Surface melting in crystalline polymethylene systems: fatty acids

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The study of the temperature-dependent infra-red spectra of selectively deuterated stearic acid shows that melting is prepared by a premelting process characterized by surface disordering on the crystalline lamellae. The origin of the phenomenon is discussed.

(Keywords: polymethylene; fatty acids; surface melting)

INTRODUCTION

It is a well known fact that organic materials containing polymethylene chains exhibit peculiar physical properties which are certainly related to the molecular flexibility and/or mobility of the long molecular chains. The precise mechanism on a molecular level which determines these properties is not yet fully understood.

As part of a study of the molecular mobility of polymethylene systems in this paper we focus on the many spectroscopic signals observed in the temperature-dependent vibrational infra-red and Raman spectra of selectively deuterated fatty acids.

The spectra show the onset of 'premelting' ~7°C below melting. The spectroscopic data collected describe such premelting as a conformational disordering at the surface of the crystalline lamellae. Such 'surface melting' can be rationalized in the light of the possible existence of 'conformational solitons' or twistons.

EXPERIMENTAL

We have studied the temperature-dependent infra-red spectra of stearic acid $CH_3-(CH_2)_{16}-COOH$ and of two dideutero stearic acids with the CD_2 group selectively located in positions 6 and 13. For brevity we refer to these molecules as C_{18}, $C_{18}(6D_2)$ and $C_{18}(13D_2)$, respectively. The synthesis of the deuterated compounds is described in reference 1. Spectra were recorded with a Nicolet 7000 FTIR interferometer. The materials were suspended in a KBr pellet and placed in a home-made thermostat. The accuracy of the temperature measurements is estimated to be ±1°C. It is known that fatty acids show polymorphism[2]: in the case of the materials studied the existence of the C modification was verified.

Room temperature structure of stearic acid and thermal behaviour

Accurate studies by X-ray diffraction[3] and vibrational infra-red and Raman spectroscopy[4–6] show that the carbon skeleton of stearic acid in the solid state at room temperature is dimeric and *trans* planar. The spectroscopic evidence that the alkyl chains are in their extended *trans* conformation comes from

(1) LAM spectroscopy of chains with bound ends[4];
(2) a study of stearic acid containing selective conformational markers[5];
(3) the unquestionable observation in the infra-red of the CH_2 wagging and rocking band progression up to the melting point[6].

The conformation of the last C–C bond adjacent to the carboxyl group is not *trans* planar but distorted[3,5].

The differential scanning calorimetry (d.s.c.) thermogram of stearic acid shows only a rather broad peak corresponding to the melting at 69.7°C. Contrary to the case for n-alkanes no solid–solid phase transitions are indicated. The broad d.s.c. thermogram suggests that premelting takes place.

The onset of 'premelting' approximately 10°C below melting has been previously indicated by nuclear magnetic resonance (n.m.r.)[2,7] and infra-red spectra[6].

Gap and resonance modes as markers of conformational defects

As a result of many molecular dynamical calculations it is known that geometry-dependent gap or pseudoresonance modes can be found in the infra-red spectrum of polymethylene chains; they have already been used in conformational analysis.

In this paper, we use the following conformational markers which we separate into two classes, namely the topologically selective and non-selective markers.

In the first class we consider the following cases:

(1) When a CH_2 is replaced by a CD_2 group, the CD_2 rocking motion becomes a typical gap mode[8,9], only slightly coupled with the host lattice, with frequencies at 622 and 650 cm^{-1} for $^{T}CD_2{}^{T}$ and $^{T}CD_2{}^{G}$ structures, respectively. It thus becomes possible to probe the conformation of the chain site by site by suitable topologically selected deuteration[10,11];
(2) When the CH_2 group adjacent to the terminal CH_3 group is placed between a T and a G conformation (end TG group), it generates a quasi-localized mode near 1342 cm^{-1} (ref. 12);
(3) It has been shown that the umbrella deformation mode of the CH_3 group at 1375 cm^{-1} is sensitive

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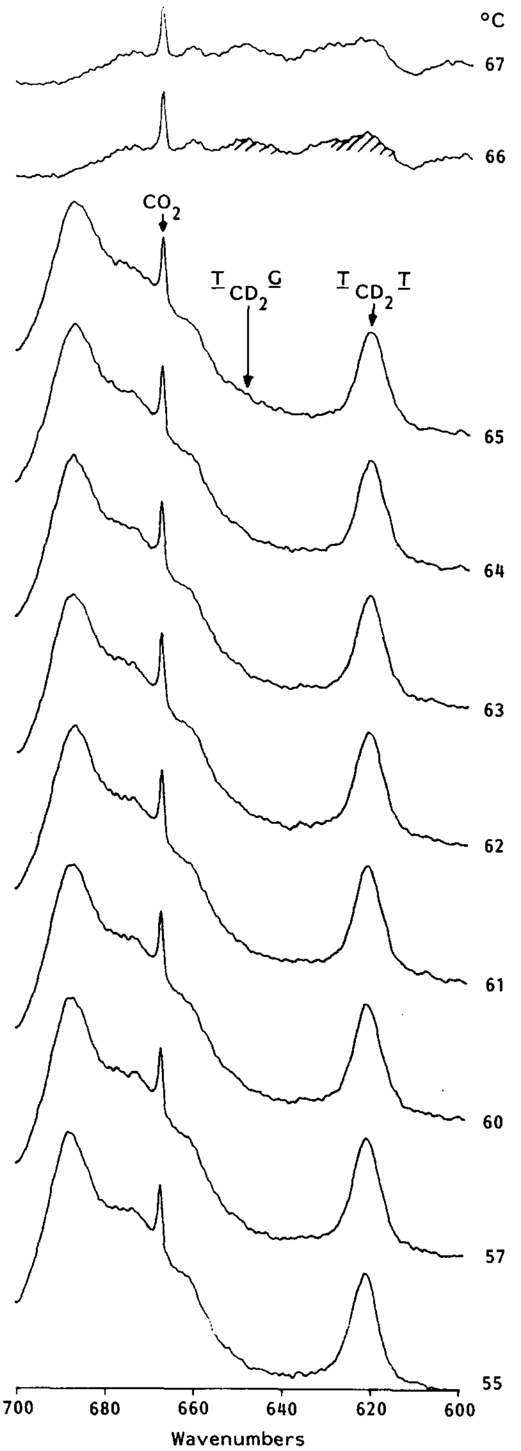

Figure 1 Temperature dependence of the infra-red spectrum of $C_{18}(13D_2)$ in the 600–700 cm^{-1} range

to the environment and to the interlamellar interactions and shifts upwards of 3–4 cm^{-1} from an ordered to a disordered phase[11,13].

The second class of topologically non-selective markers consists of the following well known and widely used quasi-localized defect modes:

(1) Calculated and observed near 1367 and 1306 cm^{-1} to be ascribed to the out-of-phase and in-phase CH_2 wagging motions of the two CH_2 groups in the GTG′ conformation[12];

(2) The defect mode calculated and observed near 1352 cm^{-1} as characteristic of the GG conformation in an otherwise T host lattice[12,14].

Temperature-dependent infra-red spectra

The infra-red spectrum of C_{18} has been already discussed in reference 6. We discuss here the evolution with temperature of the infra-red spectra of $C_{18}(6D_2)$ and $C_{18}(13D_2)$ (see *Figures 1–5*).

(i) In the CD_2 rocking range for both compounds, within the sensitivity of our measurement, we detect only the band at 622 cm^{-1} due to the TT conformation up to the melting point. At the melting point the band at 650 cm^{-1} appears, as obviously expected when the chain is in the liquid phase and the rotational isomeric state model of Flory applies ($\approx$40% of G and $\approx$60% of T conformers) (see *Figures 1* and *2*). The difference spectra obtained by subtracting the spectrum recorded at room temperature from all the other spectra, again show that no significant changes take place prior to melting (*Figure 3*).

(ii) From the spectra in the 1400–1300 cm^{-1} range we observe that starting from $\approx$63°C on the higher frequency side (1378 cm^{-1}) of the CH_3 umbrella deformation mode (1373 cm^{-1}) a new absorption increases with increasing temperature. The doublet thus formed evolves

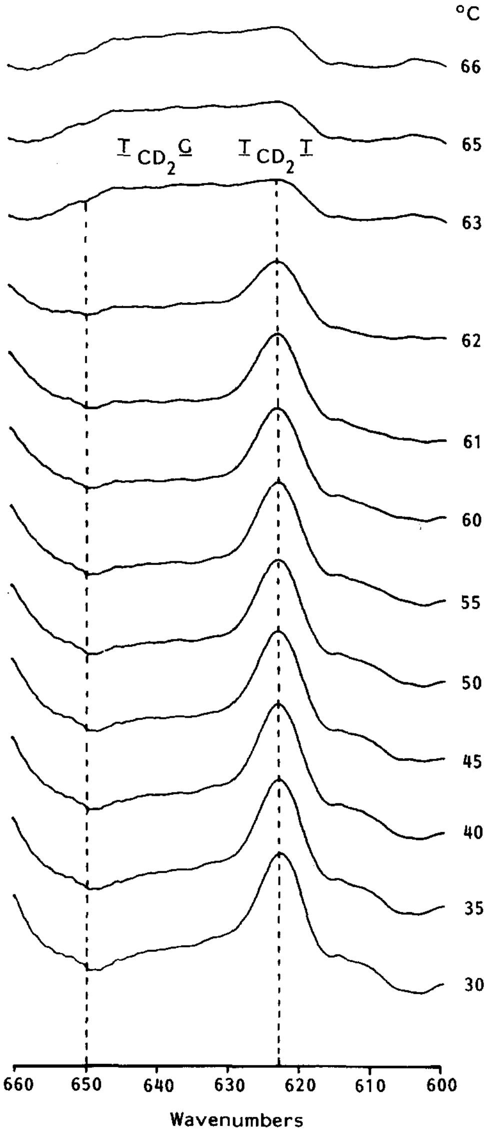

Figure 2 Temperature dependence of the infra-red spectrum of $C_{18}(6D_2)$ in the 600–660 cm^{-1} range

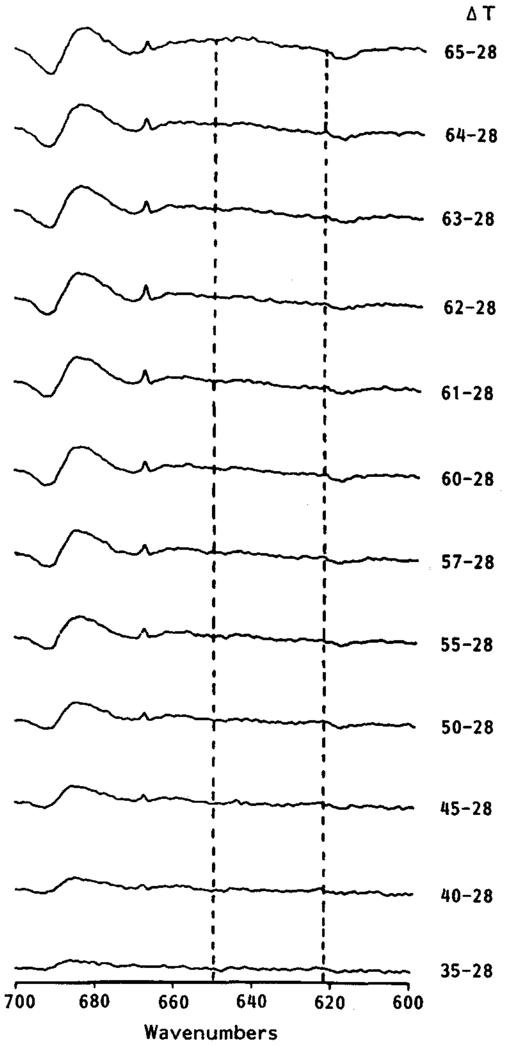

Figure 3 Difference spectra of $C_{18}(13D_2)$ in the 600–700 cm^{-1} range

toward a singlet centred at 1378 cm^{-1} at the melting point (*Figure 4*). Some kind of disordering then takes place at the interface between the molecular layers formed by the dimeric molecules.

(iii) Support to surface disordering cannot be obtained from the observation of the end-TG defect mode in the spectrum of $C_{18}(13D_2)$ because it overlaps with one of the components of the *trans* CH_2 wagging sequence, the intensity of which is enhanced by the presence of the carboxyl group. Absorption due to end-TG modes is instead observed in the spectrum of $C_{18}(6D_2)$ since it does not fully overlap with the *trans* CH_2 wag (*Figure 4*).

The above observations become clearer in the difference spectra obtained (see (i) above). From these spectra (*Figure 5*) the onset of a premelting process 5–7°C before melting becomes evident.

(iv) GTG′ defects can certainly be observed, as expected, in the spectrum of the melt. They are, however observed, also a few degrees before melting (*Figures 4* and *5*).

RESULTS AND DISCUSSION

The choice of selective deuteration in positions 6 and 13 was made in order to probe the conformation of the molecule near, but not at, the surface and inside the molecule, respectively. Results (i) show that conforma-

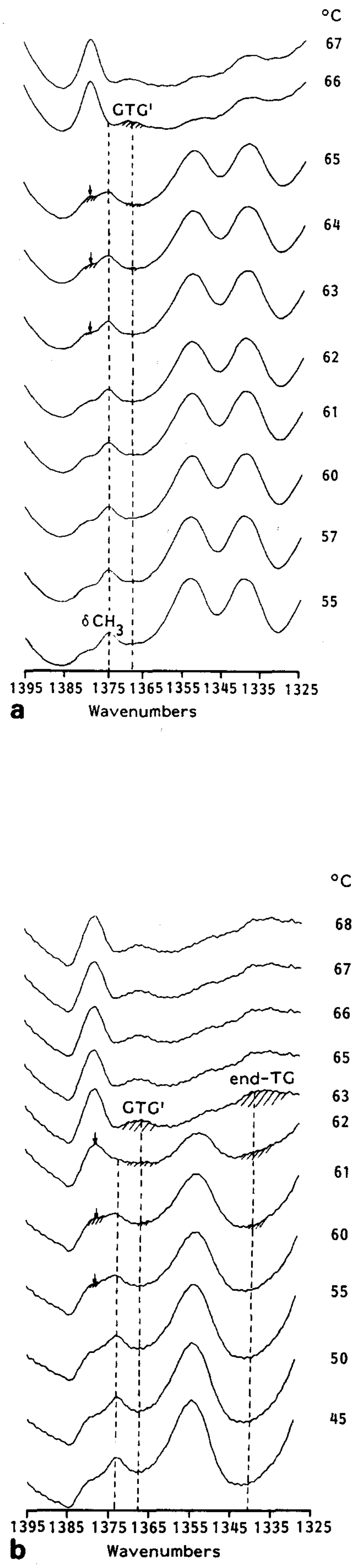

Figure 4 (a) Temperature dependence of the infra-red spectrum of $C_{18}(13D_2)$ in the 1300–1400 cm^{-1} range. (b) Temperature dependence of the infra-red spectrum of $C_{18}(6D_2)$ in the 1300–1400 cm^{-1} range

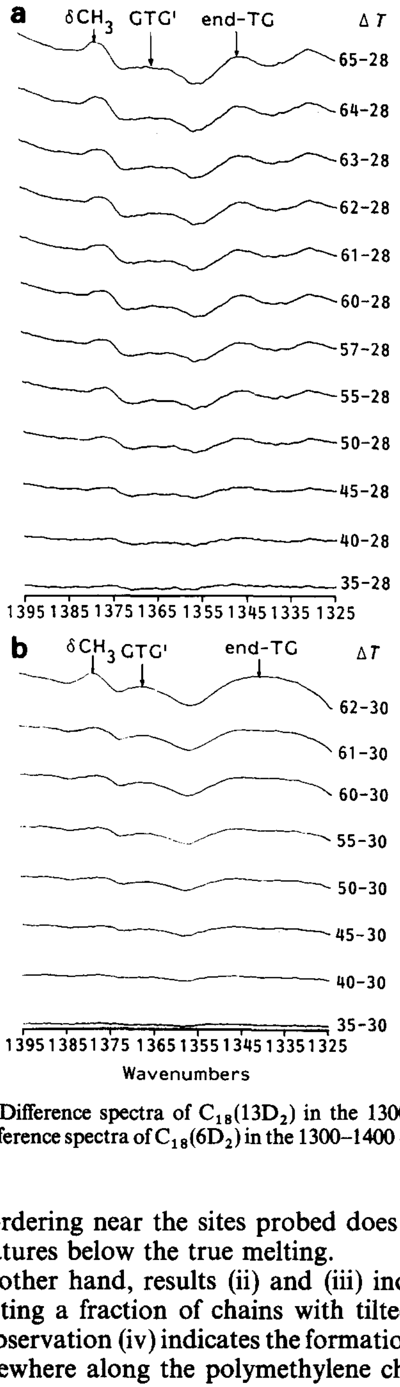

Figure 5 (a) Difference spectra of $C_{18}(13D_2)$ in the 1300–1400 cm^{-1} range. (b) Difference spectra of $C_{18}(6D_2)$ in the 1300–1400 cm^{-1} range

tional disordering near the sites probed does not occur at temperatures below the true melting.

On the other hand, results (ii) and (iii) indicate that before melting a fraction of chains with tilted heads is formed. Observation (iv) indicates the formation of GTG′ kinks somewhere along the polymethylene chain; however since the bulk, as probed by selective deuteration, does not seem to contain such kinks, they must be located near the surface of the bilayered lamella. The conformational structure of the chain is sketched in *Figure 6*.

The conclusion we reach is that the observed spectra are consistent with the fact that ≈7°C before melting a premelting process takes place consisting of a conformational disordering of the molecule at either end of the alkyl chain, thus generating a disorder at the interface between molecular layers.

Such 'surface melting' coexists with surface domains of ordered material. No 'liquid like' droplets are formed within the bulk or on the surface since markers of GG conformations are not observed until melting is reached.

By increasing temperature the surface disordering increases and it is reasonable to think that such conformational disorder may quickly move from the surface into the bulk producing, at the melting temperature, the collapse of the crystal and of the chain molecules.

The situation is identical with that already observed for the case of n-nonadecane[11]. The interesting issue raised in the spectroscopic study of n-nonadecane is that in the so called pseudorotatory phase, or 'α' phase, the surface disordering is reached by the fact that approximately 25% of the chains perform a longitudinal sliding and are capable of moving out of the lamella surface and tilt their heads at well identified molecular sites.

A highly non-even distribution of defects, in the 'α' phase of n-alkanes, has also been inferred by Snyder[10] from infra-red spectra of selectively deuterated molecules. The highest defect concentration is at the chain ends, and the concentrations at interior sites decrease exponentially going towards the middle.

Diffusion of alkane chains has been verified[15] with infra-red spectroscopy even if the longitudinal or transversal character could not be distinguished. Old and new data from neutron scattering[16,17] support the fact that longitudinal diffusion is preferred in n-alkane systems.

The origin of such longitudinal motion is not yet clear. The model of cooperative rotational libro-rotation of the chains as rigid units[18] needs to be revised since conformational flexibility becomes an important factor. Of particular interest is the theoretical study of transport of matter generated by the propagation within the alkane lattice of a conformational long twist, commonly called the Utah-Twist. It was proposed by the Utah school[19] and later reformulated in terms of a 'conformational soliton'[20]. The problem of the molecular dynamics and spectra of a 'conformational soliton' or 'twiston' has been recently treated[21].

The problem of chain motion in the solid state in terms of twistons is particularly appealing since it may have a general validity for many physical processes. It first suggests a classification of the molecular systems containing long polymethylene chains in two main classes, namely (i) systems with both ends free (n-alkanes[11], probably fatty acids) which can generate and propagate twistons, thus generating premelting phenomena due to surface melting, and (ii) systems with either one or both ends fixed (bilayered organic perowskytes[13], organic silicates[22], organic zirconates[23], phospholipids[24], biological membranes, etc.) These last systems should approach melting by forming 'liquid like' droplets of GTG′ and GG defects, whose concentration and size increase with temperature, thus generating a cooperative collapse of the crystal. If surface melting occurs additional phenomena must be considered.

From this work fatty acids seem to belong to class (i). This means that the dimeric carboxyl groups in the middle of the chain do not hinder the propagation of solitons and the occurrence of a longitudinal translation of the dimeric molecule as a whole.

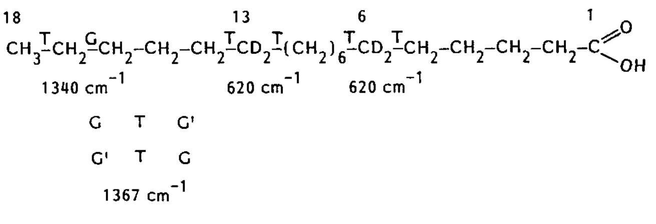
$CH_3\overset{T}{-}CH_2\overset{G}{-}CH_2-CH_2-CH_2\overset{T}{-}CD_2\overset{T}{-}(CH_2)_6\overset{T}{-}CD_2\overset{T}{-}CH_2-CH_2-CH_2-CH_2-C(=O)OH$

Figure 6 Schematic representation of the conformational structure of the chain as deduced from the analysis of the infra-red spectra of $C_{18}(13D_2)$ and $C_{18}(6D_2)$

The real existence of such twistons in solid ordered systems requires further experimental studies using various techniques.

REFERENCES

1 Tulloch, A. P. *Lipids* 1977, **12**, 92

2 Chapmann, D. 'The Structure of Lipids', Methuen, London, 1965; Von Sydow, E. G. *Acta Crystallogr.* 1954, **7**, 529; 1954, **7**, 823; Von Sydow, E. G. *Acta Chem. Scand.* 1955, **9**, 1119

3 Goto, M. and Asada, E. *Bull. Chem. Soc. Jap.* 1978, **51**, 70; 1978, **51**, 2456; 1980, **53**, 2111

4 Minoni, G. and Zerbi, G. *J. Phys. Chem.* 1982, **96**, 4791

5 Zerbi, G., Minoni, G. and Tulloch, M. P. *J. Chem. Phys.* 1983, **78**, 5853

6 Zerbi, G., Conti, G., Minoni, G., Pison, S. and Bigotto, A. *J. Phys. Chem.* 1987, **91**, 2386

7 Barr, M. R., Dunnell, B. A. and Grant, R. F. *Can. J. Chem.* 1963, **41**, 1188

8 Snyder, R. G. and Poore, M. W. *Macromolecules* 1973, **6**, 709

9 Maroncelli, M., Strauss, H. L. and Snyder, R. G. *J. Phys. Chem.* 1985, **89**, 4390

10 Maroncelli, M., Strauss, H. L. and Snyder, R. G. *J. Chem. Phys.* 1985, **82** (7), 2811

11 Zerbi, G., Magni, R., Gussoni, M., Holland Moritz, K., Bigotto, A. B. and Dirlikov, S. *J. Chem. Phys.* 1981, **75**, 3175

12 Zerbi, G. and Gussoni, M. *Polymer* 1980, **21**, 1129

13 Almirante, C., Minoni, G. and Zerbi, G. *J. Chem. Phys.* 1986, **90**, 825

14 Maroncelli, M., Qi, S. P., Strauss, H. L. and Snyder, R. G. *J. Am. Chem. Soc.* 1982, **104**, 6237

15 Piazza, R. and Zerbi, G. *Polymer* 1982, **23**, 1921

16 Ewen, B., Fisher, E. W., Piesczek, W. and Strobl, G. *J. Chem. Phys.* 1974, **61** (12), 5265

17 Guillaume, F., Doucet, J., Sourisseau, C. and Dianoux, A. J. Polymer Motion in Dense Systems, Grenoble, 1987

18 Yamamoto, T. *J. Chem. Phys.* 1988, **89** (4), 2356

19 Mansfield, M. and Boyd, R. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1227

20 Mansfield, M. *Chem. Phys. Lett.* 1980, **69**, 383; Skinner, J. L. and Wolynes, P. G. *J. Chem. Phys.* 1980, **73** (8), 4015; 1980, **73** (8), 4022

21 Zerbi, G. and Longhi, G. *Polymer* 1988, **29**, 1827

22 Lagaly, G. *Angew. Chem. Int. Ed. Eng.* 1976, **15**, 575; Lagaly, G., Weiss, A. and Stuke, E. *Biochim. Biophys. Acta* 1977, **470**, 331; Lagaly, G. *Naturwissenschaften* 1981, **68**, 82

23 Basini, L., Raffaelli, A. and Zerbi, G. *Chem. Mater.* submitted

24 Levin, I. R. in 'Advances in IR and Raman Spectroscopy', Wiley, New York, 1985, Vol. 11