Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Polymorphism in n-Fatty Acids and Vibrational Spectra: New Modifications (A_2 and A_3 Forms) of Even-Numbered n-Fatty Acids

Tohru Kobayashi [a] [b] , Masamichi Kobayashi [a] & Hiroyuki Tadokoro [a]
[a] Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka, 560, Japan
[b] Research Center, Daicel Chemical Industries Co. Ltd., Aboshi-ku, Himeji, Hyogo, 671-12, Japan

Version of record first published: 20 Apr 2011.

To cite this article: Tohru Kobayashi , Masamichi Kobayashi & Hiroyuki Tadokoro (1984): Polymorphism in n-Fatty Acids and Vibrational Spectra: New Modifications (A_2 and A_3 Forms) of Even-Numbered n-Fatty Acids, Molecular Crystals and Liquid Crystals, 104:3-4, 193-206

To link to this article: http://dx.doi.org/10.1080/00268948408070424

Mol. Cryst. Liq. Cryst., 1984, Vol. 104, pp. 193–206
0026-8941/84/1044-0193/$18.50/0

Polymorphism in *n*-Fatty Acids and Vibrational Spectra: New Modifications (A_2 and A_3 Forms) of Even-Numbered *n*-Fatty Acids

TOHRU KOBAYASHI,† MASAMICHI KOBAYASHI‡ and
HIROYUKI TADOKORO

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560 Japan.

(*Received August 29, 1983*)

From the studies of infrared and Raman spectra and X-ray diffraction, it was found that myristic and palmitic acids crystallized into a new form (referred to as A_2) different from the already-known A-super and A_1 forms. The polymethylene part of the molecules comprises the triclinic polyethylene type sublattice. The unit cell consists of two types of dimer chains that are different from each other in the conformation of the carboxyl groups. As the temperature decreases the A_2 form transforms into another A-type modification (A_3) at about 140 K. The phase transition occurs reversibly accompanied by drastic changes in the infrared absorptions associated with the carboxyl groups.

INTRODUCTION

Even-numbered *n*-fatty acids $n\text{-C}_{m-1}\text{H}_{2m-1}\text{COOH}$, abbreviated as $n\text{-C}_m$ acids, are known to crystallize in various modifications.[1] The crystal modifications are roughly divided into two categories, one being monoclinic and the other triclinic. The *B*, *C*, and *E* forms belong to the former class where the polymethylene chains comprise the sublattice of the orthorhombic polyethylene (o-PE) type.[2-5] The modifications referred to as the *A* form belong to the latter class and consist of the subcells of the triclinic polyethylene (t-PE) type.

---

†Present Address: Research Center, Daicel Chemical Industries Co. Ltd., Aboshi-ku, Himeji, Hyogo 671-12 Japan.

‡To whom correspondence should be addressed.

For the case of n-C_{12} acid, lauric acid, there are at least two types of A form: A-super[6,7] and A_1.[8] In these forms, in contrast to the monoclinic modifications, one terminal plane (the surface of the monomolecular layer) contains both the methyl and carboxyl groups. The A-super form assumes a sixfold super structure, as the name implies, and contains two types of dimer chains differing in the conformation of the carboxyl groups with respect to the polymethylene chain (the internal rotation angle around the bond between the first and the second carbon atoms). There are six dimers per unit cell. In the A_1 form, the carboxyl and the methyl groups located on the same terminal plane align alternately in the direction parallel to the a axis,[8] while the dimer chains are essentially coplanar.

The characteristic molecular packing in the A type crystals may result from the requirement that the zigzag planes of the neighboring polymethylene chains are arranged parallel to each other (constructing the t-PE sublattice) and, at the same time, that the steric hindrance owing to the bulky carboxyl groups between the neighboring molecules must be released. In order to clarify the thermodynamic stability of the specific molecular arrangement in the A type crystals, it is of importance to obtain information about the intermolecular interactions by means of vibrational spectroscopy. At present, however, we have only a few spectroscopic data about the A-super and A_1 forms of n-C_{12} acid. As for the n-C_{18} acid, stearic acid, Holland and Nielsen[5] presented the polarized infrared spectra of one of the A forms. But they did not identify the crystal modification to which the sample belonged.

In previous works[9,10] we have demonstrated that the structure of the interface between successive monomolecular layers in the crystals of long chain molecules influences markedly the phonon modes, especially those in the low-frequency region, and might control the thermodynamic behavior of the polymorphism of n-alkanes and n-fatty acids. Because of its characteristic terminal plane structure, the A type crystals of n-fatty acids are regarded as another good example for investigating the role of the interfacial structure in the polymorphism of chain molecules.

We, therefore, carried out a spectroscopic study of polymorphism of the A type crystals. In the course of the study, we found that some of n-C_m acids crystallized into a new type of A form different from A-super and A_1. A remarkable point is that this new form exhibits a reversible phase transition at a low temperature (about 140 K). The present paper aims to clarify some problems related to the polymorphism of the A type crystals on the basis of X-ray crystallographic and vibrational spectroscopic evidences. Here, we are concerned with the crystal structure of the new form in connection with differences in the nature of crystal growth as well as in the phase transition behavior between the A-super (or the A_1) and the new form.

EXPERIMENTAL

Samples: Research grade samples of n-C_m acids ($m = 12$, 14, and 16 with the purity higher than 99%) were used without further purification. n-C_{12} Acid was crystallized in a fine needle-like polycrystalline form by evaporating the solvent from CS_2 or petroleum ether solution. This sample was identified as A-super by the X-ray powder photograph.

Single-crystal specimens of n-C_{16} acid were grown from iso-C_8H_{18} solution by cooling slowly from 40° to 10°C. The crystal obtained had the shape of thin rectangular film with somewhat irregular edges and of about 7 mm × 3 mm × 70 μm (thickness) in size. As described below, the single-crystal was proved to be a new modification of the A form and referred to as the A_2 form. The A_2 form crystals were also obtained for n-C_{14} acid by the same procedure, but their size was not sufficiently large for the infrared and Raman polarization measurements.

Spectroscopic Measurements: Infrared spectra were taken using a JASCO A3 infrared spectrophotometer equipped with a wire-grid polarizer. Infrared spectra of polycrystalline samples of n-C_{12} acid (A-super) and n-C_{14} acid (A_2) were measured on powder samples spread between two KBr windows without a mulling agent. Figure 1 reproduces the spectrum of the A-super form of n-C_{12} acid at room temperature. A piece of a single-crystal specimen of n-C_{16} acid (A_2) was sandwiched between two KBr plates and the blank area was masked with aluminum foil. The incident radiation entered along the direction normal to the broad surface of the specimen, and the electric

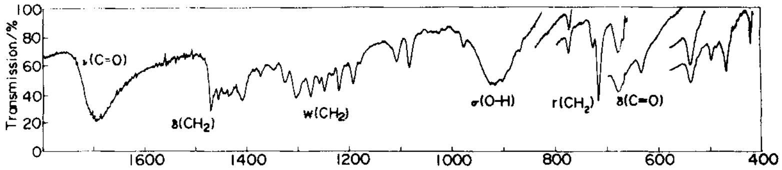


FIGURE 1 Infrared spectrum of the A-super form of n-C_{12} acid (powder) at room temperature.

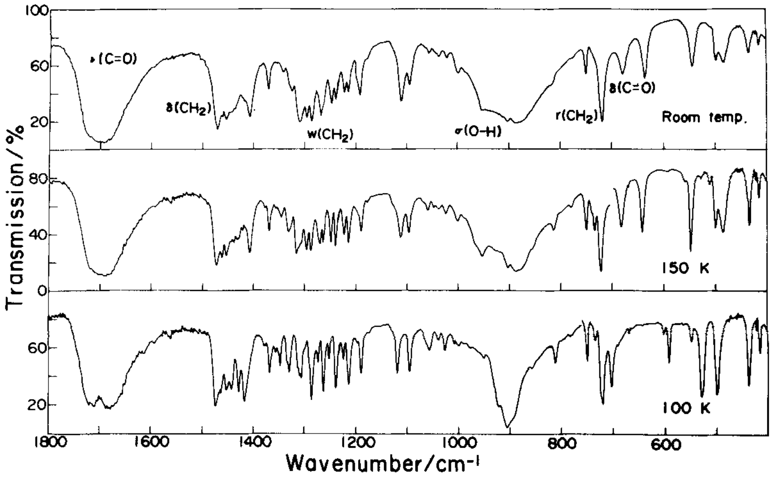


FIGURE 2 Infrared spectra of the *A*-type form of n-C_{14} acid (powder) at various temperatures.

vector of the radiation was set parallel and perpendicular to the longer edge of the specimen.

Measurements at temperatures down to liquid helium temperature were performed using an Oxford continuous flow cryostat. Figure 2 reproduces the spectra of n-C_{14} acid (powder) taken at various temperatures. The single-crystal specimen, sandwiched between small pieces

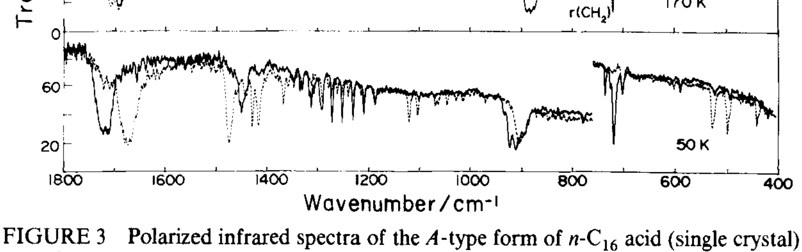


FIGURE 3 Polarized infrared spectra of the *A*-type form of n-C_{16} acid (single crystal) at various temperatures.

of KBr plates, was embedded in a cavity of a copper block with the gap filled with indium metal, and mounted on the cold finger of the cryostat through an indium plate. Figure 3 shows the polarized infrared spectra of n-C_{16} acid taken at various temperatures.

The Raman spectra were measured using a JASCO R750 triple monochromator, using the 514.5 nm line from an Ar^+ laser as the excitation light. The powder sample of the A-super form (n-C_{12} acid) was pressed into a pellet. For the polarization measurement of the A_2 form single-crystal, the orientation of the specimen mounted on the sample holder was adjusted carefully. Scattered light was collected at right angle to the incident beam. The Raman spectra are compared between the A-super (n-C_{12} acid) and the A_2 form (n-C_{16} acid) in Figure 4. The scattering geometry in the latter case is illustrated on the figure.

X-Ray Diffraction: The rotation and Weissenberg photographs of the A_2 form (n-C_{16} acid) were taken about the axis parallel to the longer edge of the specimen by using Ni-filtered Cu-Kα radiation. Figure 5 shows the rotation photograph.

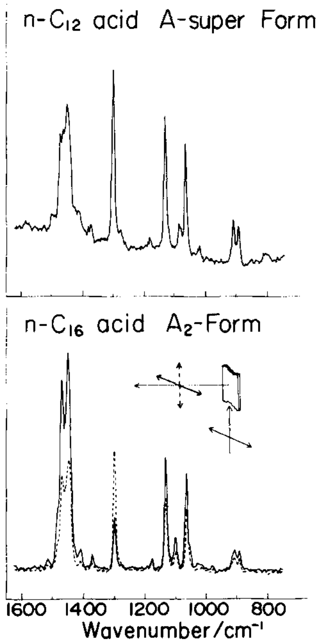


FIGURE 4 Raman spectra of the A-super form of n-C_{12} acid (upper) and the A_2 form of n-C_{16} acid (bottom) at room temperature.

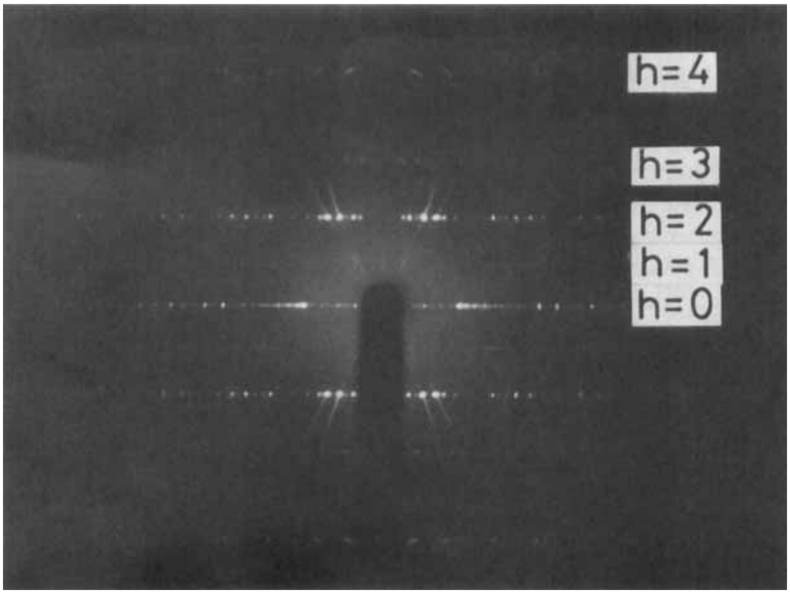


FIGURE 5 X-ray rotation photograph about the *a* axis of the A_2 form of n-C_{16} acid.

CRYSTAL STRUCTURE OF THE NEW *A* FORM

In the infrared spectra of both the *A*-super and A_2 forms, the bands due to the most in-phase modes of the methylene scissoring $\delta(CH_2)$ (around 1460 cm^{-1}) and the rocking $r(CH_2)$ (around 725 cm^{-1}) appear as singlets. This indicates that the A_2 form consists of the t-PE type sublattice, like the other *A* forms. The Raman-active most in-phase $\delta(CH_2)$ mode also gives rise to the scattering profile characteristic of the t-PE lattice, consisting of two main peaks around 1440 and 1465 cm^{-1}. The orientation of the sublattice was determined by the polarized infrared spectra (Figure 3). The observed polarization of the $\delta(CH_2)$ and $r(CH_2)$ bands, perpendicular and parallel to the longer edge of the specimen, respectively, demonstrates that the a_s axis (the subscript *s* indicates the sublattice) is parallel to the longer edge.

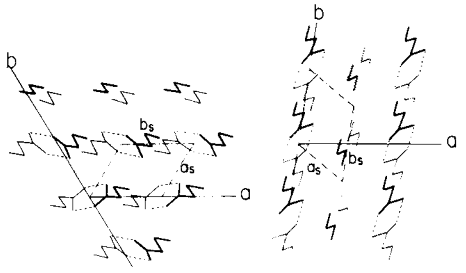
It has been pointed out that the Raman spectrum in the 900 cm^{-1} region of the fatty acids reflects sensitively the conformation of the polymethylene skeletal chain.[11] The C and E forms, consisting of the fully extended planar zigzag chains, give a simple doublet in this region, while the B form with the twisted chains gives rise to a complicated multiplet. The A_2 form, like the *A*-super form, exhibits a doublet around 900 cm^{-1} suggesting that the polymethylene skeletal chains in this form are fully extended.

The infrared spectrum in the carbonyl in-plane bending $\delta(\text{C=O})$ region of the A-super form exhibits a pair of absorption bands at 638 and 680 cm^{-1}. The doublet is due to two different conformers that coexist in the super lattice. On the contrary, the splitting due to the conformational isomerism is not clear in the hydroxyl out-of-plane bending $\sigma(\text{O—H})$ (around 920 cm^{-1}) and carbonyl stretching $\nu(\text{C=O})$ (around 1700 cm^{-1}) modes.

It is interesting that the $\delta(\text{C=O})$ and $\nu(\text{C=O})$ absorption bands of the A_2 form appear at almost the same frequencies as those of the A-super form. On the other hand, the spectra in the $\sigma(\text{O—H})$ region (800–1000 cm^{-1}) of the two forms differ from each other. The $\sigma(\text{O—H})$ absorption of the A_2 form splits clearly into two bands; one is polarized parallel (953 cm^{-1}) and the other perpendicular (880 cm^{-1}) to the longer edge of the specimen.

In the t-PE sublattice found in the triclinic *n*-alkanes and also in the A-super form of n-C_{12} acid, the polymethylene chains are so oriented that the vector normal to the zigzag plane is inclined by about 19° from the a_s axis (parallel to the longer edge of the specimen) within the $a_s c_s$ plane. Therefore, the projection of the $\sigma(\text{O—H})$ transition moment onto the film surface (the $a_s b_s$ plane) is directed parallel to the longer edge provided that the plane of the dimerized carboxyl groups is coplanar with the zigzag plane of the polymethylene chain. The 953 cm^{-1} band may correspond to the coplanar dimers. On the other hand, the transition moment is perpendicular to the longer edge (the 880 cm^{-1} band) if the carboxyl plane is twisted from the skeletal zigzag plane by about 90°. Thus, the observed infrared polarization suggests that there are two types of conformer with respect to the orientation of the carboxyl groups as in the A-super form.

The result of the X-ray diffraction is also quite significant. The rotation photograph about the longer edge (i.e., the a_s axis) of the specimen exhibits the layer reflections, corresponding to the period of 0.881 nm, among which the even layers appear ordinarily strong, while the odd layers are extremely weak (Figure 5). From the diffraction pattern, one of the crystallographic axes is proved to locate parallel to the a_s axis, with dimension essentially double the a_s. We refer to this axis as the a axis. The characteristic intensity distribution indicates that two types of dimer chains of slightly different structure are aligned alternately along the a axis spaced $a/2$ (i.e., a_s) apart. Bearing the observed infrared polarization in mind, the two dimers are thought to be different in the conformation of the carboxyl groups. The A_2



(a) A-super (b) A_I

FIGURE 6 Crystal structure of the A-super (a) and A_1 (b) forms as projected onto the *ab* plane.

form thus seems to constitute a super lattice like the case of the A-super form.

Figures 6(a) and (b) show the crystal structures of the A-super and the A_1 forms, respectively, as projected onto the *ab* plane. Here, the projections of these forms are depicted using the crystallographic data reported previously.[7,8] The steric hindrance between the bulky carboxyl groups of the adjacent molecules is avoided by their respective manners as described in the introduction. The present A_2 form does not correspond to the A-super form with respect to the identity period along the a_s axis ($6a_s$ in the A-super form). Although in the A_1 form the identity period along the a_s axis equals that of the A_2, conformational isomerism does not occur in A_1. Thus, the A_2 form is necessarily quite different from the already-known A forms.

As pointed out previously, the A-super form is obtained in the form of needle-like or elongated parallelpiped crystal which grow well in the direction of the a axis (i.e., the b_s axis), and the crystals tend to fracture in the planes parallel to the a axis. The characteristic habit of the A-super crystal is interpreted in terms of the structure. As illustrated in Figure 6(a), each terminal plane is constituted of the linear array of both the carboxyl and the methyl groups along the a axis. Every third carboxyl array then lies adjacent to one methyl array. Therefore, the dimer chains are bound together much more tightly in the a direction than in any other direction owing to the strong intermolecular forces acting between the polar carboxyl groups. Formation of hydrogen bonds between adjacent dimers may contribute to some extent.

Judging from the crystal growth of the A_2 form into a thin rectangular film, like the crystal of triclinic n-alkanes, the terminal planes in the A_2 form are assumed to be more isotropically constructed compared with those in the *A*-super. The most plausible structure is as follows: all the dimerized carboxyl groups are located at the same height, that is, the carboxyl and the methyl groups are situated in different terminal planes. This is supported by the result of X-ray diffraction.

In the *A*-super form, the odd-numbered member of the (00*l*) reflections are absent, indicating that two successive terminal planes contained in a repeat distance along the *c* direction are equivalent in structure:[6,7] both the carboxyl and the methyl groups are contained in one terminal plane. The present A_2 form gives rise to the series of the (00*l*) reflections, corresponding to the 4.15 nm period, with no systematic absence (the *c* axis defined as the axis along which the successive dimer layers are stacked together). By comparing the dimer chain length (about 4.07 nm) and the inclination angle of the chains in the t-PE sublattice (about 19°), we see that the identity period of 4.15 nm is nearly equal to the thickness of a dimer layer.

The Weissenberg photograph of the (0kl) reflections indicates also that the *c* axis is oriented perpendicular to the terminal plane. At the present stage, the unit cell dimensions as well as the space group of this new crystal form remain undetermined, because of some complexities in the diffraction pattern. In the case of n-C_{16} acid, most reflections fit tentatively to the unit cell of $a = 0.881$ nm, $b = 0.489$ nm, $c = 4.15$ nm, $\alpha = \beta = 90°$, and $\gamma = 70°$ with the triclinic space group of $P1$-C_1^1 or $P\bar{1}$-C_i^1. However, on the *c*-axis rotation photograph, there are weak but distinct reflections corresponding to the double-sized *c* dimension ($c = 8.30$ nm). This means that the present A_2 form possibly belongs to, or partially contains, a double-layered polytype similar to those found in monoclinic *n*-alkanes.[9,10]

The single- and double-layered polytypes are different in the relative orientation of the stacking lamellae, but the structure within a single lamella is identical in both cases. Even for the double-layered polytype, our structural model observed diffraction pattern, although the index *l* is doubled and the (00*l*) reflections with l = odd turn out to be absent.

Besides the complexity caused by polytypism, there is another uncertainty about the arrangement of the dimer chains: the equivalent isomers are arranged along the ⟨010⟩ or ⟨110⟩ directions of the sublattice. Figure 7(a) and (b) illustrate the structural models by the projection of the terminal plane for the two possible cases. At the present stage, we cannot decide unequivocally which is the case.

In the present work, the A_2 form was found for n-C_{14} and n-C_{16} acids. Furthermore, we recognize that the spectrum of the *A*-type

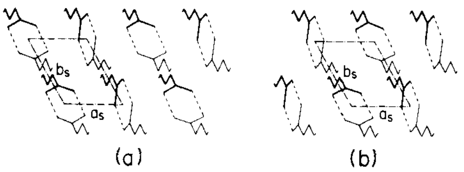


FIGURE 7 Two possible structural models of the A_2 form illustrated as the projection of the terminal plane consisting of the carboxyl groups.

crystal of n-C_{18} reported by Holland and Nielsen[5] is that of A_2. Recently, we confirmed that the A-type crystal of n-C_{18} acid belonged to the A_2 form. Therefore, we may conclude that the A-type modification of n-C_{14} and higher member of the even-numbered n-fatty acids belong to the A_2 form, rather than the A-super or A_1 so far reported in the case of n-C_{12} acid.

In A_2 the adjacent carboxyl groups must be more sterically hindered than in the other A forms. The reason for the favorable formation of the A_2 form in the higher members may be as follows: the contribution of the van der Waals forces between the polymethylene chains becomes predominant over the interaction between carboxyl groups, as the number of carbon atoms increases. This overcomes the instability due to the bulky polar groups.

Recently, Goto[12] presented the crystal structure of an A-type modification of n-C_{14} acid based on three-dimensional X-ray analysis. The main feature of the resultant structure (two-fold super lattice along the a axis, and the terminal plane structure) is quite similar to that we are proposing in the present work, but details of the diffraction patterns of n-C_{14} acid are different from ours. Furthermore, according to Goto, the reflection intensities vary from specimen to specimen. Therefore, it may be possible that "the A_2 form" of n-C_{14} acid is different from that of n-C_{16} acid. We need further extensive crystallographic investigation before a final decision concerning the structure of A_2.

PHASE TRANSITION OF A_2 TO ANOTHER A-TYPE FORM

This section deals with the spectral change accompanying the phase transition of the A_2 form of n-C_{14} and n-C_{16} acid to the low-temperature phase that is referred to as A_3. The most significant change takes place in the infrared bands due to the carboxyl groups. In A_3 the parallel and perpendicular components of the ν(C=O) absorption are separated by about 50 cm^{-1} (at 1672 and 1718 cm^{-1}), while the two components of the σ(O—H) mode overlap each other into a singlet having the peak around 900 cm^{-1}. In the region of 700–500 cm^{-1}, including the δ(C=O), w(O—C=O), and r(O—C=O) modes, the spectral pattern of A_3 is quite different from that of A_2. The pair of δ(C=O) bands owing to the two conformers (680 and 638 cm^{-1}) in A_2 disappear in A_3. Instead, there appear new bands at 700, 603, and 592 cm^{-1}. The 546 cm^{-1} band of A_2 shifts to 528 cm^{-1} in A_3. Only the band around 500 cm^{-1} appears with almost the same frequency and polarization in both A_2 and A_3. The absorption bands mentioned above appear at the same frequencies in both *n*-C_{14} and *n*-C_{16} acids, and therefore are assigned to the modes of the carboxyl groups.

The absorptions due to the most in-phase mode of r(CH_2) (725 cm^{-1}) and δ(CH_2) (1460 cm^{-1}) remain unaltered both in frequency and polarization. This indicates that the A_3 form consists of the t-PE sublattice and that the orientation of the sublattice with respect to the coordinate system fixed to the specimen is kept unchanged in the phase transition.

Comparing the progressive bands due to the methylene wagging w(CH_2) and the skeletal stretching ν(C—C) modes before and after the transition, we find that the corresponding bands appear at almost the same frequencies but with somewhat different polarizations. The progressive band series are specified by the phase difference between the adjacent methylene units, and the allowed phase differences are determined by the length of the methylene sequence that assumes the planar zigzag conformation. Therefore, the positions of the progressive bands are very sensitive to the number of carbon atoms and also to the conformation of the polymethylene chain. In the case of *n*-C_{18} acid,[5] for example, the B form, consisting of the twisted polymethylene chains, gives rise to the progressive bands at frequencies quite different from those of the C and E forms that consist of straight chains. The intensities and polarizations are influenced by the extent of coupling with the modes of the polar carboxyl groups. From the observed spectral change in the phase transition from A_2 to A_3, the structural change should occur in part of the carboxyl groups accompanied with no appreciable conformational change nor rearrangement of the polymethylene part.

In addition to the internal modes, the low-frequency Raman spectra of *n*-C_{16} acid change drastically at the transition temperature as shown in Figure 8. The spectrum in this region is strongly influenced by the spatial arrangement of the molecules. The 160 cm^{-1} band is due to the LAM (the longitudinal acoustic mode). Except for the slight high-frequency shift with lowering temperature, this band does not show an

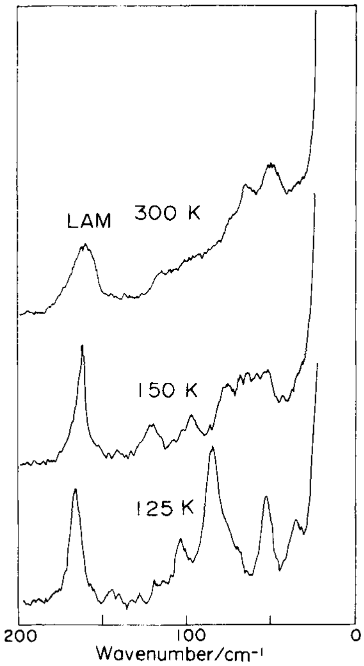


FIGURE 8 Temperature dependence of low-frequency Raman spectrum of the *A*-type form of *n*-C_{16} acid.

appreciable change in the whole temperature range investigated, indicating that the planar conformation of the polymethylene chains remains unchanged in the phase transition. This is consistent with the result of the w(CH_2) and ν(C—C) progressive bands. The most significant spectral change is observed in the region from 50 to 100 cm^{-1}. In this region there appear bands due to the carboxyl groups, and they vary sensitively depending on the polymorphic structure. Therefore, the observed spectral change indicates that rearrangement of the carboxyl groups accompanies the phase transition.

Another characteristic feature of the phase transition is that neither exo- nor endothermic peaks are detectable by DSC measurement, in spite of the clear spectral change as mentioned above.

Figure 9 shows the infrared spectra of the *A*-super form of *n*-C_{12} acid measured at various temperatures down to 30 K. The spectra measured on the powder sample without mulling agent are interfered by the strong diffuse reflection of the radiation, especially at low temperature, so that the real absorption profiles are disturbed to some extent. It is clear, however, that no discontinuous changes occur in the

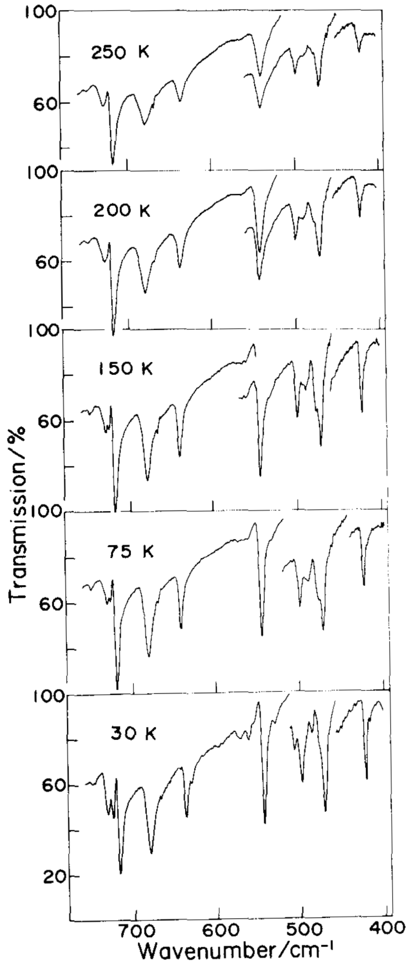


FIGURE 9 Temperature dependence of infrared spectrum of the *A*-super form of n-C_{12} acid.

temperature range investigated. Therefore, the reversible phase transition found in the *A*-type crystals of n-C_{14} and n-C_{16} acids is said to be characteristic of the A_2 structure. Probably, the terminal plane structure in the A_2 form plays a dominant role.

On the basis of the experimental results so far obtained we can describe a model of the phase transition from A_2 to A_3. As the temperature decreases the steric repulsion between the neighboring carboxyl groups increases through the thermal contraction of the crystal lattice. Then, the A_2 structure becomes less stable. At the transition temperature, the reorientation of the carboxyl groups and, presumably, the reconstruction of the hydrogen bonds occur within the terminal plane in order to be released from the steric repulsion. This mechanism requires relatively small magnitude of the activation energy as well as the heat of transition. This is the reason why the phase transition proceeds reversibly and instantaneously, and is not detectable calorimetrically.

It should be noted that in the A_2 form the fraction of the two coexisting conformers, estimated from the relative absorption intensities of the doublet around 650 cm^{-1} due to the $\delta(\mathrm{C{=}O})$ mode, does not exhibit a remarkable change with temperature, in contrast to the case of the C form.[13,14]

References

1. E. von Sydow, *Ark. Kemi*, **9**, 231 (1956).
2. V. Vand, W. M. Morley and T. R. Lomer, *Acta Crystallogr.*, **4**, 324 (1951).
3. E. von Sydow, *Acta Crystallogr.*, **8**, 557 (1955).
4. M. Goto and E. Asada, *Bull. Chem. Soc. Jpn.*, **51**, 2456 (1978).
5. R. F. Holland and J. R. Nielsen, *J. Mol. Spectrosc.*, **9**, 436 (1962).
6. E. von Sydow, *Acta Chim. Scand.*, **10**, 1 (1956).
7. M. Goto and E. Asada, *Bull. Chem. Soc. Jpn.*, **51**, 70 (1978).
8. T. R. Lomer, *Acta Crystallogr.*, **16**, 984 (1963).
9. M. Kobayashi, T. Kobayashi, Y. Itoh, Y. Chatani and H. Tadokoro, *J. Chem. Phys.*, **72**, 2024 (1980).
10. M. Kobayashi, K. Sakagami and H. Tadokoro, *J. Chem. Phys.*, **78**, 6391 (1983).
11. I. Harada, M. Tasumi, K. Sato and M. Okada, *Prep. Mol. Struct. Symp.*, 2A09, Hiroshima, Japan (1978).
12. M. Goto, *Prep. Mol. Struct. Symp.*, 3C06, Kyoto, Japan (1981).
13. S. Hayashi and J. Umemura, *J. Chem. Phys.*, **63**, 1732 (1975).
14. M. Kobayashi, T. Kobayashi and H. Tadokoro, *Polym. Preprints. Jpn.*, **29**, 2119 (1980).