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(11) Axelson, D. E.; Levy, G. C.; Mandelkern, L. *Macromolecules* **1979**, *12*, 42.
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High-Resolution Carbon-13 Nuclear Magnetic Resonance Study of Conjugation in Solid Polyimides

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ABSTRACT: Recent theoretical and instrumental advances have made it possible to record high-resolution ^{13}C NMR spectra of polymeric solids. The resolution of these spectra is such that, in general, chemically distinct carbons have separately resolved resonances. We have determined the ^{13}C chemical shifts for a series of insoluble polyimides and appropriate model compounds. The chemical shifts are used to study the electron density differences among the compounds, and the nature of the conjugation along the polyimide chains is then postulated. The conjugation is thought to be an important factor in the high mechanical and thermal stability of these systems.

Introduction

The unusually good chemical and mechanical stability at high temperatures of aromatic polyimides makes them attractive for a variety of applications. They appear promising for use as high-temperature adhesives in bonding metals such as steel and titanium.[1] Their ease in forming charge-transfer complexes with various metal dopants,[2] as well as their increase in electrical conductivity at high pressures,[3,4] suggests that they may have potential for use as organic conductors. In addition, the uniform deformation of some biaxially oriented aromatic polyimides makes them amenable for special mechanical applications.

In order to clarify the relationship between chemical structure and properties of these polyimides, we sought to characterize the nature of conjugation along the backbone. This problem has been studied previously with vibrational spectroscopy,[5,6] ultraviolet spectroscopy,[5-7] and molecular orbital calculations.[8] Recent instrumentation advances allowed us to compare these results with those obtained through ^{13}C NMR. The advantage of using NMR lies in the observation of individual resonances for specific carbon types in the structure. Various polyimides and appropriate model compounds were synthesized in an effort to follow changes in the electron densities of specific carbons by observing their chemical shifts. Once a trend in the electron densities was established, we felt that the nature of the conjugation could be postulated.

The aromatic polyimides used in this study are highly insoluble polymers. Until recently, high-resolution ^{13}C NMR spectra of polymers were obtainable only for samples in solution or in the melt—the widths of these resonances being frequently on the order of a few hertz. In contrast, the spectra of solid, glassy polymers showed lines tens of kilohertz in width, with no resolvable fine structure. The dipolar and anisotropy interactions responsible for these broad lines are averaged to zero in a normal solution or melt by rapid molecular motion. Such motion is restricted in glassy solids. However, by the application of new instrumental techniques, it has been possible to obtain ^{13}C NMR spectra of glassy polymers approaching the quality of those of solutions.[9-11] The broadening resulting from the magnetic interaction between ^{13}C nuclei and protons ($\sim$20 kHz) is removed by dipolar decoupling of the protons.[12] The line width contribution from the chemical shift anisotropy (1–5 kHz) is removed by magic-angle sample spinning.[13] This involves rotating the sample at several thousand revolutions per second about an axis oriented 54.7° from the direction of the static field. The combination of these two techniques results in line widths for glassy, amorphous polymers on the order of 100 Hz. Sensitivity enhancement is offered by a third technique, cross polarization, in which magnetization is transferred from the protons to the naturally abundant (1.1%) carbon-13 nuclei.[14,15] Since the protons repolarize in the static field much more quickly than do the carbons, an additional savings in time is given by this technique. By using dipolar decoupling, magic-angle spinning, and cross polarization simultaneously, we are able to record spectra of the insoluble polyimides and to assign individual resonance lines to magnetically inequivalent carbons. With such spectra it is possible to follow chemical shift changes and to gather information concerning conjugation along the polymer backbone.

Experimental Section

Poly[*N,N'*-bis(phenoxyphenyl)pyromellitimide] was kindly provided as a biaxially oriented film of Kapton H by Dr. J. A. Kreuz of E. I. du Pont de Nemours & Co. The syntheses of three model compounds of this polymer [*N,N'*-bis(phenoxyphenyl)pyromellitimide (DPEP), *N,N'*-diphenylpyromellitimide (DPP), and *N,N'*-dicyclohexylpyromellitimide (CHP)] have been described previously.[5] 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-methylenebis[aniline] (MDA), and nadic anhydride (NA) were obtained commercially (Aldrich Chemical Co.) and used without further purification. An aromatic imide macromer made of BTDA, MDA, and NA—hereafter designated PMR[16-19]—and the remaining model compounds were synthesized by Dr. R. Lauver of NASA, Lewis Research Center, and Mr. A. Wong of Case Western Reserve University.

The ^{13}C NMR spectra were recorded at 37.7 MHz with a Nicolet Technology NT-150 spectrometer equipped with a cross polarization accessory. Radio-frequency amplifiers delivering $\sim$550

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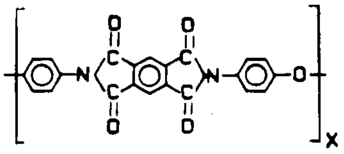
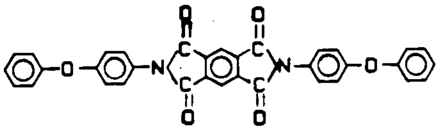
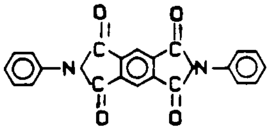
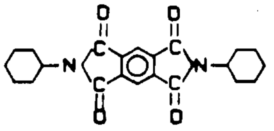
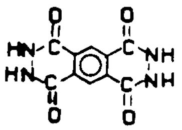
Table I
Structures and Designated Abbreviations for the Model Compound Series Based on Poly[*N*,*N*′-bis(phenoxyphenyl)pyromellitimide]

figure no.	structure	designation
1		Kapton
2		DPEP
3		DPP
4		CHP
5		PH

W at 150 MHz and ~1000 W at 37.7 MHz were adjusted to satisfy the Hartmann–Hahn condition at roughly 80 kHz.[14] A single coil was used to preserve the match throughout as much of the sample volume as possible. Isolation of the carbon and proton frequencies was obtained with a 75-Ω coaxial cable cut to a quarter wavelength of the proton Larmor frequency of 150 MHz. The isolation in the probe was typically 40 dB, to which two filters added another 50 dB. The copper coil was wound on a Kel-F cylindrical support 10 mm in diameter and 15 mm in length. Effective decoupling power under these conditions was ~20 G, as measured by the proton 90° pulse [$(\tau_{360°} - \tau_{180°})/2$] and also by off-resonance decoupling of dioxane. Dipolar decoupling fields of roughly this magnitude were required to obtain high-resolution spectra of some of the model compounds.

The samples were packed into hollow Beams-Andrew rotors,[13,20] which were machined from Kel-F and spun at speeds between 2 and 2.5 kHz. Maximizing the intensity of the carbonyl peak of glycine served to set the magic angle to 54.7 ± 0.1°. A small amount of poly(oxymethylene) was placed in each of the samples to serve as a reference; its resonance is 90 ppm downfield from that of tetramethylsilane (Me_4Si). The cross polarization contact time used was 1 ms, and the delay between pulse sequence repetitions was 3 s. Digital resolution in the free induction decays was 10 Hz. For the highly crystalline model compounds roughly 20 000 transients were accumulated, while 5000 were sufficient for the partially amorphous polymers and macromers. Spin temperature alternation was used to eliminate various artifacts.[21] The static field was not locked during accumulation.

Results and Discussion

There are two general types of compounds which are of interest here: those related to poly[*N*,*N*′-bis(phenoxyphenyl)pyromellitimide], or Kapton (registered trademark of du Pont), and those related to polyimides derived from PMR, a macromer series based on imidized 3,3′,4,4′-benzophenonetetracarboxylic dianhydride. The structures of these two groups of compounds are given in Tables I and III, along with designated abbreviations. The respective chemical shift data are tabulated in Tables II and IV. The assignments given are only tentative in the case of the various phenyl carbons. An insufficient number of appropriate model compounds was available to make the assignments certain. However, all are consistent with those spectra which we did record as well as with calculated electron densities.[8] Further work on the assignment of the phenyl carbons is complicated by the extremely low solubility of most of the compounds (making solution NMR difficult) and by the large number of transients required to obtain spectra with high signal-to-noise ratios in the cross polarization experiments (making tedious the measurement of the polarization transfer rate T_{IS}(SL)—often useful in distinguishing among carbons[10]). In any case, one of our purposes in reporting these spectra is to show the degree of resolution obtainable routinely in an NMR experiment on solid imide compounds. The primary information about conjugation will be drawn from the carbonyl carbon resonance.

Carbon-13 chemical shifts have long been recognized as a probe for assessing the electronic structure of aromatic compounds. In these systems, the shielding is governed primarily by the electron density at each carbon. In fact, the general trends have been interpreted by Alger et al.[22] using the equation

$$\delta(^{13}C) = 100\Delta Q_\pi + 67\Delta Q_\sigma - 76\Delta P$$

Table II[a]
Carbon-13 Chemical Shifts for the Poly[*N*,*N*′-bis(phenoxyphenyl)pyromellitimide] Series

compound	imide carbonyl	tertiary central phenyl	quaternary central phenyl	bound to ether oxygen	N-substituted phenyl	aliphatic
Kapton	167.8	139.3	129.5	159.5	129.5 121.7[b]	
DPEP	164.7 162.1	136.1	131.0	154.3 152.8	127.9 123.8 120.1[b] 118.1 115.5 113.4	
DPP	165.2	139.8	131.5		131.5 128.4 117.5[b]	
CHP	164.1	136.7	115.5			49.7 43.0 29.5 25.9
PH	157.9	129.5	124.3			

[a] All numbers listed in Tables II and IV are chemical shifts of indicated carbons in ppm downfield from tetramethylsilane. Estimated accuracy is ±0.5 ppm. [b] These are the phenyl carbons bound directly to the imide nitrogen.

Table III
Structures and Designated Abbreviations for the Model Compound Series Based on PMR

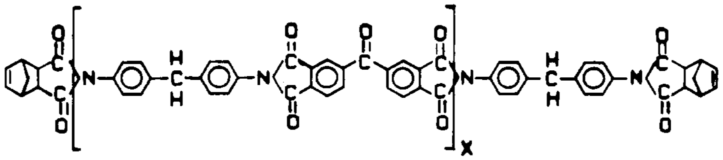
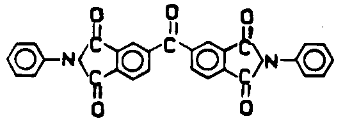
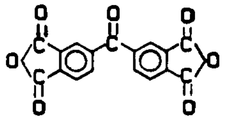
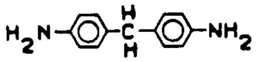
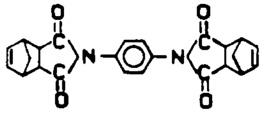
figure no.	structure	designation
6		PMR
7		BTDP
8		BTDA
9		MDA
10		PBN

Table IV
Carbon-13 Chemical Shifts for the PMR Series

compound	central carbonyl	imide carbonyl	tertiary central phenyl	quaternary central phenyl	N-substituted phenyl	backbone methylenes	norbornene aliphatics
PMR	196.2	178.1 171.3	138.2	131.5	131.5	~50	53.8 47.6 42.4
BTDP	196.2	165.7	140.3 136.7	124.2	130.5 124.2[a]		
BTDP	195.5	172.4	142.4	134.6 132.0			
MDA					145.5 142.9 132.6 130.0 128.9 126.9 117.0 115.0 113.9[a]	39.9	
PBN		177.1			133.1 131.5 127.9[a]		50.7 45.1 43.0

[a] These are the phenyl carbons bound directly to the imide nitrogen.

where ΔQ_π, ΔQ_σ, and ΔP are the π charge, the σ charge, and the sum of the mobile bond orders (relative to the values of benzene), respectively. Substituent-induced chemical shifts reflect the redistribution of charge caused by the substituent—the changes in electron density. The distribution of charges can be influenced by many factors, including mesomeric, π-inductive, steric, direct electric field, or anisotropy effects. Mesomeric effects are primarily observed for large conjugated systems and reflect the substituent's ability to produce a mesomeric release or withdrawal of electrons. Although the π-inductive effect has been studied for a variety of systems, considerable controversy still exists in its interpretive use. The electric field effect will polarize the C–H bond, decrease the electron density at the proton, and consequently increase it at the carbon nucleus. The steric effects result from several effects of a substituent: (1) polarization of nearby bonds, (2) diminishing the conjugation of perturbed groups, and (3) changing bond angles.

We are examining a series of compounds with very similar electronic structures. The electronic differences arise primarily from slight changes in bond order or conjugation, and not from drastic changes in the nature of the bonding. The chemical shift changes are then determined predominantly by differences in electron density.

A. Poly[*N*,*N*′-bis(phenoxyphenyl)pyromellitimide] and Model Compounds. The spectrum of Kapton is shown in Figure 1. Because of the electron-withdrawing effect of the oxygen, the carbonyl carbon resonance occurs at the lowest field, 168 ppm downfield from Me_4Si. The calculated electronic charge of this carbon is +0.228, on a scale in which −1 is the charge of one electron.[8] (The electronic charges reported in ref 8 are based on total valence electron densities for the specified atoms, as calculated by the Pariser–Parr–Pople method. The charges represent deviations from a neutral distribution of the π

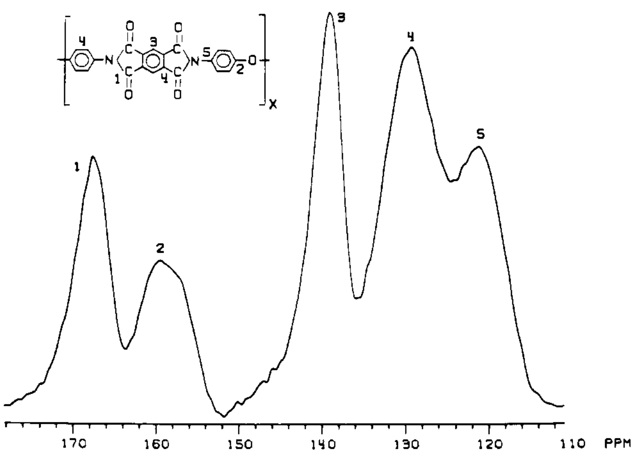


Figure 1. High-resolution ^{13}C NMR spectrum of poly[*N,N'*-bis(phenoxyphenyl)pyromellitimide], or Kapton, at 37.7 MHz. Assignments of the individual resonances are indicated. Experimental conditions are given in the text. Spinning rate: 2.5 kHz.

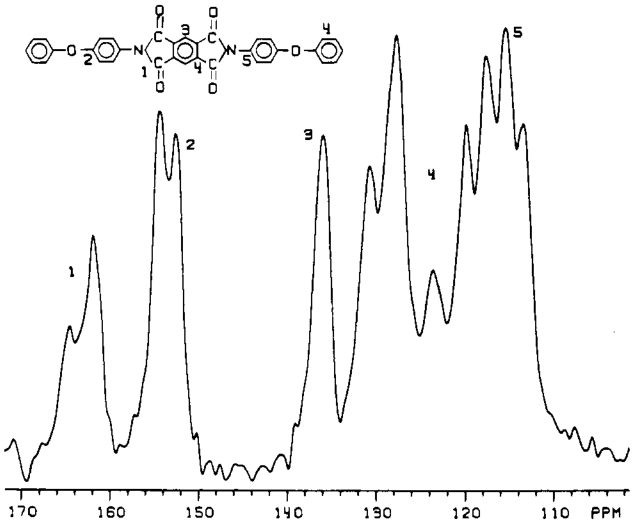


Figure 2. High-resolution spectrum of *N,N'*-bis(phenoxyphenyl)pyromellitimide (DPEP). Spinning rate: 2.5 kHz.

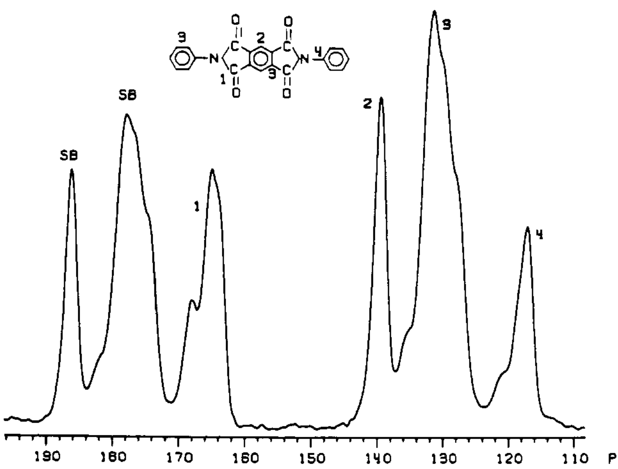


Figure 3. High-resolution spectrum of *N,N'*-diphenylpyromellitimide (DPP). Spinning rate: 1.8 kHz.

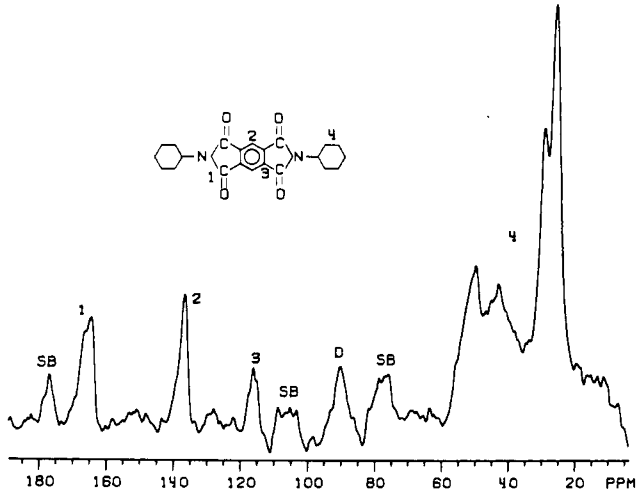


Figure 4. High-resolution spectrum of *N,N'*-dicyclohexylpyromellitimide (CHP). Spinning rate: 2.3 kHz.

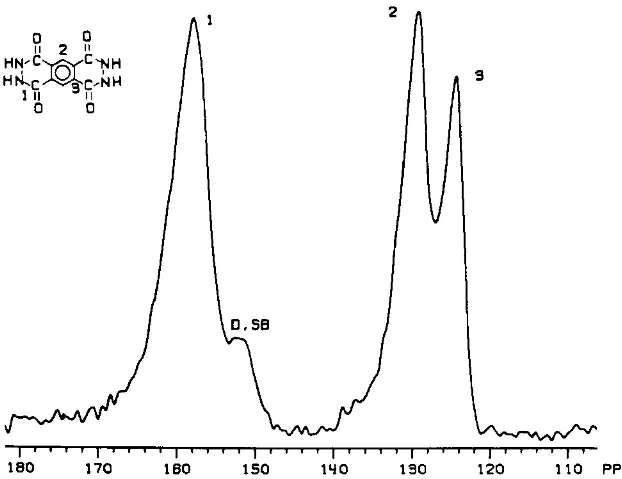


Figure 5. High-resolution spectrum of pyromellitic hydrazide (PH). Spinning rate: 2.3 kHz.

electrons in the molecules.) The carbons directly bonded to the oxygen in the phenoxyphenyl group absorb at 160 ppm. The protonated carbons of the central phenyl ring (in the pyromellitimide group) appear at 139 ppm, which is consistent with a less positive charge of +0.080.[8] All other carbons in the phenyl rings of Kapton are calculated to have higher electron densities and therefore resonate at higher fields. The phenoxyphenyl carbons directly bonded to the imide nitrogen have a charge of −0.033, the most negative of all phenyl carbons.[8] They resonate at the highest field, 122 ppm. The protonated phenoxyphenyl carbons and the quaternary central phenyl carbons have roughly the same calculated electron densities; they appear at 130 ppm.

The spectra of four model imide compounds are shown in Figures 2–5. The results of assigning specific carbons to individual resonance peaks parallel those for Kapton, with the exception of CHP (Figure 4). Here the cyclohexyl carbons resonate at much higher field, between 50 and 25 ppm. This is a result of the higher electron density near these carbons afforded by the increase in number of directly bonded hydrogens. One of the most noticeable differences among the spectra is the considerable change in line width in going from Kapton to the model compounds. The biaxially oriented Kapton film is semicrystalline with a high amorphous content.[5,23] While carbons in the crystalline domains would be expected to give rise to sharp, well-resolved peaks because of the homogeneity of their local environments (assuming no large bulk susceptibility differences), those in the amorphous regions would not. The isotropic chemical shift dispersion for glassy amorphous polymers has been observed to limit resolution previously[10] and could easily account for the

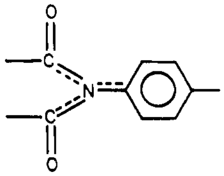
5-ppm line width seen for Kapton. (Relaxation contributions to the line width are not nearly so significant.[24]) The isotropic chemical shift dispersion is intrinsic to the sample and is not a result of instrumental limitations. It arises from differences in conformations along the chain and from differences in three-dimensional chain packing in the sample. Such variations in conformation and packing do not occur for the model compounds, which are entirely crystalline with well-defined structures. The resultant line width observed for these compounds is roughly 2 ppm, although this is by no means a lower limit.

The improvement in spectral resolution which accompanies the onset of complete crystallinity in the model compounds allows the observation of splitting of various peaks. This splitting dominates the spectrum of DPEP, Figure 2. Each peak in the displayed region is real; none are spinning sidebands (SB), which complicate some of the other spectra. (These sidebands arise when spinning at a frequency less than the range of the chemical shift anisotropy.) There are several possible contributions to the splittings; the importance of each depends upon the particular carbon under consideration. For the carbons in close proximity to the imide nitrogens, the primary cause of splitting is probably the dipolar coupling of ^{13}C and ^{14}N. This coupling is not completely removed by magic-angle spinning because the nitrogen quadrupole displaces slightly the effective field direction from that of the static field. Thus, since the angle between the effective field and the rotation axis is not 54.7° for these carbons, the dipolar coupling with nitrogen is not eliminated. The spectrum is then dependent upon the relative strengths of the quadrupolar and Zeeman fields. Most frequently (when neither the quadrupolar nor Zeeman field is overwhelmingly dominant), the result is an asymmetric doublet,[25] such as observed here for the imide carbonyl carbons. It should also be noted that these resonances are broadened by deviation from the magic angle caused by the quadrupole. The chemical shift anisotropies of the nearby carbons are not averaged completely to their isotropic values.

The carbons directly bound to the ether oxygen are also split in DPEP, probably because of the difference in the para substituents of the two phenyl rings. An additional cause of inequivalency among these and the remaining carbons is the various conformations which are possible in DPEP. X-ray diffraction has determined the oxygen bond angle in the phenoxyphenyl group to be 126° in the crystalline state.[26] Furthermore, the two phenyl rings of the phenoxyphenyl are skewed from coplanarity by 35°, where a conformational energy minimum occurs in the Morino structure.[27,28] These effects result in a magnetic inequivalence of the phenoxyphenyl carbons, the phenyl carbons, and the imide carbonyl carbons due to different electronic shieldings. The relative importance of conformational differences has not yet been determined, although they probably are not as significant as the quadrupolar and substituent influences discussed above. They may contribute only to broadening of the resonances and not to distinct splitting. In any case, however, this is a situation in which the spectrum of the solid is considerably more detailed and potentially more informative than that anticipated for the solution (assuming sufficient solubility).

The relative intensities of some of the peaks in the cross polarization spectra do not appear to be internally consistent. One case is that of pyromellitic hydrazide (PH), which is obtained by digestion of Kapton with hydrazine.[29] The spectrum and assignments are presented in Figure 5. The intensity of the carbonyl carbon peak is considerably greater than that of the quaternary phenyl carbons and relatively greater than that of carbonyl resonances in Kapton and its other model compounds. This results from the proximity of the NH group to the carbonyl. The efficiency of polarization transfer is related to the strength of the magnetic field generated by protons at the carbon nucleus. This field drops off as the cube of the distance between the carbon and the protons. The additional proton on the nitrogen of PH allows a more efficient cross polarization for the carbonyl carbon and an attendant increase in intensity of the resonance. The relative intensities of the two tertiary central phenyl and four quaternary central phenyl carbons can be explained in an analogous fashion.

Information concerning the nature of conjugation along the backbone of Kapton and its model compounds may be derived from the chemical shifts. The form of conjugation postulated by frequency shifts of bands in vibrational spectroscopy is as follows:[5,6]



The ^{13}C NMR resonances of most interest in evaluating this model are those of the carbonyl carbon and of the phenyl carbon directly bonded to the nitrogen. For the model compound DPEP the carbonyl peak is split into two peaks at 164.7 and 162.1 ppm (Table II). The corresponding resonance for DPP occurs at 165.2 ppm, and that for Kapton at 167.8 ppm. This trend of increasing chemical shifts indicates decreasing electron densities, by arguments given earlier. (The quadrupolar interaction makes it difficult to assign the center of gravity of the carbonyl carbon resonance. The changes in chemical shifts for this series of compounds are not then interpretable on a strictly quantitative basis. Nevertheless, the quadrupole splitting is not so large as to obscure, on a qualitative basis, the increasing chemical shifts for this series of compounds.) The suggestion is then that the indicated conjugation increases in the order Kapton, DPP, and DPEP, since for more highly conjugated systems the bond order of the carrbon–nitrogen bond increases and the electron density at the carbonyl carbon will be higher. This scheme is corroborated by the behavior of the phenyl carbon directly bonded to the nitrogen. Chemical shifts are recorded at 113.4, 117.5, and 121.7 ppm for DPEP, DPP, and Kapton. Again this sequence suggests decreasing electron density and therefore decreasing levels of conjugation. The vibrational spectra[5,6] support this conclusion as well. The frequencies of the imide II and imide III modes increase in the order Kapton, DPP, and DPEP, indicating an increase in the bond stiffness of the carbon–nitrogen bonds and a resultant increase in electron density of the carbonyl carbons. On the basis of this evidence, the model proposed above appears reasonable.

In order to check that the observed chemical shift changes were caused by conjugation differences, we thought it desirable to examine model compounds in which conjugation is known not to exist. In the two compounds used, CHP and PH (Figures 4 and 5), the lack of an aromatic substituent at the nitrogen precludes conjugation. This is substantiated by the low imide II and imide III frequencies in the vibrational spectra of CHP.[5] Based upon the previous NMR results, the expectation was that the lack of conjugation and correspondingly low electron density would yield a high value (~170 ppm) for the

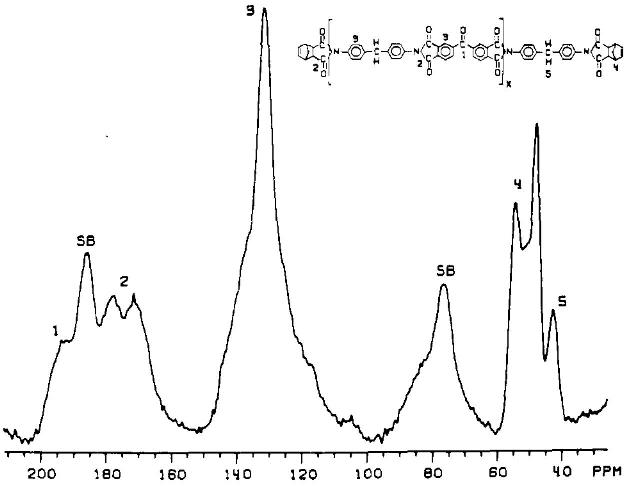


Figure 6. High-resolution spectrum of PMR, a macromer polymerized from monomeric reactants described in the text. Spinning rate: 2.1 kHz.

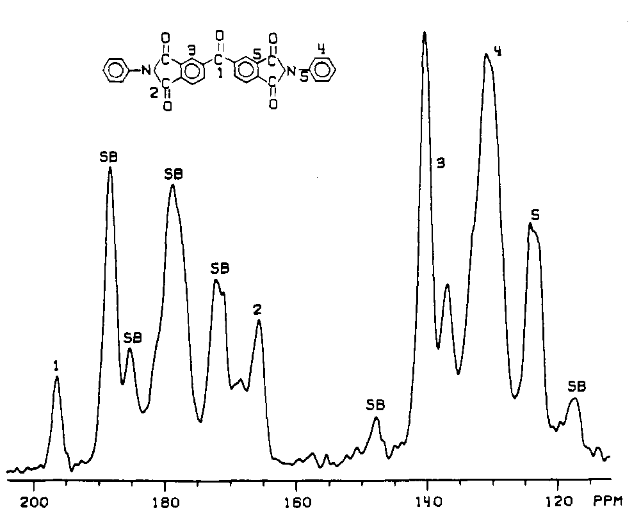


Figure 7. High-resolution spectrum of the N,N'-diphenyl imide of 3,3′,4,4′-benzophenonetetracarboxylic acid (BTDP). Spinning rate: 1.9 kHz.

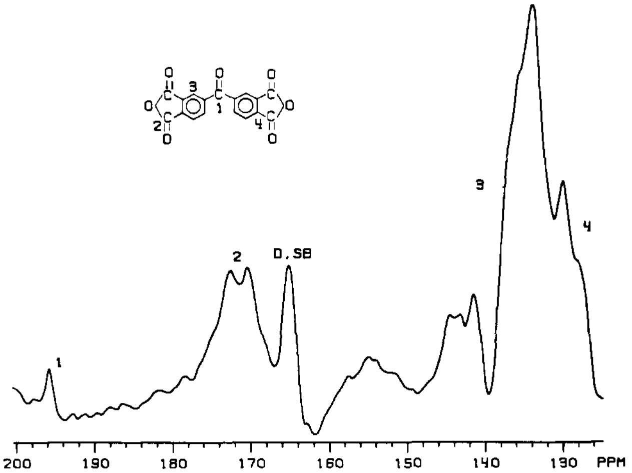


Figure 8. High-resolution spectrum of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA). Spinning rate: 2.3 kHz.

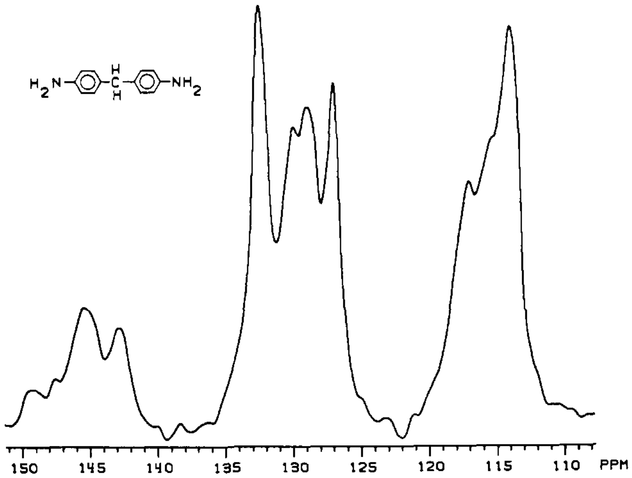


Figure 9. High-resolution spectrum of 4,4′-methylenebis[aniline] (MDA). Spinning rate: 2.3 kHz.

carbonyl carbon chemical shift. However, values of 164 ppm for CHP and 158 ppm for PH are observed. These chemical shifts at relatively high field indicate more electron density at the carbonyl carbon than for Kapton and the other model compounds, even though there is known to be no conjugation. The explanation for this behavior lies in the difference in the hybridization state of the nitrogen atom. In Kapton, DPEP, and DPP, the nitrogen is sp^2 hybridized, while in CHP and PH the hybridization is sp^3.[5] When nitrogen is sp^2 hybridized, the orbitals are coplanar and permit the increase in bond order associated with conjugation. In sp^3 hybridization, however, the arrangement of the orbitals is pyramidal, and conjugation cannot occur. The two nitrogen electrons not involved in bonding occupy one of the sp^3 hybrid orbitals. Because of the pyramidal arrangement of the orbitals, the unbonded electron pair is in close proximity to the imide carbonyls. The fact that these electrons are not directly bound to the carbonyl does not prevent them from shielding the carbon nucleus. This change in hybridization exemplifies some of the problems in correlating chemical shifts to conjugation. However, as long as the fundamental nature of the bonding is not drastically altered (a condition satisfied by Kapton, DPP, and DPEP), we feel that chemical shifts can be used as a probe of slight changes in bond order and conjugation.

B. PMR and Model Compounds. PMR is a term used by the National Aeronautics and Space Administration to designate the polymerization of monomeric reactants consisting of the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), 4,4′-methylenebis[aniline] (MDA), and the dimethyl ester of 3,3′,4,4′-benzophenonetetracarboxylic acid (BTDE).[17] The result of this reaction is a series of macromers with varying molecular weights. The PMR used in this study has an average molecular weight formulated from monomer composition[17] of 1500. The structure is shown in Table III; the average number of BTDE units in the distribution of macromers of this sample is 2.1. Various model compounds of this addition-type imide prepolymer were chosen as well: the N,N'-diphenyl imide of 3,3′,4,4′-benzophenonetetracarboxylic acid (BTDP), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 4,4′-methylenebis[aniline] (MDA), and 1,4-phenylbisnadimide (PBN).

The main objectives of recording the spectra of PMR and its model compounds were to verify the findings on the conjugation of Kapton and to analyze the effects on electronic structure of the benzophenone carbonyl. The spectra are shown in Figures 6–10, and the chemical shifts are tabulated in Table IV. The central carbonyl of the benzophenone group is observed at 196 ppm, in good agreement with previously reported solid-state NMR results.[30] At considerably higher field, roughly 170 ppm, the imide carbonyl carbons absorb. The various phenyl car-

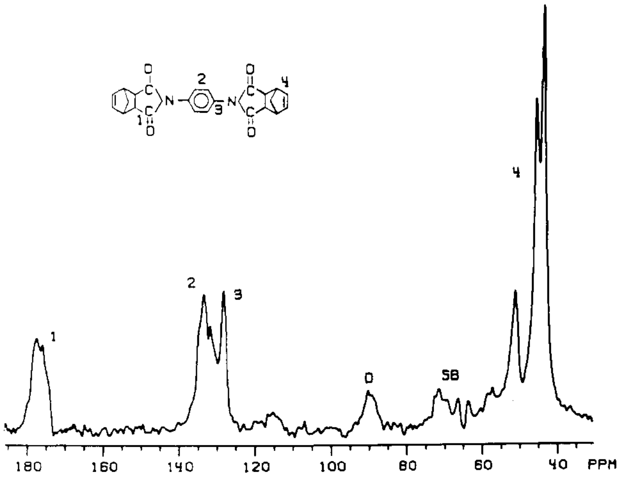


Figure 10. High-resolution spectrum of 1,4-phenylbisnadimide (PBN). Spinning rate: 2.3 kHz.

bons are observed between 145 and 115 ppm, with the lower end of this range generally attributable to the phenyl carbons directly bonded to nitrogen. The aliphatic carbons, both in the backbone and in the norbornene rings, absorb at approximately 45 ppm.

As expected from the conformational and packing variations available to PMR because of its chain length, this macromer's line width is greater than that of the model compounds. No fine structure is resolved in the phenyl carbon peak of PMR at 131.5 ppm, while in the BTDP spectrum four phenyl peaks are distinguished clearly. The line widths of PMR are considerably less than those of Kapton, however. The packing and conformational differences in PMR are not so great, because of its much shorter chain length.

Conjugation along the backbone may be followed with the same rationale as presented for Kapton and its models. The imide carbonyl resonance of BTDP occurs at 166 ppm. Since this is the carbonyl peak farthest upfield, the BTDP is the most highly conjugated of these compounds, followed by PMR at 171 ppm, BTDA at 172 ppm, and PBN at 177 ppm. These results parallel the Kapton study in that those model compounds most closely related to the macromer or polymer (i.e., BTDP for PMR and DPEP for Kapton) have the highest degree of conjugation. A lower amount of chain twisting and improved crystallinity relative to the macromer of polymer is probably the cause. The second imide carbonyl resonance in PMR at 178 ppm arises from the nadimide group and agrees well with the carbonyl chemical shift of PBM at 177 ppm. Finally, we point out that the central carbonyl of the benzophenone group resonates at 196 ppm, indicating very little electron density in the vicinity of this carbon. Conclusions about the conjugation at this point cannot be drawn on the basis of chemical shift comparison with the imide carbonyls because of the considerable difference in electronic environments. In fact, it has been shown from ^{13}C solution studies[31] that the benzophenone carbonyl resonance at 196 ppm is at relatively high field, indicating some degree of conjugation between the two phenyl rings.

Summary

We have shown that high-resolution ^{13}C NMR spectra of solid polyimides and model compounds can be obtained with magic-angle spinning, dipolar decoupling (~80 kHz), and cross polarization. The resolution of these spectra is sufficient to permit assignment of individual resonances to individual carbon types in the samples. For some of the model compounds, splitting of the resonances occurs, due to incompletely averaged ^{13}C–^{14}N dipolar couplings, to substituent effects, and possibly to conformations frozen in the solid state. The suggested correlation between chemical shift and electron density, and subsequently between electron density and the degree of conjugation, is not above suspicion. However, we feel that this assumption is justified for the compounds to be compared if the nature of the bonding does not vary significantly and if the crystal structures are reasonably similar. Both of these conditions are satisfied for many of the compounds in this study; the effect of a change in hybridization of the imide nitrogen has been examined with the remaining model compounds. The results indicate that conjugation does occur in the polyimide backbone, involving the imide carbonyls, the nitrogen, and the attached phenyl ring. Some of the low molecular weight model compounds have increased conjugation, presumably because of crystal structure differences. These conclusions agree well with those from ultraviolet and vibrational spectroscopies.

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