Transport of matter upon annealing in crystalline polymethylene systems: a calorimetric and spectroscopic study*†

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(*Received* 3 *February* 1982; *revised* 8 *April* 1982)

Following Ungar and Keller we have shown that when a mechanical mixture of two solid and crystalline n-alkanes of slightly different length is annealed at temperatures below the melting point of the shorter compound a mixed crystal is obtained. Calorimetric and spectroscopic studies indicate that n-alkane chains of one molecular species are able to move out of the crystallite and diffuse into the crystal of the other species. A detailed mechanism on a molecular level consistent with calorimetric and spectroscopic experiments is proposed. Molecules migrate substantially as rigid bodies with no distinct sharp conformational distortions. The same phenomenon is observed for a mechanical mixture of $C_{36}H_{74}$ and for its perdeutero-derivative of the same length. The conclusions of Ungar and Keller are substantiated and new structural details are presented.

Keywords Alkanes; transport phenomena; spectroscopic studies; annealing; polymethylene; calorimetric studies

INTRODUCTION

The molecular mechanics of the motion of polymethylene chain molecules has recently been the subject of extensive studies with various physico-chemical techniques, all aimed at understanding either the overall molecular motion or the motion of fragments of the chain backbone[1-12]. It is not yet clear whether these molecules move rigidly or may possess some kind of intramolecular flexibility. Either one or the other of these types of motion, on a molecular scale, may be the determinant of several macroscopic physical properties exhibited by these molecules. Of particular relevance is an understanding of the annealing mechanism of polymers containing long polymethylene sequences[13]. Such a process of annealing facilitates the preparation of materials with specific mechanical and rheological properties. n-Alkanes provide useful lower molecular weight models for linear polyethylene.

Recently, on the basis of spectroscopic data, we have tried to give a more detailed description of the crystal and molecular structure of n-alkanes in the phase which occurs between the orthorhombic form and the melt[6]. Such a phase is variously named as pseudohexagonal, rotatory, pseudo-orthorhombic[1,8,13] etc. Those authors who called this intermediate phase the 'α' phase did not commit themselves to any detailed description of the structure of these materials in such a phase. From extensive dynamic and spectroscopic studies we have recently proposed[6,14] that in the 'α' phase of odd numbered n-alkanes, about 15% of the n-alkane chains are sliding out of the crystal lamella and tilt their head with a *gauche* structure either in the 2,3 or 3,4 positions. No evidence was found that conformational defects (kinks, folds, etc.) occur inside the molecular chain not only within the orthorhombic phase, but also throughout the existence of the 'α' phase up to melting point at least for $C_{19}H_{40}$.

The 'kink model'[15] for melting polymethylene chains did not find experimental support from our study. Instead clear spectroscopic evidence for conformational defects at the end and inside the chain are found in the melt. The overall description of the molecular motion which, being initially predominant at the orthorhombic-'α' phase transition, is of a motion involving molecular chains as substantially rigid bodies with some flexibility confined only at either ends of the molecular chain. Interlamellar forces seem to be weakened as the interlamellar distances become greater[6].

The model from ref. 6 is consistent with the spectroscopic data which indicates an increase of 15% in the roughness of the lamella surfaces originating from the longitudinal sliding of the molecules together with a tilting of the chain ends.

The main question we wish to explore in this work is whether such a chain mobility, pointed out in our previous work[6], and also by other independent techniques[1-5], is restricted within the lamella or whether the onset of such a motion near and at the solid–solid phase transition generates a collective motion which also

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* Presented at the March meeting of the American Society (Dallas) (1982).

† Work partly supported by 'Progetto Finalizzato Chimica Fine e Secondaria, C.N.R.; Materiali Polimerici'.

0032-3861/82/131921-08$03.00

Table 1 Orthorhombic–α transition and melting temperatures of the n-alkanes studied in this work

	T_{trans}	T_{melt}	ref.
21	32.5	40.2	a
23	40.5	47.5	a
25	47.0	53.5	a
36	73.8	75.9	a
36D	71.5	72.0	b

[a] Ref. 18
[b] Ref. 34

drives other molecules into the adjacent lamellae.

Here we will discuss the evidence collected from calorimetric and spectroscopic experiments which shows that n-alkane molecules are able to migrate from one crystallite to another, thus generating an overall long range transport of matter upon annealing. This phenomenon was first demonstrated by Ungar and Keller for n-hydrocarbons[16]; a diffusion process was also proposed by Narang and Sherwood again for n-alkanes[17]. The experimental set up and the general philosophy of the work by the latter authors is, however, different from that of Ungar and Keller. We have worked substantially under the same experimental conditions as those proposed by Ungar and Keller using calorimetry and the more recent technique of infra-red spectroscopy to monitor the results. Ungar and Keller present X-ray diffraction data as well in support of their conclusions.

EXPERIMENTAL PROCEDURE

The experimental fact we have observed is that when a purely mechanical mixture of microcrystals of two n-alkanes of slightly different length ($C_n + C_{n\pm 2}$) is annealed at temperatures near the solid α phase transition of one of the two components, a mixed crystal is formed having the same properties as those obtained by co-crystallization of the two substances from solution. The same mixed crystal results when a solid n-hydrocarbon is mechanically mixed with its perdeuteroderivative and subjected to annealing. This effect has been followed by differential scanning calorimetry and infra-red spectroscopy.

n-Hydrocarbons have the general formula C_nH_{2n+2}. (Hereafter, for simplicity we shall only indicate the number of carbon atoms). We have mainly studied the following hydrocarbons: C_{21}, C_{23}, C_{25}, C_{36} and $C_{36}D_{74}$. Perhydrogenated samples were purchased from Carlo Erba Co. and used without further purification. The samples purchased were those used as standards for chromatography and the reported purity is not less than 99%. $C_{36}D_{74}$ was purchased from Merk, Sharp and Dohme with a reported isotopic purity of 98%. Dupont 990 DTA and Perkin Elmer DSC 2 calorimeters and a Nicolet FTIR 7199 spectrometer were mainly used in our experiments, however, some spectra were also scanned with a Perkin Elmer 125 spectrometer.

The mechanical mixtures considered ($C_{23}+C_{25}$ for calorimetry and $C_{21}+C_{23}$ and $C_{36}H_{74}+C_{36}D_{74}$ for infra-red spectroscopy) were prepared in the following way: (i) Each compound was separately dissolved in hot acetone near the boiling point; (ii) the compounds were precipitated from the hot solution by spontaneous cooling to room temperature and further cooling to 0°C. During precipitation the solutions were continuously stirred with a magnetic stirrer in order to maintain a fine suspension; (iii) the two suspensions were mixed at low temperature under continuous stirring which lasted for about 10 minutes; this was done to insure a homogeneous distribution of microcrystals; (iv) the suspension was filtered at 0°C and the solvent carefully removed. Further removal of the solvent was carried out keeping the sample under vacuum at 5 mm Hg for 15–20 minutes.

The sample obtained in this way appears to be whitish, opaque, soft and fluffy. In suspension very small platelets are observed. Since, as will become apparent in the discussion which follows, the size of the microcrystals is a basic kinetic parameter, all measurements were made on samples from the same batch of mechanical mixtures. It was assumed that the preparation of the samples, as described above, could yield, on average, a homogeneous distribution of microcrystals of the two chemical species.

The samples were kept in a thermostat and annealed at temperatures at which both compounds were independently solid, at temperatures at which the shorter compound was either in the orthorhombic or in the 'α' phase. For calorimetric measurements, scans were made on different samples at various annealing times. Alternatively, i.r. measurements were carried out on the suitably annealed samples but cooled to 10°C before each spectral scan.

EXPERIMENTAL DATA AND OBSERVATIONS

The phase transition and the melting temperatures of the compounds studied in this work are reported in *Table 1*. The data in *Table 1* are taken from the literature[18]. The calorimetric experiments carried out in our work for C_{23} and C_{25} agree with the values of the literature.

Calorimetry

The d.s.c. thermograms of pure C_{23} and C_{25} given in *Figure 1* agree well with those reported in the literature. In addition to the two peaks due to the solid-to-α and α-to-melt transition, a very small peak is observed at $T = 44.0°C$ for C_{23} (ΔH 35 cal mol^{-1}). In the case of mixed crystals, an additional heat absorption is observed after the solid-to-α transition. The precise origin of this peak is not known, but it does not affect the object of this work. Binary systems of two n-paraffins with slightly different lengths show a phase diagram typical of substances with complete miscibility at any phase[19–21]. The solid phase transition temperature shows the typical minimum in which both the orthorhombic and the α phase have the same composition. *Figure 2* shows the concentration dependent solid transition temperatures determined from calorimetric data for the system $C_{23}+C_{25}$. The heat of transition for such mixed crystals as a function of concentration measured here, (*Figure 3*) is in agreement with that predicted by Bonsor and Bloor for mixed n-alkanes[22]. The heat of transition turns out to be roughly half of that for the pure compounds and almost constant over a large concentration range. As can be seen from *Figure 2*, the transition temperature of the mixed crystals $C_{23}+C_{25}$, over a broad concentration range, occurs in the range 34.5°–35°C, i.e. below the transition temperatures of both pure compounds. If the annealing of the mechanical mixture generates mixed crystals we would expect to observe a broad peak arising at these temperatures while the two peaks of the pure material should decrease with the annealing time. This is exactly

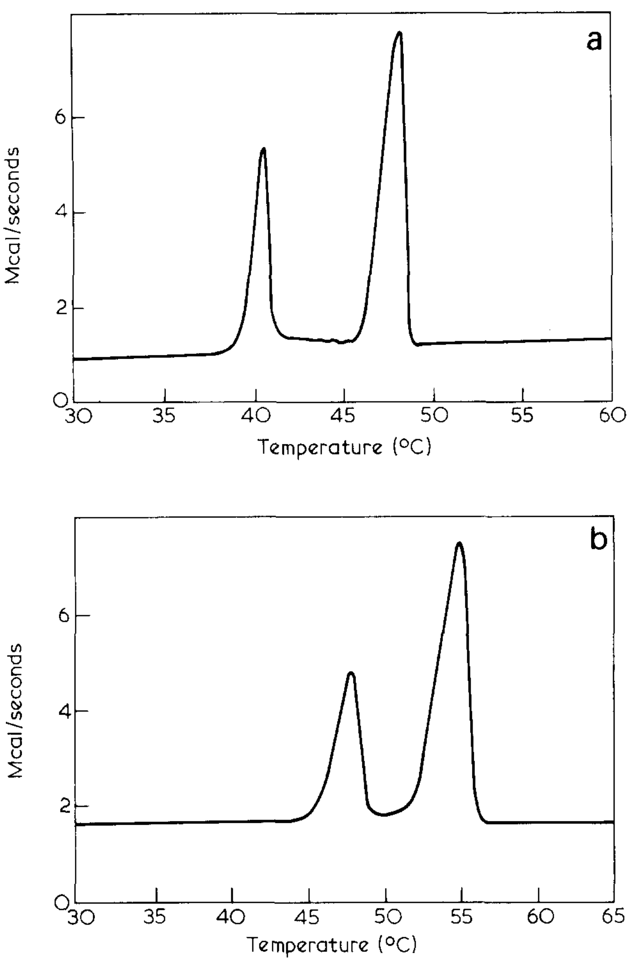

Figure 1 D.s.c. thermograms of (a) $C_{23}H_{48}$ and (b) $C_{25}H_{52}$

what is observed experimentally in the d.s.c. thermograms shown in *Figure 4* for a 1:1 molar mixture of $C_{23}+C_{25}$ at different annealing times. The formation of mixed crystals is thus confirmed.

The kinetics of the transformation (*Figure 5*) was followed by measurement of the area of the transition peak of C_{23}; this was not possible for C_{25}, whose peak is strongly overlapped by the peak due to the melting of the mixture. Possible errors in the weight of the sample were minimized by scanning a second thermogram of each sample (which at the end of the first scan has become a mixed crystal of 1:1 composition) and comparing the thermogram areas. The area differences are only due to differences in the weight of the samples.

Calorimetric measurements allow us to make the following observations (for sake of clarity in the discussion which follows we have used a suitable label for each observation):

(Cal 1): The process takes place in a narrow range of temperatures already below the transition temperature of the shorter compound. However, it can be recorded when both compounds are still in the orthorhombic phase.

(Cal 2): The rate of the process increases very rapidly when the annealing temperature approaches the transition temperature of the compound which first goes into the α phase (*Figure 5*).

(Cal 3): At annealing temperatures at which one of the two compounds is in the α phase, the process takes place so quickly (10–20 min for the complete mixing) that it cannot be followed quantitatively by calorimetry.

(Cal 4): At the end of the process the material is the same as that obtained by co-crystallization of the two n-alkane molecules at the chosen starting ratios.

(Cal. 5): The analysis of the kinetic curves seems to show that the process follows different laws at different temperatures. Often diffusion processes in solids can be analysed in terms of different contributions such as bulk or grain boundary (pipe) diffusion[23]. For the study of the diffusion processes[24], one can represent the kinetics of the processes for a given series of samples, by a law of the type $c(t)=c_0t^\alpha$, where $c(t)$ is the total amount of substance having diffused at time t. Fitting the curves of *Figure 5* with such a function one observes that α decreases with increasing temperature (*Figure 6*).

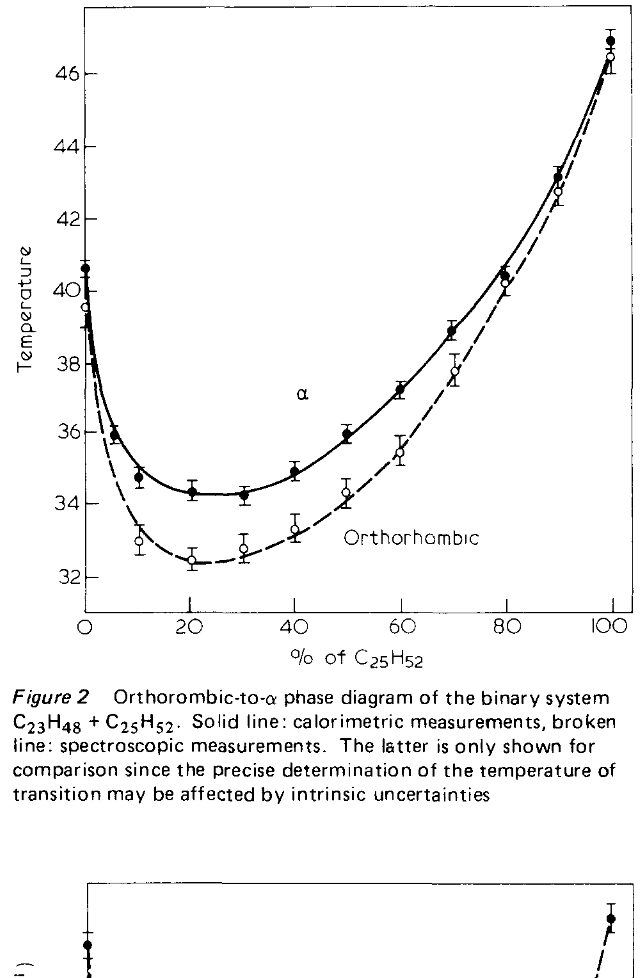

Figure 2 Orthorombic-to-α phase diagram of the binary system $C_{23}H_{48}+C_{25}H_{52}$. Solid line: calorimetric measurements, broken line: spectroscopic measurements. The latter is only shown for comparison since the precise determination of the temperature of transition may be affected by intrinsic uncertainties

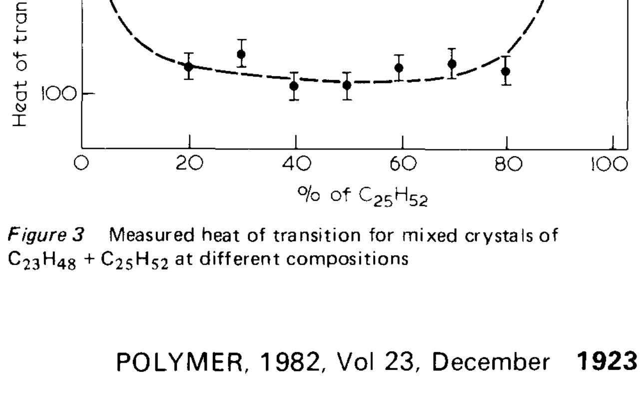

Figure 3 Measured heat of transition for mixed crystals of $C_{23}H_{48}+C_{25}H_{52}$ at different compositions

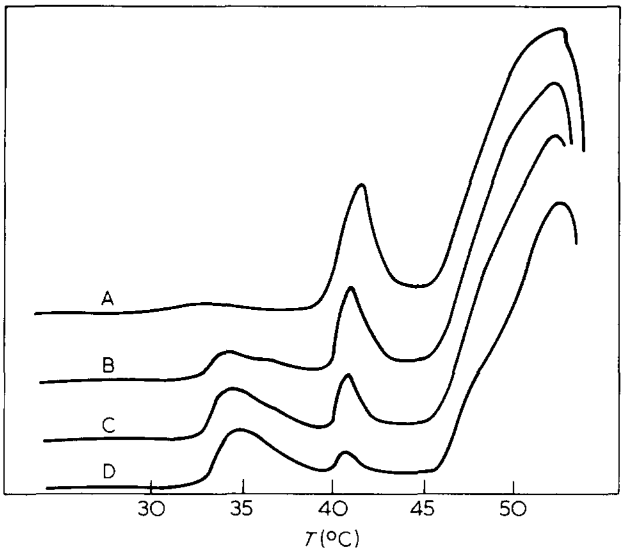

Figure 4 Evolution with the annealing time of the d.s.c. thermogram of a 1 : 1 mechanical mixture of $C_{23}H_{48}$ + $C_{25}H_{52}$. Annealing temperature 40°C. (A) t = 0; (B) t = 40 min; (C) t = 2 h; (D) t = 4 h

Infra-red spectroscopy

Solid normal hydrocarbons in the *trans* planar conformation show an infra-red spectrum which has been the subject of extensive studies in the past[25,26]. When the molecule is taken as an isolated chain (or when there is one molecule per unit cell in the crystalline state, e.g. triclinic structures) one expects to find the progressions of bands generated by typical group frequencies such as CH_2 rockings (P), CH_2 twistings (T), CH_2 waggings (W), C–C stretchings (R) etc. The components of each progression refer to normal modes characterized by a phase difference between adjacent oscillators. Letting $\varphi_j = \frac{j\pi}{m}$ ($j = 0,1,2,3 \ldots m-1$) define the phase difference for a chain of m CH_2 units[27]. The vibrational assignment in terms of j are well known and well understood for n-alkanes[28]. All the modes lie on specific dispersion curves for the corresponding one-dimensional infinite crystal (i.e. polyethylene)[25,26]. In the case of orthorhombic crystals of n-alkanes, two molecules are found per unit cell. Thus weak intermolecular interactions take place and each of the vibrational levels of the single chain splits into two components. The separation of the components depends on the extent of the dynamic interactions and their occurrence in the infra-red or Raman spectrum depends on the symmetry of the modes and their corresponding selection rules[29,30].*

Here, our attention is mainly focussed on the band progression of the CH_2 rocking modes (ω_9 dispersion curves of polyethylene) most of which show noticeable splittings. The largest split is shown for the in-phase CH_2 rocking motion near 720 cm^{-1} labelled by $j = 0$ which is the limiting mode already reached when the n-alkane molecule contains only a few CH_2 units[28].

As previously discussed[31], such group factor splitting occurs when the proper frequency of one single oscillator resonates (couples) with an identical one within the same system. The study of such a splitting by isotopic dilution[32] is based on the fact that the introduction of an isotopic impurity generates singlets, since the vibrational levels of the guest molecule cannot couple with those of the host lattice. Moreover by increasing the concentration of the guest molecules the extent of interaction of the host molecules decreases thus decreasing the extent of

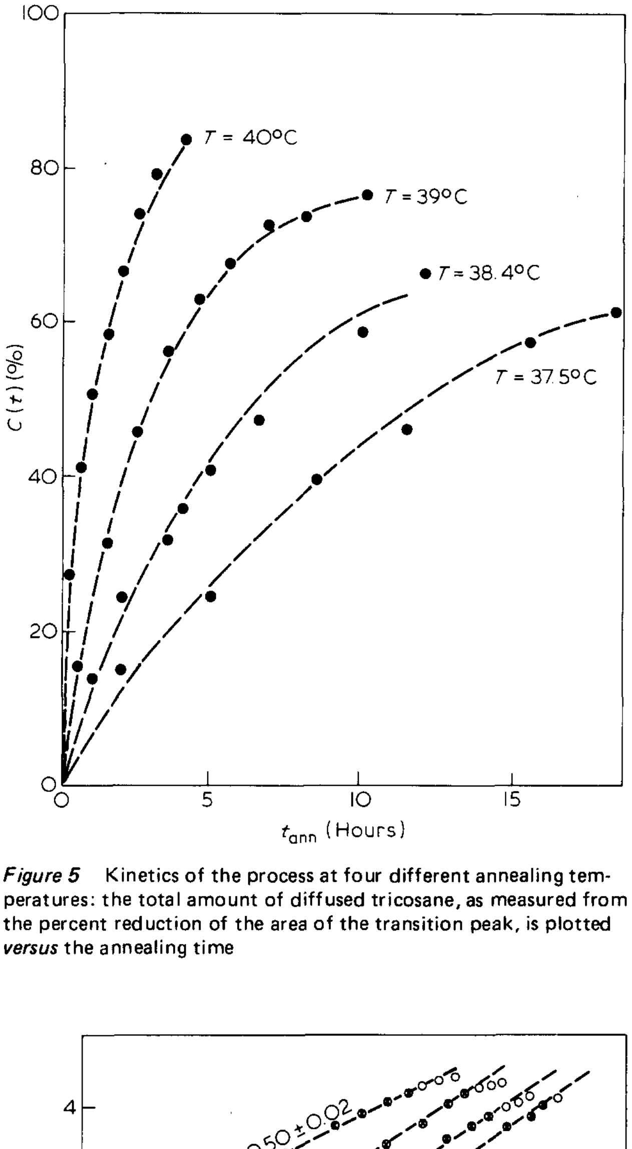

Figure 5 Kinetics of the process at four different annealing temperatures: the total amount of diffused tricosane, as measured from the percent reduction of the area of the transition peak, is plotted *versus* the annealing time

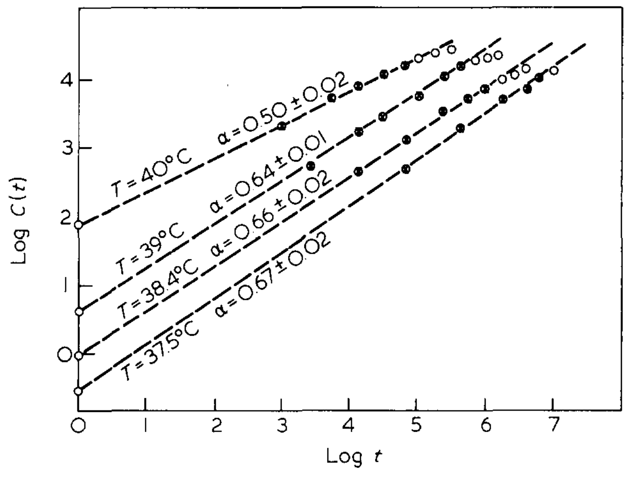

Figure 6 Logarithmic plot of the four kinetic curves of ***Figure 5.*** Best straight lines are plotted in the hypothesis that the total amount of diffused substance can follow a function of the form: $C(t) = C_0t^{\alpha}$. (See, for instance, ref. 24). The experimental values used for the interpolation are labelled with a cross

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* We can observe that this fact allows us to use i.r. spectroscopy to determine the phase diagram of a binary system of n-alkanes. The infra-red bands of n-alkanes in the α phase do not, indeed, show any splitting (or, at least, they show only a 'residual splitting'[6]). For this reason, the temperature of the orthorhombic α phase transition can be determined as that where group factor splittings disappear. Ths phase diagram of the binary system $C_{23}+C_{25}$ determined in this way is shown in *Figure 2*.

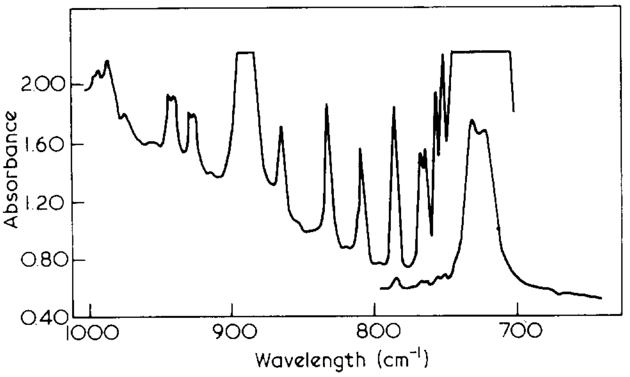

Figure 7 Infra-red spectrum of a 1 : 1 mechanical mixture of $C_{21}H_{24}$ + $C_{23}H_{48}$ in the 700 to 1000 cm^{-1} range

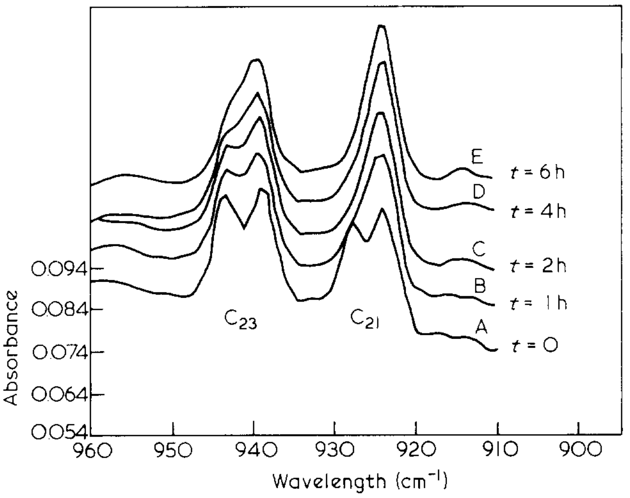

Figure 8 Evolution with the annealing time of the P_{15} band of the $C_{21}H_{44}$ and the P_{17} band of $C_{23}H_{48}$ for a 1 : 1 mechanical mixture of $C_{21}H_{44}$ and $C_{23}H_{48}$. Annealing temperature 30°C: (A) $t = 0$; (B) $t = 1$ h; (C) $t = 2$ h; (D) $t = 4$ h; (E) $t = 6$ h

splitting[33]. The same can be assumed, to a first approximation, to occur for the case of a mixed crystal[31]. For the $j = 0$ limiting CH_2 rocking mode, splitting may still occur since the $j = 0$ frequencies are the same for the two molecules mixed together. The modes with larger j values for both components of the mixture occur at different frequencies and the frequency mismatch is too large and no splitting is expected. This is a new spectroscopic feature which requires further theoretical consideration.

Our experiments are based on the above criteria. In *Figure 7* the infra-red spectrum in the 700 to 1000 cm^{-1} range is reported for a mechanical mixture of C_{21} and C_{23}. The usual well known group factor splitting of the CH_2 rocking mode for each molecule is indicated. When annealing takes place the following observations can be made:

(Vib 1): During the annealing process all the bands with $j \neq 0$, which are originally split progressively lose their splitting and coalesce into a singlet at intermediate frequencies (*Figure 8*). The $j = 0$ CH_2 rocking does not lose the splitting.

(Vib 2): *FT*i.r.-difference spectra obtained by subtracting the original spectrum from each successive scan at various annealing times clearly show the appearance of a singlet inside each starting doublet (*Figure 9*). The relative ratio of the intensity of the singlets within each spectrum is not constant, but the intensity of the peak due to C_{21} increases more rapidly.

(Vib 3): The splitting disappears more rapidly for the bands of the shorter compound (*Figure 8*).

Other observations can be made throughout the whole spectrum, namely:

(Vib 4): Spectra scanned during the annealing do not show any noticeable indication of conformational distorsions[6,14].

(Vib 5): By increasing the annealing time a weak, but unquestionable band arises near 1342 cm^{-1} (*Figure 10*).

(Vib 6): The methyl deformation mode near 1375 cm^{-1} shifts to 1378 cm^{-1} as already observed for the case of nonadecane[6].

A real case of isotopic dilution is encountered when a mechanical mixture of $C_{36}H_{74}$ and $C_{36}D_{74}$ is annealed

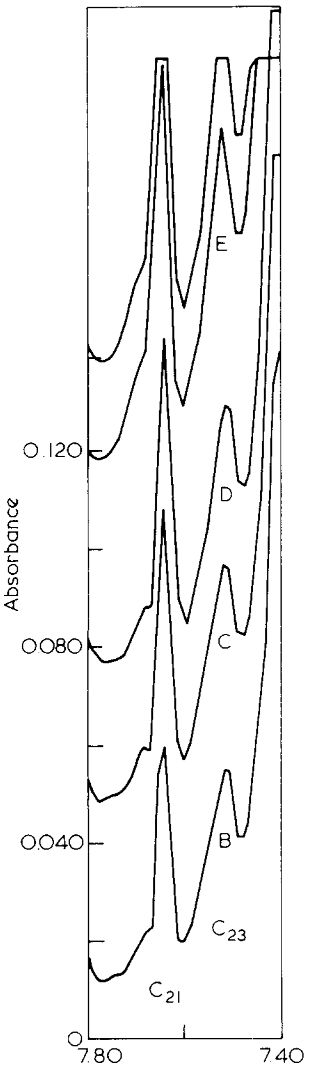

Figure 9 *FT* i.r. difference spectra. From the spectrum of a mechanical mixture of $C_{21}H_{44}$ + $C_{23}H_{48}$ kept at different annealing times the spectrum of the starting mechanical mixture with no annealing was subtracted. P_9 bands of C_{21} and C_{23} are shown at different annealing times. Since the physical properties of the samples change with annealing time the background absorption changes. Different scaling factors were used in each spectrum. No direct comparison of the intensities of the singlets in the different spectra can then be made. Only a comparison of the relative ratio of the singlets within the same spectrum is meaningful. Annealing times as in *Figure 8*

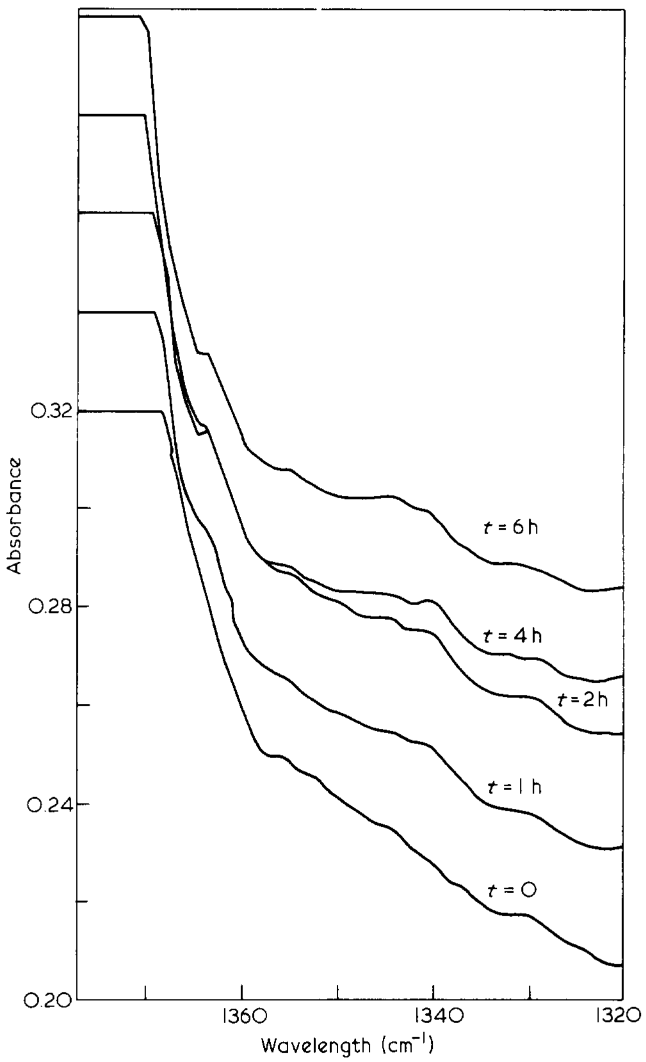

Figure 10 Evolution with time of annealing of the spectrum of the mixed crystals in the 1330–1380 cm^{-1} range showing the peak arising near 1342 cm^{-1}. These spectra were taken at low temperature (where no chain mobility is allowed) by quenching the sample before each scan. The peak observed must then be ascribed to the static conformation of the molecules in the mixed crystal. (See refs. 6 and 14)

and spectra examined as in the former case. We take the CD_2 bending absorption which is free from strong overlapping and the following observations can be made (*Figure 11*):

(Vib 7): An absorption starts rising within the doublet filling the valley between the two peaks.

(Vib 8): The splitting between the two components decreases with annealing time.

From the CH_2 rocking made (*Figure 12*) a final observation can be made:

(Vib 9): While the splitting decreases along with annealing time the valley is partially filled supposedly by a singlet but whose existence is not so clear.

DISCUSSION

From the experiments reported here there seems to be no doubt that, upon annealing, a mechanical mixture of crystalline n-alkanes of slightly different length (or of isotopic species of the same length) mixed crystals are formed. This fact implies that an intermixing of the microcrystals of the two substances must somehow take place. The physical aspect of the material before and after annealing is also different: it starts, as already mentioned, as an opaque polycrystalline mixture and ends as a glass-like transparent homogeneous material.

The structure of the new material can be described as crystallites of an orthorhombic lattice (vib 1) with a rough lamella surface due to the fact that longer chains tilt their heads (or tails) (vib 5)[6,14] and interlamellar forces are, on average, weaker (vib 6)[6,31].

In more detail the process is a diffusion which starts below the phase transition of the shorter compound and becomes rapid when the shorter compound is in the 'α' phase (Cal 1, Cal 2, Cal 3). The temperature dependence of the diffusion law can be tentatively interpreted as a variation with temperature on the diffusion mechanism (Cal 5). In analogy with other systems, one may suggest that at the temperature at which the process starts, a pipe diffusion dominates and evolves with temperature towards a bulk diffusion[23]. However a precise analysis of the kinetics is impossible because of the extent of physical

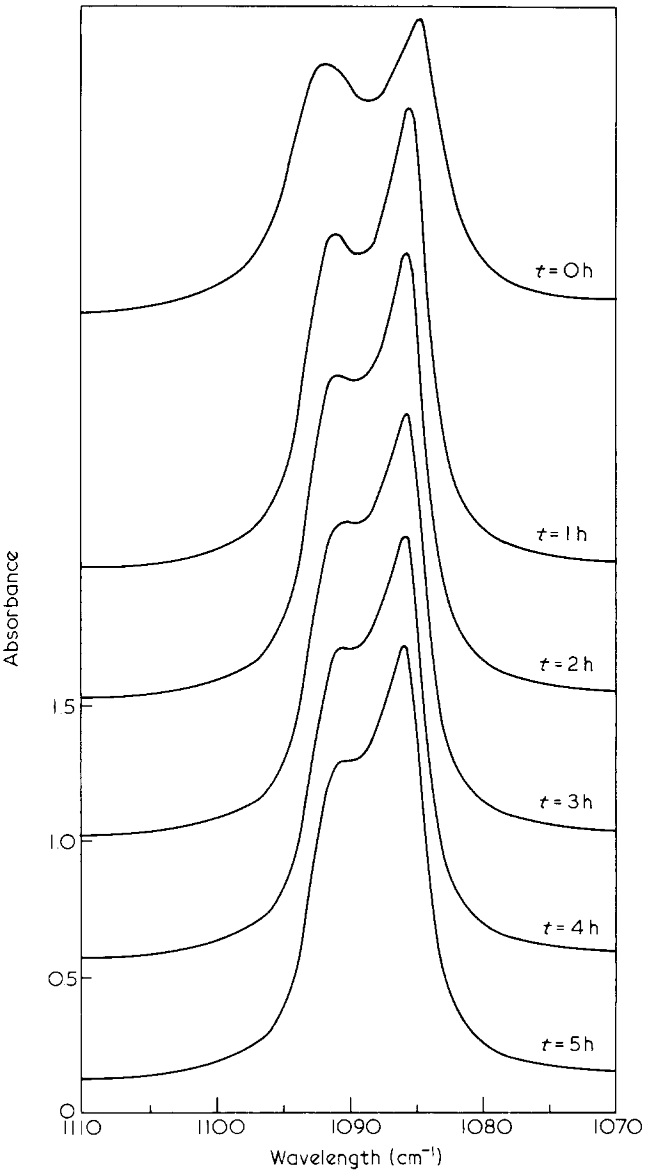

Figure 11 Evolution with the annealing time of the CD_2 bending band in the spectrum of a 1 : 1 mechanical mixture of $C_{36}H_{74}$ + $C_{36}D_{74}$. Annealing T = 68°C

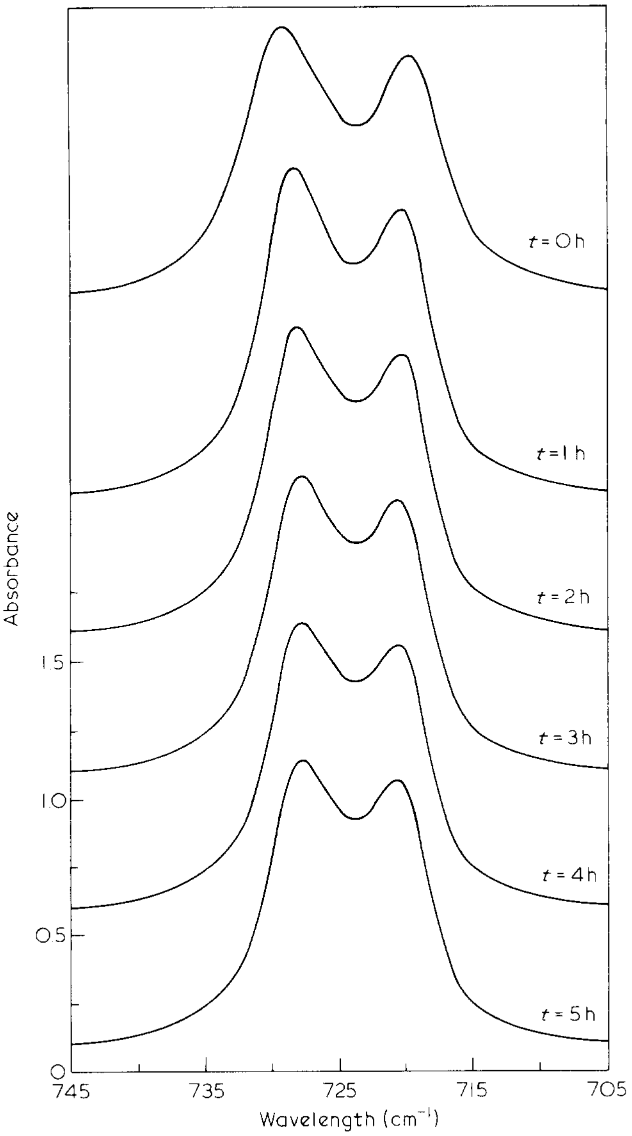

Figure 12 Evolution with annealing time of the CH_2 rocking band for the spectrum of the sample of *Figure 11*

contacts of the crystallites in the mixture can never be determined and reproduced in two different samples.

Going towards a molecular model for the process, it can be pointed out that the experiments show that molecules of both crystals move during diffusion. Indeed islands of C_{21} in C_{23} and islands of C_{23} in C_{21} are observed (vib 2). Likewise islands of $C_{36}D_{74}$ are certainly observed in a host matrix of $C_{36}H_{74}$ (vib 7). There seems to be some experimental suggestion that the rate of diffusion is different for the two species with the shorter compound being the faster mover (vib 2 and vib 3). Of particular interest is the experiment on the isotopic binary system. Indeed the singlet appearing in the middle of the CD_2 bending, originates from molecules of $C_{36}D_{74}$ which have migrated in the crystal of $C_{36}H_{74}$. Related to the motion of the deuterated molecule is the large reduction of the splitting of the CH_2 rocking band. However, molecules of $C_{36}H_{74}$ have migrated into the $C_{36}D_{74}$ matrix as suggested, but to a lesser extent, by the CH_2 rocking singlet and as confirmed by the minor reduction of the splitting of the CD_2 bending.

The possibility of a different rate of migration seems to be reasonable if we consider that the shorter compound is nearer the α phase, hence it is always more mobile. It has to be added, however, that the mobility of the longer compound is also certainly enhanced by the diffusion of the shorter compound since the solid–solid transition temperature of the longer compound is lowered by the impurity[19,20].

The same situation also occurs for the isotopic binary mixture since the perdeuterated compound has a lower phase transition temperature[34]. However, in this case we cannot claim an 'induced activation' of $C_{36}H_{74}$ by $C_{36}D_{74}$, the latter migrating first, since the phase diagram of the binary system does not exhibit any minimum[34] as with binary mixtures of n-alkanes of different length. This is probably the reason for the very limited mobility of $C_{36}H_{74}$ derived from vib 9.

If the rate of migration is different for the two species a correlated one-to-one exchange of the molecules of the two species is ruled out.

In the discussion so far we have not specified whether there is any experimental indication of the fact that molecules migrate longitudinally or transversly to the direction of the chains. From our experiments a decision cannot be taken, but the body of physical measurements and calculations, collected by many authors, on the dynamics of polymethylene molecules seems to point more towards a longitudinal mobility, also suggesting that chains may move more easily by longitudinal rototransational jumps[1–12]. Intuitively it seems reasonable because of the highly anisotropic character of these systems.

The longitudinal mobility of substantially rigid molecules which stems out of this work must have the following characteristics as derived from the experimental data collected here: (i) the process must be active both in the orthorhombic and α phase even if at very different extents; (ii) large conformational distorsions should not be allowed; (iii) the longitudinal mobility must favour easy penetration of the guest molecule into the host lattice.

Case (i) suggests that the motion of the alkane molecules in the crystal cannot be reduced only to a cooperative rotational motion[8], which should only be active in the α phase.

Case (ii) confirms the information derived in more detail on noadecane[6], that drastic conformational distorsions do not occur and thus cannot be the basic origin of the α modification (e.g. a Pechold's type kink cannot bring the chain out of the crystal).

Case (iii) asks for some overall flexibility of the molecular chains which may generate small holes in the crystal into which the incoming molecule can fit and proceed by a supposed rototranslational motion[2–5].

This work favours (even if cannot be taken as proof) the type of lattice dynamics for polymethylene molecules recently presented by Mansfield and Boyd[10] and more recently reformulated by Mansfield *et al.* as a 'soliton like motion'[11,12]. Namely the crystal seems to be able to host a certain number of chain molecules containing a gentle twist of the whole chain over a considerable number of CH_2 units. Such a conformational distorsion is subject approximately to a sine–Gordon potential. The solution of the equation of motion describes a 'conformational soliton' which moves rapidly and easily along the chain without being trapped either inside the chain, into one of the localized and immobile conformational defects[10], or at the end of the molecule (i.e. on the surface of the lamella).

The main problem with soliton is the energy of formation which still is calculated to be too large[10] for the generation of a sizable population. Further studies on this problem are under way in our laboratory.

CONCLUSIONS

This work gives further support to the conclusions of Ungar and Keller that n-alkane molecules are able to migrate from one crystal to another covering large distances almost on a macroscopic scale[16]. In this work we verified the phenomenon and have provided a description of it on a molecular scale.

The role played by the 'α' phase in supervising such a transport-of-matter process is pointed out. The migration of a chain in the 'α' phase cannot be overlooked when one tries to describe the 'structure' or the 'nature' of the solid 'α' phase. In such a modification, chains acquire such a large mobility that they give the system a 'plastic' character. Our findings provide a description of the 'α' phase which is very similar to that discussed by Piesczek *et al.* on the D form of $C_{33}H_{68}$[1]. From X-ray diffraction experiments these authors conclude that 'the structure of modification D of $C_{33}H_{68}$ cannot be understood from static packing considerations without taking into account the dynamics of the chain'. So far only rotational motions of the chain accompanied by small translations were found for n-paraffins. Here, evidence is collected for the fact that chains can migrate over much larger distances. On a short time scale the sublattice may seem to be ordered, even if strongly perturbed, but on a longer time scale one chain has travelled a long way into another lamella.

The process of migration is observed in binary mixtures of solid n-alkanes of slightly different length, or for n-alkanes of the same length, but isotopically different. There seems to be no particular reason to think that the same mobility should not occur in homogeneous systems. A temperature dependent self-diffusion process in any crystalline n-alkanes should then be considered.

Of particular relevance in the field of transport phenomena in organic materials is the fact that, in spite of such a large molecular mobility, chains substantially keep an overall *trans* conformation thus moving almost as rigid bodies. While de Gennes has pointed out that chains are mobile in an amorphous phase by a 'reptation' model when the conformational chain flexibility is the dominant factor[35]. The 'reptation mechanism would require the existence of a large fraction of amorphous or liquid like structures; this has not yet been demonstrated. Hence the chain mobilities in amorphous and crystalline phases must have different origins.

This work sheds some light on the yet unsolved problem of the chain mobility which facilitates the process of annealing of polymeric materials. The question still unsettled is whether the annealing process is accompanied by a transport of matter across subgrain boundaries[13]. This work shows that, at least in the case of polymethylene chains, transport of matter does take place and can be maximized when the system is brought into the 'α' phase.

ACKNOWLEDGEMENTS

We wish to thank Dr A. Provasoli of ICM, Milano, for his help in the d.s.c. measurements; Drs E. Mantica, D. Botta and L. Castellani for their advice during the crystallization of the substances. We wish to thank Professor A. Cesaro of the University of Trieste and Drs G. Minoni and G. Zannoni of the Polytechnic of Milan for helpful and friendly discussions.

REFERENCES

1 Piesczek, W., Ewen, B., Fischer, E. W. and Strobl, G. *Colloid Polym. Sci.* 1974, **252**, 896
2 Even, B. and Richter, D. *J. Chem. Phys.* 1978, **69**, 2954
3 Richter, D. and Even, B. in 'Neutron Inelastic Scattering' 1977 (IAEA, Wien, 1978)
4 Bonsor, D. H., Barry, J. F., Newbery, M. W., Smalley, M. V., Granzer, E., Koberger, C., Nedwed, P. H. and Scheidel, J. *Chem. Phys. Lett.* 1978, **62**, 576
5 Bloor, D., Bonsor, D. H., Batchelder, D. N. and Windsor, C. G. *Mol. Phys.* 1977, **34**, 939
6 Zerbi, G., Magni, R., Gussoni, M., Holland-Moritz, K., Bigotto, A. and Dirlikov, S. *J. Chem. Phys.* 1981, **75**, 3175
7 McCullough, R. L. *J. Macromol. Sci., Phys.* 1974, **B9**, 97
8 McClure, D. *J. Chem. Phys.* 1968, **49**, 1830
9 Kobayashi, M. *J. Chem. Phys.* 1977, **68**, 145
10 Mansfield, M. and Boyd, R. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1227
11 Mansfield, M. *Chem. Phys. Lett.* 1980, **69**, 383
12 Skinner, J. L. and Wolynes, P. G. *J. Chem. Phys.* 1980, **73**, 4022
13 Wünderlich, B. 'Macromolecular Physics', II, Academic Press, N.Y. (1976) ch. VII
14 Zerbi, G., Magni, R. and Gussoni, M. *J. Mol. Struct.* 1981, **73**, 235
15 See, for instance: Pechold, W. *Colloid Z. Z. Polym.* 1968, **228**, 1
16 Ungar, G. and Keller, A. *Colloid Polym. Sci.* 1979, **257**, 90
17 Narang, R. S. and Sherwood, J. N. *Mol. Cryst. Liq. Cryst.* 1980, **59**, 167
18 Broadhurst, M. G. *J. Res. Natl. Bur. Stand.* 1962, **66 A**, 241
19 Mazee, W. M. *Anal. Chim. Acta* 1957, **17**, 97
20 Mazee, W. M. *Erdol u. Kohle* 1960, **13**, 88
21 Kieras, J., Turner, W. R. and Melpolder, F. W. *ACS Div. Chem. Prepr.* 1964, **9**, 257
22 Bonsor, D. H. and Bloor, D. *J. Mater. Sci.* 1977, **12**, 1559
23 Harrison, L. G. in 'Comprehensive Chemical Kinetics', Elsevier, Amsterdam, vol. II, pp. 377–463 (1969)
24 Rogers, C. E. in 'Physics and Chemistry of the Organic Solid State', Interscience Publ., vol. II, p. 509 (1965)
25 See, for instance: Tasumi, M. 'Intra and Intermolecular Vibrations of n-Alkanes and Polyethylene', in 'Vibrational Spectroscopy — Modern Trends', (Eds. A. J. Barnes, W. J. Orville-Thomas), Elsevier, Amsterdam (1977)
26 See, for instance: Zerbi, G. 'Applied Spectroscopy Review', 1969, **2**, 193
27 Zbinden, R. 'Infra-red Spectroscopy of High Polymers', Academic Press, NY (1964)
28 Schachtschneider, J. H. and Snyder, R. G. *Spectrochim. Acta*, 1963, **19**, 17 and references therein
29 Tasumi, M. and Shimanouchi, T. *J. Chem. Phys.* 1965, **43**, 1245
30 Tasumi, M. and Krimm, S. *J. Chem. Phys.* 1967, **46**, 755
31 Zerbi, G. in 'Advances in Chemistry Series', Am. Chem. Soc., in press
32 Wedder, W. and Hornig, D. F. *Adv. Spectrosc.* 1962, **2**, 189
33 Krimm, S. and Cheam, T. S. *Faraday Soc. Disc.* 1979, **68**, 244
34 Stehling, F. C., Ergos, E. and Mandelkern, L. *Macromolecules* 1971, **4**, 672
35 de Gennes, P. G. *J. Chem. Phys.* 1971, **55**, 572