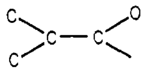

of predominant enolate character for the akali metal derivatives of butyric esters in THF, carbanion character increasing somewhat with the heavier alkali metals. The OR group must, however, have considerable freedom of rotation except for the lithium derivatives at low temperature, where complete planarity is attained of the whole structure.

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Carbon-13 Nuclear Magnetic Resonance Study of Ethylene–Butene Copolymers

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ABSTRACT: The ^{13}C NMR spectra of ethylene–1-butene copolymers prepared by both a titanium and a vanadium catalyst system show peaks which can be assigned to a large number of sequences expected from copolymerization. We do not, however, detect any head-to-head polymerization of butene as reported recently. Moreover, we feel that peaks attributed to a head-to-head butene dyad are due rather to an isolated ethylene in a BEB sequence. Further, the three peaks observed in the methyl region of the spectrum are assigned to B-centered triads, as opposed to branches in positions having different tacticities as reported earlier. Finally, these data suggest that the ethyl brances in low-density polyethylene are not all isolated branches.

Introduction

Recently, Dechter and Mandelkern[1] (D–M) reported on the ^{13}C NMR spectrum of an ethylene–1-butene copolymer (hereafter referred to as ethylene–butene copolymer) containing about 10 mol % 1-butene. Their spectra clearly show the presence of 1,3-diethyl branching, as evidenced by several discrete peaks in their spectrum due to this moiety. They also claim to have 1,2-diethyl branches, which would arise from head-to-head polymerization of two butene units.

We have studied several ethylene–butene copolymers where the 1-butene level has ranged from 10 to 80 mol %. Furthermore, these polymers have been prepared with both a titanium-based catalyst system and a vanadium-based catalyst system. We have shown[2] that with ethylene–propylene copolymers the titanium catalyst gives isotactic propylene sequences and exclusively head-to-tail propylene polymerization even when up to two ethylene units are inserted between propylene units. On the other hand, vanadium catalyst causes an atactic polymerization of propylene and also gives tail-to-tail, as well as head-to-tail, propylene dyads. Head-to-head polymerization of propylene is usually not found in ethylene–propylene copolymers.[3]

We have analyzed our ethylene–butene copolymers in a manner analogous to that used for ethylene–propylene copolymers and, although we confirm the assignment of D–M for 1,3-diethyl branches, we see no evidence for 1,2-diethyl branches caused by head-to-head polymerization of butene. Instead, we feel that the peak at 24.57 ppm used by D–M for assignment of this branch type is due instead to the central methylene of a BEB sequence of a random ethylene–butene copolymer.

Experimental Section

Samples prepared with the titanium-based catalyst system were made by a small-scale copolymerization of ethylene and 1-butene carried out in 500-mL bottles at 70 °C and 25-psi comonomer pressure. The composition of the comonomers was held relatively constant by maintaining a 10 mol/h flow of gasses through the bottle.

Samples prepared with the vanadium-based catalyst were made by copolymerizing ethylene and 1-butene in a hexane solution at 1 atm and 25 °C. A soluble vanadium catalyst was used with ethylaluminum dichloride as a promoter. The composition of the copolymer was regulated by controlling the ratio of the monomers in the gas phase. Methanol was added to the hexane solution to precipitate the polymer after polymerization was completed.

Samples were prepared as approximately 30% (w/v) solutions in dideuteriotetrachloroethane and run at approximately 120 °C

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in a 20-mm-o.d. tube. The copolymer prepared with V catalyst was run at about 130 °C because this gave better resolution of the $\alpha\beta$ and $\gamma\gamma$ peaks.

Spectra were obtained on a Nicolet NTC-200 spectrometer which operates in the Fourier transform mode at 50.3 MHz. The spectral width, acquisition time, and data points were ±2000 Hz (quadrature detection), 2.05 s, and 16 384, respectively. Noise-modulated broad-band decoupling was used on all samples to remove $^{1}H-^{13}C$ couplings. A 90° (23.5 μs) excitation pulse was used with a 30-s delay between pulses. Because the longest T_1 was found to be about 6 s in several ethyl-branched polyethylenes, these conditions are considered to be quantitative. The number of scans accumulated for each spectrum was about 200. Chemical shift calibration was made by assuming that the $(CH_2)_n$ peak falls at 30.00 ppm. Intensity measurements were made by using the spectrometer's integration software. A 0.2-Hz line broadening was used to reduced noise, and to eliminate interference from spinning sidebands, samples were not spun.

Nomenclature

We have adopted a nomenclature system based on that suggested for ethylene–propylene copolymers by Carman and Wilkes.[4] In this scheme, methylene carbons in the polymer backbone are assigned two Greek letters designating their position relative to the nearest methine carbon on both sides. For example, an $\alpha\gamma$ carbon would be the boldfaced carbon in the sequence ^{t}CCCC^{t}C. The symbol δ is used to indicate that there are at least four, but possibly more than four, bonds separating a given methylene from the nearest methine. The symbols ^{t}C, CH_3, and CH_2 are used to designate the branch carbon, the branch methyl, and the branch methylene, respectively. Where appropriate, these symbols are accompanied by subscripts to indicate the types of sequence in which the specific carbon occurs. For example, $^{t}C_{BBE}$ designates the branch carbon of a butene unit bonded on one side to another butene unit and on the other side to an ethylene unit. A bar over a B ($\bar{B}$) is used to indicate a butene unit which has added tail-to-tail (○— —○) rather than head-to-tail (—○—○). Thus $^{t}C_{BBE}$ represents the central butene unit methine carbon in the sequence ○— —○. The symbol $\bar{B}\bar{B}$ is used to designate a head-to-head butene dyad. Thus $^{t}C_{BB}$ is either ^{t}C in the dyad —○○—.

Results and Discussion

Table I contains the possible sequences that can occur in ethylene–butene copolymers and the chemical shifts associated with these sequences. This table also contains the calculated chemical shifts for these sequences as well as the chemical shifts for certain reference polymers. Table I also gives the chemical shifts reported by D–M, and these shifts are positioned in the table adjacent to structures that we feel are more plausible than those assigned by D–M. Our assignments are based on the chemical shifts calculated by the empirical method of Lindeman and Adams[5] and on comparisons of peak intensities as a function of monomer composition. Furthermore, strong use was made of the fact that these spectra strongly resemble those of ethylene–propylene copolymers when one takes into consideration the differences expected from branches that are ethyl rather than methyl. Finally, comparison of the spectra of hydrogenated polybutadienes[6] with those shown here reveals excellent agreement. From Table I it can be seen that a one-to-one correspondence is found for all peaks in hydrogenated polybutadienes and those peaks found in ethylene–butene copolymer prepared with Ti catalyst except that the latter have additional peaks in the 34- and 24-ppm regions. The ethylene–butene copolymer prepared with a V catalyst shows several additional peaks not found in the copolymer prepared with Ti catalyst. These additional peaks are interpreted in terms of BEB sequences and, in the case of the polymer prepared with vanadium, sequences involving tail-to-tail butene dyads.

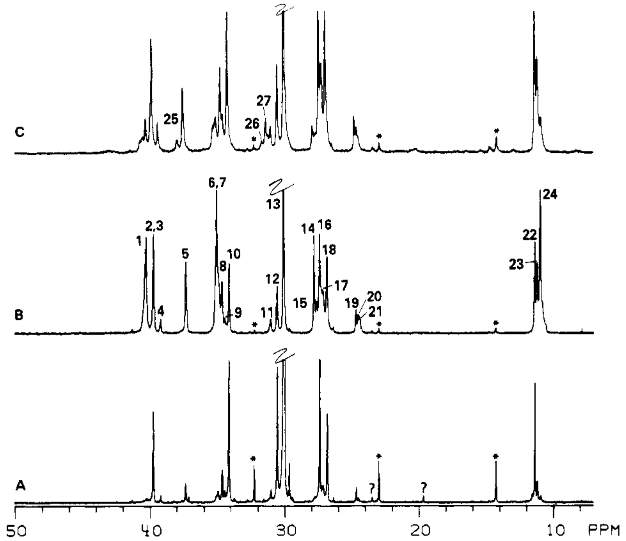

Figure 1. ^{13}C NMR spectra of ethylene–butene copolymers: (A) copolymer prepared with titanium-based catalyst–14% butene; (B) copolymer prepared with titanium-based catalyst–58% butene; (C) copolymer prepared with vanadium-based catalyst–42% butene. Asterisks denote peaks due to chain termination.

Figure 1 shows the ^{13}C NMR spectra of two types of ethylene–butene copolymers. D–M report three types of sequences in their ethylene–butene copolymers—isolated butene units, head-to-tail butene units, and head-to-head butene units. They assign peaks at 24.57 and 34.53 ppm to the ethyl CH_2 of a head-to-head unit and the $\alpha\beta$ of a BBEE unit, respectively. A peak at 31.73 ppm is assigned by D–M to the $\alpha\delta$ of a $\bar{B}\bar{B}$EE unit. In the polymer prepared with a Ti catalyst we do not see a peak at 31.73 ppm. We do see peaks at 24.62 and 34.59 ppm, which we feel correspond to D–M's peaks at 24.57 and 34.53 ppm. However, we assign these peaks to the $\beta\beta$ and $\alpha\gamma$ carbons arising from a BEB sequence. We see a small peak at 34.41 ppm, which we assign to the resonance of an $\alpha\delta$ carbon in the sequence BBEE. This assignment is based on the agreement of the chemical shifts in the copolymer with those found for hydrogenated polybutadiene. Table II contains the observed peak intensities for $\alpha\gamma$ and $\beta\beta$ resonances. For a copolymer low in butene content the $\alpha\gamma$ peak at 34.59 ppm is twice as intense as the peak at 24.62 ppm. At higher butene levels, additional peaks are observed at 24.62 and 24.47 ppm, which we assign to the $\beta\beta$ carbons in the sequences BBEBE and BBEBB, while the peak at 24.77 ppm is due to the $\beta\beta$ carbon in the sequence EBEBE. The $\alpha\gamma$ resonance at 34.59 ppm is clearly not twice as intense as the total intensity of the $\beta\beta$ region in the polymer containing high levels of butene. By analogy to the $\alpha\delta$ resonances, this anomaly can be explained by the presence of an $\alpha\gamma$ carbon in the sequence BBEB giving a peak at ~35.0 ppm, a region that also contains a peak due to $^{t}C_{BBB}$. Figure 2 shows an expansion of this region of the spectrum for a copolymer containing only 14 mol % butene. This expansion clearly shows five peaks which can be assigned to $^{t}C_{BBB}$, $\alpha\gamma$-BBEB, $\alpha\gamma$-EBEB, $\alpha\delta$-BBEE, and $\alpha\delta$-EBEE. Polymers containing higher levels of butene give rise to a broad $^{t}C_{BBB}$ peak which overlaps and obscures the peak due to BBEB sequences. Given these assignments, we are forced to conclude that copolymers prepared with Ti catalyst do not contain head-to-head butene dyads.

A spectrum of an ethylene–butene copolymer prepared with a V catalyst is shown in Figure 1. In addition to the

Table I
Chemical Shifts of Ethylene–Butene Copolymers and Various Reference Polymers

Line	Type	Sequence	Structure[a]	Chemical Shifts[b]						
				CALC[c]	PE[d]	PB[e]	PBD[f]	EB(Ti)[g]	EB(V)[h]	D & M[i]
1	αα	BBBB	^{t}c c^{t}c **c**^{t}c c^{t}c c	39.0		40.6	40.37	40.22	40.28	
2	αα	BBBE	^{t}c c^{t}c **c**^{t}c c c c	38.8			39.60	39.69	39.85	39.75
3	^{t}C	EBE	c c^t**c** c c c	39.1	39.7		39.60	39.69	39.85	
4	αα	EBBE	c c^{t}c **c**^{t}c c c c	38.5			39.05	39.15	39.38	39.10
5	^{t}C	BBE	^{t}c c^t**c** c c c	37.0			37.22	37.30	37.30	37.27
6	^{t}C	BBB	^{t}c c^t**c** c^{t}c c	35.0		35.0	34.88	35.00	35.15	
7	αγ	BBEB	^{t}c c^{t}c **c** c c^{t}c c	34.7			–	34.89	35.15	
8	αγ	EBEB	c c^{t}c **c** c c^{t}c c	34.5			–	34.59	34.73	34.53
9	αδ	BBEE	^{t}c c^{t}c **c** c c c c	34.5			34.33	34.41	34.41	
10	αδ	EBEE	c c^{t}c **c** c c c c	34.3	34.3		33.97	34.09	34.08	34.14
11	γγ	BEEB	^{t}c c c **c** c c^{t}c c	30.5			30.87	31.00	30.97	
12	γδ	BEEE(B or E)	^{t}c c c **c** c c c c (^{t}cc or cc)	30.2	30.4		30.36	30.50	30.50	
13	δδ	BEEE(B or E)	^{t}c c c c **c** c c c (^{t}cc or cc)	30.0	30.0		29.84	30.00	30.00	
14	CH_2	BBB	^{t}c c^t**c** c^{t}c c	27.7		27.9		27.74	27.89	34.88
15	CH_2	?		–				27.54	27.64	
16	βδ	BEE(B or E)	^{t}c c **c** c c c (^{t}cc or cc)	27.5	27.3		27.22	27.33	27.39	27.30
17	CH_2	?						27.18	27.22	
18	CH_2	EBE	c c^t**c** c c c	27.2	26.8		26.67	26.77	26.90	26.78
19	ββ	EBEBE	c c^{t}c c **c** c^{t}c c c c	24.9			–	24.62	24.76	24.57
20	ββ	BBEBE	^{t}c c^{t}c c **c** c^{t}c c c c	24.8			–	24.47	24.60	
21	ββ	BBEBB	^{t}c c^{t}c c **c** c^{t}c c^{t}c c	24.7			–	24.34	–	
22	CH_3	EBE	c c^t**c** c c c	11.4	11.2		11.11	11.31	11.30	11.22
23	CH_3	BBE	^{t}c c^t**c** c c c	11.4			10.91	11.14	11.12	
24	CH_3	BBB	^{t}c c^t**c** c^{t}c c	11.4		10.8	10.52	10.89	10.87	
25	^{t}C	BB$\bar{\mathrm{B}}$	^{t}c c^t**c** c c^{t}c	37.1					37.97	
26	αβ	BB$\bar{\mathrm{B}}$	^{t}c c^{t}c **c** c^{t}c	32.0					31.66	
27	αβ	EB$\bar{\mathrm{B}}$	c c^{t}c **c** c^{t}c	31.8					31.33	
28	^{t}C	$\bar{\mathrm{B}}\bar{\mathrm{B}}$	c^t**c**^{t}**c** c	41.6						
29	CH_2	$\bar{\mathrm{B}}\bar{\mathrm{B}}$	c^t**c**^{t}**c** c	24.7						31.73
30	CH_3	$\bar{\mathrm{B}}\bar{\mathrm{B}}$	c^t**c**^{t}**c** c	11.9						

a) For backbone methylene carbons and ^{t}C's, the particular carbon designated by type and sequence is underlined. For CH_2 (branch) and CH_3 carbons, the methine carbon carrying the branch which the type and sequence designate is underlined.

b) Chemical shifts calibrated by assuming the δδ carbon falls at 30.0 ppm from TMS.

c) Ref. 5

d) Chemical shifts obtained from an ethylene-butene copolymer with < 3% butene.

e) Chemical shifts for a polybutene prepared with a titanium-based catalyst.

f) Ref. 6

g) Ethylene-butene copolymer (41 mole-% butene) prepared with a titanium-based catalyst.

h) Ethylene-butene copolymer (37 mole-% butene) prepared with a vanadium-based catalyst. Chemical shifts differ slightly because this sample was run at 130°C and chemical shifts in these polymers are temperature dependent (Ref. 6).

i) Ref. 1.

Table II
Intensities[a] of the αγ and ββ Peaks

sample[b]	αγ-BBEB	αγ-EBEB	ββ(total)	αγ/ββ
A	0.2	1.7	0.9	2.1
B	*c*	2.8	2.7	1.0

[a] Intensity of complete spectrum equals 100. [b] Samples A and B gave spectra shown in parts A and B of Figure 1, respectively. [c] Not measurable due to overlap by $^tC_{BBB}$ resonance.

resonances found for the copolymer prepared with Ti catalyst, a number of additional resonances are observed. These lines are assigned to sequences which involve a tail-to-tail butene dyad in the various sequences or to variations in stereoregularity of sequences containing long runs of butene. The polymer prepared with Ti catalyst has a peak at 40.22 ppm, which was assigned to αα-BBBB carbons. The polymer prepared with V catalyst has additional lines in the region 40.5–40.3 ppm which we believe are due to αα-BBBB carbons in a different stereochemical environment. The lines at 31.66 and 31.32 ppm are assigned to αβ carbons in BB$\bar{\mathrm{B}}$ and EB$\bar{\mathrm{B}}$ sequences, respectively. These carbons have calculated shifts of 32.0 and 31.8 ppm. The peak at 31.66 ppm is believed to correspond to the peak that D–M observed at 31.73 ppm

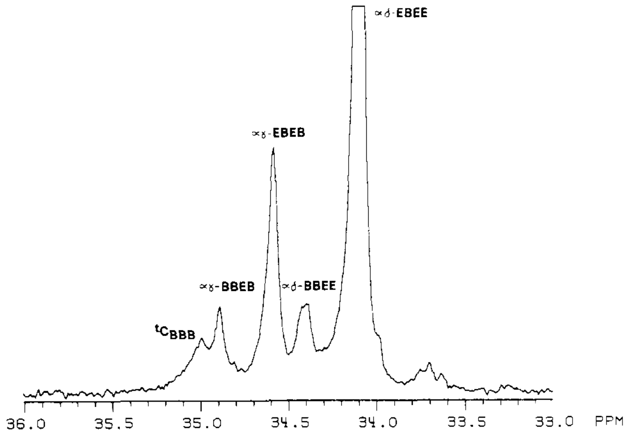

Figure 2. Expansion of the 33–36-ppm region of the spectrum shown in Figure 1A.

and assigned to an *αδ* carbon in the sequence —○○———. The ethyl-branch CH_2 and CH_3 carbons associated with *αβ* sequences have calculated chemical shifts which are too similar to those calculated for CH_2 and CH_3 in head-to-tail sequences to expect them to be resolved. The $^tC_{EBB}$ has a calculated chemical shift of 39.1 ppm, which is identical with that of a $^tC_{EBE}$ and again would fall in a region where it would be obscured by other peaks. The $^tC_{BBB}$ has a calculated shift of 37.1 ppm and is assigned to the peak occurring at 37.53 ppm. Chain-terminating carbons give small resonances at 32.25, 22.89, and 14.17 ppm.

In an attempt to prove that head-to-head linkages were not present in either of the copolymers studied, we prepared a copolymer from the decomposition of diazomethane and diazopropane. The polymer prepared by this process would have ethyl methine and methylene repeat units which should be incorporated randomly. A spectrum of such a polymer is shown in Figure 3 and closely resembles the spectra of ethylene–butene copolymers except for new resonances at 42.6 and 12.5 ppm. Although a complete assignment of the resonances in this spectrum has not been made (a fuller assignment of the resonances seen in this spectrum will be given elsewhere), we believe the peaks at 42.6 and 12.5 ppm can be assigned to the ^tC and CH_3 carbon, respectively, in a head-to-head unit. The CH_2 of the 1,2-diethyl branch occurs at 24.22 ppm, near, but to the high-field side of, the *ββ* resonance. Careful examination of the spectrum of the spectrum of the ethylene–butene copolymer prepared with V shows a broad peak at ~43 ppm and a small peak at 12.5 ppm. Given that there are some other small unidentified peaks in this spectrum and that the peak intensities of the 43- and 12.5-ppm peaks are not 1:1 as expected for a head-to-head butene dyad, we are reluctant to assign these peaks to this structure. Therefore we conclude that no head-to-head butene units exist in any of the ethylene–butene copolymers that we have studied and we believe that the assignments made by D–M are more reasonably explained by the presence of BEB sequences in their spectrum.

The only other published data on ethylene–butene copolymers with high butene content of which we are aware are those of Cudby and Bunn.[7] They show a spectrum of an ethylene–butene copolymer containing 30 mol % butene, but the only assignments they give are to three methyl signals, which they report as 11.2, 10.8, and 10.4 ppm. They assign these peaks to the methyl of an isolated ethyl branch and to the meso and racemic dyads of adjacent ethyl branches, respectivly. We believe these peaks correspond to the ones we observe at 11.31, 11.12, and 10.87 ppm in this study because of the high similarity between the remaining peaks in both spectra. Consequently, we believe that these peaks are due to sequence distribution rather than stereochemical effects, and we assign the peaks at 11.31, 11.12, and 10.87 ppm to the methyl resonance of the new central butene in the sequences EBE, BBE, and BBB, respectively. Examination of poly(1-butene) made with the same catalyst employed in this study shows that the effect of racemic linkages is most clearly seen in the branch CH_2 region of the spectrum. We, therefore, attribute the extra lines at about 27 ppm to CH_2 resonances which are a combination of sequence effects and stereochemistry, but no assignments could be made.

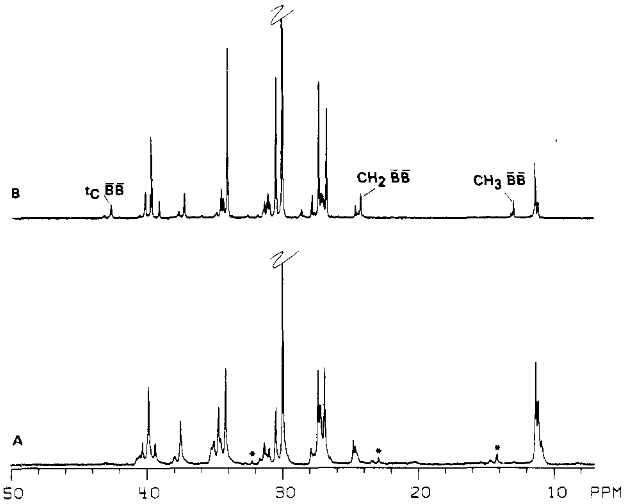

Figure 3. ^{13}C NMR spectra of (A) ethylene–butene copolymer prepared with vanadium-based catalyst and (B) polymer prepared by decomposition of diazopropane and diazomethane. Asterisks denote peaks due to chain termination.

Finally, the data presented here support the hypothesis that the ethyl branching in low-density polyethylene (LDPE) may not all be due to isolated ethyl branches. Nearly all spectra of LDPE show that the resonance for the methyl group of an ethyl branch is more intense than the resonance for the ^tC. Furthermore, the methyl peak is usually broader than that of the remaining peaks in the spectrum. However, for ethylene–butene copolymers prepared with sufficiently low butene content to ensure isolated ethyl branches, both the ^tC and the methyl peaks have the expected intensities, and the methyl peak is not broadened.[8,9] The variation in intensities cannot be attributed to differences in relaxation time because the ^tC relaxation time for an ethyl branch is 2.3 s, while that of the methyl group is 5.1 s.[10] Therefore, if relaxation factors are involved, the ^tC peak would be expected to be more intense that the methyl peak. As reported by others,[11,12] we believe the discrepancy in intensity and peak width can be attributed to the occurrence of 1,3-diethyl branching. The $^tC_{BBE}$ peak should fall at 37.4–37.8 ppm in LDPE, and peaks have been seen in this region by Bowner and O'-Donnell.[12] However, even when these peaks are not seen due to low signal-to-noise, an estimate of the number of 1,3-diethyl branches could be obtained by the difference in the integrated intensity of the peak due to the CH group and the peak due to the methyl group of an ethyl branch. Provided the data were obtained under quantitative conditions, this difference would be a measure of nonisolated ethyl branches.

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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 (~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 ~550

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