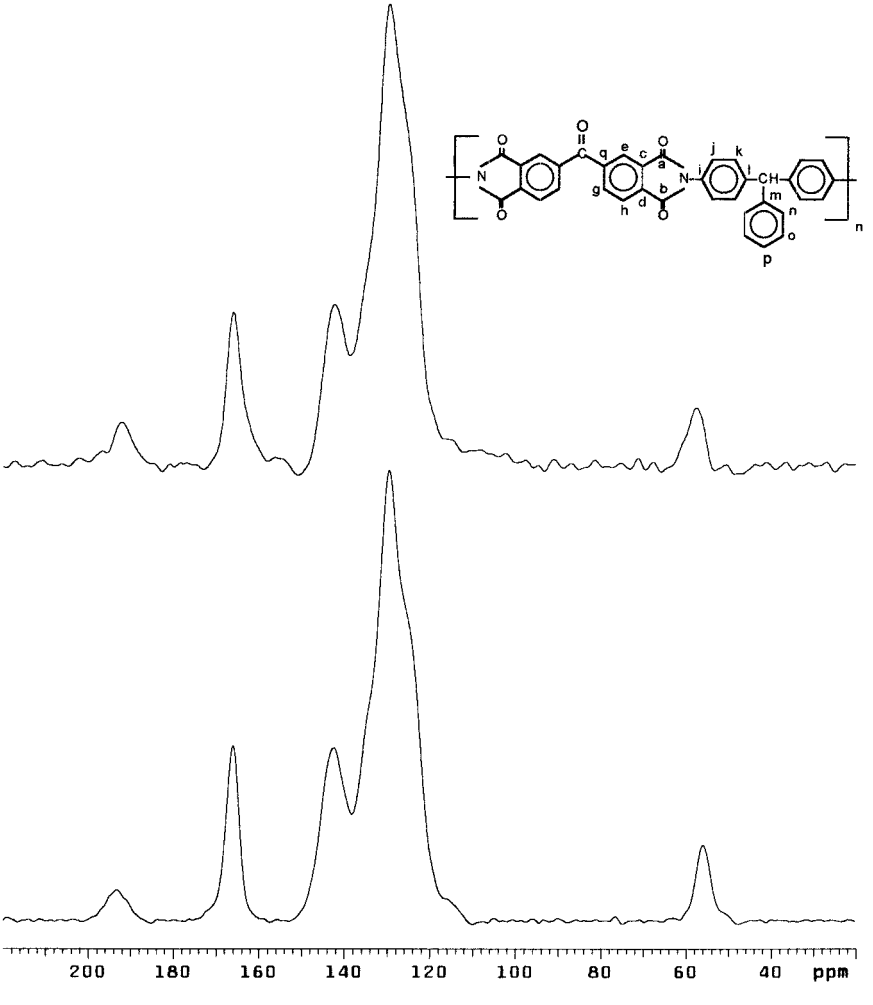



**Figure 5** High-resolution CP-MAS $^{13}$C-NMR spectra of BZP-TPM obtained by (top) two-step chemical imidization and (bottom) one-step high-temperature polycondensation.

ferences in the thermal history and content of isoimide moities in the samples.

An analysis by UV-visible spectroscopy reveals that polymers treated with a mixture of acetic anhydride and *N,N,N′,N′*-tetramethylethylenediamine (50/50 by volume) at room temperature for 20 h (chemical imidization) contain about 13–15% of the isoimide units. Postcyclization heating at 230°C gradually decreases the amount of isoimide to 4–5%.[20]

The presence of isoimides induces important changes in the intermolecular packing of rodlike polypyromelitimides.[16] The thermal isomerization at elevated temperatures is difficult to be completed because of the lack of mobility of the polyimide chains in the glassy state. When PM-TPM is heated at 275°C for 30 min, the isoimide content drops below the sensitivity of the UV-visible spectroscopy. These changes imply an increase in the intermolecular packing order observed by WAXD. However, even after this treatment, the diffraction patterns of the films obtained by chemical imidization did not resemble those for PM-TPM obtained from the one-step high-temperature polycondensation. Similar WAXD patterns and $^{13}$C-CP/MAS NMR spectra were obtained only when the former polymer was heated 60 min at 275°C or 10 s at 350°C.

NMR spectra of polyimide films of BZP-TPM prepared by chemical imidization of PAA, along with that obtained by the one-step high-temperature polycondensation, are shown in Figure 5. Broader lines are observed in the spectrum of the former polyimide as a consequence of the less regular chemical structure obtained by this route. In this spectrum, the position of the methine peak is shifted downfield by 1.2 ppm, in agreement with a carbon with a lower electronic density. As relaxation contributions are not significant in the line shapes of the polyimides spectra, the observed differences for PM-TPM and BZP-TPM evidence that the aryl–imide system shows a lower degree of conjugation in the polyimide obtained by chemical imidization and (to a lesser extent) by thermal imidization of the same precursor, with respect to that obtained by the one-step route. The consequence of conjugation is the shielding due to the electron density present at carbons in the aromatic system.[4]

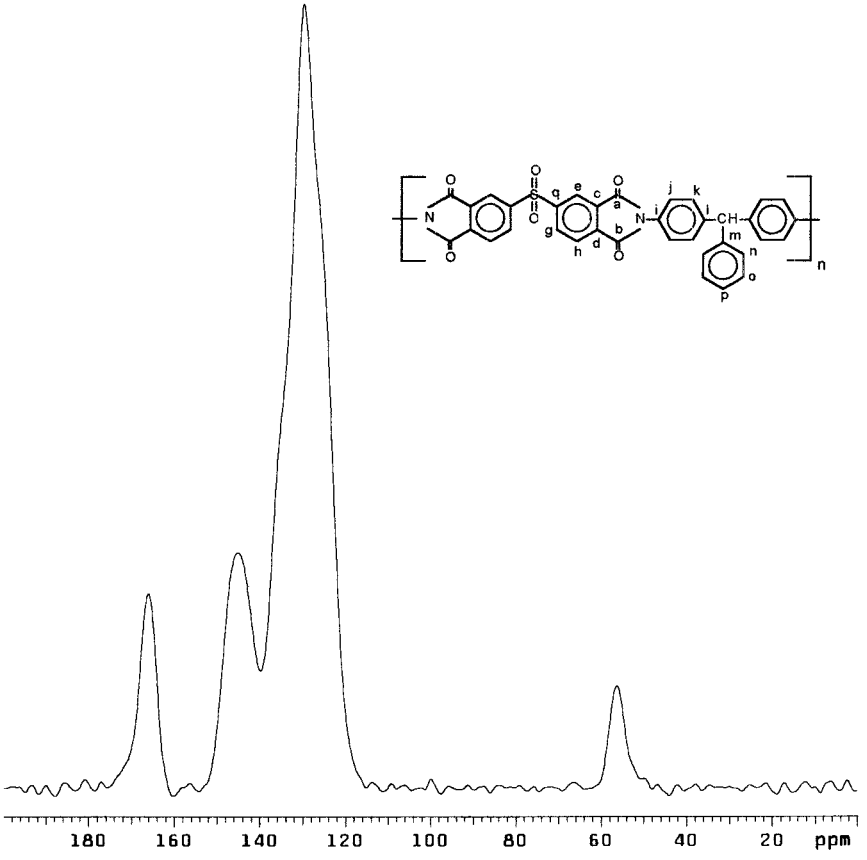



**Figure 6** High-resolution CP-MAS $^{13}$C-NMR spectrum of BSA-TPM.

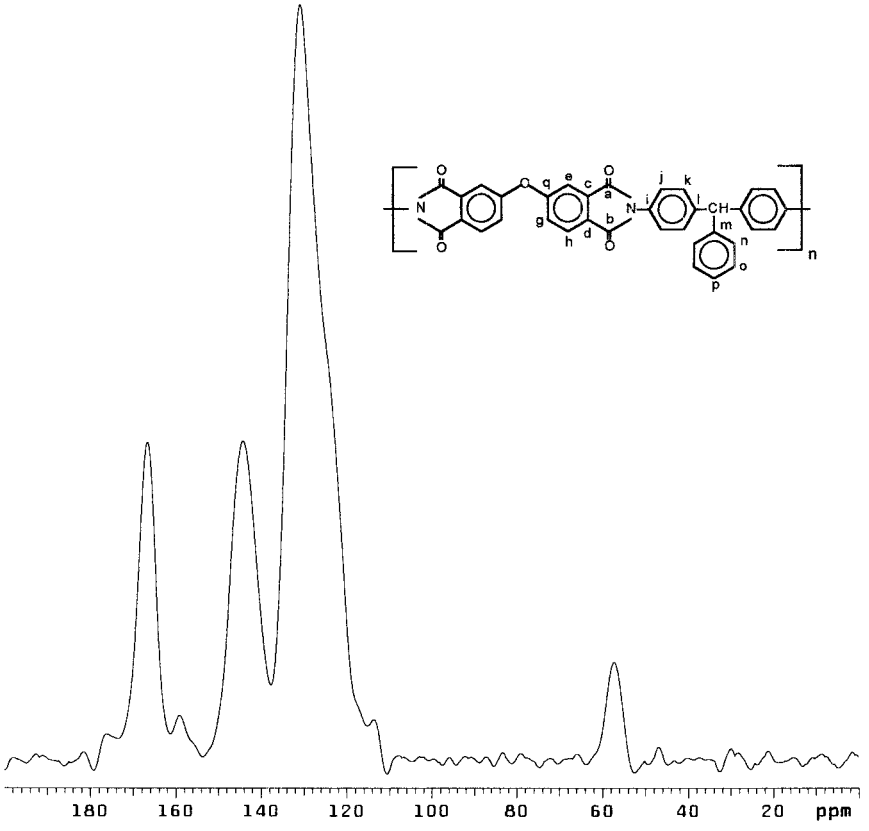



**Figure 7** High-resolution CP-MAS $^{13}$C-NMR spectrum of ODP-TPM.

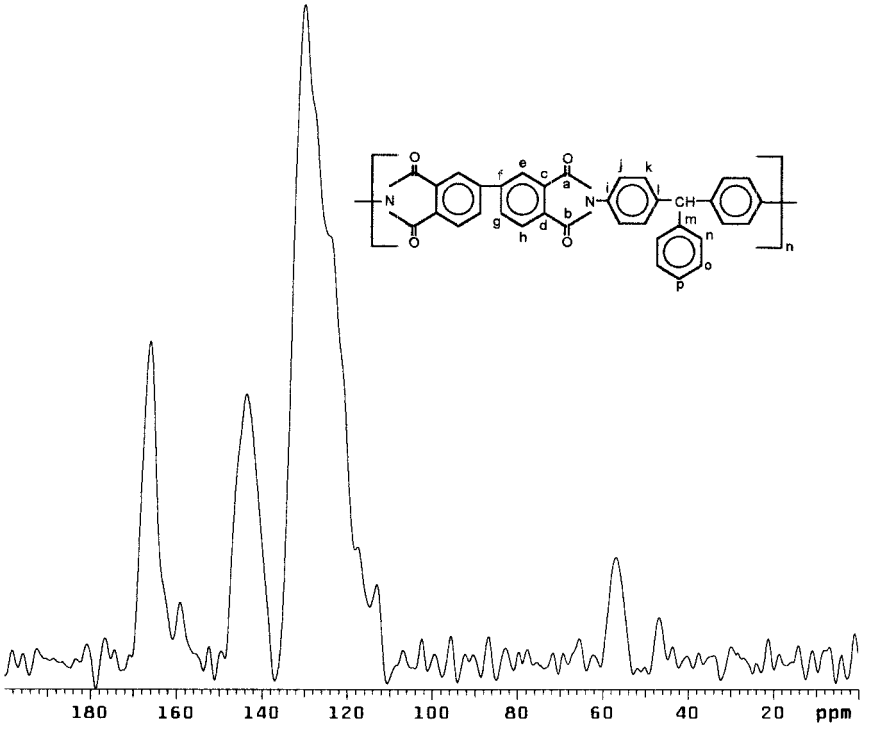



**Figure 8** High-resolution CP-MAS $^{13}$C-NMR spectrum of BP-TPM.

The CP-MAS spectra of BSA-TPM, ODP-TPM, and BP-TPM polyimides prepared by the one-step high-temperature polycondensation are shown in Figures 6–8, respectively. The same peak pattern is observed for these samples and for the BZP-TPM spectrum (see Fig. 5): a broad signal for the imide carbonyl peak, another for substituted aromatic carbons (carbons *l*, *m*, and *q*), one to three signals for the aromatics, and one peak for the methine carbon. There are small differences in the chemical-shift positions and line shapes, but because of the broadness and asymmetry of the peaks, a further analysis is precluded.

The CP-MAS spectra of PM-ODA obtained by the thermal imidization of the corresponding PAA at 300°C for 30 min ($\eta_{inh}$ = 2.4 dL/g, 0.5 g/dL in DMF at 25°C) and a commercial polyimide film Kapton are shown in Figure 9. Assignments were taken from the literature (see Table I).[4,7] Similar features are observed in both spectra, but broader peaks are distinguished for the PM-ODA sample. The most noticeable difference between the spectra is the shape of the carbon directly bound to the phenoxy group (*carbon q*). Two peaks, at 158.1 and 155.1 ppm, can be resolved for the PM-ODA sample (see Table I). These features can indicate differences in chemical composition, conformation, and three-dimensional packing, which result from imidization procedures and postcyclization thermal and mechanical treatments used in the production of Kapton H.

## CONCLUSIONS

The present results show that NMR is particularly valuable in the detection of differences in the three-dimensional structure of aromatic polyimides. The final structures of these polymers are a consequence of the different reaction mechanisms

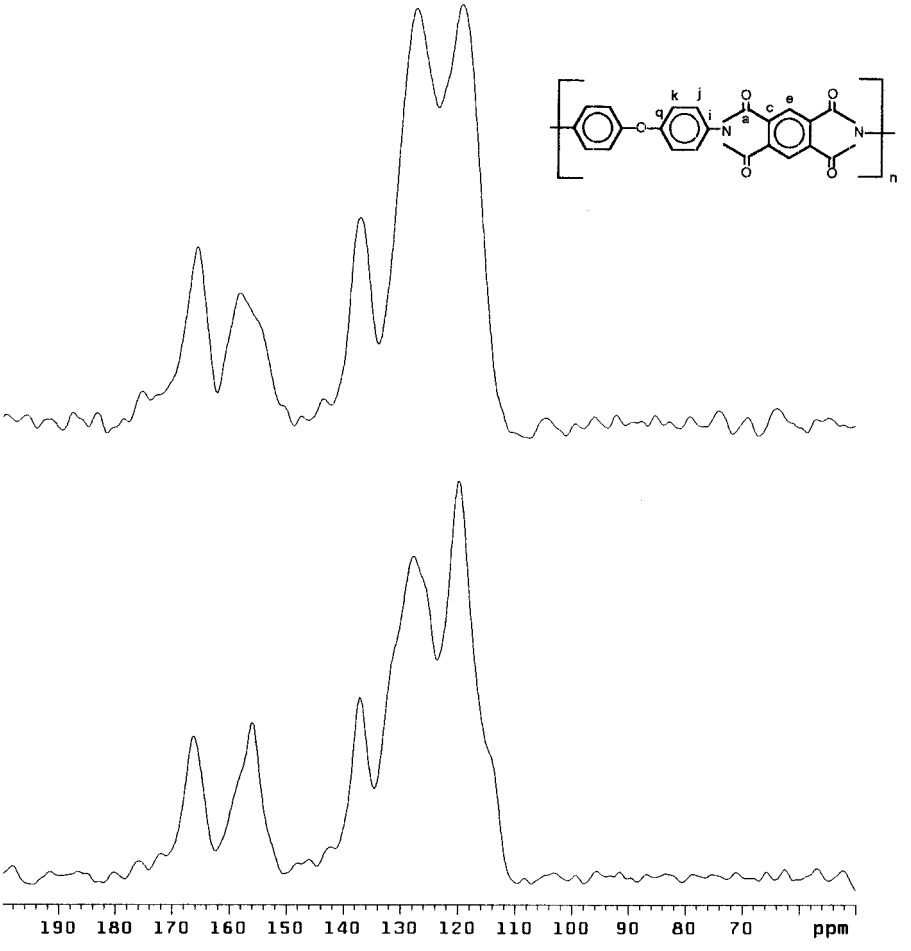



**Figure 9** High-resolution solid-state $^{13}$C-NMR spectra of (top) a home-made pyromellitimide polyamide and (bottom) a Kapton sample.

of the imidization involved during their synthesis. Studies of these systems by solution and 2-D NMR techniques are in progress.

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