

Structure of the Lowest Temperature Crystalline Phase and Its Annealing Effect of Potassium Pentadecanoate

Tsutomu ISHIOKA* and Isao KANESAKA

*Department of Chemistry, Faculty of Science, Toyama University,
Gofuku, Toyama 930, Japan*

(Received August 16, 1993)

ABSTRACT: The structure and the thermal behavior of potassium pentadecanoate (99% purity), $\text{CH}_3(\text{CH}_2)_{13}\text{CO}_2\text{K}$, having low water content were investigated by differential scanning calorimetry, IR and Raman spectroscopies, and X-ray diffraction. Six phases were observed by thermal measurements. The molecular and crystal structures of the lowest temperature crystalline phase (phase I) and its annealing effect were studied. The molecular conformation was confirmed to be all-*trans*, comparing IR observed frequencies in the methylene progressive region with calculated ones. The crystal structure was speculated to be analogous to the B-form in even-numbered potassium soaps from analyzing the X-ray powder pattern. When a specimen was annealed in the temperature range from 110 to 150°C, a new structural modification appeared. The molecular conformation of the annealed specimen in phase I was speculated as slightly differed from all-*trans*. The crystal structure of the annealed one was different from both the A- and B-forms. The annealed specimen was unstable and converted to the initial one over a few days.

KEY WORDS Potassium Pentadecanoate / Vibrational Analysis / X-Ray Diffraction / Differential Scanning Calorimetry /

A structural study of metal salts of long-chain saturated fatty acids is important to reveal the structure of ethylene-based ionomers¹ which consist of the long methylene sequences with a part of the polar groups such as methacrylate or acrylate in their main chain. So, we started a detailed structural study for the metal soaps under various physical conditions.

Among the metal soaps, the crystal structures and the thermal structural transition behavior have been precisely investigated for the even-numbered potassium soaps, $\text{CH}_3(\text{CH}_2)_n\text{CO}_2\text{K}$, where n is the number of the methylene groups. They take the successive phase transitions from the crystalline phase to the liquid crystalline phase with an increase in temperature.² The lowest temperature crystalline phase of $n=2-10$ belongs to the

monoclinic A-form (space group $P2_1/a$),³ where the unit cell contains four molecules which have all-*trans* conformation and packed in a cross-chain structure. The crystalline phase of $n=10-16$ is ascribed to the triclinic B-form ($P\bar{1}$),⁴ where the unit cell contains two molecules which have all-*trans* conformation and packed in a perturbed version of the triclinic T_{\parallel} subcell.² With the elevation in temperature, both the A- and B-forms are transformed to the monoclinic C-form ($P2_1/a$) at 50–80°C. The molecules in the C-form are supposed to have partially conformational disorder at the methyl end.⁵ On the other hand, little has been known about the definite structure and the thermal transition behavior of odd-numbered soaps, except for the work in 1980 by Cingolani *et al.*⁶ In this study, we investigated the structure of the lowest tem-

* To whom correspondences should be addressed.

perature crystalline phase and its annealing effect of potassium pentadecanoate ($n=13$) by means of vibrational spectroscopies, X-ray diffraction, and differential scanning calorimetry (DSC).

EXPERIMENTAL

Potassium pentadecanoate was synthesized from pentadecanoic acid (Sigma Company, 99%) by the titration of potassium carbonate in dry ethanol solution kept at 70°C. The product was purified by reprecipitation from a diethyl ether solution and dried at 90°C *in vacuo* for 24 h over ten times. At each step of reprecipitation and drying, the product was checked by a DSC measurement until a reproducible thermal data was obtained. Neutralization was confirmed from the IR spectrum. The content of water was evaluated to be less than 1 wt% from the elementary analysis.

DSC measurements were carried out with a Rigaku DSC using sealed pans at the heating rate 10 Kmin⁻¹. Infrared spectra were recorded in the KBr disk on a JASCO IR-810 spectrophotometer. Raman spectra for the polycrystalline sample were observed using a JASCO R-800 spectrometer and 514.5 nm exciting beam from an Ar⁺ laser. Observed wavenumbers were calibrated with an indene standards. X-Ray diffractions were measured for a powder specimen sealed in a glass capillary with a Rigaku RAD-C system using nickel-filtered Cu-K_α radiation at room temperature.

RESULTS AND DISCUSSION

The result of DSC measurement of potassium pentadecanoate obtained freshly (hereafter called a fresh salt) is shown in Figure 1(a). With increasing temperature from room temperature to 300°C, the five endothermic peaks were observed. The transition temperatures agreed well with those reported by Cingolani

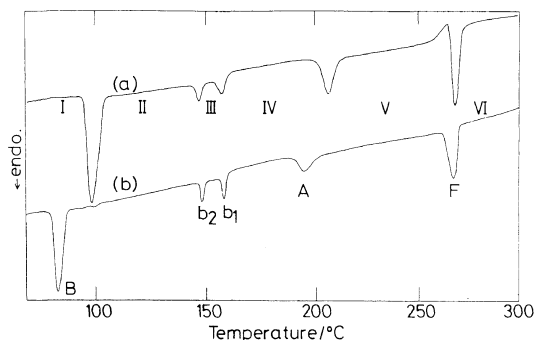


Figure 1. DSC traces of (a) fresh salt and (b) annealed salt of potassium pentadecanoate.

et al., who notate the transition points by symbols from B to F, as shown in Figure 1(b). Six phases are designated as phase I (crystalline phase) to phase VI (lamellar liquid crystalline phase). We focused our attention to the molecular and crystal structures of crystalline phase I.

First, we examined the molecular conformation of the fresh salt by means of the infrared spectrum. The infrared bands in the 700–1400 cm⁻¹ region are sensitive to a molecular conformation in the alkyl chain. Their assignments were made on the basis of a normal coordinate calculation, which was carried out for the all-*trans* conformation by the Wilson GF matrix method using an NEC computer (ACOS 1000) at Tokyo University of Agriculture and Technology, as described before.⁷ The calculated frequencies in the methylene progressive region satisfactorily agreed with the observed ones, as listed in Table I. Therefore, the molecular conformation in phase I is concluded to be all-*trans*.

Second, we investigated the crystal structure of the fresh salt by means of X-ray diffraction. The observed powder pattern at room temperature in the 2θ region from 3 to 38° is shown in Figure 2(a). We compared the observed pattern ($n=13$) with those previously determined for two crystal forms A ($n=8$) and B ($n=14$),^{3,4} as follows. Lomer has determined the cell dimensions for a series of even-numbered potassium soaps and revealed that in

Structural Study of Potassium Pentadecanoate

Table I. Observed and calculated frequencies (cm^{-1}), and P.E.D. (%) in the methylene progressive region of potassium pentadecanoate

A' mode				A'' mode			
$\nu_{\text{obs.}}$	Relative intensity ^a	$\nu_{\text{calc.}}$	P.E.D. ^b	$\nu_{\text{obs.}}$	Relative intensity ^a	$\nu_{\text{calc.}}$	P.E.D. ^b
1418	s	1414	$\delta(\alpha)$ 50, W 17, $\nu_s(\text{COO})$ 15, R 13			1302	T 96
		1409	W 58, R 32			1302	T 96
		1402	W 59, R 29, δ 11			1299	T 97
		1392	W 60, R 27, δ 10			1299	T 97
1382	m	1379	W 59, R 23			1296	T 99
1363	m	1372	U 78, W 11	1294	vw	1296	T 93
		1362	W 68, R 18			1290	T 87
1349	m	1342	W 76, R 14	1273	vw	1279	T 82, P 15
1332	m	1322	W 83			1265	T 75, P 21
1309	m	1301	W 88	1244	vw	1246	T 65, P 29
1283	m	1282	W 88	1219	vw	1223	T 52, P 40
1260	m	1262	W 84			1198	P 57, T 33
1235	m	1239	W 79, ω 10	1178	w	1178	P 81
1211	m	1212	W 76, ω 11	1109	m	1103	T 64, P 32
1189	m	1182	W 83	1040	w	1034	T 86, P 11
1130	m	1129	R 38, ω 32, W 13, β 10	1001	m	1000	T 68, P 26
1095	m	1091	R 41, ω 26, W 22	963	m	960	T 53, P 37
		1068	R 79, W 16	917	m	918	P 47, T 42
		1066	R 82, W 17	877	m	876	P, 56, T 32
1063	m	1062	R 80, W 17	834	m	835	P 64, T 24
		1060	R 81, W 15	795	m	795	P 72, T 18
		1056	R 82, W 16	765	m	759	P 79, T 13
1048	m	1055	R 75, W 12	744	m	727	P 85
1033	w	1035	R 65, ω 15, W 13	728	w, sh	702	P 91
1018	w	1026	R 82			682	P 95
		1003	R 78, ω 10			669	P 98
982	vw	986	R 73, ω 14	715	vs	661	P 100
973	w	975	R 80, ω 11				
917	m	892	R 47, β 32				
888	m	888	R(α) 49, $\delta(\text{COO})$ 39				

^a s, m, w, v, and sh mean strong, medium, weak, very, and shoulder.

^b P.E.D. = potential energy distribution where W, R, P, T, U, β , ω , δ , $\nu_s(\text{COO})$, and $\delta(\text{COO})$ indicate methylene wagging, C-C stretch, methylene rocking-twisting, twisting-rocking, methyl symmetric bending, rocking, C-C-C bending, methylene bending, carboxylate symmetric stretching, and bending, respectively. (α) means mode of $\text{C}_\alpha\text{H}_2$ group.

the A-form, the dimensions remain at constant values regardless of the chain length except that the long spacing c increases with an increase in the chain length.⁸ This is also the case for the B-form. Thus, the cell dimensions assumed for the hypothetical A- and B-forms of $n=13$ except for c were the same as those reported. The c dimension was evaluated according to Lomer's equation.⁸ They are summarized in Table II. We calculated the

powder patterns using structure factors reported^{3,4} and arbitrary full-half-width of each reflection. They are shown for the hypothetical B- and A-forms in Figures 2(c) and (d), respectively.

In Figure 2, we find a resemblance between the observed curve of the fresh salt and the simulated one owing to the B-form, especially near $[0\ 1\ 4]$, $[1\ 0\ 4]$, and $[1\ \bar{1}\ 0]$ reflections. On the other hand, the observed curve is quite

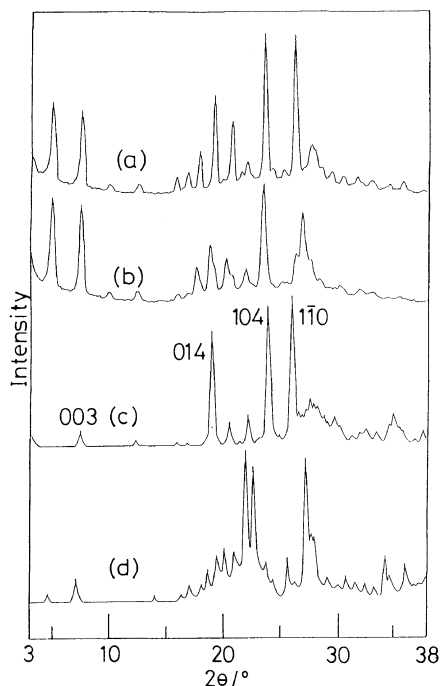


Figure 2. X-Ray powder patterns of (a) fresh salt observed, (b) annealed salt, (c) B-form simulated, and (d) A-form simulated.

Table II. Hypothetical crystal data of potassium pentadecanoate.

	A-form	B-form
$a/\text{\AA}$	8.03	4.15
$b/\text{\AA}$	5.69	5.60
$c/\text{\AA}$	38.70	36.03
$\alpha/^\circ$		93.0
$\beta/^\circ$	100.2	91.4
$\gamma/^\circ$		92.4
	Monoclinic	Triclinic

different from the calculated one owing to the A-form. Hence, the crystal structure of the fresh salt is speculated to be similar to that of the B-form. The large discrepancies were found in the intensity of the reflections below 10° between Figures 2(a) and (c). Since they are ascribed to $[0\ 0\ 1]$ reflections, the discrepancies may be attributed to some structural differences along the chain direction between the B-form and the fresh salt.

From the analysis of the X-ray diffraction patterns, the crystal structure of the fresh salt was revealed to be similar to the B-form in the even-numbered potassium soaps. On the other hand, the even- and odd-numbered saturated fatty acids exhibit different crystal polymorphic behavior. The reason is considered as follows. There are three factors governing the crystal structure of the potassium soaps: (1) van der Waals packing energy between the hydrocarbon chains, (2) non-bonded interlayer interactions between the end-methyl groups, and (3) Coulomb interactions between the COOK groups. The even-odd effect on the crystal structure is mainly due to the interactions between the methyl groups. However, when the Coulomb cohesive energy among the head groups is sufficiently larger than the cohesive energy among the methyl groups, the former interactions govern the crystal structure. According to the crystal geometry of the B-form and the equilibrium atomic charges,⁹ the Coulomb potential energy between the COOK groups is roughly estimated to be several times larger than the interlayer cohesive energy of the end-methyl groups.¹⁰ Thus, the even-odd effect may be minimized.

Next, we investigated the annealing effect on the structure in phase I. A specimen of the fresh salt was submitted to subsequent heating runs in DSC experiments, where the ending temperature was progressively increased in the range of 110 and 150°C, as shown in Figure 3. Then, the gradual disappearance of peak B in the fresh salt was found with the appearance of a new peak at 355.6 K. The simultaneous shift from 474.3 to 462.6 K was also observed in peak A. We call this heated specimen as the annealed salt. The DSC curve of the annealed salt is given in Figure 1(b). This characteristic thermal behavior was first found for $n=11$ by Cingolani *et al.*⁶

The X-ray powder pattern of the annealed salt at room temperature is given in Figure 2(b). This pattern is different from both the simulated ones assuming the A- and B-forms,

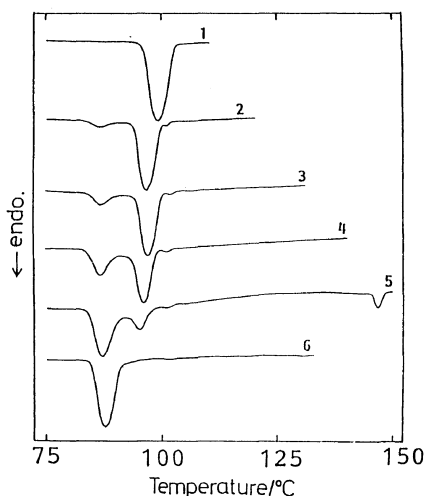


Figure 3. DSC traces in subsequent heating runs. Curve 1 is fresh salt. Curves 2–6 were measured after heating runs 1–5 up to 110, 120, 130, 140, and 150°C, respectively.

which indicates that the crystal structure is different from both the A- and B-forms. The infrared spectrum of the annealed salt coincided well with that of the fresh salt. Hence, the molecular conformation of the annealed salt was speculated to be also all-*trans* at first sight, by also referring that no infrared band sensitive to conformational disorder at the methyl end was found in the methylene progression region ($700\text{--}1400\text{ cm}^{-1}$).⁷ Two Raman bands were observed at 921 and 895 cm^{-1} in the annealed salt, which also indicates no *gauche* defect around the $\text{C}_2\text{--C}_3$ axis at the COO^- end, by referring that the bands sensitive to the *gauche* conformer are absent at 890 , 870 , 850 , and 820 cm^{-1} .¹¹

To get further information on the annealed salt, the temperature dependence of the infrared and the Raman spectra were measured. In phase II, the satellite bands owing to the methyl end-*gauche* conformation appeared at 1076 , 935 , and 778 cm^{-1} in the infrared spectrum with decreasing the intensities of the progressive bands owing to the all-*trans* conformation. The Raman band profile of the methylene bending mode ($1400\text{--}1500\text{ cm}^{-1}$) became broad in phase II, indicating packing disorder in the alkyl chains. These increases in

the disorder of the alkyl chains during the successive annealing process may result in the structural change. That is, these disorders induced during the annealing remain in the annealed salt, although we did not detect the evidence. The fraction of the conformational disorder in the annealed salt is evaluated less than 0.1% per chain from the identification limit by infrared and Raman spectra.^{12,13} The resultant annealed specimen was unstable and converted to the fresh salt over a few days. The transition point in the annealed salt at 355.6 K is lower than the fresh salt at 369.0 K . A similar example that the unstable phase has the lower transition point than the stable phase is seen in the two crystal modifications α and β of oleic acid,¹⁴ where they melt at 286.5 K and 289.4 K , respectively. Thermodynamically, β phase is confirmed to be more stable than α phase. α phase transforms irreversibly to β phase slowly, as found here.

REFERENCES

1. T. Ishioka and M. Kobayashi, *Macromolecules*, **23**, 3183 (1990); T. Ishioka, *Polym. J.*, **25**, 1147 (1993).
2. D. M. Small, "Handbook of Lipid Research," Vol. 4, Plenum Press, New York and London, 1986.
3. E. L. V. Lewis and T. R. Lomer, *Acta Cryst.*, **B25**, 702 (1969).
4. J. H. Dumbleton and T. R. Lomer, *Acta Cryst.*, **19**, 301 (1965).
5. D. M. Glover, *Acta Cryst.*, **A37**, 251 (1981).
6. A. Cingolani, G. Spinolo, M. Sanesi, and P. Franzosini, *Z. Naturforsch., A*, **35**, 757 (1980).
7. T. Ishioka, *Bull. Chem. Soc. Jpn.*, **64**, 2174 (1991).
8. T. R. Lomer, *Acta Cryst.*, **5**, 11 (1952).
9. H. Noma, Y. Miwa, I. Yokoyama, and K. Machida, *J. Mol. Struct.*, **242**, 207 (1991).
10. M. Kobayashi, T. Kobayashi, Y. Cho, and F. Kaneko, *Makromol. Chem., Macromol. Symp.*, **5**, 1 (1986).
11. I. Harada, M. Tasumi, K. Sato, and M. Okada, Preprints of Molecular Structure Symposium, Hiroshima, The Chemical Society of Japan, Tokyo, 1978, p 230.
12. M. Maroncelli, H. L. Strauss, and R. G. Snyder, *J. Chem. Phys.*, **82**, 2811 (1985).
13. Y. Kim, H. L. Strauss, and R. G. Snyder, *J. Phys. Chem.*, **93**, 485 (1989).
14. M. Kobayashi, F. Kaneko, K. Sato, and M. Suzuki, *J. Phys. Chem.*, **90**, 637 (1986).