Macromolecules **1983,** *16,* 492–496

J. Skolnick* and Robert Yaris: Damped Orientational Diffusion Model of Polymer Local Main-Chain Motion. 2. Application to Poly(vinyl acetate). Volume 15, Number 4, July–August 1982, page 1046.

All of the qualitative conclusions of the paper summarized on p 1050, i–vi, remain unchanged when the corrected expressions for the autocorrelation function and the spectral density are employed. Thus, the important conclusion that the damped diffusion model gives a good phenomenological description of local main-chain motions remains valid. On the scale of the figures presented in the papers, the corrected calculations produced no change in any of the figures.

Tables I–IV should be corrected to read as shown.

Table I
SY Model[d]

temp, °C	T_{AA}, ms	T_{XX}, ms	N_A	N_X	β,[c] rad/s	δ,[c] rad/s	$R^{c,f}$
−45	202	279	−0.88	−0.61	2.50 +8	2.39 +7	3.0 −3
10	470	270	−0.315	−0.091	5.19 +7	5.05 +10	5.0 −32
30	550	250	−0.062	−0.014	2.31 +8	3.53 +10	4.1 −29
110	970	400	0.063	0.013	3.88 +8	1.21 +11	1.3 −23

Table II
Activation Energies by NMR Parameterization

model	ϵ_a (short-range motion), kcal/mol	E_a (dissipation), kcal/mol
SY	2.26[c]	3.7[d]

Table III
Frequency of Maximum Loss Using Parameters Fit to NMR Results for PVA[a] in 5% Toluene at 10 °C

model	log ω_{max}	parameters[c]
SY	10.25	β = 5.19 +7, δ = 5.05 +10 (rad/s)

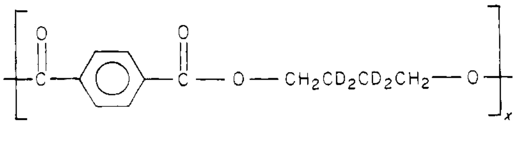
Table IV
Frequency of Maximum Loss Using a One-Parameter Fit for PVA[a] in 5% Toluene at 10 °C

model	log ω_{max}	ϵ_{max}[b]	parameters[d]
SY	8.6	0.355	β = 5.19 +7, δ = 1.23 +9 (rad/s)

Communications to the Editor

Motions about Three Bonds in Polymers: Solid-State Deuterium NMR Studies

Defect or kink diffusion in polymers has captured the interest of chemists and physicists for several decades.[1] Although numerous theories and much debate have been set forth, the experimental basis on which to test these theories has been scant or nonexistent. We now report experimental evidence for three-bond motion as an isolated motional mode in the deuterium-labeled poly(butylene terephthalate) homopolymer:



The alkyl portion of poly(butylene terephthalate) is ideally set up to undergo a three-bond type of motion. It contains the shortest sequence that is able to undergo these motions[2] ($(CH_2)_4$) and does not have available to it longer range motional modes, such as a Schatzki crankshaft reorientation[3] or 10-bond motions.[4] Further, we have shown by solid-state ^{13}C NMR experiments that the terephthalate groups act as molecular "anchors". Carbon NMR relaxation data[5,6] and carbon chemical shift anisotropy considerations[7] indicate that the terephthalate residues can be considered static in comparison to the motions exhibited by the alkyl residues. The alkyl carbon relaxation times point to a fairly large amount of spectral density in the megahertz frequency regime and suggest a correlation time of ca. 10^{-5}–10^{-6} s.[6] Motions of this frequency are in the intermediate exchange region for solid-state deuterium NMR spectroscopy, and for this reason we initiated a deuterium NMR study of this polymer.

Deuterium NMR spectroscopy in the solid state offers some distinct advantages for the study of molecular motion in solid polymers. Relaxation of the deuterium nucleus is dominated by the quadrupolar interaction,[8] thus eliminating the need to establish relaxation mechanisms. Also, the deuterium field gradient tensor for most C–D bonds is axially symmetric, with the unique principal axis along the C–D bond direction.[9] Thus there is a one-to-one correspondence between frequency and orientation, and the orientation of the field gradient tensor is known with respect to the molecular framework.[10,11] In addition, deuterium NMR quadrupolar powder patterns are sensitive to motions that have correlation times proportional to the reciprocal of the quadrupolar splitting,[12] making deuterium the nucleus of choice for the study of molecular motions that have correlation times of ca. 10^{-4}–10^{-7} s.

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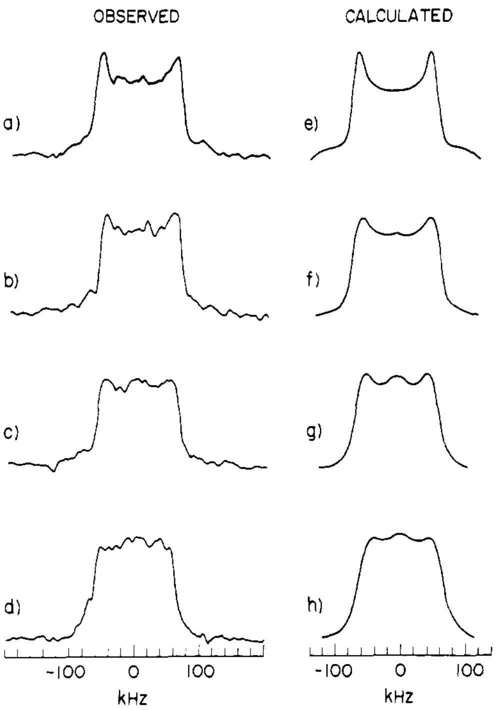

Figure 1. Observed (a–d) and calculated (e–h) solid-state deuterium NMR spectra of poly(butylene terephthalate) in which the "center" butanediol carbons bear deuterium: (a) −88, (b) −32, (c) −11, and (d) +5 °C. The calculated spectra assume a quadrupolar splitting of 124 kHz and a two-site hop between sites separated by 103° with rate constants (e) $\ll 1 \times 10^4$, (f) 1.9×10^4, (g) 4.7×10^4, and (h) 7.1×10^4 s^{-1}.

Finally, the low natural abundance of deuterium eliminates background signals due to unlabeled material in natural abundance,[13] thereby providing completely selective observation of isolated residues.

Experimental Section. The selectively labeled poly(butylene terephthalate) sample was prepared according to literature methods,[14] using butylene-*2,2,3,3-d*$_4$ glycol (Merck) as the starting diol. The polymer was characterized by thermal measurements and by solution-state deuterium and carbon NMR spectroscopy. No end groups were observed by carbon spectroscopy,[15] and the deuterium spectrum attested to the integrity of the labeling pattern.

The samples for NMR spectroscopy were melted into glass tubes and allowed to cool from the melt. The observed deuterium NMR spectra are reproducible with temperature cycling, thus providing evidence that the necessary thermal history (caused by acquiring temperature-dependent spectra of the samples) does not greatly affect the properties that we are measuring.

Solid-state deuterium NMR spectra were recorded on a home-built spectrometer operating at 55.26 MHz for ^{2}H. The spectrometer employs a Nicolet 1180E computer, data system, and pulse programmer, Novex radio-frequency gear, an Amplifier Research 200L amplifier, Rockland audio filters and frequency synthesizer, and a Nicolet Explorer III digital oscilloscope with parallel data transfer to the computer.

The probe coil is surrounded by a Dewar, and a Varian temperature controller unit and a digital thermometer with a copper–constantan thermocouple are used for temperature control. The temperatures are considered accurate to ±1 °C and stable to ±2 °C. The coil accepts tubes 5 mm in diameter and samples ca. 10 mm in length. The weight of a sample was typically 100 mg.

Spectra were obtained in quadrature using the quadrupolar echo pulse sequence $(90_{\pm x}-\tau_1-90_y-\tau_2)$,[16–18] 4K data points, a digitization rate of 200 ns/point (5 MHz), and a 4.3-μs 90° pulse width. The length of τ_1 was generally set at 30 μs. The value of τ_2 was set several microseconds shorter than the time needed to start digitization at the top of the quadrupolar echo maximum. After data accumulation, the FID was left-shifted by the correct number of points, so that for each spectrum, the part of the FID that was transformed began at the exact top of the echo.

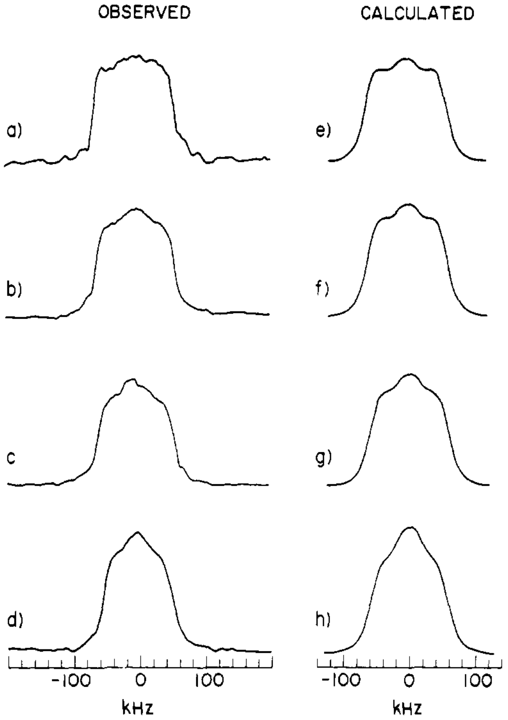

Figure 2. Observed and calculated deuterium NMR spectra as described in the legend for Figure 1: (a) 21, (b) 44, (c) 63, and (d) 85 °C; (e) rate constant 1.4×10^5, (f) 2.1×10^5, (g) 2.8×10^5, and (h) 5.7×10^5 s^{-1}.

The calculated deuterium spectra were corrected by taking into account pulse power falloff as a function of frequency,[19] the distortions that arise when motions occur during the quadrupolar echo delay time,[20] and the spectrum that is obtained when the rate of motion is intermediate on the time scale of the quadrupolar splitting.[21]

Results. The spectrum of poly(butylene terephthalate) at −88 °C is the quadrupolar powder pattern of a rigid material (Figure 1a). A quadrupolar coupling constant (e^2qQ/h) of 165 kHz can be measured from this spectrum, and the quadrupolar splitting $(\Delta\nu_Q)$ is thus 124 kHz. As the temperature is raised, the static quadrupolar pattern becomes motionally averaged (Figures 1 and 2). Although the center of the pattern fills in, the total width of the pattern is still ca. 120 kHz. In the fast-exchange limit, the spectrum is essentially an $\eta = 1$ pattern (Figure 2d). Beyond the fast-exchange limit, other spectral changes begin to take place, and a spike grows in the center of the spectrum (not shown). The temperature-dependent spectra are fully reversible.

The $\eta = 1$ (axially asymmetric) spectrum in Figure 2d has an ~120-kHz breadth. The observation of an axially asymmetric spectrum[21] suggests that the motional process leading to collapse of the static powder pattern has twofold or lower symmetry.[22] Further, the breadth of the pattern $(2\omega_\perp = 120$ kHz) suggests that the motional process involves a conformational transition through an angle whose bisector is approximately the "magic angle", or 54.7°.[21] Such a spectrum can arise from a gauche–trans conformational transition.[11,22] Some examples are shown in

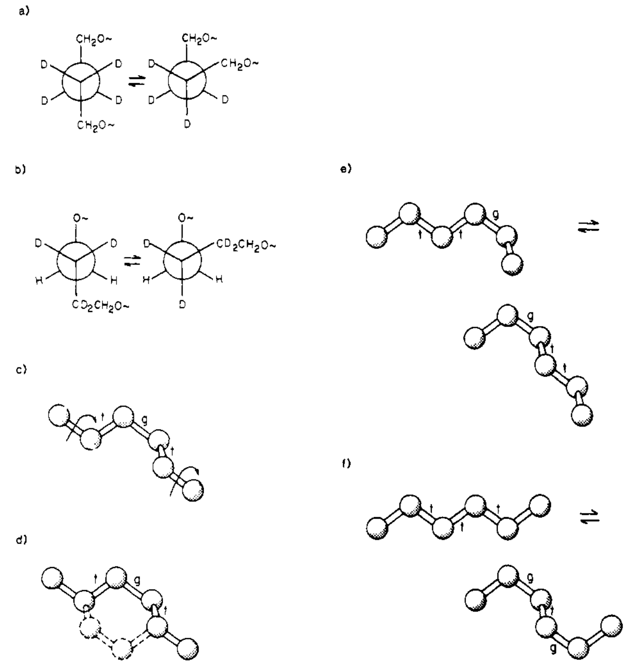

Figure 3. Possible mechanisms for trans–gauche conformational transitions in the alkyl region of poly(butylene terephthalate). (a) A discrete isomerization about the central bond; (b) discrete isomerization about an end bond; (c) a crankshaft type of motion about the O–CH_2 bonds; (d) a three-bond motion in which the bonds change positions as if they were on a cyclohexane skeleton; (e) a motion involving gauche migration ($ttg^{\pm} \leftrightarrow g^{\pm}tt$); (f) a motion causing pair gauche production, consisting of counterrotation about second-neighbor parallel bonds ($ttt \leftrightarrow g^{\pm}tg^{\mp}$). The data presented here indicate that mechanisms e and f are most likely to occur.

Figure 3. The source of the $\eta = 1$ spectrum can be readily visualized if we affix an xyz coordinate system to the Newman projection in Figure 3a, where the z axis is parallel to the chain axis (and thus perpendicular to the plane of the paper), and the y axis bisects the CD_2 bond angle. In the rapid-motion limit, the z component of the electric field gradient tensor is unaffected, as it is parallel to the reorientation axis. Thus, the component of the tensor perpendicular to the C–D bond, $\omega_\perp$, is unchanged, and remains ca. 60 kHz. The component of the electric field gradient tensor along the y axis is at approximately the "magic angle" with respect to the C–D bond vector orientations and thus has a motionally averaged frequency of zero. The tensor must remain traceless, which thus requires that the third component be at $-\omega_\perp$. Consequently, in the rapid-motion limit, a gauche–trans conformational transition of a C–D bond is expected to give rise to an axially asymmetric pattern with ca. 120-kHz breadth.

The spectra obtained at temperatures between the static and the fast-exchange limits can be interpreted as arising from trans–gauche conformational isomerizations, which occur at intermediate rates. Representative spectra are shown in Figures 1 and 2, along with the corresponding calculated spectra. The spectra are calculated by assuming that the C–D bond hops between two equally populated sites separated by a dihedral angle of 103°.[36]

All of the calculated spectra employ the 124-kHz quadrupolar splitting, which was determined from the static spectrum in Figure 1a. The rate constant for isomerization was varied in order to calculate the spectra for the intermediate-exchange region. Figures 1 and 2 show that the agreement between the calculated and observed spectra is very good. The calculated spectra are very sensitive to the jump angle, and jump angles of 100° or 110° clearly do not produce calculated spectra that fit the observed ones. The sensitivity of the spectra to the rate constant is not as extreme as the angular sensitivity. The rate constants are considered accurate to 10%.

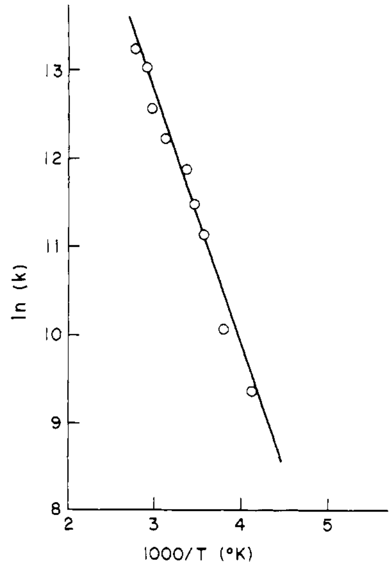

Figure 4. Arrhenius plot of the natural logarithm of the rate constant vs. $1/T$. An apparent activation energy of 5.8 kcal/mol is obtained from the slope of the line.

The rate constants are listed in the figure captions. The correlation time for reorientation is 7×10^{-6} s at 20 °C. The activation energy for this conformational transition can be estimated from a plot of the natural log of the rate constants vs. the inverse temperature. A plot of these data is shown in Figure 4. These data yield an activation energy of 5.8 kcal/mol, corresponding to slightly more than one barrier height.[37]

Discussion. The spectra of poly(butylene terephthalate) are consistent with the occurrence of gauche–trans isomerization as an isolated motional mode.[38]

It now remains to establish the nature of the conformational transition that is responsible for the experimental observations. The requirements are that the process must result in a ca. 103° reorientation of the C–D bond (103° is the *dihedral* angle of reorientation), that the two conformations must be of nearly equal energy, and that only one barrier height is required for the transition. We can envision several reorientation mechanisms that satisfy these requirements: (a) discrete isomerization about the center bond ($ttt \leftrightarrow tg^{\pm}t$); (b) isomerization about the outer bond ($ttt \leftrightarrow g^{\pm}tt$); (c) crankshaft rotation about both C–O bonds; (d) three-bond motions constituting half of a cyclohexane ring flip; (e) gauche migration ($ttg^{\pm} \leftrightarrow g^{\pm}tt$); and (f) counterrotation about second-neighbor parallel bonds (pair gauche production) ($ttt \leftrightarrow g^{\pm}tg^{\mp}$). Mechanisms a–f are shown in Figure 3. We shall explore each of these in turn.

An example of discrete isomerization about the center bond is shown in Figure 3a. Although the NMR data reported here are consistent with this model, this type of reorientation requires large-scale motion of the chain ends and is dismissed for this reason. Single isomerization about the end bond ($ttt \leftrightarrow g^{\pm}tt$) (Figure 3b) also requires large-scale reorientation of the tails of the polymer.[1] Further, these models are not consistent with carbon relaxation data,[5,6] which suggest that the OCH_2 groups undergo motions that are of less amplitude and/or rate than those of the "central" CH_2 carbons, nor are they consistent with the preferred conformation of an $OCH_2CH_2CH_2CH_2O$

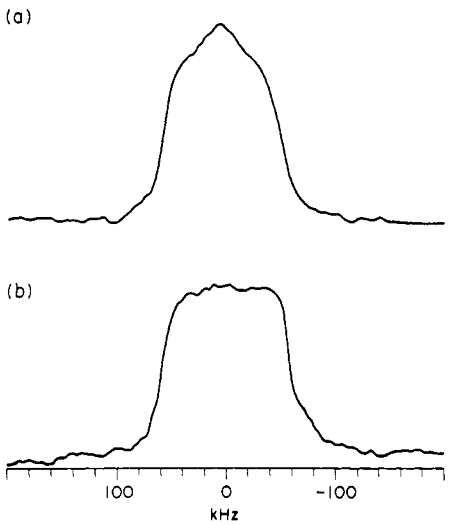

Figure 5. Solid-state deuterium NMR spectra of ^2H-labeled poly(butylene terephthalate) at 85 °C: (a) spectrum of poly(butylene terephthalate) in which the "center" carbons of the alkyl moiety bear deuterium; (b) spectrum that represents the OCD_2 deuterons of a different labeled poly(butylene terephthalate) sample.[31]

unit (see below). Thus, we can eliminate mechanisms a and b.

Crankshaft rotations about $O-CH_2$ bonds (Figure 3c) have been proposed as the most likely motions for butanediol-containing polyesters in solution.[25] This proposal is based on the assumption that the barrier to internal CH_2-CH_2 rotation is sufficiently high compared to the barrier for CH_2-O rotations, so that motion about C–C bonds does not lead directly to significant spin–lattice relaxation.[25] This type of crankshaft motion requires that the $O-CH_2$ bonds be collinear—a condition that can be met if the butanediol moiety adopts a distorted tgt conformation (Figure 3c). We dismiss this type of crankshaft motion for solid poly(butylene terephthalate) on several grounds. First, in the rapid-motion limit, this type of crankshaft motion is expected to produce a narrowed Pake deuterium spectrum.[11] Figure 2d illustrates that the observed rapid-exchange pattern is clearly not a narrowed Pake pattern. Secondly, the compressed tgt conformation is not consistent with X-ray fiber diffraction[26,27] and infrared studies,[28,29] which find that the conformation of unstressed PBT is "approximately" $g^{\pm}tg^{\mp}$. Finally, the crankshaft motion causes the OCH_2 and "central" CH_2 carbons to move with the same rates and angular ranges. This is not consistent with our carbon relaxation[5,6] and chemical shift anisotropy measurements.[7,30] A crankshaft type of motion about the $O-CH_2$ bonds clearly does not fit our data.

The mechanism for three-bond motion proposed by Monnerie and coworkers is shown in Figure 3d.[2] The gauche bond and both of its neighbors form what can be visualized as half of a cyclohexane ring. Motion carries the bonds to the other half of the cyclohexane ring. Such motions would give rise to the deuterium spectra we observe for the labeled poly(butylene terephthalate). However, these motions require identical motions for the protons on the central carbons and the protons on the OCH_2 carbons. Preliminary solid-state deuterium NMR work on OCD_2-labeled poly(butylene terephthalate) indicates that the OCD_2 deuterons do not undergo motions that are identical with those of the central CD_2 deuterons (Figure 5). The spectra shown in Figure 5 show that the OCD_2 deuterons are not involved in large-scale and/or rapid motions at temperatures where the deuterium spectra for the central CD_2 groups are in the fast-exchange limit.[31] These observations, in conjunction with previous carbon NMR data,[5-7] tend to mitigate against this model for three-bond motion.

Gauche migration ($g^{\pm}tt \leftrightarrow ttg^{\pm}$), proposed by Helfand,[1,32,33] can occur by pathways requiring less than two barrier heights. This type of transition is an attractive one for polymers, as it does not require large-scale reorientation of the tails of the polymer (Figure 3e). Further, the two states are expected to have nearly equal energies. This type of motion does not require large-amplitude motion of the OCH_2 groups and is thus consistent with the carbon NMR data. This type of motion does require translation of the ends of the polymer chain, a motion that may be taken up by O–C bond angle deformation in this polymer.

Pair gauche production, also proposed by Helfand[1,32,33] (Figure 3f), carries ttt into $g^{\pm}tg^{\mp}$. This reorientation also requires slightly more than one barrier height. Furthermore, the $g^{\pm}tg^{\mp}$ conformation is predicted from rotational isomeric state calculations to be the most stable one for the $OCH_2CH_2CH_2CH_2O$ unit.[34] In addition, this conformation is consistent with the IR[28,29] and X-ray[26,27] conclusions, which find that the unstressed polymer adopts an "approximately" gauche–trans–gauche conformation.[39] This type of counterrotation about the two nearest-neighbor parallel bonds does not require large-scale reorientation of the OCH_2 carbons, a result consistent with our chemical shift anisotropy considerations and relaxation studies.

Both of the Helfand mechanisms (Figure 3e,f) require counterrotation about second-neighbor parallel bonds. These formal mechanisms reduce to the same motions; i.e., the gauche migration is part of the pathway for pair gauche production. It is likely that the actual reorientation does not entail one discrete process but rather involves some combination of mechanisms a–f, with ttt $\leftrightarrow$ $g^{\pm}tg^{\mp}$ and $ttg^{\pm}$ $\leftrightarrow$ $g^{\pm}tt$ (mechanisms e and f) as the predominant modes. The two sites for the motional model are likely to be g^+tg^- and g^-tg^+. Solid-state deuterium NMR studies involving OCD_2-labeled poly(butylene terephthalate) are in progress.[31] Analysis of the results for this polymer should enable us to establish more thoroughly the modes of reorientation for the OCH_2 deuterons.

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Registry No. Poly(butylene terephthalate) (repeating unit), 24968-12-5; poly(butylene terephthalate) (copolymer), 26062-94-2; poly(butylene-*2,2,3,3-d*$_4$ terephthalate) (copolymer), 84081-58-3; poly(butylene-*2,2,3,3-d*$_4$ terephthalate) (repeating unit), 84081-59-4.

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(36) It is noted that similar line shapes can be obtained with a diamond lattice jump model, a dihedral angle of 109°, and unequal populations of g^+, g^-, and t conformers.[22,24] However, in the absence of additional chemical information, we adopt here the simplest model that explains the data well.

(37) The potential for C–C bond rotation in butane (ca. 3.7 kcal/mol) is considered to be one barrier height.[23]

(38) It should be noted that the temperature-dependent deuterium NMR spectra of polyethylene are very different from those shown here in Figures 1 and 2. In the amorphous regions of polyethylene many types of motional modes may occur, and the observed spectra are a superposition of them.[4,11] Spectra similar, but not identical with those reported here, have been observed in glycolipids.[22,24]

(39) A critical comparison and evaluation of the published X-ray structures for poly(butylene terephthalate)[35] lists a value of 76.2° as the "best estimate" for the dihedral angle between the gauche carbons shown in the structure in Figure 3b. This value is in excellent agreement with our results, which predict that the dihedral angle between these groups is 77° (180°–103°).

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