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Local Order in Liquid *n*-Alkanes: Evidence from Raman Spectroscopic Study

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ABSTRACT: The study of the temperature-dependent Raman spectra of *n*-alkanes from the solid through melting and in the melt phase reveals that short intermolecular correlation can occur in the melt forming at T_m and just above T_m a sizable concentration of extended trans C−C bonds sequences. The mean length of these trans sequences is not less than approximately 5 units. The implications of these observations regarding the mechanism of crystallization of *n*-alkanes are discussed.

1. Introduction

The issue of local order in amorphous polymers has been very controversial and is still the center of interest in polymer circles. In the past many authors have tackled the problem with a variety of theoretical and/or experimental studies. The understanding of these phenomena implies the possibility of detecting short or long-range correlation between polymeric chains.

It has been generally recognized that the study of short chain model molecules may be an easier way to approach the problem. This was the approach taken by some authors[1] in the study of molecular orientational correlation and local order in liquid *n*-alkanes as models of the structure of amorphous polyethylene. These studies were aimed at deriving information capable of describing the structure of *n*-alkanes in the melt phase either as a collection of unperturbed conformationally distorted molecules (as in solution) or as systems with a liquid-crystal-like structure. The authors of ref 1 present measurements of depolarized light scattering, magnetic birefringence, small-angle neutron scattering, Raman spectroscopy, and wide-angle X-ray scattering. They conclude that in liquid *n*-alkanes there exists a very weak orientational correlation which is far from a nematic-like state and which can be characterized by a correlation length <10 Å. They stress that the correlation length is extremely small (approximately 8−9 CH_2 units). From SANS and Raman experiments they conclude that no conformational changes with temperature occur in the melt.

In this paper we present temperature-dependent Raman spectra and reconsider the whole vibrational problem with the aim to extract from the experiments more details on the molecular structure of liquid *n*-alkanes. The analysis consists of a combined use of frequency and intensity data[2−4] and is based on concepts of molecular dynamics of one-dimensional crystals.[5,6] Our particular interest is also focused at the evolution of the intra- and intermolecular structures of *n*-alkanes with temperature, from the solid through the pseudorotatory "α" phase and in the melt.[7] We are interested in detecting signals to be possibly associated with the intra- and intermolecular organization of molecules just above the melting point in order to ascertain whether some sort of memory of the structure of the solid is retained within a certain range of temperatures. We wish also to find some spectroscopic indication of the molecular ordering, if any, in the melt in preparation of crystallization.

2. Experimental Section

A large family of odd and even *n*-alkanes (from C_5 to C_{44}) has been considered in our experiments. For sake of simplicity, the data reported in this work are restricted only to a few molecules as prototypical cases. Chromatographically pure materials were purchased from Aldrich and were used without further purification. The purity of the compounds was checked by differential scanning calorimetry (Mettler DSC 30). The samples were sealed in capillary tubes, and the Raman spectra were recorded with a DILOR $X-Y$ Raman spectrometer equipped with a multichannel detector; all measurements were made with the exciting line at 514.5 nm of an Ar^+ laser, and the average laser power on the sample was ≈20 mW. The temperature of the samples was controlled with a Mettler FPH82 hot stage suitably modified for recording Raman spectra. Temperature measurements and stability were accurate within 0.1 °C. The spectra at very low temperatures were recorded with a closed-circuit cryostat of Galileo (accuracy ±1 °C). Raman band intensities were measured as peaks heights with respect to a suitably chosen baseline.

For a few prototypical cases great care has been taken to check the reversibility of the observed temperature-dependent spectra during the heating and cooling processes with small ΔT through the melting temperature, hereafter referred to as T_m. Typical Raman spectra of a few *n*-alkanes in the solid and in the liquid phase are given as examples in Figures 1−3.

3. Spectroscopic Probes

When polymers are considered as one-dimensional crystals, phonon dispersion curves $\omega(k)$ can be and have been calculated.[5] The shape of the frequency branches in $\omega(k)$ is related to the extent of intramolecular coupling. Some of the modes are almost k-independent while some show large frequency dispersion with k, thus indicating the local and collective character, respectively, of the corresponding phonons.[2,3,8]

We focus our attention to a few $k \approx 0$, Raman-active, modes which we use as probes of the existence of trans-planar segments. In this paper we do not study polyethylene (PE) but short oligomers of general chemical

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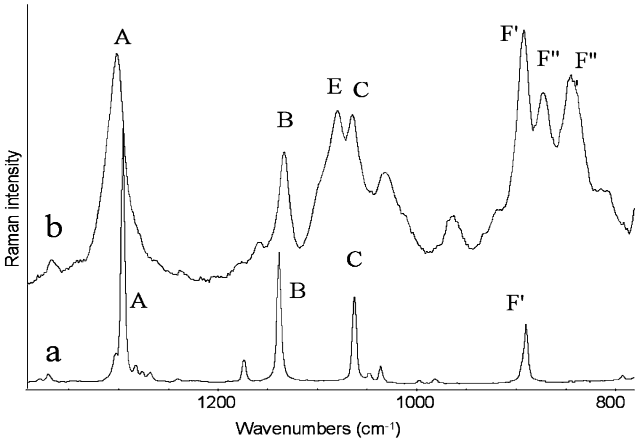

Figure 1. Raman spectrum of n-dodecane (C_{12}) in the range 1400−800 cm^{-1}: (a) solid at −260 °C; (b) liquid at room temperature. For the labeling of the lines see text.

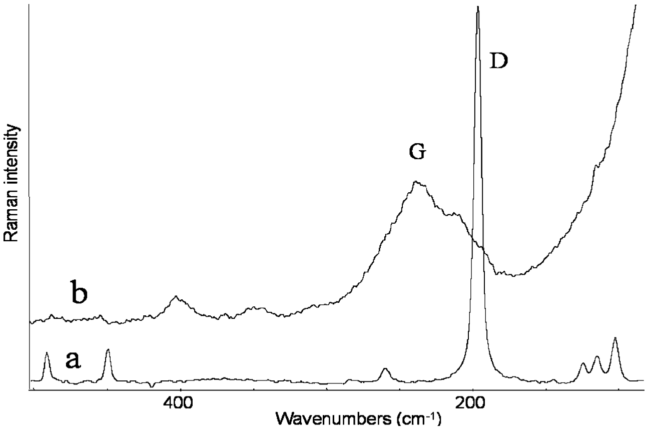

Figure 2. Raman spectrum of n-dodecane ($C_{12}H_{26}$) in the range 500−100 cm^{-1}: (a) solid at −260 °C; (b) liquid at room temperature. For the labeling of the lines see text.

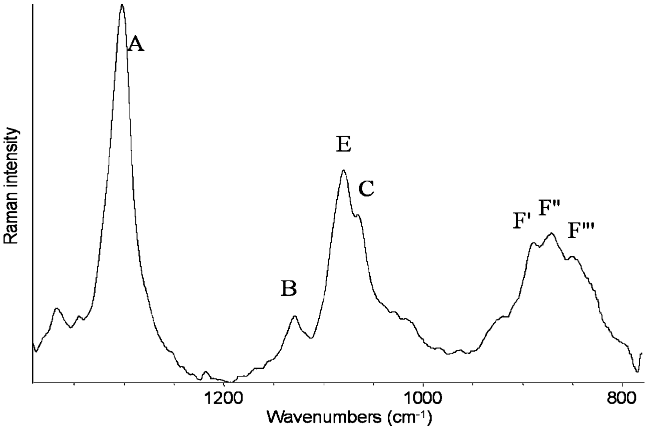

Figure 3. Raman spectrum of liquid n-tetratriacontane ($C_{34}H_{70}$) at 80 °C in the range 1400−800 cm^{-1}. For the labeling of the lines see text.

formula $CH_3-(CH_2)_N-CH_3$. Throughout this paper the number of CH_2 unit in each oligomer will be identified by N.

When relatively short oligomers of ethylene (i.e., n-alkanes) are considered, the dynamical characteristics of PE are not lost. The IR and Raman bands of the oligomers still correspond to the $k \neq 0$ phonons of the "infinite" 1-d lattice, and end effects can be neglected unless very short oligomers are considered where the distinction between end group modes and phonons becomes meaningless because of strong intramolecular coupling.[8] If the Brillouin zone of the 1-d crystals is considered in k space, the $k \neq 0$ phonons we will be focusing on are those closest to the zone center ($k = 0$) which show the strongest spectroscopic activity since they approach the $k = 0$ modes of a perfect infinite crystal.[9] The value of k, or of the corresponding phase coupling φ,[8] is determined by the number of repeating CH_2 units making up the oligomer molecule. On the other hand, characteristic end-group modes can be located in the spectra and used as diagnostic tools.[7,8,10,11] The Raman lines labeled A−G in the spectra of Figures 1−3 are those used in this work:

- Line A (Figures 1 and 3). The CH_2 twisting $k \approx 0$ phonon is observed as a strong Raman line near 1295 cm^{-1} for any polymethylene system and is characteristic of a highly localized motion. The frequency of this phonon is practically independent from the number of CH_2 units[8] and by the conformation of the molecular chain and its intensity is linear with the number of CH_2 units.[12] This Raman line is sharp and strong for solid polymethylene systems and broadens slightly when conformational disorder is introduced.[12]

- Lines B and C (Figures 1 and 3). The two $k \neq 0$ phonons observed for all-trans chains near 1130 and 1060 cm^{-1} are due to the in-phase and out-of-phase stretching of the C−C bonds (lines B and C, respectively).[8] These two phonons belong to a phonon branch strongly dispersed,[7] thus indicating that the vibrations are largely collective as a result of intramolecular couplings which extend throughout a certain length of the molecular chain. These lines are known to occur only when all-trans sequences exist in the materials. The first line due to the in-phase C−C stretching shows a slight dependence on the length of the trans-planar segment ($\Delta v \approx 15$ cm^{-1});[8] the larger shift is observed for very short chains. This shift originates from the intramolecular coupling with the end groups.[8]

- Line D (Figure 2a). The chain length dependent LAM(1) vibration (longitudinal accordion motion) occurs at low frequencies and is generally used for measuring the length of the polymethylene chain in the all-trans conformation.[13]

When conformational disorder (C−C bonds in a gauche conformation G) is introduced in the n-alkane chain, conformational defects (e.g., G, GTG, GTG′, end-TG, and end-GT) are generated, and the following spectroscopic markers of well-known defects are observed in the Raman spectra[7,10,14] as discussed below:

- Line E (Figures 1b and 3). The stretching of the C−C bond involved in the G conformation becomes a highly localized mode which gives rise to a characteristic Raman line[15] located near 1080 cm^{-1}.

- Lines F (Figures 1 and 3). A group of lines associated with the C−C stretching of the end groups (F′ end-TT at 890 cm^{-1}, F″ end-TG at 870 cm^{-1}, and F‴ end-GT at 840 cm^{-1}).[7,10] These lines float on top of a nonselective broad background which is generally observed in the Raman spectra of conformationally disordered chains.[16]

- Line G (Figure 2b). A broad and weak scattering near 220 cm^{-1} associated by Snyder to a motion of conformationally disordered chains. The mode is described as disordered-Lam (D-LAM).[17] This broad scattering can also be taken as the envelope of LAM-1 modes of short trans-planar sequences (number of $CH_2 \leq 8-9$). This concept will be used later in this paper.

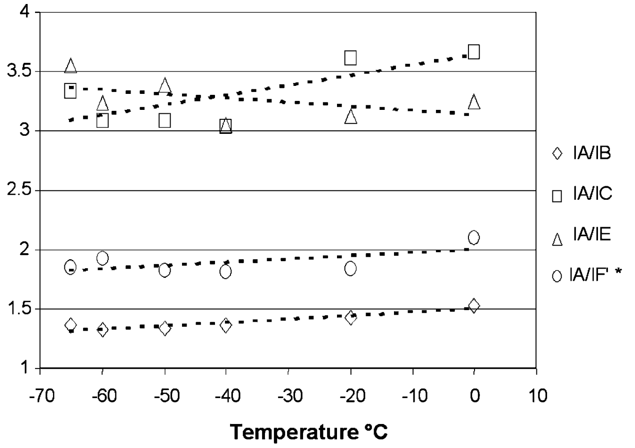

Figure 4. Temperature dependence of the intensity ratios between Raman lines A, B, C, E, and F′ for *n*-octane (C_8) in the liquid phase. For the labeling of the lines see text. The values of the ratio $I_A/I_{F'}$ turned out to be superimposed to the I_A/I_B; they are shown upshifted by 0.5 for clarity.

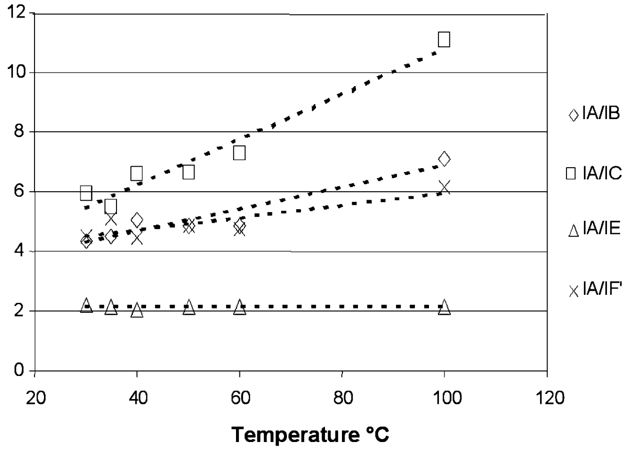

Figure 5. Temperature dependence of the intensity ratios between Raman lines A, B, C, E, and F′ for *n*-octadecane (C_{18}) in the liquid phase. For the labeling of the lines see text.

4. Chain Flexibility of Single *n*-Alkane Chain

In the comparison which follows we analyze the changes of the intensity ratios between some of the lines discussed above (which are more relevant to the issue of this paper; other possible correlations are purposely neglected and will be treated elsewhere) as a function of the temperature for three chains C_8H_{18}, $C_{18}H_{38}$, and $C_{34}H_{70}$ (hereafter labeled as C_8, C_{18}, and C_{34}) considered as the prototypes of short, medium, and long molecules, respectively. The data from other *n*-alkanes of different length will obviously be taken into account. We examine the spectra of the samples in the liquid phase from T_m to higher temperatures.

- C_8 (Figure 4). Both the intensity ratios I_A/I_B and $I_A/I_{F'}$ indicate a small decrease of the fraction of trans-planar sequences with increasing temperature; a consequently small increase of uncorrelated G conformations is indicated by I_A/I_E. The use of these conformational probes is, however, not fully safe for *n*-octane since end effects may still be active in such a short molecule.
- C_{18} (Figure 5). The *T* dependence of I_A/I_B (and also of I_A/I_C) indicates that the fraction of matter organized in trans-planar sequences decreases with increasing T; this is confirmed also by $I_A/I_{F'}$, which probes the structure of the ends of the molecules some of which keep their ends straight-trans even in the liquid phase. The intensity ratios I_A/I_E with the increase of *T* maintains a constant value. This trend suggests that the gauche population, in the range of temperature considered, increases more slowly than the decrease of the trans-planar sequences as indicated by I_A/I_B.
- C_{34}. The observations for this molecule are not as easy as for the other cases because the Raman line associated with trans-planar sequences are more broad and weak. The spectroscopic data are, however, similar to those derived for C_8 and C_{18}.

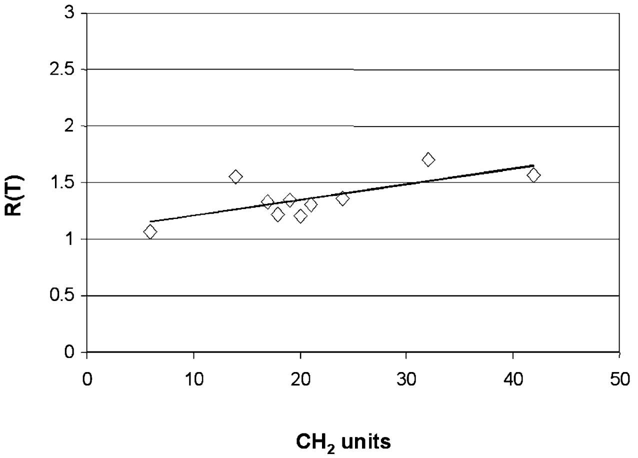

Figure 6. Intensity ratio between the Raman-active CH_2 twisting mode (line A) and the Raman-active C−C stretching mode (line B) of all-trans *n*-alkanes molecules in the solid state studied in this work.

5. Concentration of Trans-Planar Sequences

From the temperature-dependent Raman spectra discussed in section 4 we have derived in a qualitative way the idea that relatively “long” trans sequences may still exist in the melt just above T_m and that they may persist when temperature increases at least within a limited temperature range.

In what follows we present an attempt of a quantitative evaluation of the fraction of matter organized in all-trans conformation. Let us first consider the intensity ratios I_A/I_B we have measured for a series of *n*-alkanes ($N = 4-40$) in the solid state at a temperature at which all chains can be safely taken to be all-trans-planar. Such a ratio is slightly increasing with *N* (Figure 6) with an average value that can be taken as ≈1.3, thus indicating the linear dependence of the intensity of the line B with *N*. Because of the collective character of the vibrational mode associated with line B, the intensity of this line can be taken as a measure of the amount of material organized in all-trans chains. If it is assumed that this ratio remains approximately the same also for trans-planar sequences in the liquid phase, we can estimate the approximate concentration of trans C−C bonds organized in sequences which contribute to the intensity of the line B in liquid phase. For a solid *n*-alkane with N CH_2 units let α_A and α_B be the contributions by each CH_2 to the intensity of the lines A and B. One can write

$$I_A/I_B = N\alpha_A/N\alpha_B = 1.3 \qquad (1)$$

For a liquid *n*-alkane with *N* CH_2 groups let $N^*(T)$ be the number of CH_2 organized in all-trans sequences at a temperature *T*. The following relation can be written:

$$N\alpha_A/N^*(T)\,\alpha_B = R(T) \qquad (2)$$

where $R(T)$ is the experimental intensity ratio I_A/I_B measured at the temperature T. The percent concentration $C_{trans}(T)$ of C−C bonds in all-trans sequences is given by

$$\%\,C_{trans}(T) = (100\cdot\alpha_A/\alpha_B)/R(T) \qquad (3)$$

From the experimental values of $R(T)$, shown in Figure 7, the concentration of trans-planar sequences as a function of T can be easily calculated and are plotted in Figure 8. It is immediately seen that the amount of matter in the trans conformation is nonnegligible even at temperature higher than T_m.

The evidence so far collected indicates that line B originates from the existence of trans segments of a sizable, but yet undetermined, length. From the values of $R(T)$ just above T_m we can estimate that for C_8, C_{16}, C_{18}, C_{21}, and C_{34} the fraction of the material organized in trans sequences is ≈85%, ≈37%, ≈32%, ≈23%, and ≈15%, respectively. It follows that if it is assumed that every chain in the sample contains the measured % C_{trans}, it becomes possible to estimate the minimum mean length of the trans-planar sequences. Such a length is obviously the minimum mean average length compatible with the measurements. The mean length estimated from our experiments turns out to be ≈4 C−C bonds in the trans conformation, as shown in Figure 9.

6. Disordered Matter

Unlike the case of the all-trans chains, the direct experimental determination of the amount of conformationally disordered matter cannot be made from the Raman spectrum since an all-gauche internal standard does not exist. As already stated, Raman lines F′, F″, and F‴ can reveal the conformations at the end of the n-alkane chains; analogously, the infrared absorption spectra provide information on the existence of other specific conformational defects such as GTG′, GG, GTG, and end-TG. On the other hand, let us assume that the intensity of the Raman line indicated above as E near 1090 cm^{-1} may be taken as an approximate indication of the total amount of G structures. In such a case the concentration of G conformations as a function of temperature in the liquid phase from T_m upward may be probed by the ratio I_A/I_E. Within experimental errors the values of I_A/I_E vs T of all n-alkanes are practically similar and decrease very slowly with increasing temperature (see Figures 4 and 5). If X is the fraction of matter organized in relatively long trans sequences as measured by line B, $1 - X$ is the fraction of matter which may reasonably consist both of G structures, as measured by the line E, and of a population of trans structures not organized in long sequences (∼1−4 CH_2 units). Any further speculation is not supported by clear experimental data.

7. Toward Long Straight Trans-Planar Chains Approaching the Temperature of Crystallization

The existence of a nonnegligible concentration of entirely trans-planar chains in liquid short n-alkanes (e.g., C_5−C_8) at low T, just above T_m, is proven by the observation of the LAM-1 mode. As shown in Figure 10 for n-octane, LAM-1 of the all-trans molecules in the solid (−75 °C) is unquestionably observed also for the liquid at −20 °C. Raman spectra of these materials were already reported in ref 1 and are in agreement with a series of spectra recorded by us during this work. The concentration of entirely trans-planar chains decreases with increasing N, and the LAM-1 band becomes hardly observable for $N \approx 7$.

We have extended our experiments to the study of the Raman spectrum of n-dodecane at room temperature and at −11 °C, approaching its crystallization temper-

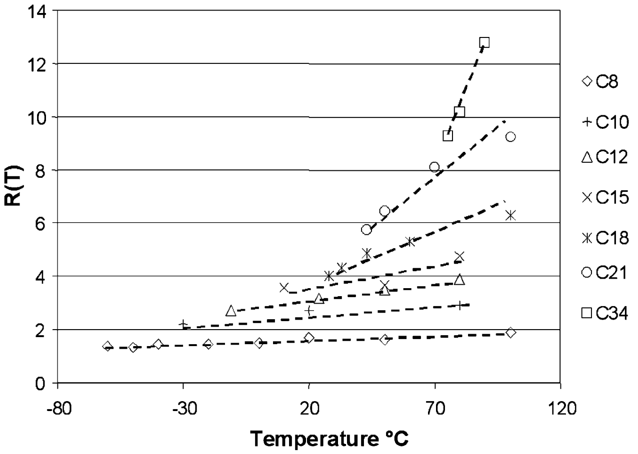

Figure 7. Experimental values of $R(T)$ for some n-alkanes in the liquid phase.

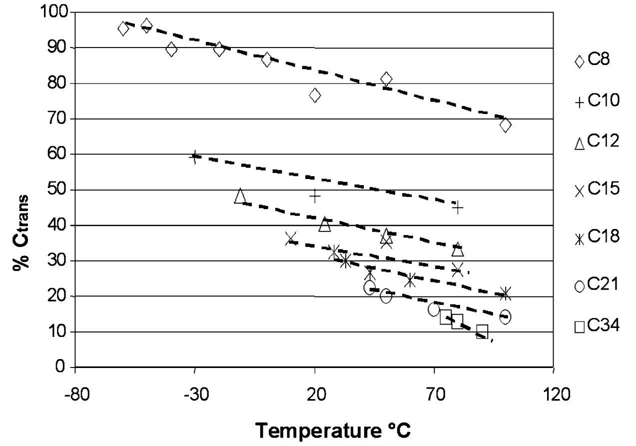

Figure 8. Temperature evolution of predicted concentration of trans-planar sequences in the liquid phase for various n-alkanes.

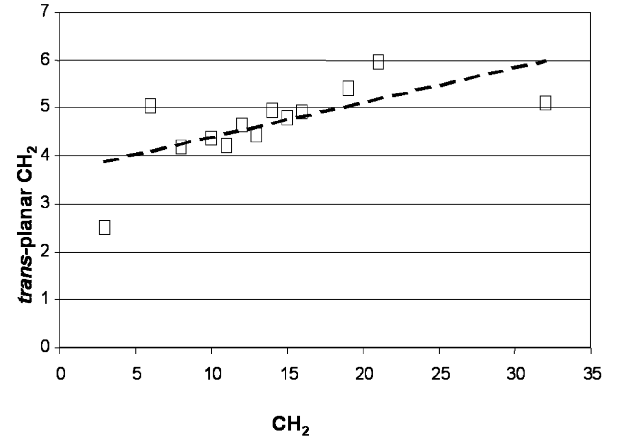

Figure 9. Predicted minimum mean number of CH_2 units organized in a trans-planar sequences for every chain just above T_m.

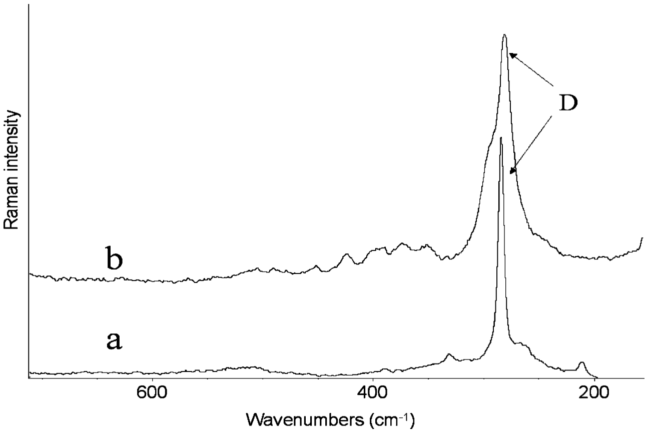

Figure 10. LAM(1) mode of *n*-octane: (a) in the solid phase at −75 °C and (b) liquid at −20 °C.

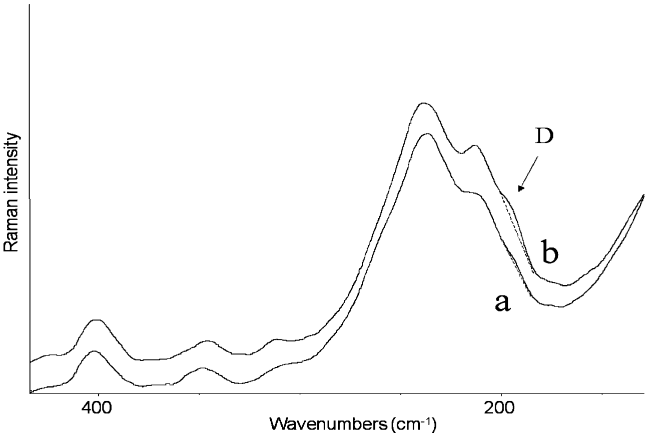

Figure 11. Temperature dependence of the Raman spectra in the LAM-1 region for *n*-dodecane: (a) at room temperature and (b) at −11 °C. The appearance of line D is taken as evidence of the onset of formation of fully trans-planar molecules.

ature. As shown in Figure 11, the scattering of LAM-1 at 196 cm^{-1}, hardly noticeable at 28 °C, becomes clearly more noticeable at −11 °C (line D).

Through the observation of LAM-1 modes at just above T_m for relatively short (but not too short *n*-alkanes), as seen above in the case of C_{12}, we believe we are probing the elementary act of formation of the seed of crystallization which goes through a transplanarization of a few molecules which, on their turn, may favor the formation of bundles of molecules and then of the crystal. It should be noticed that the length of the straight trans-planar chains, mentioned above, which are detected by LAM-1 near crystallization is that of the entire molecule. As previously discussed, shorter trans chains should show their LAM mode just in the frequency range covered by the scattering described by Snyder as D-LAM.[17] We do not find anything conceptually wrong to take an alternative interpretation of D-LAM proposed by Snyder and to consider D-LAM as the envelope of LAM-1 modes of trans chains with $N \leq 5$, i.e., just the average length compatible with the data reported in Figure 9.

8. Discussion

The scenario which emerges from the study of the Raman spectra of *n*-alkanes is that from the crystal to the melt just above T_m molecules may keep a "memory" of their crystalline organization through weak intermolecular cohesive forces. When liquid *n*-alkanes approach crystallization, molecules (if short) or section of molecules (if long) may become trans-planar, favoring the formation of bundles which evolve into a crystal. These concepts lead again to the "fringed micelle model" proposed for the crystallization of polymers.

The suggestion that intermolecular cohesive correlations may still exist just above T_m comes from the analysis of several *T*-dependent physical parameters of *n*-alkanes in going from the solid to the liquid phase. We consider first the experimental values of viscosity and density as given by Rossini et al.[18] From the density of the liquid-phase one can derive the average volume V_m occupied by each chain and the average volume V_{CH_2} (hereafter expressed in Å^3) occupied by each CH_2 group. If V_{CH_2} is the volume of a sphere associated with each CH_2, a radius r_{CH_2} (hereafter expressed in Å) can be derived.

Let us consider C_{18} as a prototypical molecule. In the solid phase both V_{CH_2} and r_{CH_2} can be derived from crystallographic data: $V_{CH_2} = 26.44$ and $r_{CH_2} = 1.85$. In the melt phase we calculate $V_{CH_2} = 30.03$, $r_{CH_2} = 1.93$ at 20 °C; $V_{CH_2} = 31.96$, $r_{CH_2} = 1.97$ at 90 °C; $V_{CH_2} = 36.16$, $r_{CH_2} = 2.05$ at 210 °C; and $V_{CH_2} = 42.17$, $r_{CH_2} = 2.16$ at 330 °C. We notice that in the temperature range in which the changes of viscosity are large the changes of V_{CH_2} and r_{CH_2} are relatively very small and close to the values derived for the solid. This fact makes it logical to think that the mobility of chains should be very restricted (thus implying large values of the viscosity), suggesting that just above T_m molecules are forced to be somewhat organized in loose "bundles" with intermolecular contacts which may allow only longitudinal mobility and possibly some kind of chain twisting.[7,19] At higher temperatures V_{CH_2} increases substantially with the consequent increase of molecular mobility.

It is interesting noticing that when *n*-alkane molecules crystallize in the orthorhombic lattice ($r_{CH_2} = 1.77$ Å for polyethylene) with two molecules per unit cell, sizable *T*-dependent correlation field splittings are observed in both the IR and Raman spectra for the vibrations of CH_2 bending ($\Delta v \approx 20$ cm^{-1}) and rocking ($\Delta v \approx 10$ cm^{-1}).[7,20,21] This means that the kind and strength of intermolecular correlations acting at $r = 1.77$ Å can be revealed in the spectra. Upon heating the orthorhombic lattice expands anisotropically,[22] intermolecular forces weaken very rapidly, and the splittings decrease and then disappear[7,23,24] even if interchain distances have increased only slightly.

On the basis of the study of the intermolecular potential in such apolar and hardly polarizable polymethylene chains, these observations are consistent with the fact that intermolecular correlation are very short range.[25]It has to be noticed that the phenomenon of lattice expansion and longitudinal diffusion occurs while chains are still organized in the solid phase. The idea that just above T_m some sort of short-range intermolecular correlation may still occur, keeping a "memory" of the previous "ordered" structure, is thus justified since r_{CH_2} is still close to that of the crystal.

On the other hand, the description, at the molecular level, of the melting process of finite polymethylene chains presently available adds further rationale to what is being studied in this work. Experimental and theoretical evidence has been offered, and never disclaimed, that the process of melting of crystalline lamellae develops with the onset of a longitudinal motion[7] (possibly caused by the propagation of twistons[19]) which pushes the molecules out of the lamella surface.[7,10,19,26–28] Surface disordering takes place as a premelting phenomenon.[10,29] (For a full discussion of the spectroscopic experiments on this subjects see ref 29.) When T_m is approached, it is likely that conformational disordering proceeds further from the disordered surface into the "core" of the lamella. It is quite conceivable that the bundled trans chains, whose existence is suggested in this work, are the "pseudo-ordered trans-planar" domains which remain in the material as the results of weak intermolecular correlations and which oppose the disordering coming from either ends of the chains. The model of "fringed micelles" may still be used conceptually for the description of the internal structure of polymethylene systems near and above T_m. The dimensions of the micelles and the mobility of the chains forming such domains are strongly T dependent. Micelles tend to collapse when the disrupting forces due to conformational disorder from either surfaces overcome the "cohesive" forces between trans-planar chains.

The results obtained in this work seem to contradict the description given by the RISM model on the structure of n-alkanes in the melt.[30] RISM predicts that (i) for an infinite noninteracting chain the trans/gauche ratios are 64.5/35.5 at 300 K and 60/40 at 400 K; (ii) the T-dependent concentrations of trans segments of various lengths are much smaller that those estimated from Raman intensity ratios for long chains. The reason for such differences may be that this work seems to tell us that nonnegligible intermolecular interactions take place especially when approaching T_m, thus suggesting that the RISM model be nonadequate to describe what happens near T_m.

Since the spectroscopic data have been shown to be reversible when samples are heated or cooled through T_m, the bundling up of the chains through intermolecular correlation, as presented in this work, can be taken as the elementary step in the crystallization process of n-alkanes.

The existence of intermolecular correlations, at least for chains of a certain length, and the consequent formation of domains of straight trans-planar chains is in full agreement with theoretical and experimental studies. The numerical simulations by Klein[31] on polymethylene systems show the possible existence (i) of parallel ordered chains at low temperature and (ii) of thermally activated longitudinal motions of single chains or of an ensemble of chains with the consequent formation of conformational disordering on the lamella surface and possibly of chain mismatching.

Of great interest are also experimental data from scanning tunneling microscopy (STM) of n-alkanes.[32,33] In these works variable-temperature STM was used to observe molecular dynamics and structure in the vicinity of order–disorder transitions in n-alkane monolayers at the interface between graphite and organic fluids. The lattice dimensions of graphite are incommensurate with the geometry of the trans-planar structures of n-alkane chains, thus removing the possibility of preferential matching of the molecules with the substrate. Clear evidence is reported of parallel organization, longitudinal displacements, surface disordering, molecular mobility, intermolecular diffusion.

9. Conclusions

The analysis of the T-dependent vibrational Raman spectra of n-alkanes of various lengths indicates that just above the melting temperature and in a nonnegligible temperature range above T_m weak and short-range intermolecular correlation can occur. Intermolecular correlations activate the formation of segments (possibly forming bundles) of trans-planar chains with a minimum length of approximately 5–6 CH_2 units.

From this work it clearly emerges the fact that the crystallization in an n-alkane system goes through the formation of seeds consisting of weakly bundled segments of trans-planar chains with an minimum average length of $\geq$5–6 CH_2 units. When the temperature is raised, bundles are quickly destroyed; the collapse depends on temperature and chain length.

Our work agrees with most of the conclusions derived with independent techniques in ref 1, namely (i) the model of a nematic-like structure for liquid n-alkane melts is not applicable and (ii) the proposal of the existence of weak orientational correlation characterized by a short correlation length and/or the existence of pretransitional ordering of very short segments ($\approx$8–9 CH_2).

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