Vibrational spectroscopic studies of linear and cyclic alkanes C_nH_{2n+2}, C_nH_{2n} with $24 \leqslant n \leqslant 288$: Chain folding, chain packing and conformations

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Evidence of chain folding in long chain linear alkanes C_nH_{2n+2} with $n \geqslant 168$ was obtained by Raman and *FT*i.r. spectroscopy. Investigation of cyclic alkanes C_nH_{2n} with $24 \leqslant n \leqslant 288$ using vibrational spectroscopy allows for identification of specific bands due to folding as well as determination of conformational sequences in the fold region. The cyclic alkanes with $n = 48$, 72 and 96 were crystallized from solution with monoclinic structures, whereas the alkanes with $n = 144$ and 288 were obtained as orthorhombic crystals. It has been found that the cyclic alkanes with $n = 72$ and 96 crystallize from the melt as crystallites with a high degree of orthorhombic character.

(Keywords: linear and cyclic alkanes; chain folding; chain packing; conformation; vibrational spectroscopy)

INTRODUCTION

It is well known that semicrystalline polymers such as polyethylene usually crystallize in a two phase system of crystalline and amorphous regions, where the ratio of these phases can easily be changed depending on crystallization conditions. In particular, determination of configurations and conformations in the amorphous region resulting from chain folding in the polymers has been one of the important basic problems in polymer science for over three decades. Two main models of folded-chain lamellae in polymers have been proposed: (a) the adjacent re-entry (sharp) fold model[1,2] and (b) the random re-entry (switchboard) fold model[3] as well as several modifications of (a) and (b)[4–6]. Analysis of g.p.c., i.r. and ^{13}C n.m.r. spectroscopy data, along with neutron scattering on perdeuteropolyethylene or polyethylene, have shown that solution grown crystals have structures consistent with the adjacent re-entry fold model[7–13]. This type of sharp chain folding can be closely related to the structures of long chain cyclic alkanes because they crystallize with well-defined conformations having two parallel all-*trans* stems, combined with two loops at both ends of the ring structure.

In this paper we report the results of Raman and i.r. spectroscopic investigations of chain folding phenomena in long chain linear alkanes C_nH_{2n+2} with $n > 100$ as well as the peculiar packing behaviour and fold conformations of cyclic alkanes C_nH_{2n} with $24 < n < 288$.

EXPERIMENTAL

Materials

Samples of linear and cyclic alkanes used for this study were synthesized as reported elsewhere[17,18].

Measurements

I.r. spectra were obtained on a Bruker FT-IR spectrometer IFS 113V. Spectral resolution was maintained at 1 cm^{-1}. Measurements on solution grown crystals (SC) were performed using KBr pellets. Although grinding and pressing can introduce defects and/or phase transformations this method was used, as the results from the i.r. investigations showed excellent agreement with X-ray, electron microscopic and Raman-investigations where the crystalline samples were used directly. This seems to indicate that even if some defects were produced during the KBr sample preparation, they do not contribute significantly to the overall results. For melt grown crystals (MC), the following method was used: samples of thickness 100–200 μm were sandwiched between KBr windows. For the preparation of films, the samples were melted between KBr windows and slowly cooled. Raman spectra were obtained using a Spex double monochromator model 1403. The minimum band pass was 0.5–1.0 cm^{-1}. Excitation was provided by an argon ion laser from Coherent (model CR-12). The plasma lines of the ion laser were eliminated by a Spex

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Lasermate monochromator. Temperature (80–340 K) was controlled using an Oxford cryostat. Wide-angle X-ray scattering diagrams were obtained using nickel-filtered CuKα ($\lambda = 1.542$ Å) radiation on a Philips plate film camera.

RESULTS AND DISCUSSION

In previous papers we have reported evidence of chain folding in long chain linear alkanes by characterization of longitudinal acoustic modes (LAM) observed by Raman spectroscopy, with its frequency being inversely proportional to the length of an all-*trans* chain[1][7]. It was found that linear alkanes with $n \geqslant 168$ no longer crystallize in the fully extended form, but on annealing at high temperatures, the extended form is again observed. Furthermore, evidence of chain folding can be obtained by vibrational spectroscopic analysis from the appearance of bands due to *gauche* conformers arising from chain folding. In addition, information about chain packing in cyclic alkanes can be obtained from vibrational spectroscopic analysis.

Raman spectroscopy

CC stretching region. Raman spectra in the CC stretching region for extended linear alkanes C_nH_{2n+2} with $n = 48$ and 72 and a folded chain alkane with $n = 168$ (crystal thickness L_{LAM}: 111 Å at crystallization temperature 10°C)[17] in the crystalline or molten state are illustrated in *Figure 1*. In general, perfect crystalline linear alkanes with $n = 48$ and 72 possessing orthorhombic chain packing show two narrow bands, representing asymmetric ($\Delta\tilde{\nu}_{as}$) and symmetric ($\Delta\tilde{\nu}_s$) stretching vibrations at 1131 and 1063 cm^{-1}, respectively. In the molten state of the alkane with $n = 24$, these bands virtually disappear in intensity and one broad scattering region centred at *ca.* 1080 cm^{-1} resulting from *gauche*-conformers appears. By comparison of spectra from the solid and molten states, the broad band with a maximum at *ca.* 1080 cm^{-1} near the $\Delta\tilde{\nu}_{as} = 1063$ cm^{-1} band in the linear alkanes with $n = 168$ may be assigned to *gauche*-conformers in the folding region arising from the supermolecular structure. These spectral features are similar to those observed in semicrystalline polyethylene by Strobl and Hagedorn[19].

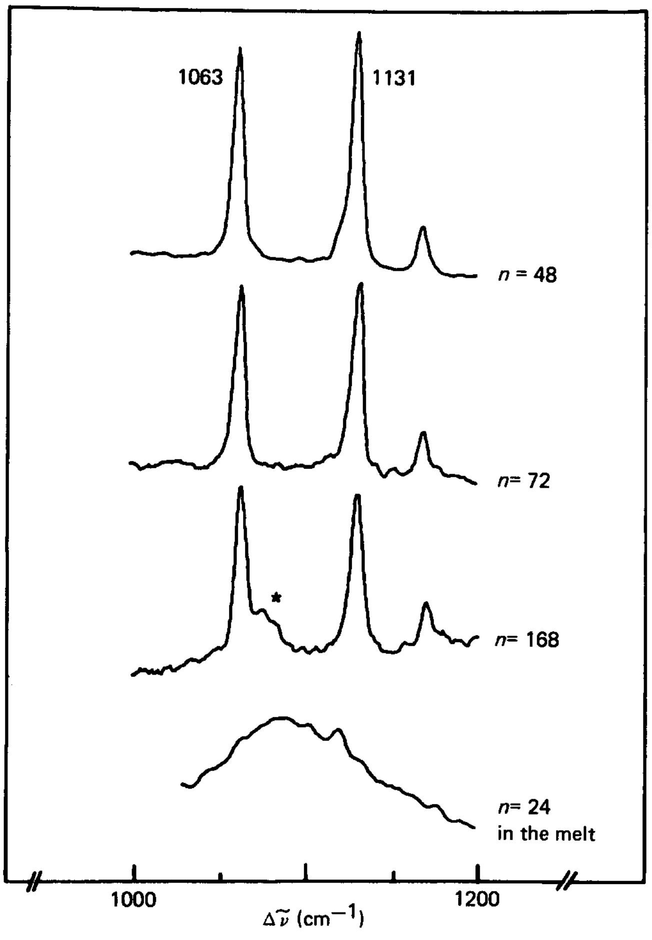

Figure 1 CC-stretching region of Raman spectra of linear alkanes C_nH_{2n+2} with $n = 24$, 48, 72 and 168 in the solid or molten state. The alkane with $n = 168$ was crystallized from n-heptane at 10°C. An asterisk (*) attached to the spectrum indicates the *gauche* components

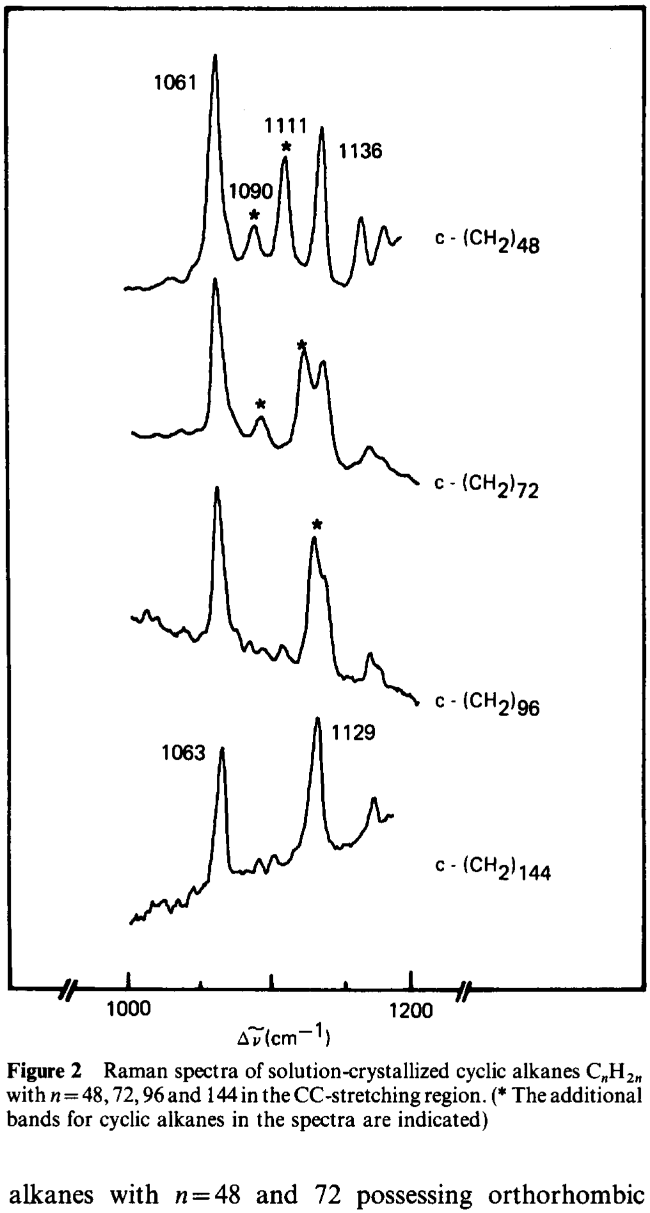

Figure 2 Raman spectra of solution-crystallized cyclic alkanes C_nH_{2n} with $n = 48$, 72, 96 and 144 in the CC-stretching region. (* The additional bands for cyclic alkanes in the spectra are indicated)

The spectra of cyclic paraffins in this region are complicated by the definite fold conformation and chain packing effects as shown in *Figure 2*. The X-ray structural analysis of single crystal c-$(CH_2)_{24}$ and c-$(CH_2)_{36}$ at −160°C was carried out by Groth[15] and Trzebiatowski *et al.*[16], respectively. These studies showed both molecules crystallize as two parallel *trans* stems connected by two *–gauche/gauche/trans/gauche/gauche(ggtgg)–* loops (*Figure 3*) and the unit cells are monoclinic. In particular, Trzebiatowski *et al.*[16] have compared the c-$(CH_2)_{36}$ crystal structure with those from

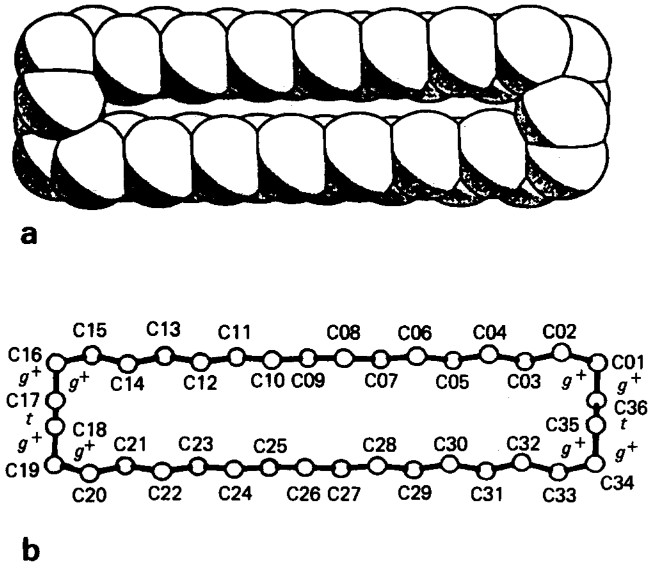

Figure 3 Molecular models of the crystal conformation of c-$(CH_2)_{36}$ from X-ray diffraction data[16]. (a) Space-filling model; (b) atomic model

a homologous series of cyclic alkanes with $n=48$, 60 and 72 measurements obtained with a Guinier camera and found both of these molecules also crystallize in a monoclinic lattice. The effect of chain packing can be seen from the fact that the two bands at $\Delta\tilde{\nu}_{as}=1063$ and $\Delta\tilde{\nu}_s=1131\,cm^{-1}$, observed in orthorhombically packed linear alkanes, appear at $\Delta\tilde{\nu}_{as}=1061$ and $\Delta\tilde{\nu}_s=1136\,cm^{-1}$ in monoclinic cyclic alkanes. There are two additional bands at 1090 and $1111\,cm^{-1}$ in the case of c-$(CH_2)_{48}$, the latter band at $1111\,cm^{-1}$ shifting to higher frequencies nearer the $\Delta\tilde{\nu}_s$ symmetric band with increasing chain length. The exact interpretation of this remarkable spectral change is not yet fully understood.

Furthermore, the cyclic alkanes with $n=72$ and 96 exhibit large spectroscopic differences depending on the crystallization conditions as shown in *Figure 4*. After crystallization melt crystallized samples exhibit only two stretching vibration bands, the frequency $\Delta\tilde{\nu}_s$ of the symmetric band deviating from the band positions for orthorhombic chain packing observed in linear alkanes but the frequencies in the case of the asymmetric vibration of all these compounds are in good agreement. X-ray analysis was used in the investigation of this interesting phenomenon. *Figure 5* shows X-ray powder diagrams of cyclic alkanes crystallized from the melt and their *d*-values are given in *Table 1*. The typical monoclinic unit cell (202_m), (020_m), (120_m) and (122_m) reflections of cyclic alkanes with $n=24$, 48, 72 and 96[16] diminished with increasing chain length for melt crystallized samples, and the (110_o) and (200_o) reflections appeared, in accordance with an orthorhombic unit cell. For c-$(CH_2)_{48}$, reflections due mainly to a monoclinic unit cell were observed, whereas for c-$(CH_2)_{72}$ both monoclinic (202_m) and (120_m), (122_m) and orthorhombic (110_o) and (200_o) reflections were observed together and for c-$(CH_2)_{96}$ mainly orthorhombic (110_o) and (200_o) reflections were observed. From these X-ray diffraction experiments it appears that the change of chain packing in cyclic alkanes with $n=48$, 72 and 96, crystallized from the melt, is very much dependent on ring size. Hence, the asymmetric band at $1127\,cm^{-1}$ of melt crystallized samples with $n=72$ and 96 can be demonstrated to be the effect of a mixture of monoclinic and orthorhombic lattices. However, for the large ring c-$(CH_2)_{144}$, orthorhombic subcell (110_o) and (200_o) reflections were always observed independent of the crystallization conditions. In the Raman spectra (*Figure 2*), it can also be seen that the band frequencies of c-$(CH_2)_{144}$ in the CC stretching region are in good accord with those of orthorhombic packed linear alkanes at $\Delta\tilde{\nu}_{as}=1063$ and $\Delta\tilde{\nu}_s=1129\,cm^{-1}$. Both observations thus suggest that the chain packing of C-$(CH_2)_{144}$ crystals is orthorhombic. Finally, the data for the asymmetric and symmetric vibration frequencies of several linear and cyclic alkanes are given in *Table 2*. It can be seen that, for all alkanes studied, band positions depend inherently on packing type. This effect is more clearly illustrated when the frequencies are given as the difference between $\Delta\tilde{\nu}_s$ and $\Delta\tilde{\nu}_{as}$. By comparison, $\Delta\tilde{\nu}_{s-as}=74$–$75\,cm^{-1}$ for monoclinic, 66–$68\,cm^{-1}$ for orthorhombic, $69\,cm^{-1}$ for hexagonal, $74\,cm^{-1}$ for triclinic and $64\,cm^{-1}$ for a mixture of monoclinic and orthorhombic chain packed crystals were observed.

CH_2-bending region. Information about chain folding and molecular packing of linear and cyclic alkanes can also be obtained from the CH_2-bending region using Raman spectroscopy. For orthorhombic crystals containing two molecules in the unit cell there are three bands at 1417, 1441 and $1460\,cm^{-1}$. The appearance of

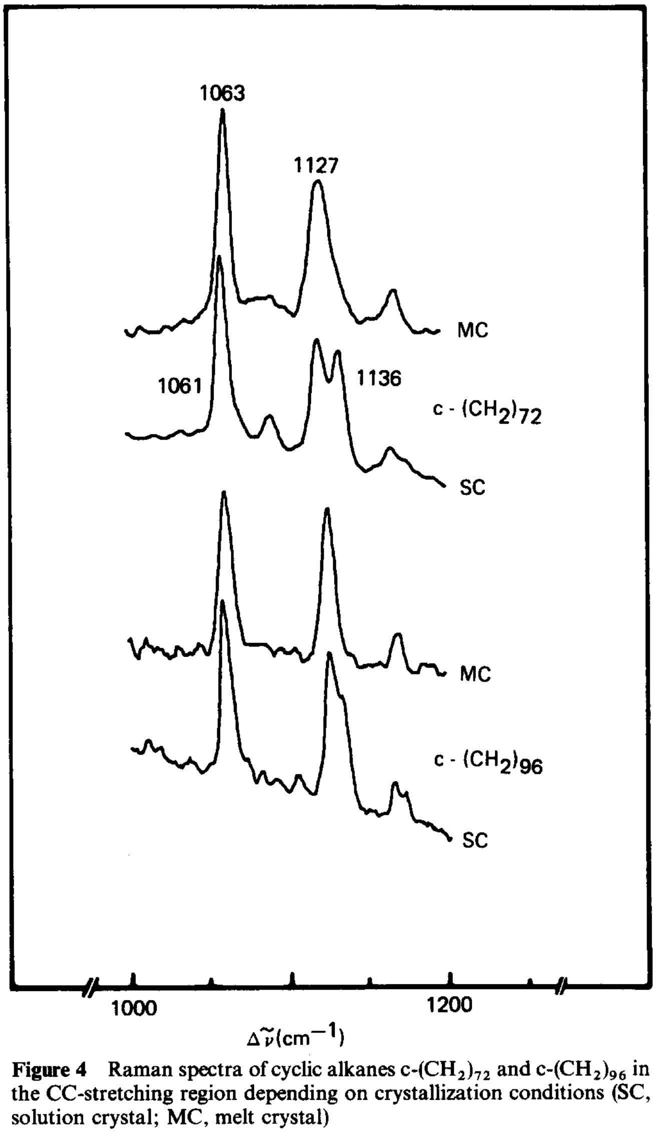

Figure 4 Raman spectra of cyclic alkanes c-$(CH_2)_{72}$ and c-$(CH_2)_{96}$ in the CC-stretching region depending on crystallization conditions (SC, solution crystal; MC, melt crystal)

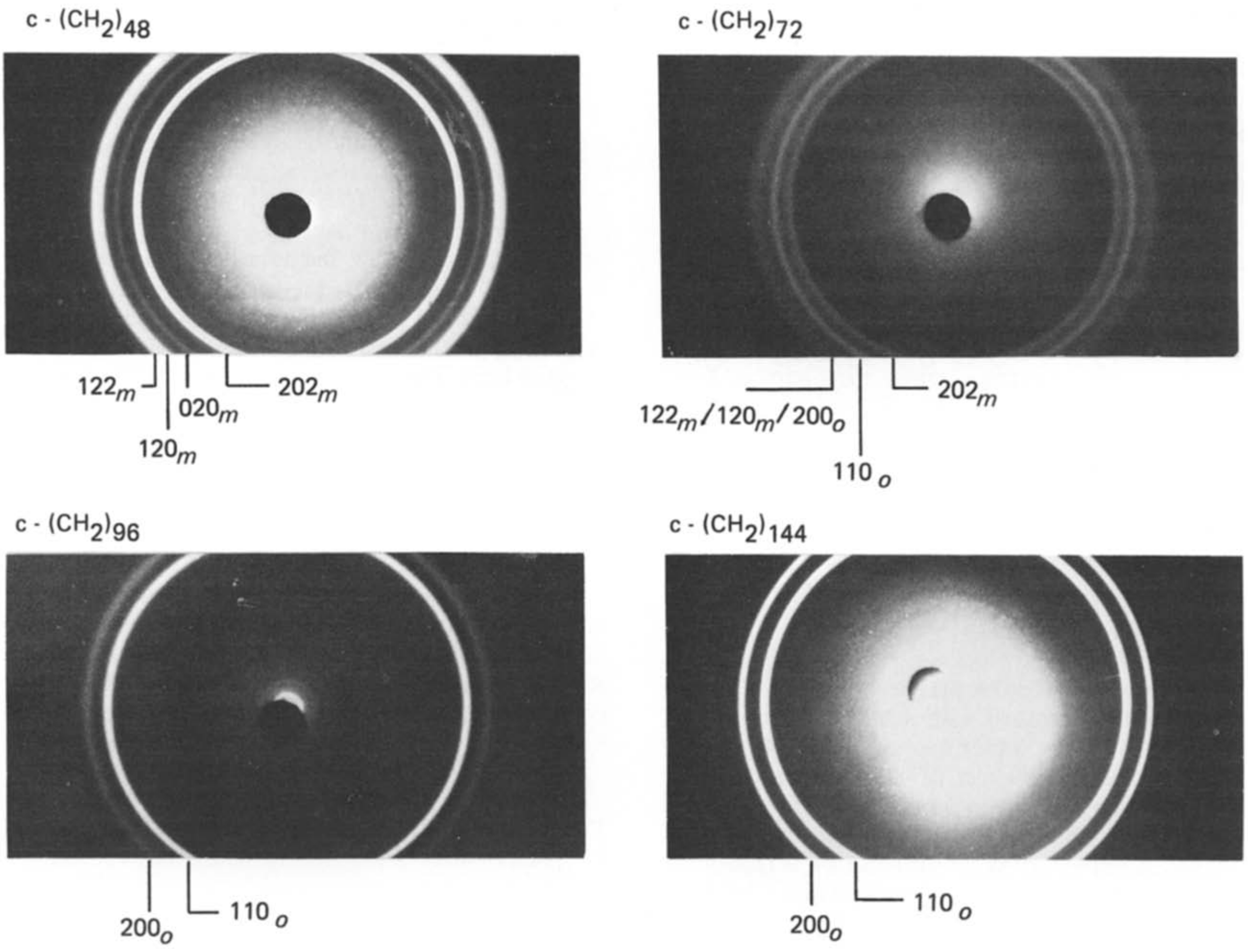

Figure 5 Wide-angle X-ray diffraction patterns of melt crystallized cyclic alkanes with $n=48$, 72, 96 and 144

Table 1 Wide-angle X-ray diffraction data for the samples as shown in *Figure 5*

$c\text{-}(CH_2)_{48}$		$c\text{-}(CH_2)_{72}$		$c\text{-}(CH_2)_{96}$		$c\text{-}(CH_2)_{144}$		Polyethylene	
d (Å)	*hkl*	*d* (Å)	*hkl*	*d* (Å)	*hkl*	*d* (Å)	*hkl*	*d* (Å)	*hkl*
4.62	202_m	4.58	202_m						
4.14	020_m	4.17	110_o	4.16	110_o	4.16	110_o	4.13	110_o
3.80	120_m	3.78	120_m	3.75	200_o	3.74	200_o	3.70	200_o
		3.75	200_o						
3.68	122_m	3.66	122_m						

the two bands at 1441 and 1460 cm^{-1} has been interpreted as arising from Fermi-resonance[20,21] interaction between the CH_2-bending fundamental vibration with overtones of the infra-red active B_{2u} CH_2 rocking vibration at 720 cm^{-1}. The band at 1417 cm^{-1} is only found to be associated with the orthorhombic crystal lattice. In particular, Strobl *et al.*[19] and Glotin *et al.*[22] have shown that this band can serve as an internal standard for the determination of the degree of crystallinity in semicrystalline polyethylene because its intensity decreases with increasing conformational disorder of CH_2-chains. *Figure 6* presents the spectra of linear alkanes with $n=48$, 120 and 288 in the crystalline state and $n=24$ in the molten state. For the crystalline samples with $n=48$ and 120 with orthorhombic crystal structures, all three discrete bands at 1417, 1441 and 1460 cm^{-1} were observed for the reasons discussed above. The melt spectrum for $n=24$ has only a broad band having a maximum at about 1440 cm^{-1}. The band frequencies of the spectrum for $n=288$ measured in the crystalline state is in agreement with those for $n=48$ and 120 but its spectral features are different; the intensity of the band at 1417 cm^{-1} in the case of $n=288$ is diminished and the bands at 1441 and 1460 cm^{-1} are not clearly separated. From this band shape it can be supposed that $n=288$ is a mixture of amorphous and crystalline phases, resulting from chain folding. In addition, defects within the crystalline phase could cause broadening and may represent at least a contribution to the overall band shape.

Figure 7 shows the Raman spectra in the CH_2-bending vibrational region for the solution and melt crystallized cyclic alkanes with $n=72$, 96, 144 and 288. For samples with $n=72$ and 96 crystallized from solution, the band at 1417 cm^{-1} was not observed since no crystal field splitting is usually associated with monoclinic crystals having one molecule per unit cell. However, the appearance of the 1417 cm^{-1} band in the corresponding

Table 2 Raman frequencies depending on chain packing type of linear and cyclic alkanes in the CC-stretching region

Alkanes		Chain packing	$\Delta\tilde{\nu}_{as}$ (cm^{-1})	$\Delta\tilde{\nu}_{s}$ (cm^{-1})	$\Delta\Delta\tilde{\nu}_{s\text{-}as}$ (cm^{-1})
n-$C_{24}H_{50}$	SC[a]	triclinic	1061	1135	74
n-$C_{48}H_{98}$	SC	orthorhombic	1063	1131	68
n-$C_{72}H_{146}$	SC	orthorhombic	1063	1131	68
n-$C_{96}H_{194}$	SC	orthorhombic	1063	1131	68
n-$C_{120}H_{242}$	SC	orthorhombic	1063	1130	67
n-$C_{144}H_{290}$	SC	orthorhombic	1063	1130	67
n-$C_{168}H_{338}$	SC	orthorhombic	1063	1130	67
n-$C_{192}H_{386}$	SC	orthorhombic	1063	1130	67
n-$C_{216}H_{434}$	SC	orthorhombic	1063	1129	66
n-$C_{288}H_{578}$	SC	orthorhombic	1063	1129	66
Polyethylene	SC	orthorhombic	1063	1130	67
c-$(CH_2)_{24}$	SC	monoclinic	1061	1135	74
c-$(CH_2)_{48}$	SC	monoclinic	1061	1136	75
c-$(CH_2)_{72}$	SC	monoclinic	1061	1136	75
c-$(CH_2)_{96}$	SC	monoclinic	1061	1136	75
c-$(CH_2)_{144}$	SC	orthorhombic	1063	1129	66
c-$(CH_2)_{288}$	SC	orthorhombic	1063	1129	66
c-$(CH_2)_{24}$	34°C	hexagonal	1063	1131	69
n-$C_{24}H_{50}$	50°C	hexagonal	1063	1131	69
c-$(CH_2)_{72}$	MC[b]	orthorhombic + monoclinic	1063	1127	64
c-$(CH_2)_{96}$	MC	orthorhombic + monoclinic	1063	1127	64
c-$(CH_2)_{144}$	MC	orthorhombic	1063	1129	66
c-$(CH_2)_{288}$	MC	orthorhombic	1063	1129	66

[a] Crystallized from solution
[b] Crystallized from the melt

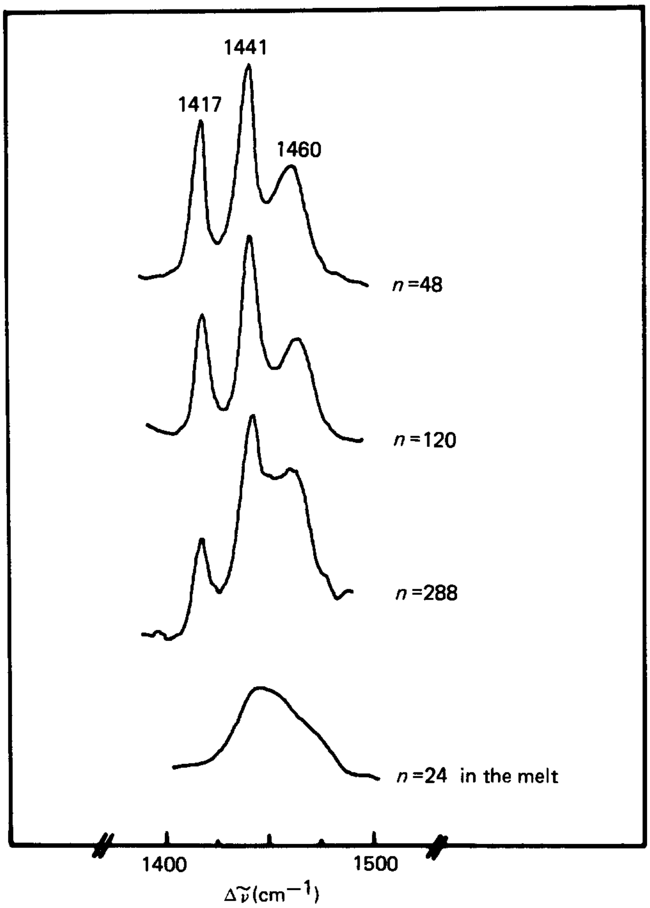

Figure 6 CH-bending region of the Raman spectra of linear alkanes with n = 24, 48, 120 and 288 in the solid or molten state. The alkane with n = 288 was crystallized from o-xylene at 25°C

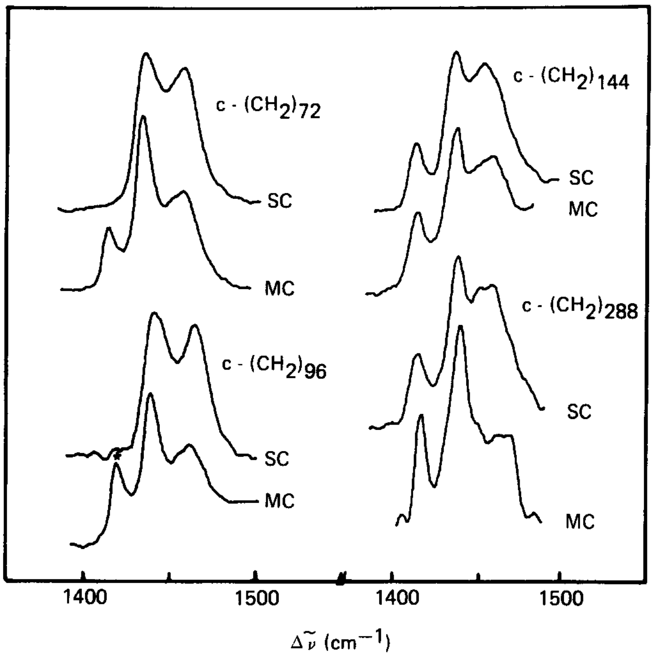

Figure 7 Raman spectra of solution- and melt-crystallized cyclic alkanes with n = 72, 96, 144 and 288 in the bending region (* the band characteristic of orthorhombic packing is indicated in the spectra)

samples crystallized from the melt suggests that these crystals contain at least some orthorhombic structure. We have not determined the relative amount of the orthorhombic crystal form but it increases with increasing chain length by comparison of the intensity of the 1440 cm^{-1} band with the intensity of the 1417 cm^{-1} band. The long chain cyclic alkanes with n = 144 and 288, on the other hand, give a band at 1417 cm^{-1}, independent of crystallization conditions. It can be seen that solution grown crystals of $n = 144$ and 288 have an orthorhombic lattice as discussed in the previous section.

CH-stretching region. The complexity of spectral features of extended polymethylene chains of the Raman spectrum has been extensively discussed by several authors[20,23,24], focussing on three factors; conformation, mobility and chain packing but a satisfactory analysis has not yet appeared in the literature. In order to acquire a better understanding of the phenomena in this region, it would seem reasonable that the influences of position, intensity and shape of these bands be studied in detail.

As shown in *Figure 8*, Raman spectra of the crystalline alkanes generally exhibit one relatively broad band at 2848 cm^{-1} and one intensive band at 2882 cm^{-1} which can be unambiguously assigned to symmetric and asymmetric CH-stretching vibrations, respectively. As far as packing effects are concerned, the spectra of linear alkanes with $n = 72$, 120, 288 and c-$(CH_2)_{144}$, shown to have orthorhombic crystal structures by studies of other vibrational regions and X-ray investigation, are all essentially identical. However, the spectral features of triclinic and hexagonal n-$(CH_2)_{24}$, and monoclinic c-$(CH_2)_{72}$ are clearly different than those of the orthorhombic crystals. The monoclinic and triclinic structures exhibit two maxima at 2850 and 2860 cm^{-1}, and at 2847 and 2860 cm^{-1}, respectively. Band splitting in the case of triclinic structures was also observed by Snyder *et al.*[20] who has explained these as binary combinations of HCH bending modes at 2860 cm^{-1} and pure CH symmetric modes at 2847 cm^{-1}. However, according to our observations, c-$(CH_2)_{72}$ with a monoclinic structure exhibits band splitting even though it has the same packing as n-$C_{20}H_{42}$ which has been reported by Snyder *et al.* Therefore, the band splitting in this region can not be confidently assigned as a characteristic feature of only triclinic structures. As shown in the spectrum of triclinic n-$C_{24}H_{50}$, CH_3-end group absorption gives bands at 2964 cm^{-1} (asymmetric:in-skeletal plane) and 2953 cm^{-1} (asymmetric:out-of-skeletal plane) but the symmetric mode is hidden by the symmetric CH-stretching vibration of the methyl groups. Those bands are too weak to distinguish in the spectra of the higher homologues as shown.

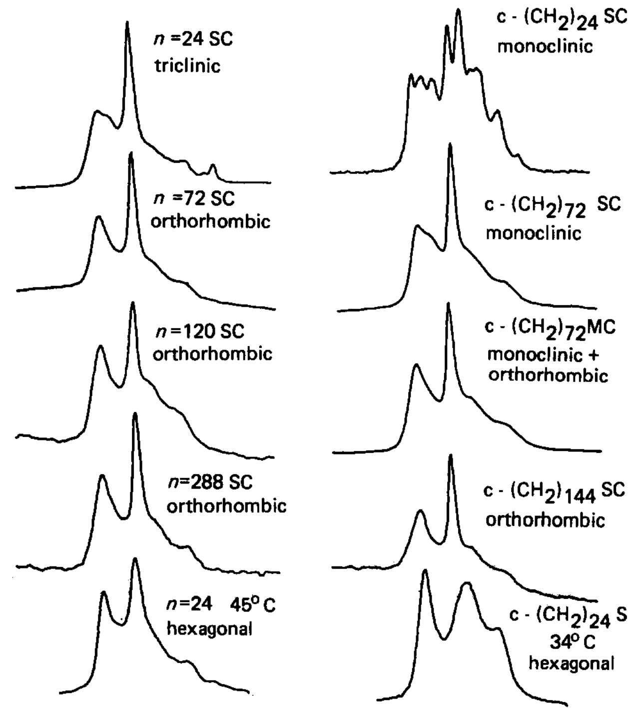

Figure 8 Raman spectra for linear and cyclic alkanes of various chain packing types in the CH-stretching region

The cyclic alkane c-$(CH_2)_{24}$ shows extremely complex spectral features which can be discussed as resulting from splitting of fundamental vibrations arising from fold formation in the small ring system. The high temperature phase of c-$(CH_2)_{24}$, with hexagonal symmetry, displays three discrete bands; a narrow band at 2850 cm^{-1}, a broad band near 2898 cm^{-1} and a weak shoulder at 2931 cm^{-1}. This spectral shape is very similar to the melt spectrum for polyethylene at atmospheric pressure reported by Wunder[25]. The reason for this similarity can be explained from thermal data; by the quantitative analysis of d.s.c. curves, the enthalpy change of the solid state phase transition of c-$(CH_2)_{24}$ ($\Delta H_{Tr} = 35\,kJ\,mol^{-1}$) is about 3.5 times larger than that for the melting transition ($\Delta H_m = 10.85\,KJ\,mol^{-1}$)[26]. This suggests that the molecular state of c-$(CH_2)_{24}$ at high temperature is almost melt-like, similar to condis crystals[27] having a high defect concentration.

However, there is a broad band near 2935 cm^{-1} whose interpretation has been controversial. Spiker and Levin[23] have proposed that this band is an asymmetric fundamental of the CH_3-end groups at 2871 cm^{-1} split by Fermi resonance into two components at 2935 and 2895 cm^{-1}. However, Snyder *et al.*[20] have assigned this broad band as arising from symmetrical CH-stretching of methylene groups. Our observation shows the 2935 cm^{-1} band in cyclic alkanes without the terminal methyl groups. This result is consistent with the assignment by Snyder *et al.* In the case of linear alkanes, of course, this band is more intense, so a relationship with the end groups cannot be fully eliminated.

I.r. spectroscopy

CH_2-rocking region. In cyclic paraffins crystallized from solution, a band appears at 700 cm^{-1} due to chain folding. Zerbi *et al.*[28] have found that this band can be interpreted as arising from coupling of rocking vibrational modes in the *-ggtgg-* chain folded region of cyclic alkanes. It can be seen in *Figure 9* that the intensity of this band decreases with increasing chain length because the ratio of folded chains to *trans* conformation methylene groups in the alkane chains decreases. The band at 714 cm^{-1} is typical for solution crystallized cyclic alkanes with $n = 24$, 48, 72 and 96 that exhibit monoclinic chain packing. This band and the correlation of its intensity with the size of the chains was first reported by Grossmann, Arnold and Bürkle[32]. The chains with this packing are basically aligned in the parallel fashion and the resulting interactions between chains are so weak that no band splitting is observed. However, the rocking band of orthorhombically crystallized linear alkanes clearly splits into two peaks at 720 and 730 cm^{-1} due to interchain interactions in the crystals. The solution

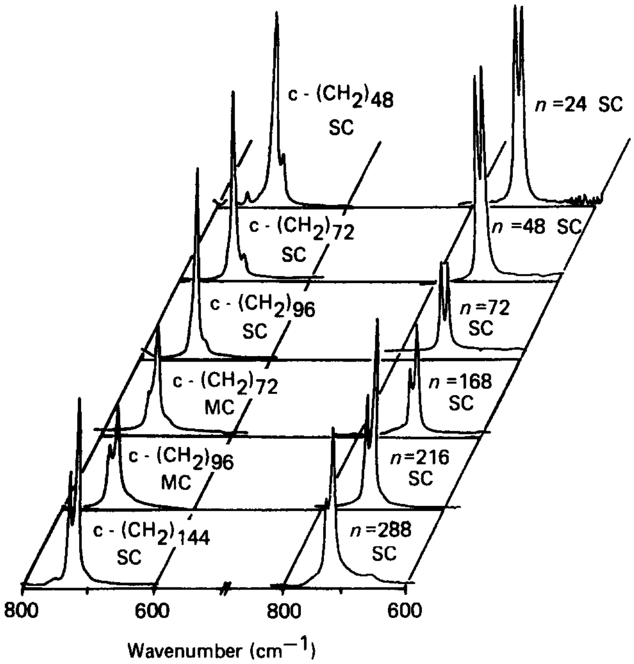

Figure 9 *FT*i.r. spectra of solution- or melt-crystallized linear and cyclic alkanes in the rocking region. $n = 168$, 216 and 288 were crystallized from n-heptane at 25°C, *o*-xylene at 10°C and *o*-xylene at 25°C, respectively

crystallized cyclic alkane c-$(CH_2)_{144}$ also exhibits this splitting due to its orthorhombic packing as discussed earlier. Melt crystallized cyclic alkanes with $n = 72$ and 96 show only a weak shoulder at 730 cm^{-1}, indicative of a mixture of orthorhombic and monoclinic crystal packings. From this one can see that the influence of crystallization conditions is as important as that of chain length.

The long chain linear alkane n-$C_{216}H_{434}$ possesses a total length of 274 Å in its fully extended configuration. When one compares this length with the lamellar thickness of about 100 Å for crystalline polyethylene, it could be expected that n-$(CH_2)_{216}$ would also crystallize in a chain folded conformation. This has already been investigated by calculation of the lamellar thickness of crystalline n-$C_{216}H_{434}$ by measurement of the Raman–LAM vibrational frequency^{17}. Furthermore, i.r. spectroscopy allows, in principle, calculation of the degree of crystallinity of linear alkanes and polyethylene. The orthorhombic chain packing of linear alkanes shows two rocking bands at 720 and 730 cm^{-1}. The band at 720 cm^{-1} is characteristic of segments with *trans* and *gauche* conformations while the band at 730 cm^{-1} is only found in orthorhombic unit cell. By comparison of the integrated intensity of the two bands, it is therefore possible to determine the degree of crystallinity quantitatively.

The spectra in *Figure 10* show two samples of linear n-$C_{216}H_{434}$ with different histories. Sample (A) was annealed 14 h at 125°C and sample (B) crystallized by quenching a solution in xylene rapidly from the boiling temperature to 10°C. By annealing (sample (A)), the lamellar thickness is increased ($L_{LAM} = 264$ Å) and defects are rapidly eliminated; one then observes approximately equal intensities for both bands. By fast cooling (sample (B)) the molecules have little time to crystallize and therefore the resulting crystal structure has many kinks and point defects that decrease the degree of crystallinity. It can be seen qualitatively in the spectrum of sample (B) that the intensity of the band 730 cm^{-1} is reduced. At the same time a shoulder at about 714 cm^{-1} appears, the frequency of which is typical for the spectra of monoclinic samples. One can then suggest in sample (B) the orthorhombic regions contain domains with monoclinic structure. These metastastable monoclinic crystalline phases has also been detected in polyethylene by X-ray scattering^{29}, electron diffraction^{30} and ^{13}C n.m.r.^{31}

CH-bending region. Figure 11 shows the i.r. spectra of linear and cyclic alkanes in the bending vibration region. The solution-crystallized cyclic alkanes with $n = 48$, 72 and 96 have an intense band at 1472 cm^{-1} and a shoulder at 1442 cm^{-1} which is not observed in fully extended linear alkanes with $n \leqslant 96$. Therefore, the latter can be

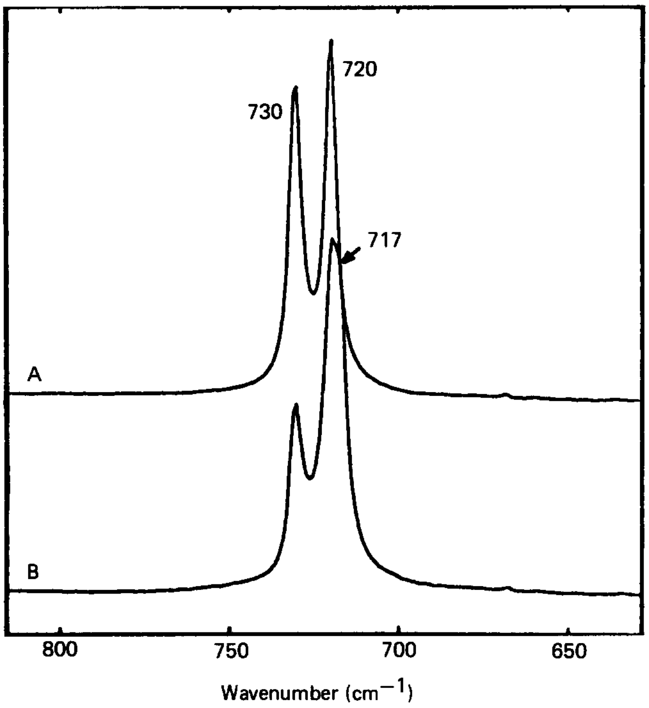

Figure 10 Spectra dependence on thermal histories of n-$C_{216}H_{434}$ (A) annealed 14 h at 125°C after melting and (B) crystallized at 10°C from *o*-xylene

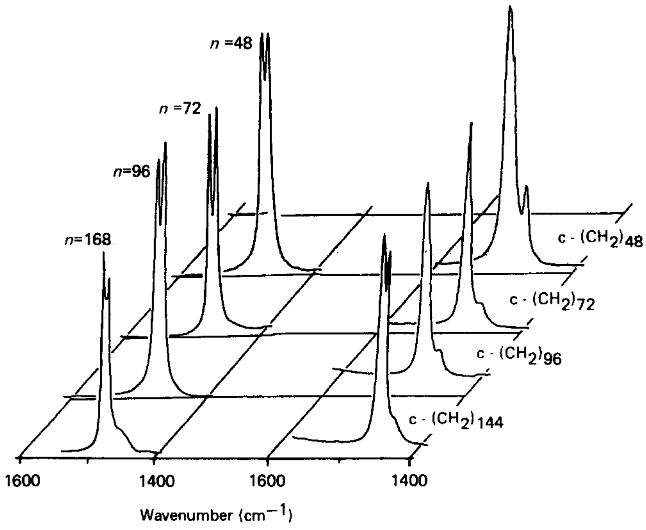

Figure 11 *FT*i.r. spectra of solution crystallized linear and cyclic alkanes in the bending region. The $n = 168$ was crystallized from n-heptane at 25°C

assigned as a specific band resulting from conformational defects in the fold region[32]. For linear alkanes with $n = 48$, 72, 96 and 168, two maxima at 1463 and 1473 cm^{-1} arise from Davydov-splitting, which is characteristic for orthorhombic crystals. However, the linear alkane with $n = 168$ gives an additional band near 1442 cm^{-1}, indicative of chain folding. This shoulder is broader than those of the cyclic alkanes. From this difference we can suppose that the fold conformation of n-$C_{168}H_{338}$ is not a well-defined *–ggtgg–* fold as in cyclic alkanes, or it contains other *gauche*-conformation groups along with *–ggtgg–* chain folds. The observation of band splitting in the c-$(CH_2)_{144}$ spectrum again clearly demonstrates that the molecule possesses orthorhombic chain packing.

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