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NMR study of the energy difference and population of the *gauche* and *trans* conformations in solid polyethylene

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Abstract

High-resolution, solid-state ¹³C NMR spectra have been obtained for four polyethylene samples, at temperatures from 20 to 100°C. The samples varied in crystallinity, lamellar thickness and molecular weight. From the chemical shift of the peak corresponding to the amorphous phase, the fraction of *gauche* conformers was determined. By assuming a Boltzmann distribution of *trans* and *gauche* conformations, the energy difference between the *trans* and *gauche* states was found to be 6.4 ± 0.5 kJ mol⁻¹. This is higher than values found previously for polyethylene and alkane chains in melt and solution states, and can be attributed to effects of the semi-crystalline morphology. The degeneracy of the *gauche* state was found to be significantly greater than the value of 2 expected for equilibrium in the melt. This is explained in terms of an additional number of *gauche* conformations due to chain folding at lamellar surfaces. The variation in the value of the *gauche* state degeneracy shows an understandable trend with changes in crystallinity and lamellar thickness. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

It is well known [1] that the polyethylene (PE) chain is comprised of lower energy *trans* (*t*) conformations of methylene sequences, and higher energy *gauche* (*g*⁺ and *g*⁻) conformations. There have been a number of studies, experimental and molecular dynamics (MD) simulations, which have produced values for the energy difference between *t* and *g* states, and for the torsional barrier, for short and long alkanes, and cyclic paraffins and polyethylene. There appears to be a wide variation in the value for the energy difference found. For example, in a MD study of amorphous PE below the glass transition, Jin and Boyd [2] found a value of approximately 2.5 kJ mol⁻¹. For butane and pentane, Darsey and Rao [3] found a value of 4.98 kJ mol⁻¹. In a MD simulation of dioctadecyldimethylammonium chloride monolayers, Adolf et al. [4] produced a value of 4.41 or 2.93 kJ mol⁻¹, depending on the expression used for the potential. Other values range from [1]

about 2–4 kJ mol⁻¹; ab initio crystal orbital calculations [5] gave 3.64 kJ mol⁻¹, Raman measurements [6] on *n*-alkanes 2.1 kJ mol⁻¹. ¹³C NMR studies [7] on *n*-alkanes, cyclic paraffins and polyethylene in solution, using methodologies similar to the present work, give a value of about 3.5 kJ mol⁻¹. However, the common feature in all these studies is that they relate to solution, melt or purely amorphous states, and there appears to be no data concerning the *t* – *g* energy difference in the amorphous phase of semi-crystalline PE, which is one objective of the present work.

At an early stage in its development, solid-state ¹³C NMR was shown to clearly distinguish between the crystalline and non-crystalline regions of PE [8]. The chemical shift difference, between the resonances, is the result of conformational differences between these phases. In the crystal, the carbons adopt an all-*t* conformation, resulting in an isotropic chemical shift of 33.5 ppm. In contrast, fast exchange between the *t* and *g* conformations occurs in the amorphous phase. When a carbon, separated by three bonds, is in a *g* rather than a *t* conformation, the resulting resonance has a smaller chemical shift. Thus, this γ -*gauche* effect moves the amorphous resonance upfield from the crystalline signal. The lowest chemical shift would be reached when the chain assumes the all-*g* conformation. Liquid cyclohexane is constrained in such a conformation, and exhibits a

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Table 1

Physical properties of the four PEs. The crystallinity was measured by DSC and the lamellar thickness by TEM experiments [11]

PE sample		Crystallinity (%)	Lamella thickness (nm)
No.	Name		
(1)	SC RCH1000	45	15
(2)	PA RCH1000	71	65
(3)	SC 00660	70	20
(4)	PA 00660	88	60

chemical shift of 27.84 ppm. Assuming that the isotropic chemical shift is determined by a linear relationship between the values of the all-*t* and all-*g* conformations, the fraction of *g* conformers, f_g , can be estimated [9] as

$$f_g = \frac{\delta(\text{trans}) - \delta(\text{amorphous})}{\delta(\text{trans}) - \delta(\text{gauche})} \quad (1)$$

where δ is the isotropic ^{13}C chemical shift.

The energy of the *g* conformations relative to *t* can be described by a Boltzmann relationship

$$\frac{n_g}{n_t} = A \exp(-E/RT) \quad (2)$$

where E is the energy difference, $n_{g,t}$ is the number of *g* or *t* conformations, and A is a pre-exponential factor. For PE chains in equilibrium in the melt, the double degeneracy of the *g* states would lead to a value for A of 2. Experimentally, the chemical shift of the amorphous phase leads to a value for f_g (Eq. (1)). Since $f_g = n_g/(n_g + n_t)$, n_g/n_t in Eq. (2) can be related to f_g by

$$\frac{n_g}{n_t} = \frac{f_g}{1 - f_g} \quad (3)$$

Therefore, from a measurement of f_g with temperature, the average energy difference E between *t* and *g* states can be

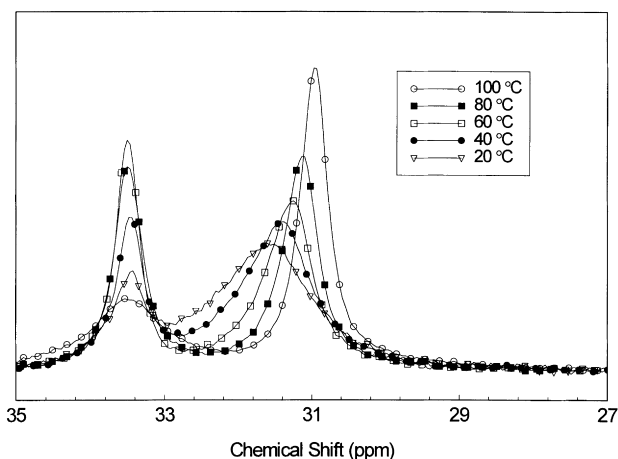


Fig. 1. Solid-state ^{13}C NMR spectra for pressure-annealed Rigidex 00660 at temperatures from 20 to 100°C, as indicated. For clarity, only every fifth data point has been plotted. It can be seen that the chemical shift of the non-crystalline resonance moves upfield as the temperature is increased. A similar effect was observed for all the PEs.

Table 2

The fraction of *gauche* conformers in the non-crystalline component, determined from the isotropic chemical shift (Eq. (1))

PE sample		Temperature (°C)				
No.	Name	20	40	60	80	100
(1)	SC RCH1000	0.321	0.357	0.386	0.411	0.445
(2)	PA RCH1000	0.349	0.377	0.410	0.441	0.468
(3)	SC 00660	0.309	0.344	0.360	0.418	0.436
(4)	PA 00660	0.323	0.338	0.391	0.422	0.448

determined, along with the pre-exponential factor A , characterising the relative population of the *g* states. In this paper, we use this methodology to determine E and A for four PE samples varying in crystallinity and lamellar thickness. The results are discussed in terms of the influence of the crystalline morphology on the amorphous phase.

2. Experimental

Solid-state ^{13}C NMR spectra were acquired at 50.3 MHz, at temperatures from 20 to 100°C on a Chemagnetics CMX-200 spectrometer. A single pulse excitation sequence, with a 4 μs 90° excitation pulse and on-resonance high power ^1H decoupling equivalent to $B_{1\text{H}} \approx 80$ kHz, was used to collect the data. Experiments were performed with magic angle spinning at 3.5 kHz. The recycle delay was 20 s. This is considerably shorter than the longitudinal relaxation time associated with the crystalline phase, and therefore this peak was partially saturated. This had the advantage of reducing the overlap between the crystalline and amorphous peaks, allowing an accurate determination of the chemical shift of the amorphous peak [10].

Four different PE samples, varying in crystallinity, lamellar thickness and molecular weight were studied (Table 1). A high molecular weight PE (RCH1000, molecular weight about 4.5×10^6 g mol $^{-1}$) and a high-density PE (Rigidex 00660, molecular weight about 1.6×10^5 g mol $^{-1}$) were used in slow-cooled and pressure-annealed forms. Details of the processing conditions can be found in a previous publication [11].

3. Results and discussion

The *gauche* population in the amorphous phase at each temperature was calculated using Eq. (1), by measurement of the chemical shift of the amorphous peak (Fig. 1), and the results are shown in Table 2. The number of *g* conformations can be seen to increase with temperature, as expected from consideration of Eq. (2).

Fig. 2 shows the plot of $\ln(n_g/n_t)$ versus $1/T$ for each sample, from which E and A can be calculated from the slope and intercept, respectively. It should be noted here that the barrier height between the *trans* and *gauche* conformations is in the range 16–22 kJ mol $^{-1}$ [12] whereas at the

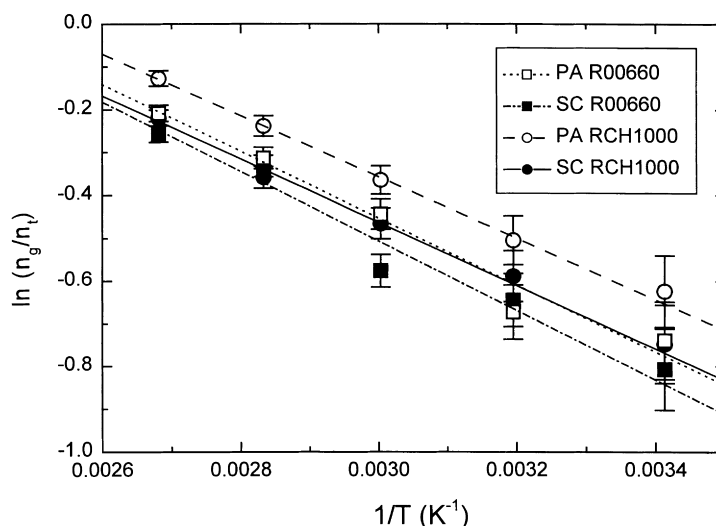


Fig. 2. $\ln(n_g/n_t)$ versus $1/T$ for the four PE samples, as indicated. The lines are fits to Eq. (2).

lowest temperature employed in this work (20°C), the thermal energy RT is only 2.4 kJ mol^{-1} . The assumption of fast exchange at this temperature may not therefore, be strictly appropriate. However, the points on the plot in Fig. 2 relating to this temperature ($1/T = 0.00341$) do not show a departure from the linear relationship. Furthermore, in Fig. 1, there is still a single peak, at 31.6 ppm, demonstrating fast exchange between t and g conformations on the NMR time-scale. The asymmetry of this peak is due to some overlap with the crystalline peak. The results are shown in Table 3. The calculated value of E , the energy difference between the states, has an average value of $6.4 \pm 0.5 \text{ kJ mol}^{-1}$. This is higher than the range of values previously found [1–7] experimentally and theoretically ($2\text{--}5 \text{ kJ mol}^{-1}$). However, to our knowledge, this is the first attempt at an experimental measure of this parameter in semi-crystalline PE, as opposed to melt and solution studies.

The value of A is consistently higher than 2, which demonstrates that a higher population of g states exist than the equilibrium distribution would predict. However, the morphology of solid PE imposes constraints on the conformational equilibrium that the non-crystalline region can exhibit. In particular, chain folds, which are present in

the interfacial material, consist of relatively short sections of chain fixed at both ends by the crystal. Folding is achieved with the majority of bonds exhibiting the g conformation [13]. Entanglements, tie chains between different crystallites and other morphological and structural constraints present in the non-crystalline region also restrict the PE chains to a limited set of conformations. As a result, the pre-exponential factor A , is only equivalent to 2 when the conformational equilibrium is unrestricted. The fact that A is greater than 2 for all samples can immediately be attributed to the significant levels of crystallinity of all the samples. The majority of the amorphous phase is contained within the fold surfaces, which will constrain the chain [13] to adopt more g conformations than would be the case for a melt at equilibrium. The magnitude of the uncertainties on the values of A obtained in Table 3 mean that comparisons between samples must be taken with a degree of caution, but in general, some tentative conclusions can be reached. The differences in the value of A obtained between the samples can, in general terms, be related to the morphology of each sample. The highest number of folds, and hence the highest value of A , would be obtained in a sample of high crystallinity and small lamellar thickness, such that the total lamellar surface area is maximised. In Table 1, it can be seen that samples 2 and 3 have very similar crystallinities, but the lamellar thickness of the pressure annealed sample 2 is three times that of 3. This is consistent with $A(3) > A(2)$. Similarly, the lamellar thickness in the two pressure-annealed samples, 2 and 4 is similar, but the crystallinity of sample 4 is significantly higher, hence the larger value of A . The crystallinity effect again dominates in the comparison between the two slow-cooled samples 1 and 3, where the lamellar thickness is similar. $A(3)$ is greater than $A(4)$, which suggests the effect of the smaller lamellar thickness is dominant in producing more fold surface in samples of not too different crystallinity.

Table 3

The energy separation E (between the t and g states) and the pre-exponential factor A , calculated from the slope and intercept, respectively, in Fig. 2, for each PE sample

PE sample		E (kJ mol^{-1})	A
No.	Name		
(1)	SC RCH1000	6.2 ± 0.4	5.8 ± 1.1
(2)	PA RCH1000	6.0 ± 0.1	6.0 ± 1.0
(3)	SC 00660	6.8 ± 1.0	6.9 ± 1.4
(4)	PA 00660	6.5 ± 0.5	6.6 ± 1.2

4. Conclusions

We have presented a NMR method for determining the $t - g$ energy difference and relative g state population in the amorphous phase of semi-crystalline polyethylene. The value was found to be $6.4 \pm 0.5 \text{ kJ mol}^{-1}$, higher than the values reported in the literature for PE and alkanes in solution or melt states (approximately $2\text{--}5 \text{ kJ mol}^{-1}$). This difference is probably due to the complex morphology of the amorphous phase, resulting from the constraining effects of the crystalline lamellae. MD simulations are currently underway to investigate this further. The degeneracy of the gauche state appears to show a correlation with the lamellar surface area, which can be qualitatively assessed from crystallinity and lamellar thickness data, although the uncertainties associated with the determination of the pre-exponential factor make this conclusion tentative at present.

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