Thermally-Induced Molecular Motion and Premelting in Hexacontane

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ABSTRACT: A combination of careful differential scanning calorimetry, solid-state NMR, small- and wide-angle X-ray diffraction, and selected area electron diffraction studies of pure $C_{60}H_{122}$ (hexacontane) were carried out to evaluate its thermal behavior in the crystalline state with increasing temperature. Solution-crystallized material showed only a single sharp endothermic peak at 99 °C corresponding to the melting transition, while bulk crystallized material showed an additional small endothermic peak at 71 °C. Variable-temperature ^{13}C CP/MAS spectra showed a loss of cross-polarization and peak intensities between 40 and 74 °C which indicated increased molecular motion. A complete loss of signal occurred above 74 °C, confirming relatively large-scale rotational, translational, and/or librational motion. Alternative use of high-power decoupling (^{13}C HPD/MAS) spectroscopy allowed observation of the mobile components of the samples, especially at the higher temperatures from 77 to 99 °C. Peak sharpening due to increased molecular motion plus chemical shift changes characteristic of increasing populations of gauche conformations near the chain ends were observed. These confirm a gradual increase in the conformational mobility of segments near the crystal surface with increasing temperature (probably related to translational movement at the α transition) that generates a rough surface able to accommodate the end-group trans–gauche jumps. The interior methylene segments, however, maintain their all-trans conformation up to the melt temperature of 99 °C. Wide-angle X-ray patterns of solution-crystallized samples confirmed orthorhombic structure, while bulk-crystallized material possessed the monoclinic structure. The combination of techniques employed clearly confirmed the occurrence of premelting (as described above) at ca. 30 °C below the melting point for both samples that involves increased terminal group mobility coupled with chain translation. The lack of a DSC transition for the high-purity solution-crystallized sample plus the gradual change in the NMR behavior which occurs with increasing temperature is consistent with a nonconcerted process related to the concerted α transition observed for various molecular weight samples of polyethylene and impure *n*-alkanes.

Introduction

The *n*-alkanes, although having a relatively simple chemical repeat unit, have yielded a plethora of structural changes with temperature. These changes have involved several different phase transitions, including the transformation to a hexagonal phase for alkanes having a carbon number ≤45. The recent synthesis of pure, very high molecular weight *n*-alkanes,[1-3] up to C_{400}, has made available a new set of chain molecules for further study. In particular, thermodynamic studies of dononacontahectane, $C_{192}H_{286}$, led to the conclusion that a premelting process takes place about 30–40 °C below the true melting temperature. The specific premelting process of interest here is one where the end sequences (but not the internal methylenes) become disordered; i.e., some gauche units are introduced. Thus, at temperatures well below complete melting, these molecular crystals develop surface disorder which disrupts the planar array of the terminal methyl groups. This premelting phenomenon is unique to chain molecules. The thermodynamic analysis of the fusion of the *n*-alkanes by Flory and Vrij[4] predicted that this phenomenon would occur under certain circumstances. Solid-state NMR,[5] vibrational spectroscopy,[6,7] differential calorimetry,[3] dilatometry,[8] and selected area electron diffraction[9] studies have all given evidence for this type of premelting in a variety of *n*-alkanes.

Solid-state NMR spectroscopy has proven especially valuable in investigating the molecular conformations and structures of the polyethylenes and *n*-alkanes since it is a direct molecular-level probe of conformation and motion.[5,10-14] For example, segment chemical shifts are sensitive to crystal packing conformation about the C–C backbone (the γ-gauche effect).[15,16] In particular, it has been shown by Möller et al. that the α, β, and γ carbon atoms can be resolved for various linear alkanes including octahexacontahectane, $C_{168}H_{238}$, and that chemical shift changes can be observed that correlate with crystal packing and motion.[5] Solid-state ^{13}C NMR peak position changes for crystal–crystal transitions, formation of the "rotator phase", and premelting were all described.[5] Thus, this is a very useful method to directly observe premelting of the type described and to separate out other possible transformations which occur for shorter chain molecules.

Hexacontane, $C_{60}H_{122}$, appears to be near a pivotal position in the homologous series of alkanes with a chain length such that the summation of intermolecular forces in the crystalline state changes the molecular behavior possible with increasing temperature: lower analogs are capable of concerted *molecular* rotational motions within the crystal lattice (rotator phase) while longer chain alkanes can only undergo nonconcerted *segmental* motions

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combined with lateral translations below the melting transition which allow crystal surface disordering and end-group rotation (premelting). We report here the results of a variable-temperature solid-state ^{13}C NMR study performed on hexacontane samples crystallized from the melt and from solution. We then compare these results with selected area diffraction[9] and vibrational spectroscopic studies[7] on the same material.

Experimental Section

The *n*-hexacontane sample was purchased from Fluka. Two crystallization procedures were used. In one of these the sample was rapidly crystallized from the pure melt. In the other it was rapidly crystallized from a butyl acetate solution.

Solid-state ^{13}C NMR spectroscopy was performed on a Bruker MSL-200 spectrometer operating at a field of 50.32 MHz for carbon. Data were acquired using the techniques of magic-angle spinning with cross-polarization (CP/MAS) and without cross-polarization (MAS). In both cases high-power proton decoupling (HPD) was employed during signal acquisition. All chemical shift values were referenced to the upfield shift of adamantane at 300 K (29.5 ppm). The sample spinning rate was maintained at ~3000 Hz, ensuring that the pressure gradient inside the rotor was ≤6 atm. A standard double-air-bearing Bruker CP/MAS probe was used for the variable-temperature CP/MAS study, while a special Bruker high-temperature CP/MAS probe was used for the variable-temperature HPD/MAS experiments. The standard CP/MAS probe was calibrated using ethylene glycol.[17] The high-temperature probe was used without calibration. A Bruker VT-1000 controller was used to regulate probe temperatures. Actual temperature values reported in this study are believed to be accurate to ±2 °C as confirmed by calibration with ethylene glycol and correlation of spectral changes with DSC peaks of small-molecule crystals displaying known solid–solid transitions. Samples were allowed 20–30 min to equilibrate before spectral data were acquired. Data were processed off-line using Spectra Calc[18] and SC_NMR, an Array Basic program written in-house for analyzing NMR data files on microcomputers.[19]

The thermograms were obtained with a Perkin-Elmer DSC 2B calibrated with indium. About 1 mg of sample was used at a heating rate of 5 K/min. The sensitivity range was set at 2. This range is about 5 times more sensitive than in the conventional operation of this instrument.

The small-angle X-ray patterns were obtained at room temperature by means of a Rigaku-Denki slit-collimated camera using filtered Cu Kα radiation. Exposure times were about 24 h. The observed first-order maximum was converted to crystallite thickness by the application of Bragg's law. The uncertainty in the thickness was ±0.5 Å. The wide-angle X-ray patterns were obtained at room temperature using a slit-collimated Siemens D-500 diffractometer were Cu Kα radiation. The experimental voltage/current conditions were 40 kV/30 μA with incident beam divergent slits 0.3°/0.3° and antiscatter slits 0.3°/0.05°. The diffractometer was calibrated using the NBS 640b silicone powder standard.

Selected area electron diffraction patterns were obtained at 100 kV with a JEOL JEM-100CXII electron microscope, taking the usual precautions to minimize the electron beam dosage (low beam flux, sensitive photographic emulsion), thus avoiding significant radiation damage to the specimen. With a Gatan 626 heating/cooling sample stage, it was possible to obtain diffraction spacings from solution-crystallized samples at increasing temperatures. All microcrystals studied by electron diffraction were crystallized onto carbon-film-covered 400-mesh electron microscope grids by evaporation of a dilute solution in toluene. The crystals were predominately in the orthorhombic form with $R(0,0)$ rectangular layer packing of the methylene subcell, as evidenced by the characteristic $hk0$ diffraction pattern.[9] It was also possible to recrystallize the sample in situ from the melt after the initial heating experiments. In this case the chain packing reverted to a monoclinic form in the same methylene subcell so that the layer packing was $R(2,0)$ with subcell axes of $a(s)$ = 7.42 Å and $(b)s$ = 4.96 Å.

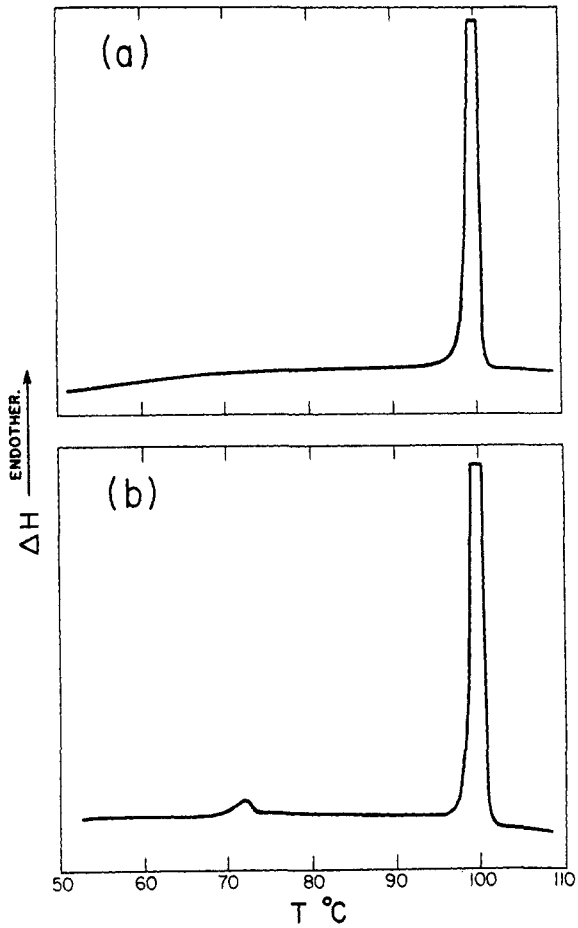

Figure 1. DSC thermograms for *n*-hexacontane: (a) sample rapidly crystallized from butyl acetate solution; (b) sample crystallized from the pure melt.

Results

The wide-angle X-ray patterns showed that rapid crystallization from solution gives only an orthorhombic unit cell. This result is similar to that reported by Takamizawa et al. for $C_{48}H_{98}$.[20] Crystallization from the pure melt resulted primarily in a monoclinic unit cell with, however, a small amount of the orthorhombic structure being present. The long periods that are observed are consistent with these assignments. The long period of the bulk-crystallized sample was 68 ± 0.5 Å, which is consistent with the value of 69.5 Å expected for the monoclinic structure. The long period for the sample rapidly crystallized from solution was 80.5 ± 0.5 Å as compared with the expected value of 78.0 Å for the orthorhombic structure. The selected area diffraction studies showed that the planar zigzag-ordered chain conformation is maintained up to the melting temperature for both unit cells. This is consistent with the IR results reported earlier which indicated only gradual and low loss of trans conformation at temperatures approaching the melting point.[7]

The thermograms for samples generated with the two different crystallization methods are given in parts a and b of Figure 1. The thermogram for the solution-crystallized sample shows only one sharp endothermic peak at 99 °C that can be identified with the melting temperature. This is the melting temperature that is expected based on reports in the literature.[4,20,21] The thermogram for the bulk-crystallized sample is given in Figure 1b. A small endothermic peak is observed at 71 °C followed by the sharp melting peak at 99 °C. The origin of the endotherm at 71 °C is unknown at present. A similar behavior was observed for $C_{50}H_{102}$: a carefully annealed sample showed

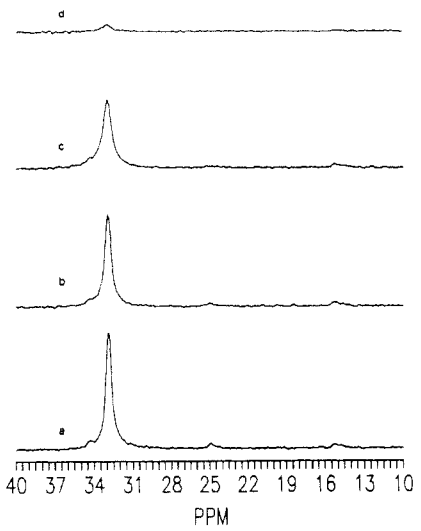

Figure 2. Variable-temperature ^{13}C CP/MAS spectra of melt-crystallized hexacontane acquired at (a) 40, (b) 51, (c) 63, and (d) 74 °C. The cross-polarization contact time was 2 ms, and the recycle time between acquisitions was 3 s. An exponential line-broadening factor of 5 Hz was applied to the raw data before Fourier transformation. The number of scans varied from 768 to 3600. The spectra were scaled by a factor of (no. of scans/768)$^{-1/2}$ in order to compare the signal-to-noise of b–d to a.

Table I
CP/MAS ^{13}C Chemical Shift Values (ppm) for Melt-Crystallized Hexacontane

temp (°C)	γ-CH_2	inner-CH_2	β-CH_2	$-CH_3$
40	34.2 (0.4)[a]	32.9 (0.3)	24.9 (0.2), 24.3[b]	15.3 (0.4), 14.8
51	34.3 (0.4)	32.9 (0.3)	24.9 (0.3)	15.2 (0.4) 14.6
63	34.2 (0.5)	33.0 (0.4)	24.9 (0.8)	15.3 (0.5)
74		33.0 (0.4)		

[a] Values in parentheses are the half-widths at half-height in ppm for the listed peak. [b] Values listed beside the main peak values are for upfield shoulders which could be clearly detected.

no DSC transitions prior to melting, while a sample quenched from the melt displayed additional transitions at ca. 5 and 23 °C below the melting point.[22]

Figure 2 shows the variable-temperature ^{13}C CP/MAS spectra for melt-crystallized hexacontane acquired over a temperature range of 40–74 °C. The chemical shifts and line widths are given in Table I. The methyl carbon is observed at 15.3 ppm, along with the β and γ carbons (24.9 and 34.2 ppm, respectively). The intense peak at 32.9 ppm corresponds to inner methylene carbons predominately in the all-trans conformation.[13,14] As the temperature increased, the overall signal-to-noise decreased. The β and γ carbon peaks were no longer detectable by 59 °C. In addition, the line widths for peaks of the inner methylene and methyl carbons began to broaden. By 74 °C, only a broad inner methylene carbon peak was detectable. At temperatures above 74 °C, no signal could be detected using cross-polarization and the measuring method was changed (to HPD/MAS) in order to obtain meaningful spectra.

Variable-temperature ^{13}C HPD/MAS spectra for melt-crystallized hexacontane were acquired between 77 and 99 °C and are presented in Figure 3. This method allows observation of more mobile materials for which signal enhancement by cross-polarization is not efficient or even possible.[23] Möller et al. used this technique extensively in their observations of various linear alkanes.[5] Table II summarizes the observed ^{13}C shifts. At 77 °C the methyl carbon peak had shifted upfield to 14.3 ppm, compared

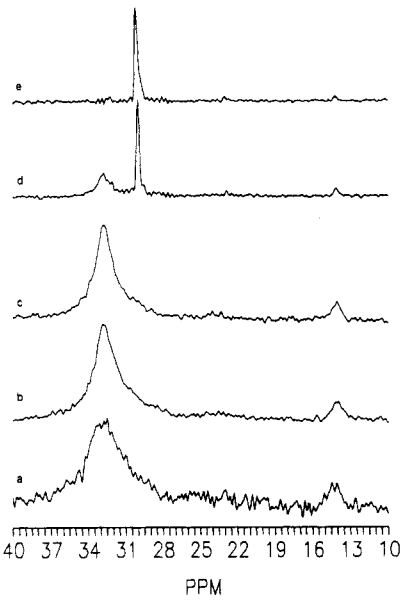

Figure 3. Variable-temperature ^{13}C HPD/MAS spectra of melt-crystallized hexacontane acquired at (a) 77, (b) 83, (c) 85, (d) 89, and (e) 99 °C. The ^{13}C 90° pulse length was 3.8 μs, and the recycle time was 30 s between scans. An exponential line-broadening factor of 10 Hz was applied to the raw data before Fourier transformation. The number of scans varied from 32 to 843.

Table II
HPD/MAS ^{13}C Chemical Shift Values (ppm) for Melt-Crystallized Hexacontane

	inner-CH_2			
temp (°C)	trans	gauche	β-CH_2	$-CH_3$
77	32.9 (1.8)[a]			14.3 (0.7)
83	32.8 (0.9)			14.0 (0.7)
85	32.8 (0.9)			14.0 (0.4)
89	32.7 (0.7)	30.0 (0.2)	22.7 (0.2)	14.1 (0.2)
99		30.1 (0.2)	22.8 (0.3)	14.1 (0.2)

[a] Values in parentheses are the half-widths at half-height in ppm for the lisited peak.

to a room-temperature value of 15.3 ppm, and had begun to narrow significantly. The β carbon peak had broadened to the extent that is was no longer visible. The γ carbon peak was obscured by the broad peak of inner methylene carbons. Spectra obtained at 83 and 85 °C showed a gradual narrowing of the peaks with a reappearance of the β carbon peak. At 89 °C, another much narrower peak was observed at 30.1 ppm, characteristic of methylene carbons undergoing rapid trans–gauche conformational isomerization.[5,11] A corresponding decrease in the all-trans methylene carbon peak was observed. Further peak narrowing was observed that results from rapid reorientation of the molecular segments which reduces line-broadening effects such as chemical shift dispersion and chemical shift anisotropy.[13] At 94 °C, the β carbon was observed as a relatively sharp peak which had shifted upfield to 22.8 ppm, a change of ~2 ppm from the value observed in the CP/MAS spectrum at room temperature. The all-trans methylene carbon peak was detectable up to the melt temperature of 99 °C.

Discussion

CP/MAS Results. We focus attention on the melt-crystallized sample. The chemical shifts of the methyl, β, and γ carbons remained constant up to ~74 °C, with only the relative spectral intensities decreasing. This decrease

in intensity indicates the onset of molecular-level motion which interferes with signal enhancement by cross-polarization. However, since the chemical shifts remain constant for all of the observable carbons, the average *conformation* of the alkane chains has not changed. This conclusion is in accord with the direct structural observations by selected-area electron diffraction which showed that the ordered, planar zigzag conformation is maintained up to the melting temperature.

Table I summarizes the values of chemical shifts and peak widths obtained. Between 63 and 74 °C, the alkane chains begin to undergo 180° flips of the entire chain (unlikely), small-angle librations of short segments, and/or lateral displacement of entire chains. None of these would disrupt the all-trans conformation of the inner methylene chain, but the latter two could reduce the ^1H $T_{1\rho}$ to the point where cross-polarization is not possible. Lateral displacement is typical of the α transition that is observed in both *n*-alkanes and polyethylene.[24] In fact, extrapolation of the dielectric loss data for the *n*-paraffins to *n*-hexacontane indicates this transition should be in the vicinity of 70 °C.

At a temperature of 74 °C, the methyl and β carbon peaks disappeared and the inner methylene carbon peak began to broaden. The loss of cross-polarization for the two end carbons indicates a more disordered and liquid-like environment, consistent with a premelt combining longitudinal disordering and rapid conformational motion of the terminal carbons. Premelting, with end sequences being disordered, is a unique feature of chain molecules,[4] and its onset is expected in this temperature region.[3] In fact, Snyder and co-workers have observed premelting in *n*-hexacontane for this temperature range using infrared and Raman spectroscopy. Electron diffusion measurements on the *n*-alkanes, including *n*-hexacontane, substantiate these conclusions since the degree of lateral chain packing (as monitored by the a/b axes ratio) gradually starts to increase in this temperature range.[9] Takamizawa et al.[20] found that the long period of *n*-hexacontane began to decrease at about 80 °C, consistent with the onset of premelting. Thus, the molecular interpretation of the CP/MAS results receives confirmation from independent diffraction studies. We have been able to confirm here the existence of chain premelting in *n*-hexacontane which involves the disorder of end-group sequences. This is a distinctly different phenomenon from both the rotator phase and that where complete chain conformational disordering occurs [as for poly(1,4-*trans*-butadiene)] but with sufficient linear chain integrity so that some element of lateral order is maintained.[25,26]

HPD/MAS Results. The HPD/MAS spectrum of 77 °C shows an upfield shift of approximately 1 ppm for the methyl carbons. This shift indicates a larger population of the gauche conformation[5,8] and is consistent with the analysis of the CP/MAS spectra given above. The appearance of the sharp peak at 30.1 ppm at 89 °C indicates that the disorder has moved farther in from the exterior of the crystallites to significantly effect the motion of the inner carbons, consistent with vibrational spectroscopy studies[7] and theoretical expectations.[4] Confirming this interpretation is the 33 ppm peak for the all-trans conformational population of the very middle methylene carbons which is not altered until the molecule completely melts.

Comparison of Melt-Crystallized versus Solution-Crystallized Hexacontane. The NMR thermal behavior of solution-crystallized *n*-hexacontane was qualitatively similar to that of the melt-crystallized material. Neither

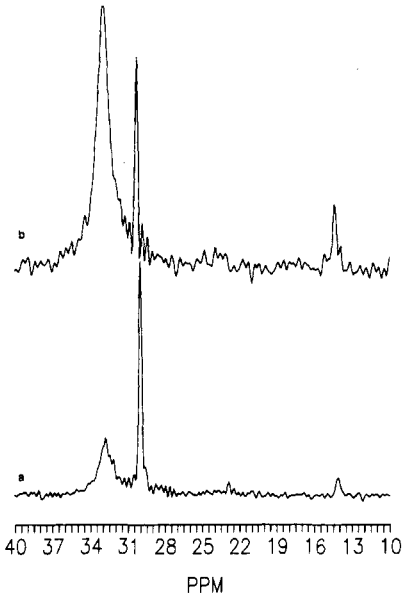

Figure 4. ^{13}C HPD/MAS spectra for (a) melt-crystallized hexacontane acquired at 89 °C and (b) solution-crystallized hexacontane acquired at 91 °C. The number of scans obtained for the spectra was 160 for the melt-crystallized sample and 249 for the solution-crystallized sample. The recycle time for both samples was 30 s. An exponential line-broadening factor of 5 Hz was applied to the raw data prior to Fourier transformation. The ^{13}C 90° pulse length used for the solution-crystallized sample was 4.6 μs.

sample could be cross-polarized at temperatures above 74 °C, and the shift in the methyl group resonance to 14.0 ppm was observed in both cases. These observations indicate that premelting occurs at approximately the same temperature. Figure 4 demonstrates, however, that there is a quantitative difference in the populations of conformations of the inner methylene carbons with increasing temperatures. From the relative areas of the peaks at ~33 and ~30 ppm at 89 and 91 °C, respectively, we find that about 50% of the detectable inner methylene carbons have become disordered for the melt-crystallized sample as compared to only 15% for the solution-crystallized samples. While these differences are not strictly quantitative, they do reflect differences in the relative number of chain segments able to undergo conformational averaging as the melting point is approached. This may be due to better crystal perfection for the solution-crystallized sample or, conversely, to the presence of interior or surface imperfections in the melt-crystallized sample which facilitate lateral motion and premelting.

The gradual, nonconcerted onset and increase in disorder for the $C_{60}H_{122}$ (and the $C_{50}H_{102}$ sample, for that matter[7,22]) confirms previous observations that, first, the orthorhombic and monoclinic crystal forms are maintained up to the melt, second, no hexagonal or rotator phase forms with increasing temperature, and, third, end-group disorder related to longitudinal diffusion occurs. This is in contrast to other samples which display concerted transitions observable by thermal analysis, including lower *n*-alkanes (which adopt the hexagonal, rotator phase), impure longer *n*-alkanes,[24] and polydisperse polyethylene samples of similar and higher molecular weight (which display observable thermal transitions apparently induced by interior or surface defects).[24] Solid-state NMR methods clearly allow the observation of both concerted and nonconcerted transitions in these materials at the segmental level and make possible the correlation of such molecular level behavior with macroscopic properties and transitions.

Conclusions

The observed loss of spectral intensity in the CP/MAS spectra as a function of temperature is a result of the increased mobility of the molecules which, however, does not change the ordered conformation of the entire alkane chain. Consequently, we were able to investigate the question of premelting in *n*-hexacontane by a combination of solid-state NMR methods. Both CP/MAS and HPD/MAS solid-state variable-temperature ^{13}C NMR spectroscopy show that the thermal behavior of melt-crystallized hexacontane is best described by the concept of premelting, where the regular packing of the end-group sequence is disrupted and the chain ends develop a disordered state allowing trans-gauche conformational isomerization. The observed shifts for the methyl and β carbons are consistent with the end sequences undergoing partial "melting" at temperatures well below that of the disordering of the inner all-trans methylene carbons which involves complete chain melting. These observations are in accord with theoretical expectations and studies of other *n*-alkanes. These results are also in very good agreement with a recent study of the vibrational spectra of *n*-hexacontane,[6] which shows that the temperature dependence of the number and location of gauche bonds along the chain is essentially the same as observed by NMR.

There is now a substantial body of evidence, both theoretical and experimental, to support the kind of premelting that has been described here. This phenomenon should not be confused with premelting due to impurities, phase transitions, or the development of conformational disorder along the entire chain molecule. It is a phenomenon unique to chain molecules and has a firm theoretical basis.[4]

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