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Vibrational Spectra and Phase Transitions in Intercalated Layered Alkylammonium Zirconium Phosphates

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Temperature-dependent infrared spectra of two samples of layered zirconium phosphates intercalated with n-$CH_3(CH_2)_{10}CH_2NH_2$ and n-$CH_3(CH_2)_{12}CH_2NH_2$ have been recorded and studied. The purpose of the work is to understand the mechanism of phase transitions at the molecular level. Collective phonons and localized defect modes have been identified, and their thermal behavior has been studied. The transition is not first order and proceeds through several steps. Upon heating, chains contain GTG′ kinks but no liquidlike structures are observed.

Introduction

This work is part of research aimed at understanding the molecular phenomena that form the basis for phase transitions in materials containing polymethylene chains. The justification of this research is that in nature many polymethylene systems exist, each one showing peculiar physical properties that are certainly related to the flexibility and mobility of the long alkyl chain.

In this paper we use the vibrational infrared spectrum as a tool for probing the detailed molecular conformation of the alkyl chains as function of temperature. Molecular dynamical calculations and experiments have shown that the vibrational spectra provide information on normal modes topologically localized at specific sites and/or on collective motions involving the whole molecular chain.[1-3] The classes of molecules so far treated are the simple n-alkanes,[4,5] fatty acids,[6] biological materials,[7] organic perovskites as models of bilayered membranes,[8] and polyethylene.[1-4,9]

One of the main results of this work is that new insight has been gained on the molecular processes that take place at phase transitions (either solid–solid or solid–melt and/or solid–nematic). Spectroscopic indications have been found that the molecules of n-alkanes, and possibly fatty acids, while still in the solid can perform longitudinal translations when energy is provided as heat.[5,10,11] Such longitudinal motions produce first conformational disordering on the surface of the crystalline lamellae;[5] melting is than approached with the disorder increasing from the surface into the core.[12]

On this basis we have proposed a first approximate classification of these molecules into systems with free ends (which can perform translational diffusion) and systems with fixed ends.[3]

In this paper we focus our attention on a class of new compounds in which alkyl chains are sandwiched between two planes of zirconium phosphate ions (hereafter referred to as α-ZP). According to our tentative correlations between structure and phase transitions, these compounds should be classified as fixed-end systems similar to the organic perovskites previously studied.[8]

Experimental Section

The structure of these systems is given in Figures 1 and 2. Chemically each layer of α-ZP consists of a plane of zirconium atoms between two planes of PO_4^{2-} ions. Three oxygen atoms of the phosphate group are bound to three zirconium atoms, while the fourth is bound to a proton that can be easily exchanged with other counterions that then separate the inorganic layers. Many counterions have been studied;[12] in our case we are interested in systems such as $CH_3(CH_2)_n\mathit{CH}_2NH_3^+$. Many alkyl chains with various values of n have been introduced; in our case we study molecules with n = 10 and 14 (which we label as C12 and C16, respectively).

Details on the chemistry and on the thermal and crystallographic properties are reported in a review article by Alberti and Costantino.[13] Samples of α-ZP C12 and α-ZP C16 were kindly provided by Prof. Costantino of the University of Perugia and were used as received without further purification. In this work we have recorded the vibrational infrared spectra of the intercalated zirconium phosphate as untreated powders between NaCl windows and as KBr pellets. The spectra reported in this paper are those obtained from samples as KBr pellets. No substantial differences were found in the spectra of the powders. Temperature-dependent infrared spectra were obtained from room temperature up to 250 °C in vacuo in a Specac heating cell with FTIR interferometers Nicolet 7199 and 20SXC; data manipulations were made using standard software. Differential scanning calorimetry (DSC) experiments were made with Mettler instruments.

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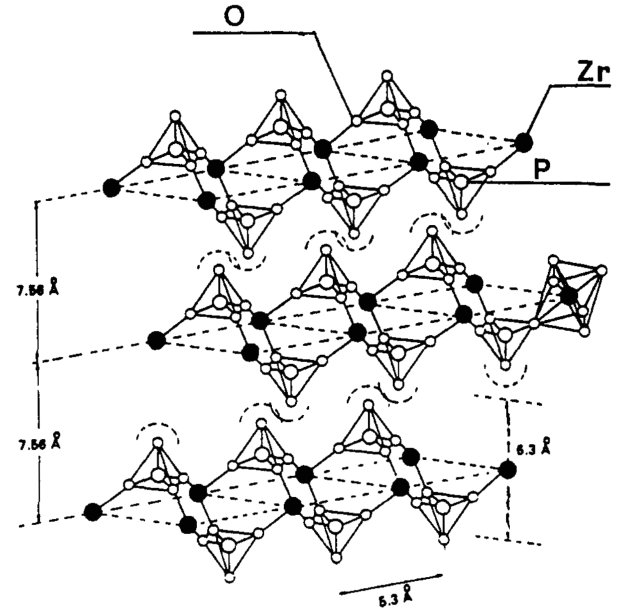

Figure 1. Crystal structure of zirconium phosphates layer between which organic molecules can be inserted (from ref 13).

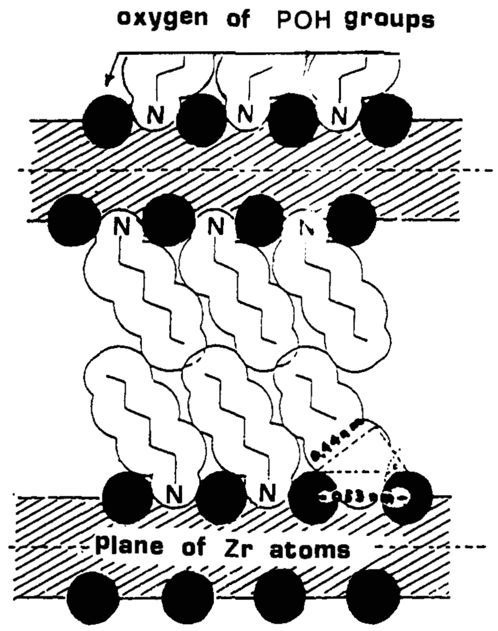

Figure 2. Sketch of the arrangement of alkyl chains between layers of zirconium phosphates consistent with X-ray diffraction data (from ref 14).

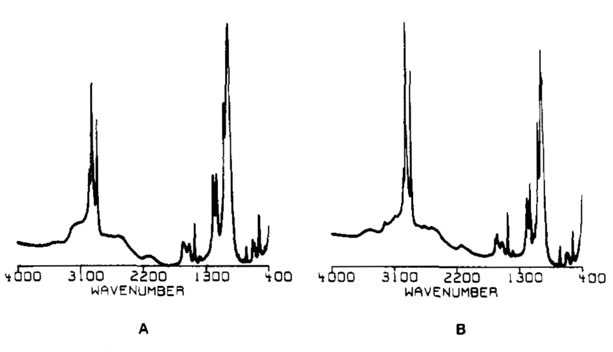

Figure 3. Spectra in the mid-IR range of the intercalated zirconium phosphates: (A) α-ZP intercalated with $CH_3(CH_2)_{10}CH_2NH_2$; (B) α-ZP intercalated with $CH_3(CH_2)_{12}CH_2NH_2$.

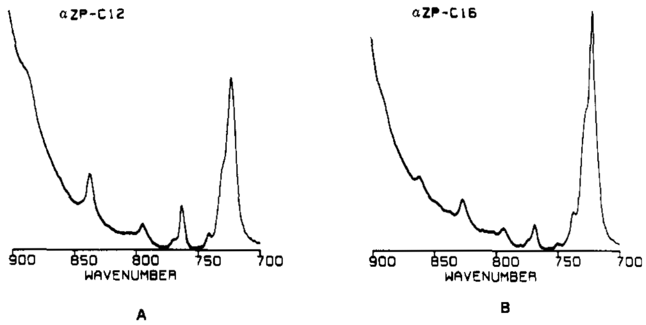

Figure 4. Band progressions of the CH_2 rocking modes: (A) α-ZP intercalated with $CH_3(CH_2)_{10}CH_2NH_2$; (B) α-ZP intercalated with $CH_3(CH_2)_{12}CH_2NH_2$.

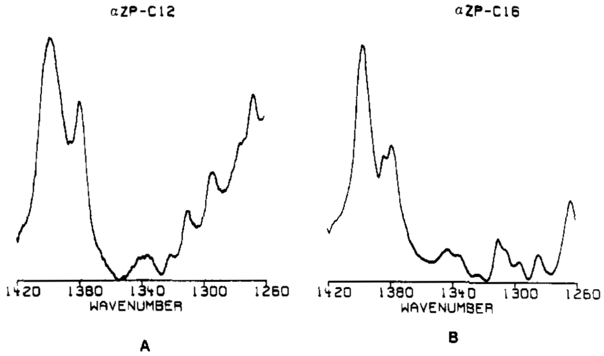

Figure 5. Band progressions of CH_2 wagging modes and methyl deformations (umbrella motion): (A) α-ZP intercalated with $CH_3(CH_2)_{10}CH_2NH_2$; (B) α-ZP intercalated with $CH_3(CH_2)_{12}CH_2NH_2$.

Results and Discussion

Structure and Spectrum at Room Temperature. The overview vibrational spectra of α-ZP C12 and α-ZP C16 reported in Figure 3 show the well-known features due to the vibrations of polymethylene chains[2,3] together with the spectrum of the inorganic moiety. To disentangle the contributions of the organic and inorganic parts, we have recorded the infrared spectrum of α-ZP prior to intercalation. No attempt is made here to assign the bands of the inorganic part since our main purpose is to focus on the conformational flexibility of the alkyl chains. We notice, however, that the observed spectra of the intercalated α-ZP are not just the superposition of the two independent materials (as should occur in a mechanical mixture). Some coupling of the counterion with the inorganic matrix can be noticed, but this does not affect the analysis we wish to carry out in this work.

Trans Planarity. The structure in Figure 2 is inferred from the X-ray diffraction measurements of the interlayer distance as function of the number of carbon atoms in the alkyl chain.[13,14] The first question we wish to address is whether spectroscopic data can support the trans-planar structure of the alkyl residues. For this purpose we search in the spectra signals known to be characteristic of CH_2 sequences in a trans conformation. We make the following observations:

(i) In the room-temperature spectra of Figures 4 and 5, CH_2 rocking and wagging modes show band progressions typical of $k \neq 0$ phonons of a chain in the trans conformation for both α-ZP C12 and α-ZP C16.

(ii) In the CH_2 bending region we observe the band at 1475 cm^{-1} which generally occurs in the trans structure

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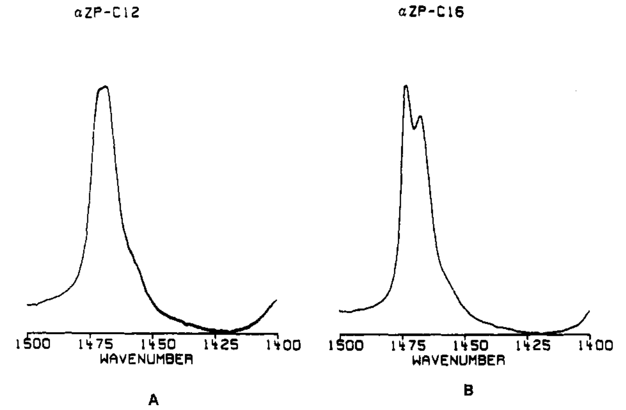

Figure 6. Absorption peaks in the CH_2 bending region: (A) α-ZP intercalated with $CH_3(CH_2)_{10}CH_2NH_2$; (B) α-ZP intercalated with $CH_3(CH_2)_{12}CH_2NH_2$.

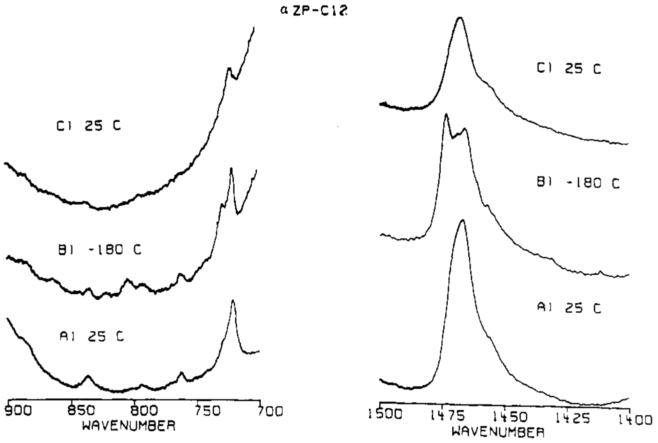

Figure 7. Thermal evolution during a low-temperature thermal cycle of the IR absorption spectrum of α-ZP C12 in the CH_2 rocking and bending regions: (A) spectra at room temperature; (B) spectra at −180 °C; (C) spectra of sample B at room temperature.

without the broad asymmetry at the lower frequency side and the weak absorption near 1445 cm^{-1} originating from gauche structures[15] (Figure 6).

(iii) In the CH_2 stretching range the antisymmetric and symmetric C–H stretchings (S^- and S^+) are observed near 2918 and 2850 cm^{-1} as in all *trans-n*-alkanes. When G conformations exist, absorption on the higher frequency side of either bands is observed.[16]

Tridimensional Order. The symmetry of the crystal lattice formed by the alkyl chains can be inferred from the observed spectrum. When the chains are arranged in an orthorhombic lattice or orthorhombic sublattice, the bands due to CH_2 bending and rocking are split into a doublet due to correlation field effects. When chains form a triclinic lattice (and sometimes monoclinic), the unit cell contains only one chain and the vibrational levels are not split.[9,14] The observed spectra in the range of the CH_2 rocking (Figure 4) show one sharp and strong single band with a fine structure on the higher frequency side; the sharp band is the quasi $k = 0$ mode, and the fine structure is the progression of the $k \neq 0$ CH_2 rocking modes with very weak infrared intensity. The conclusion that follows is that the lattice is either triclinic or distorted monoclinic.

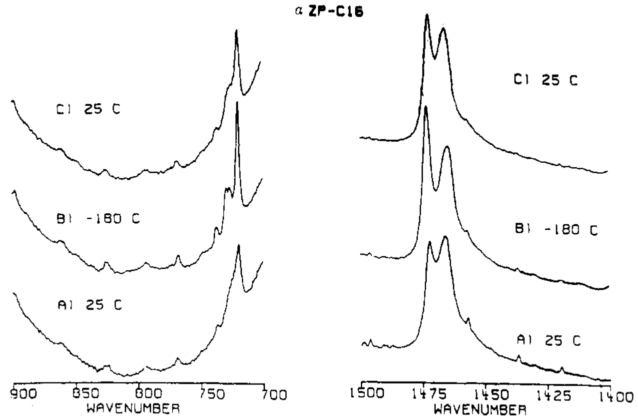

Figure 8. Thermal evolution during a low-temperature thermal cycle of the IR absorption spectrum of α-ZP C16 in the CH_2 rocking and bending regions: (A) spectra at room temperature; (B) spectra at −180 °C; (C) spectra of sample B at room temperature.

A check of this conclusion should come from the CH_2 bendings (Figure 6), which should behave in a similar way. Such a check is weakened by the fact that a doublet is observed, in contradiction with the CH_2 rocking. Such an apparent discrepancy could be removed by assigning the 1460-cm^{-1} band to the deformation mode of the NH_3^+ ion. For a better understanding of this spectral range we have recorded the spectra of both α-ZP C12 and α-ZP C16 at liquid nitrogen temperature (Figures 7 and 8). The doublet becomes further resolved, and for α-ZP C16 a third band at 1468 cm^{-1} is observed in the valley between the peaks at 1473 and 1465 cm^{-1}. We take the observed three peaks as originating from an unsplit CH_2 bending, CH_3 deformation, and NH_3^+ deformation; without any information from deuterated derivatives any choice of the bands is, however, arbitrary. Even at low temperature the CH_2 rocking band is not split. The nonexistence of an orthorhombic lattice or sublattice inferred from room-temperature CH_2 rockings bands is in this way supported. Any hope to obtain some information from the Raman spectra failed since in all the Raman spectra we tried to record we observed only a strong fluorescence.

Conformational Disorder. It is known that specific conformational defects such as GG, GTG′, and end-TG give rise in the spectrum to absorptions characteristic of the normal modes topologically localized on the defect (GG 1353 cm^{-1}, GTG′ 1367 and 1306 cm^{-1}, and end-TG 1340 cm^{-1}). These localized defect modes have often been used as probes of the disordered structure of polymethylene chains.[2-5,9,15] At room temperature there is no clear evidence of spectroscopic signals due to the above conformational defects, thus giving further support to the coplanarity of the polymethylene chains as discussed in above. The fine structure observed in the spectrum in the 1300–1370-cm^{-1} range is ascribed to the well-resolved components of the progression of the CH_2 wagging modes for the chain in trans conformation.

Temperature-Dependent Spectrum and Structure. Calorimetry. From the works by Alberti and Costantino,[13,14] we learn that upon heating, the interlayer distances, as measured from X-ray diffraction, shrink stepwise. This fact has been interpreted in terms of the formation of conformational kinks as also proposed by Lagaly[18] on other layered systems.

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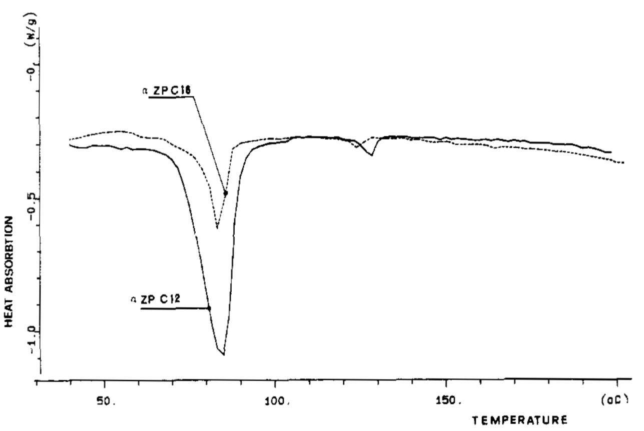


Figure 9. Differential scanning calorimetry for α-ZP C12 and α-ZP C16.

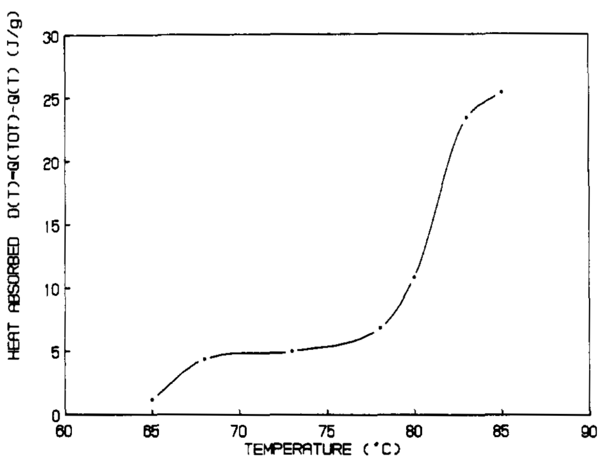


Figure 10. Variations vs temperature of the amount of the heat adsorbed during the endothermic transition of α-ZP C16.

For a better description of the phase transition we have made several experiments of differential scanning calorimetry (DSC). DSC spectra obtained for both α-ZP C16 and α-ZP C12 show two endothermic peaks near 85 and 125 °C and indicate that the amount of heat exchanged is larger for the α-ZP C12 sample (Figure 9).

A further insight into the mechanism of the transition can be obtained from the following DSC measurements. Let $Q(\text{tot})$ be the total heat absorbed for the main-phase transition, which starts near 65 °C and ends near 90 °C, and let $Q(T)$ be the heat absorbed during a DSC experiment that starts at T (65 °C < T < 90 °C) after having annealed the sample for 5 min. The plot of the quantity $D(T) = Q(\text{tot}) - Q(T)$ vs T is given in Figure 10. The results indicate that the transition is not first order since for an ideal first-order transitions $D(T)$ should be zero for any annealing. It follows that pretransitional phenomena are activated below the maximum in the DSC curve as indeed shown by the IR spectra.

Infrared Spectra. The identification of the molecular phenomena that take place upon heating can be attempted using vibrational spectroscopy, as discussed below.

(a) Thermal Evolution of the CH_2. Sequences in Trans Conformation. The clearest information on the effect of heating on the transplanar chains is given by the observation of the progression of the CH_2 rocking modes. For samples not subjected to annealing, the progression can be followed practically up to the "transition" temperature, T_{max}, indicated by the maximum of the DSC curve for both α-ZP C12 and α-ZP C16 (Figure 11A). Upon annealing, the progression can be observed through and well above T_{max} (Figure 11B). In both cases each component of the progression becomes broader but does not change its peak frequency. The existence of transplanar chains is also confirmed by the T-dependent infrared spectra in the C–H stretching region. The peak frequencies of the antisymmetric and symmetric CH_2 stretching modes are observed near 2918 and 2850 cm^{-1}, characteristic of a trans planar structure. Upon heating, the absorption due to gauche structures should be observed on the higher frequency side of these two bands; at large concentration of disorder the two main peaks shift to higher frequencies of about 5 and 2 cm^{-1}.[3,4,16] This is indeed experimentally observed. The plots of ν/T for these bands (Figures 12 and 13) describe the phase transition for both α-ZP C12 and α-ZP C16 annealed and unannealed.

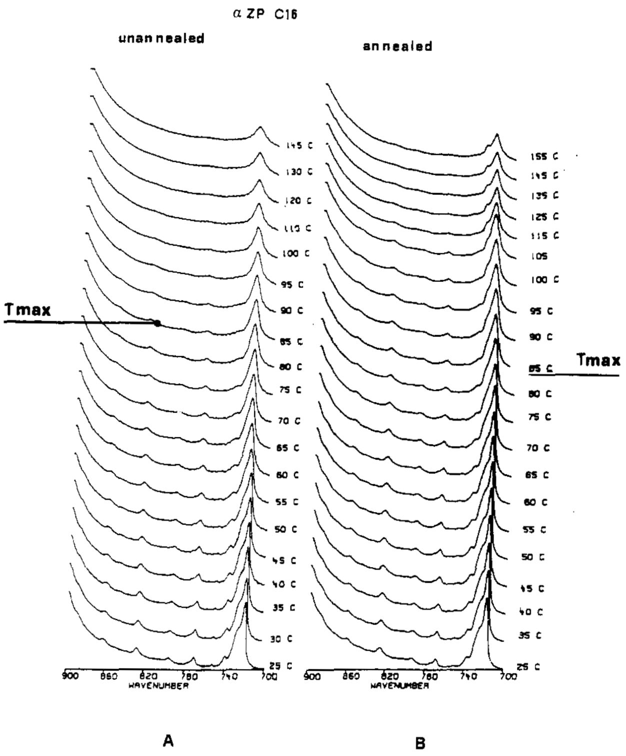


Figure 11. Variations in the CH_2 rocking sequences for α-ZP C16 during the heating treatment: (A) annealed sample; (B) unannealed sample.

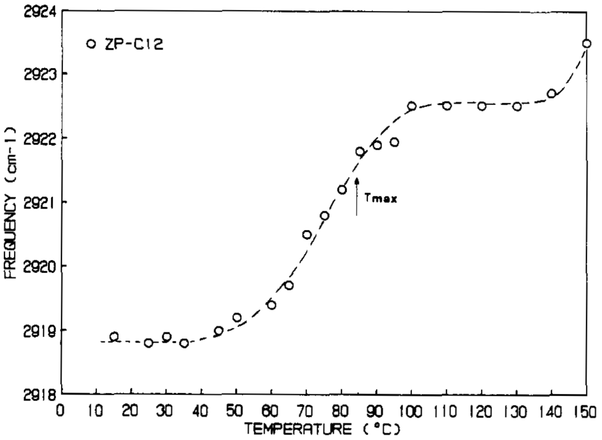


Figure 12. Frequency shifts of the antisymmetric CH_2 stretching vibrations in alkyl chains of α-ZP C12 during the thermal treatment.

(b) Thermal Generation of Defects. This phenomenon is followed by the evolution with T of the defect

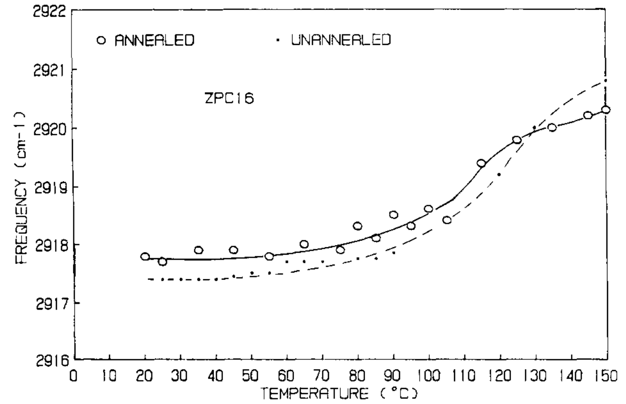


Figure 13. Frequency shifts of the antisymmetric CH_2 stretching vibrations in alkyl chains of α-ZP C16 during thermal treatment.

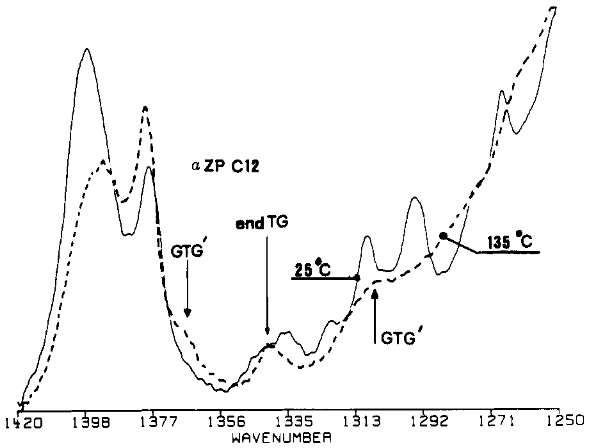


Figure 14. Room-temperature and 135 °C spectra in the CH_2 wagging region for α-ZP C12.

modes at the frequencies listed above. We studied the spectra and difference spectra as a function of T and, when possible, measured the integrated intensities. For the sake of conciseness we report in Figure 14 the spectra of α-ZP C16 at room temperature and well above the observed DSC transitions. Clearly one observes the disappearance of the CH_2 wagging progression due to the trans conformation and the appearance of the absorptions due to the defect modes of the type GTG′ (near 1365 and 1306 cm^{-1}) and end-GT (near 1343 cm^{-1}). GG defects are not formed since there is no absorption near 1350 cm^{-1}. The thermal evolution of the concentration of GTG′ modes is reported in the plot of Figure 15, parts A and B, for α-ZP C12 and α-ZP C16, respectively. The integrated intensities were measured on difference spectra; these have been obtained by subtracting the room-temperature absorptions from the spectra recorded at higher temperatures.

Our experiments were extended to temperatures well above the known transition T_{max} in a search of a "liquidlike" structure in which the polymethylene chains should be coiled in a disordered conformational structure (thus showing GG defects), similar to what is observed for liquid n-hydrocarbons or other similar systems. From out experiments it does not seem possible to reach such a state since chemical decomposition takes place before this is reached.

On the contrary we have observed both for annealed and unannealed samples, during thermal cycles from 25 to 150 °C (Figure 16), an almost complete thermal reversibility of the conformational disorder.

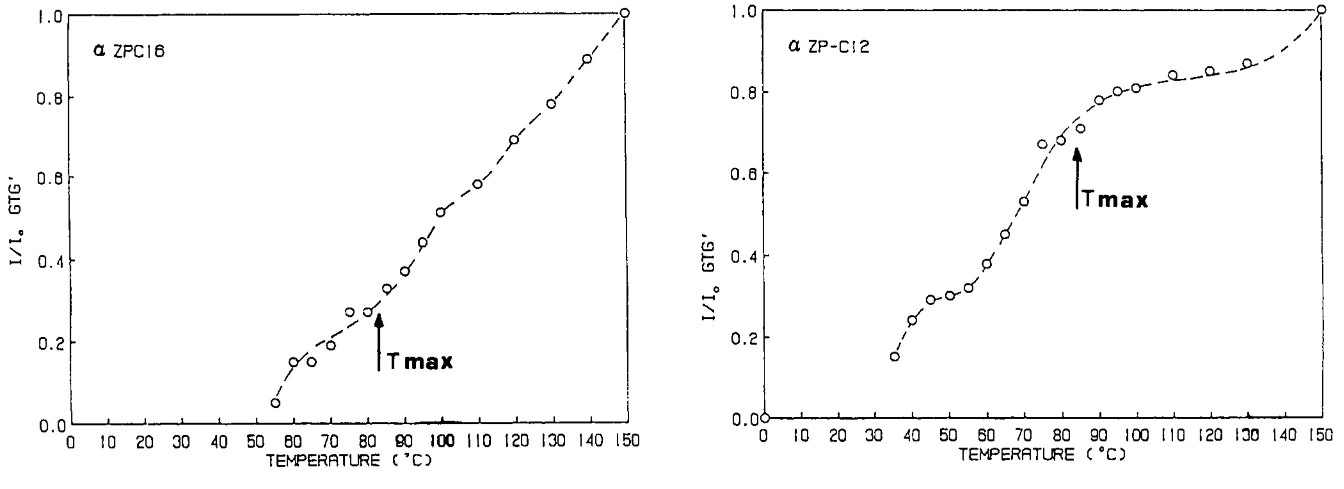
Conclusions

The description of the phase transition at the molecular scale for these systems based on the spectroscopic data collected in this work is as follows:

(a) Starting from approximately 50 °C both annealed and unannealed samples must be described as "two-phase systems" with the coexistence of a fraction of transplanar chains with unchanged length and fraction of conformationally disordered material. The relative amount of trans-planar chains is dominant at room temperature and it is still sizeable up to or through the transition at T_{max} measured with DSC. The environment of the trans-planar chain becomes increasingly perturbed with increasing temperature as indicated by the broadening of the observed bands.

(b) The conformational isomers generated by heating are identified as kinks of the type GTG′ and end-TG. It is known that GTG′ defects keep the direction of the chain unchanged while generating a small local perturbation in the lattice; end-TG defects are characteristic of a disorder that occurs on the surface of the lamella formed by the alkyl chains. No droplets of "liquidlike" chains are formed since no GG defects are observed.

(c) The location of the GTG′ defects along the chain cannot be determined in these experiments since no to-



B

A

Figure 15. Thermal evolution of the normalized intensity of the GTG′ defect band; $I(T)$ integrated intensities at variable temperatures between 25 and 150 °C, I_0 integrated intensity at 150 °C: (A) α-ZP C12; (B) α-ZP C16.

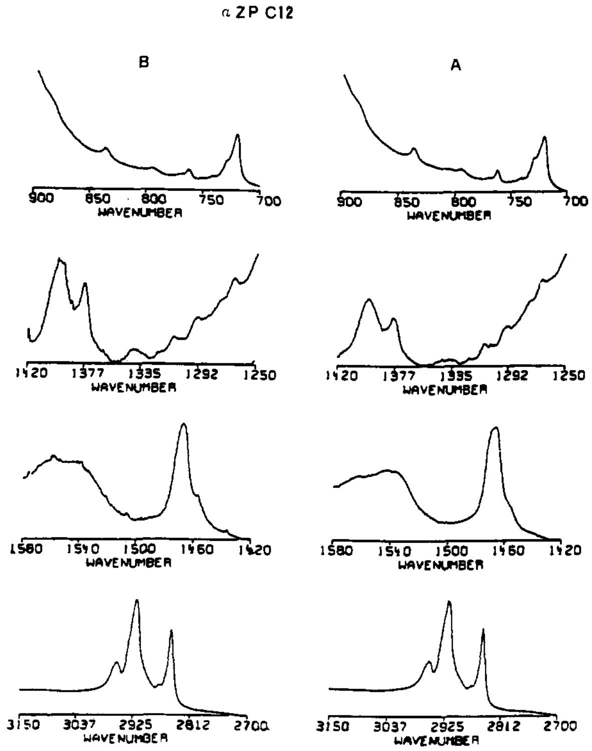


Figure 16. Comparison between the CH_2 rocking, wagging, bending, and stretching regions of an α-ZP C12 sample: (A) before thermal treatment up to 150 °C; (B) at 25 °C after cooling.

pologically selectively deuterated molecule are available (see for instance ref 5). They might be located in the bulk of the crystal and/or near the surface of the lamella. A sketch of the possible models consistent with the spectroscopic observations is given in Figure 17. Disordering may start either in the bulk (model c in Figure 17) or on the surface of the lamella (see model b in Figure 17). In the first case a cooperative propagation of the kinks must occur across chains starting anywhere in the crystal. Since the overall length of the chain shrinks for each defect created, voids must be generated on the surface of the lamella with consequent generation of surface domains of end-TG defects. In the second case domains of roughening of the surface to a depth of approximately 5–6 CH generate GTG′ defects that may propagate across the lamella. In either case a sizeable fraction of trans-planar chains coexist with or host the conformational defects.

(d) DSC experiments as already discussed and the plot of Figure 10 clearly establish that the transition is not first order. We can distinguish three main temperature domains of evolution of the relative concentration of GTG′ kinks in the range 25–150 °C. In the first domain (25–60 °C) probably a few and isolated kinks are generated that may gain some cooperativity in the second domain (60–85 °C) tending, in a third domain, toward a concentration plateau at higher temperatures. Following the progression of the concentration of the defects the overall mean thickness of the lamellae shortens stepwise as also measured by the X-ray diffraction experiments by the school of Perugia.[13,14] A second "transition" involving a small amount of energy is observed near 135 °C in both the DSC and X-ray experiments. The nature of this transition is yet to be determined.

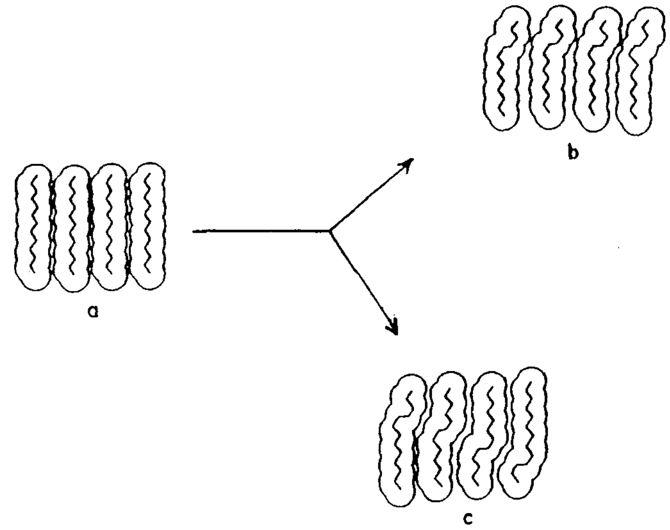


Figure 17. Sketch of the possible conformational changes, induced by the thermal treatment, consistent with IR spectroscopic data.

In conclusion this work clearly shows that the observed transitions are not of the first order, that heat absorption is related to the formation of kinks in the original trans-planar chains, and that pretransitional phenomena take place. The phase above 85 °C is characterized by the occurrence of only GTG′ and end-TG defects while no liquidlike domains are observed. This partially disordered chain packing arrangement is not easily modified without removing the intercalating molecules. The system does not allow the formation of GG defects upon further heating and at temperatures higher than 200 °C decomposes. We believe that this could be a consequence of the linkages between the polar amino group at one end of the chains and the inorganic layer. Longitudinal motions observed in systems with free ends[5,10,11] cannot take place in these systems since "solitonlike" conformational defects[19] are not allowed. The GTG′ defects with the lowest formation energies[20] are formed and are pinned at a given site possibly with the formation of a locally clustered disorder. We have already observed an analogous case in intercalated organic perovskites of the type $CH_3(CH_2)_{12}NH_3^+$.[8] The situation is very similar to that already discussed by Lagaly.[18]

Acknowledgment. We thank Mr. Aragno and Barabino for their friendly help in the experimental part of the work and Professors Alberti and Costantino in providing us with samples and data on the compounds studied and for enlightening discussions.

Registry No. α-ZP C12, 129150-29-4; α-ZP C16, 129150-30-7.

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