projections are largely determined by the position of the cross-links. This is evident in the anisotropy $R_{\parallel}/R_{\perp}$ at high k as shown in Figure 4.

The model chosen for calculation is simpler than a real randomly cross-linked network. All submolecules contain n segments, the number of cross-links per chain is constant, and the functionality of junction points adjoining chain ends is assumed to be the same as in the rest of the network. These assumptions are quite good if $k = 10$ or more. For small k, a random distribution of cross-link points will leave some molecules with 1 or 0 cross-links. These do not contribute to network elasticity nor are they deformed at equilibrium after stretching. This must be kept in mind if cross-links are introduced at random.

The direct relationship between polymer chain deformation and the theory of rubber elasticity makes SANS a unique tool for assessing the validity of several theoretical models. The theory also predicts swelling phenomena and elastic forces exerted by rubber in retraction. A comprehensive theory must account for these several phenomena, and ideally the different classes of experiment should be performed on identical samples. This is still an unfinished task.

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Monomer Sequence Distributions in Ethylene–1-Hexene Copolymers

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ABSTRACT: A ^{13}C NMR method is presented for a quantitative determination of the respective comonomer distributions, the triad distributions, average sequence lengths, and run numbers in ethylene–1-hexene copolymers. Complete ^{13}C NMR chemical shift assignments were formulated after observation of two reference systems, a poly(1-hexene) and an ethylene–1-hexene copolymer containing only 1.9 mol % 1-hexene. A second copolymer having 17.3 mol % 1-hexene allowed an observation of all the intermediate connecting sequences between the extremes of the two reference systems. A subsequent quantitative procedure, which avoids errors from peak overlap and uncertainties in configurational assignments, was developed by using relative areas from well-spaced ^{13}C NMR spectral regions, defined uniquely in terms of contributing triad sequences. The method is designed to obtain a triad distribution with the highest possible accuracy, after which, structural information meaningful to the polymer chemist is extracted.

Introduction

Polyethylene density can be controlled through incorporation of a low amount of a 1-olefin, which maintains polymer chain linearity in an overall configurational sense but leads to short chain branches randomly spaced along the polymer backbone. The linear 1-olefins 1-butene, 1-hexene, and 1-octene are important commercially for this purpose and result in ethyl, butyl, and hexyl branches in the respective copolymers. It is interesting to establish just how these secondary comonomers are incorporated, that is, the extent to which they exist as isolated branches or as "clusters" such as 1,3-dialkyl branches, 1,3,5-trialkyl branches, and so forth. ^{13}C NMR is a useful technique for detecting comonomer sequencing; resonances from as many as five consecutive units have been uniquely detected in the ^{13}C NMR spectra of ethylene–propylene[1-3] and ethylene–1-butene[4,5] copolymers. We recently reported a ^{13}C NMR method[4] for measuring quantitatively the complete triad sequence distributions and subsequent run numbers, sequence lengths, and mole fractions in ethylene–1-butene copolymers and have now extended this method in principle and technique to a corresponding analysis of ethylene–1-hexene copolymers. The method is most dependent upon a set of correct assignments and an establishment of experimental conditions that lead to accurate measurements. A complete set of assignments, based on model copolymers, poly(1-hexene), and known polymer chemical shift behavior, is reported along with a discussion of the selection of discrete spectral regions that ensure an accurate quantitative analysis.

Experimental Section

The ^{13}C NMR spectra were recorded on a Varian XL-200 NMR spectrometer at 50.3 MHz. Instrument conditions were as follows: pulse anlge, 90°; pulse delay, 15 s; acquisition time, 1 s; spectral width, 8000 Hz; number of data points per spectrum, 16K and double-precision arithmetic employed during data acquisition.

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Table I
Chemical Shift Assignments in ^{13}C NMR Spectra of Ethylene-1-Hexene Copolymers and Poly(1-hexene)

region	assignment: carbon	assignment: sequence	E/H copolymer B [H] = 17.3%	E/H copolymer A [H] = 1.9%	poly(1-hexene) homopolymer	peak no.
A	$\alpha\alpha$	HHHH	41.40		41.38	1
	$\alpha\alpha$	HHHE	40.86			2
	$\alpha\alpha$	EHHE	40.18			3
B	CH	EHE	38.13	38.14		4
C	CH	HHE	35.85			5
	4B	HHH	35.37		35.29	6
	$\alpha\gamma$	HHEH	35.00			7
	$\alpha\gamma$	EHEH				
	$\alpha\delta^+$	HHEE				
	4B	HHE	34.90			8
	$\alpha\delta^+$	EHEE	34.54	34.53		9
	4B	EHE	34.13	34.13		10
	CH	HHH	33.47		33.57	11
D	$\gamma\gamma$	HEEH	30.94			12
	$\gamma\delta^+$	HEEE	30.47	30.47		13
	$\delta^+\delta^+$	$(\mathrm{EEE})_n$	29.98	29.99		14
	3B	EHE	29.51			15
	3B	HHE	29.34			16
	3B	HHH	29.18		29.21	17
E	$\beta\delta^+$	EHEE	27.28	27.28		18
	$\beta\delta^+$	HHEE	27.09			19
F	$\beta\beta$	EHEHE	24.53	24.53		20
	$\beta\beta$	HHEHE	24.39			21
	$\beta\beta$	HHEHH	24.25			22
G	2B	EHE + HHE + HHH	23.37	23.36	23.52	23
H	1B	EHE + HHE + HHH	14.12	14.12	14.15	24

The temperature was maintained at 125 ± 1 °C during data acquisition and the polymer solutions were uniformly prepared at 10% by weight in 1,2,4-trichlorobenzene. Hexamethyldisiloxane (HMDS) was used as an internal standard and the observed chemical shifts were converted to a tetramethylsilane ($\mathrm{Me_4Si}$) internal standard by adding 2.03 ppm. Approximately 5000 transients were collected to obtain the signal-to-noise level displayed in the spectra in Figure 1. The superconducting magnet system was sufficiently stable to obtain spectra without using an internal lock.

We reported previously in a study of ethylene-1-butene copolymers that the NMR solution concentrations should be maintained at or below 15 wt % to avoid a concentration dependence of the observed resonance areas.[4] It was also recommended that integrated peak areas be utilized instead of relative peak heights. The necessity for using peak areas is vividly illustrated in Figure 1 by the observed spectrum of poly(1-hexene). The six resonances have precisely the same relative areas but display six different peak heights.

The nomenclature used to designate the different carbon types is that suggested by Carman.[1] Methyl and methine carbons are identified by the appropriate triad, which is given as a subscript. Backbone methylene carbons are designated by a pair of Greek letters, which specify the location of the nearest methine carbon in each direction. For example, an $\alpha\alpha$ methylene carbon is sandwiched between two methine carbons, an $\alpha\delta^+$ methylene carbon has one immediated methine neighbor and the second methine carbon located at least four carbons away, and so forth. The terminal carbons in a saturated end group are labeled 1s, 2s, and 3s for the first three carbons starting with the methyl carbon as 1s. Branch carbons are labeled 1B, 2B, 3B, and 4B starting again with the methyl carbon as 1B.

Results and Discussion

^{13}C NMR spectra of ethylene-1-hexene copolymers, containing principally isolated butyl branches, have been reported previously[6-8] as reference systems for the identification of the presence of butyl branches in low-density polyethylenes produced from high-pressure processes. A similar system containing 1.9 mol % 1-hexene has been reexamined in this study to establish precise chemical shift data for the resonances assigned to EHE, EHEE, and HEEE sequences. Our ultimate objective is to obtain a complete set of assignments encompassing all of the possible arrangements of ethylene and 1-hexene that are possible in ethylene-1-hexene copolymers containing more than just a few mole percent of 1-hexene. This information should lead to a method of characterizing ethylene-1-hexene copolymer structures independent of the overall comonomer composition. For this purpose, a poly(1-hexene) and an ethylene-1-hexene copolymer containing 17.3 mol % 1-hexene were prepared so that chemical shift assignments could be established for contiguous 1-hexene units as well as for the various possible ethylene-1-hexene connecting sequences. The ^{13}C NMR spectra at 50.3 MHz for each of these systems is shown in Figure 1 and complete chemical shift assignments are given in Table I. Twenty-four peaks are listed for identification in Table I even though some of these are actually multiple resonances that are closely spaced; specifically, these are peaks 6, 7, 11, 17, 23, and 24. The reference polymer systems, poly(1-hexene) and the copolymer containing 1.9 mol % 1-hexene, lead to 13 positive assignments as shown in Table I. With the HHH vs. EHE limits established, many of the remaining assignments evolve quite naturally. For example, the resonance from $\mathrm{CH_{EHH}}$, which can be confirmed by off-resonance decoupling, falls approximately halfway between the corresponding methine resonances for HHH and EHE. Similar arguments lead to the location of $\mathrm{1B_{EHH}}$, $\mathrm{2B_{EHH}}$, $\mathrm{3B_{EHH}}$, and $\mathrm{4B_{EHH}}$. Resonances from HHEH ($\alpha\gamma$), EHEH ($\alpha\gamma$), $\mathrm{4B_{EHH}}$, and HHEE ($\alpha\delta^+$) apparently overlap in peaks 7 and 8 and can be treated collectively without hazardous guesses as to detailed assignments. Some of the other remaining assignments EHEE ($\beta\delta^+$), HHEE ($\beta\delta^+$), EHEHE ($\beta\beta$), HHEHE ($\beta\beta$), and HHEHH ($\beta\beta$) follow from the analogous ethylene-1-butene copolymer assignments because the two extra branch carbons do not contribute to these observed chemical shifts. A comparison of these two sets of resonances from corresponding

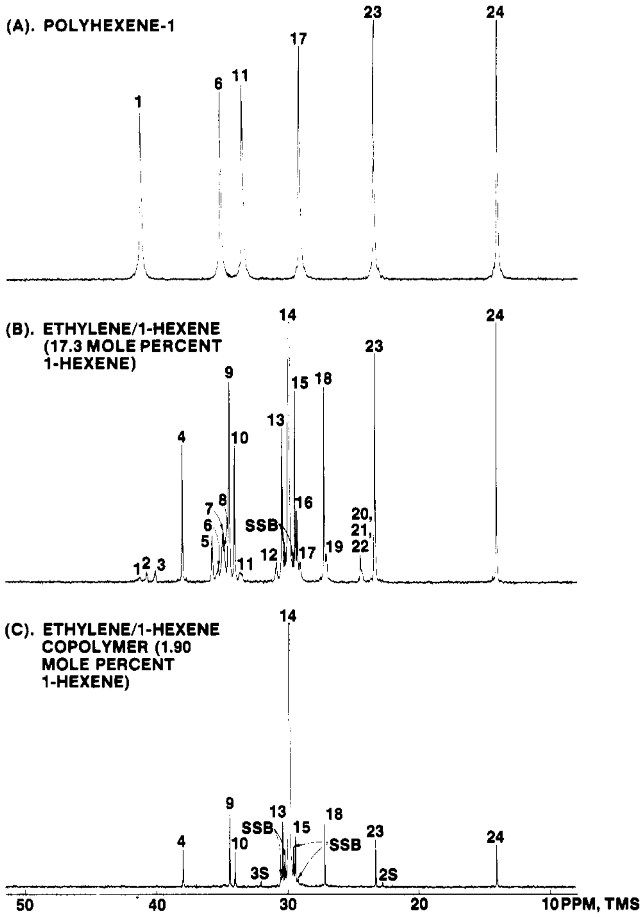

Figure 1. ^{13}C NMR spectra at 50.3 MHz and 125 °C of (A) poly(1-hexene), (B) ethylene–1-hexene copolymer ([H] = 17.3 mol %), and (C) ethylene–1-hexene copolymer ([H] = 1.9 mol %) at 10% by weight in 1,2,4-trichlorobenzene.

Table II

$\beta\delta^+$ and $\beta\beta$ Chemical Shifts in Ethylene-1-Butene and Ethylene-1-Hexene Copolymers

		chemical shift,[a] ppm	
carbon	sequence	X = 1-butene	X = 1-hexene
$\beta\delta^+$	EXEE	27.27	27.28
$\beta\delta^+$	XXEE	27.10[b]	27.09
$\beta\beta$	EXEXE	24.54	24.53
$\beta\beta$	XXEXE	24.37	24.39
$\beta\beta$	XXEXX	24.24	24.25

[a] Relative to Me_4Si. [b] Exact peak position is obscured by the presence of the multiple splittings of the 2B (BBE) resonance.

ethylene–1-butene and ethylene–1-hexene copolymers is given in Table II. It is easily seen that the observed chemical shifts for these specific sequences are precisely the same, a result that is also predicted through application of the Grant and Paul parameters.[9] Finally, the $\alpha\alpha$ resonances for HHHH, HHHE, and EHHE (peaks 1, 2, and 3) are also assigned by analogy to the ethylene–1-butene copolymers because they should occur in the same order but shifted to lower field by approximately 0.5 ppm because the effect of the additional branch carbons can be exercised here, again as required by the Grant and Paul parameters. Additional line splitting is expected to show up as broadening for the resonances associated with contiguous 1-hexene units either from configurational differences (tacticity) or a sensitivity to longer sequence lengths than described by the assignment. Such broadening does occur for peaks "1", "6", "11", and "17". More specific assignments are not required in a subsequent development of a quantitative method as it is only necessary to recognize the basic contributing sequences in a method based on collective assignments.[4]

The key advantage in utilizing collective assignments for a quantitative measurement is that an observed spectrum is divided into regions based on the accuracy with which relative spectral area measurements can be made. Closely spaced and overlapping resonances are grouped together and described algebraically, which removes any further need to prove specific assignments resulting from configurational contributions or longer range sequence effects that contribute only to line broadening or an occasional line splitting. The spectra of the ethylene–1-hexene copolymers are divided into eight regions, defined as A–H, as shown in Table I. A reduction of a spectrum containing 24 or more spectral lines to eight regions leads to a loss of spectral detail that was present originally. Although this may seem to offer a disadvantage, it should be recognized that there is a limit to the analytical accuracy with which the most detailed sequence distribution can be obtained. If one foregoes detail and requires accuracy, a reliable triad distribution that possesses far greater accuracy than a complete tetrad or higher order distribution can be obtained. The desired quantitative information for polymer characterization is still available as it does not improve or depend upon the knowledge of higher order distributions as will be seen later. The utility of using collective assignments and combined spectral regions is enhanced by invoking Bovey's necessary relationships[10] between triads, tetrads, and pentads. A detailed description of each spectral region for ethylene–1-hexene copolymers is given below in terms of triads only. Also listed are the specific contributing carbon resonances and the required necessary relationships to obtain each derivation.

Region A

Contributing carbons: $\alpha\alpha$

Specific *n*-ads: HHHH, HHHE, and EHHE

Required necessary relationship:

$$[\mathrm{HH}] = [\mathrm{HHHH}] + [\mathrm{HHHE}] + [\mathrm{EHHE}] \tag{1}$$

$$= [\mathrm{HHH}] + (1/2)[\mathrm{HHE}] \tag{2}$$

In terms of triads only, the total area of region A, T_A, is defined by

$$T_A = k([\mathrm{HHH}] + (1/2)[\mathrm{HHE}]) \tag{3}$$

Region B

Contributing carbon: methine

Specific *n*-ad: EHE

$$T_B = k[\mathrm{EHE}] \tag{4}$$

Region C

Specific *n*-ads and contributing carbons:

EHH and HHH from methine carbons

EHE, EHH, and HHH from the 4B carbons

EHEE and HHEE from $\alpha\delta^+$

EHEH and HHEH from $\alpha\gamma$

Required necessary relationships:

$$[\mathrm{HE}] = [\mathrm{EHEE}] + [\mathrm{HHEE}] + [\mathrm{EHEH}] + [\mathrm{HHEH}] \tag{5}$$

$$= 2[\mathrm{EHE}] + [\mathrm{EHH}] \tag{6}$$

$$T_C = k(2[\mathrm{HHH}] + 3[\mathrm{HHE}] + 3[\mathrm{EHE}]) \tag{7}$$

Region D

Specific *n*-ads and contributing carbons:

HEEH from $\gamma\gamma$

HEEE from $\gamma\delta^+$

Table III

A. Observed Triad Distributions and Comonomer Mole Fractions, Run Numbers, Monomer Dispersity, and Average Sequence Lengths for Ethylene-1-Hexene Copolymers Containing 1.9 and 17.3 mol % 1-Hexene

copolymer	mole fractions		triad distributions					
	[H]	[E]	[EHE]	[EHH]	[HHH]	[HEH]	[HEE]	[EEE]
ethylene-1-hexene (1)	0.019	0.981	0.017_8	0.001_3	0.000_3	0.001_4	0.034_1	0.945_2
ethylene-1-hexene (2)	0.173	0.827	0.097_8	0.054_6	0.021_0	0.039_0	0.172_1	0.615_5

copolymer	monomer dispersity	run no.	average sequence lengths	
			E	H
ethylene-1-hexene (1)	96.8	1.48	53.3	1.03
ethylene-1-hexene (2)	72.3	12.51	6.6	1.38

B. Corresponding Bernoullian Triad Distributions, Run Numbers, Monomer Dispersity, and Average Sequence Lengths for Copolymers with the Same Composition As Above

copolymer	[X]	[E]	[EXE]	[EXX]	[XXX]	[XEX]	[XEE]	[EEE]
Bernoullian (1)	0.019	0.981	0.0183	0.0007	0.0000	0.0004	0.0366	0.9440
Bernoullian (2)	0.173	0.827	0.1183	0.0495	0.0052	0.0248	0.2366	0.5656

copolymer	monomer dispersity	run no.	average sequence lengths	
			E	X
Bernoullian (1)	98.1	1.87	52.5	1.02
Bernoullian (2)	82.7	14.31	5.8	1.21

$(EEE)_n$ from $\delta^+\delta^+$
EHE, EHH, and HHH from the 3B carbons
Required necessary relationship:

$$\delta^+\delta^+ = k(2[EEE] - (1/2)[HEEE]) \qquad (8)$$

$$T_D = k(2[EEE] + (1/2) \times [HEE] + [EHE] + [EHH] + [HHH]) \qquad (9)$$

Region E
Contributing carbons: $\beta\delta^+$
Specific *n*-ads: EHEE and HHEE
Required necessary relationship:

$$[HEE] = [EHEE] + [HHEE] \qquad (10)$$

$$T_E = k[HEE] \qquad (11)$$

Region F
Contributing carbons: $\beta\beta$
Specific *n*-ads: EHEHE, HHEHE, and HHEHH

$$T_F = k[HEH] \qquad (12)$$

Region G
Contributing carbons: 2B
Specific *n*-ads: HHH, HHE, and EHE

$$T_G = k([HHH] + [HHE] + [EHE]) \qquad (13)$$

Region H
Contributing carbons: methyl
Specific *n*-ads: HHH, HHE, and EHE

$$T_H = k([HHH] + [HHE] + [EHE]) \qquad (14)$$

The factor k in the above equations is the NMR constant, which is later removed through normalization. In all, eight equations are available to solve for six relative triad concentrations or mole fractions. Even so, not all of these equations are of the same value experimentally and eq 13 and 14 are redundant. Practical considerations must also be invoked from the standpoint of data acquisition. The methyl carbon T_1's are sufficiently long to require substantial pulse delays to ensure achieving equilibrium conditions between data acquisition.[11] A 15-s pulse delay was found to be satisfactory for all but region H and is still sufficiently short to obtain the required quantitative data in a reasonable time span as shown by varying the delay between data acquisitions. Consequently, region H was omitted from the quantitative analysis. The second consideration in establishing a reliable quantitative approach is the location of the end group resonances. The 1s terminal methyl carbon resonance overlaps in region H and gives us another reason for precluding region H. The remaining two end group resonances from carbons 2s and 3s are observed at 22.86 and 32.18 ppm, respectively, and present no problems with overlap. One must also be concerned about the relative numbers of end groups that are 1-olefin and produce an allylic carbon resonance at 33.91 ppm, which falls into region C. Some catalyst systems give rise to as many as 50% 1-olefin terminal groups while other catalyst systems produce a substantially lesser amount. Since this resonance will always be obscured in the ^{13}C NMR spectra of ethylene-1-hexene copolymers, one may have to inspect the olefinic region for resonances at 114 ppm ($=CH_2$) and 140 ppm ($CH=$) or utilize an independent technique such as infrared analysis to establish the presence or absence of terminal 1-olefin groups. This problem can be avoided by eliminating region C from the quantitative treatment as there is still sufficient information to solve for the six relative triad concentrations if one continues to invoke the necessary relationships. Utilizing regions A, B, D, F, and G and the necessary relationship

$$2[EHE] + [EHH] = 2[HEH] + [HEE] \qquad (15)$$

one can readily derive the following equations for the relative triad concentrations:

$$k[EHE] = T_B \qquad (16)$$

$$k[EHH] = 2(T_G - T_B - T_A) \qquad (17)$$

$$k[HHH] = 2T_A + T_B - T_G \qquad (18)$$

$$k[HEH] = T_F \qquad (19)$$

$$k[HEE] = 2(T_G - T_A - T_F) \qquad (20)$$

$$k[EEE] = (1/2)(T_A + T_D + T_F - 2T_G) \qquad (21)$$

It should be noted that T_E was not used to obtain [HEE]. A systematically high result occurred when T_E was used; its close proximity to the strong resonances in region D may offer the best explanation.

As we have reported previously, a triad distribution is sufficient to characterize average sequence lengths, run numbers, and mole fractions.[4] The total number of 1-hexene runs per average molecule, N, is given by

$$N = n_1 + n_2 + n_3 + \ldots + n_x = \sum_{i=1}^{i=x} n_i = (1/2)\mathrm{HE} \qquad (22)$$

$$[\mathrm{N}] = (1/2)[\mathrm{HE}] \qquad (23)$$

$$= [\mathrm{EHE}] + (1/2)[\mathrm{EHH}] = [\mathrm{HEH}] + (1/2)[\mathrm{HEE}] \qquad (24)$$

and leads to the run number, as defined by Harwood:[12]

$$\text{run number} = 100[\mathrm{N}]$$

The mole fractions of each monomer are given by the respective sums of the three like-centered triads and the average sequence lengths for each type of unit are simply

$$\bar{n}_\mathrm{E} = [\mathrm{E}]/[\mathrm{N}] \qquad (25)$$

and

$$\bar{n}_\mathrm{H} = [\mathrm{H}]/[\mathrm{N}] \qquad (26)$$

The tendency of the 1-hexene units to form contiguous series or "clusters" can be described by a term that we will define as the "monomer dispersity", MD (the inverse of the sequence length).

$$\mathrm{MD} = 100[\mathrm{N}]/[\mathrm{H}] \qquad (27)$$

An MD value of 100 would indicate that the 1-hexene units are all "isolated" as ethylene–1-hexene–ethylene sequences. Any value below 100 is indicative of a tendency to "cluster" or form contiguous 1-hexene–1-hexene sequences.

Observed triad distributions, run numbers, comonomer mole fractions, the monomer dispersity, and average sequence lengths are given in Table IIIA for the copolymers used to obtain the assignments. For comparison, the corresponding parameters calculated for perfect Bernoullian distributions with the same overall composition as the copolymers are given in Table IIIB. The copolymer having 1.9 mol % 1-hexene and a monomer dispersity of approximately 97 is clearly a good model for establishing chemical shift assignments associated with EHE, EHEE, and HEEE sequences as shown in Table I. The 17.3 mol % 1-hexene copolymer has a monomer dispersity of only 72, which is considerably less than that predicted for a Bernoullian distribution of the same comonomer composition. The monomer dispersity appears to be a more sensitive indicator of a deviation from the perfectly random distribution than either the run number or an inspection of observed vs. calculated triad distributions. A comparison with Bernoullian distributions is useful because the latter serves as a reference point for the unbiased incorporation of a comonomer.

It should be pointed out that a tetrad distribution can be obtained from the data in Table I if the appropriate necessary relationships are used after carefully selecting the required tetrad ^{13}C NMR resonances. A higher order n-ad distribution would be useful in fitting statistical models as more observations are available for a fixed number of parameters. Aside from statistical considerations, the higher order n-ads are only useful in observing the lower end of the complete sequence distribution. Since it is doubtful that ^{13}C NMR can ever be used to measure sequence lengths of 10–20 contiguous units, it may be better to concentrate on obtaining one very reliable lower n-ad distribution to extract desired quantitative information about the copolymer structure.

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Carbon-13 Spin–Lattice Relaxation in Solid Poly(oxymethylene)

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ABSTRACT: Carbon-13 spin–lattice relaxation parameters of solid poly(oxymethylene) (Delrin) have been measured by means of high-resolution solid-state carbon-13 NMR. Carbon-13 spectra and relaxation parameters clearly show two different types of carbon-13 nuclei. They are assigned to carbons in "amorphous" regions and to carbons in "crystalline" regions, respectively, in accord with the accepted two-phase model of semicrystalline poly(oxymethylene). The data indicate that molecular motions do take place in the crystalline regions as well as in the amorphous regions. Our data are compared with results of dielectric and mechanical relaxation data, as well as other (proton) NMR studies, in order to gain insight into the nature of the motions as well as their correlation frequencies. It is argued that the motions in the amorphous and crystalline regions differ in their amplitudes rather than in their correlation frequencies.

Introduction

Nuclear magnetic resonance has been extensively used in the study of structural and physical properties of polymers in solution as well as in the solid state.[1] Wide-line proton NMR studies of linear semicrystalline polymers such as polyethylene and poly(oxymethylene) generally show NMR signals arising from more or less mobile components, giving rise to a (partially) narrowed NMR line,

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