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Infrared study on annealing effect on conformation of zinc stearate

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Abstract

The molecular conformation and thermal transition behavior of two zinc stearate specimens, unannealed one and annealed one, were compared. The unannealed specimen has one thermal transition at 134 °C. Annealing was made by increasing temperature to 150 °C and cooling to room temperature slowly. This annealed specimen has an exothermic peak at 103 °C, and endothermic shoulders and a peak at 118, 124 and 131 °C, respectively. The observed frequencies of all bands of the unannealed specimen at room temperature are assigned to the all-trans conformation. We found new bands at 858, 823, 793, 766, 688, and 604 cm^{-1} for the annealed specimen. Based on the normal mode analyses, these bands are assigned to the TGT conformation at the COO end, where T means trans and G means gauche. The annealed specimen consists of almost all-trans molecule but partial molecules have the TGT conformation.
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1. Introduction

Zinc soaps are useful for industrial usage as lubrication powder, but their molecular level structure and thermal transition behavior have not been fully clarified yet. We have carried out the study on the structure of the alkyl chains and the coordination structure of the COO groups around the zinc cation for zinc stearate by the infrared and XAFS study. As a result we found the conformation of the alkyl chain takes the all-trans, and the coordination structure was bridging bidenteta type [1]. The thermal transition behavior of zinc soaps depends on the chain length and thermal history [2]. In this study we investigate anneling effect on the thermal structural transition behavior of zinc stearate.

2. Experimental

Zinc stearate was synthesized from stearic acid (Σ company, 99% purity) as follows. Potassium hydroxide aqueous solution was added dropwise to stearic acid ethanol solution slowly and stirred 2 h. Then, zinc sulphonate aqueous solution was added to the above solution and stirred for 2 h. Resultant solution was put into a refrigerator one night. Precipitate was filtered and washed by distilled water, ethanol, and acetone and recrystallized from benzene. The precipitate was dried under vacuum at 60 °C over night. Resultant material was confirmed by the infrared spectrum. Differential scanning calorimetry (DSC) measurements were made by a Rigaku DSC 8230 with a heating rate 10 K/min. Infrared spectra were measured with a JASCO IR-810 with KBr disk method.

3. Results and discussion

Fig. 1 shows the DSC traces of two zinc stearate specimens: trace (a) is for the unannealed specimen and trace (b) for the annealed specimen. The annealed specimen was made by increasing the temperature to 150 °C and then cooled to room temperature slowly. The trace (a) has one phase transition peak at 134 °C. This is ascribed to the structural phase transition from the all-trans conformation of the alkyl chain and the bridging bidentate coordination structure of the COO groups at room temperature to the liquid-like conformation of the alkyl chain and slightly distorted bridging bidentate coordination structure of the COO groups [1]. The trace (b) has an exothermic peak at 103 °C, and endothermic shoulders and a peak at 118, 124 and 131 °C, respectively. The structural change in this temperature range of these DSC peaks of anneadled specimen is unknown.

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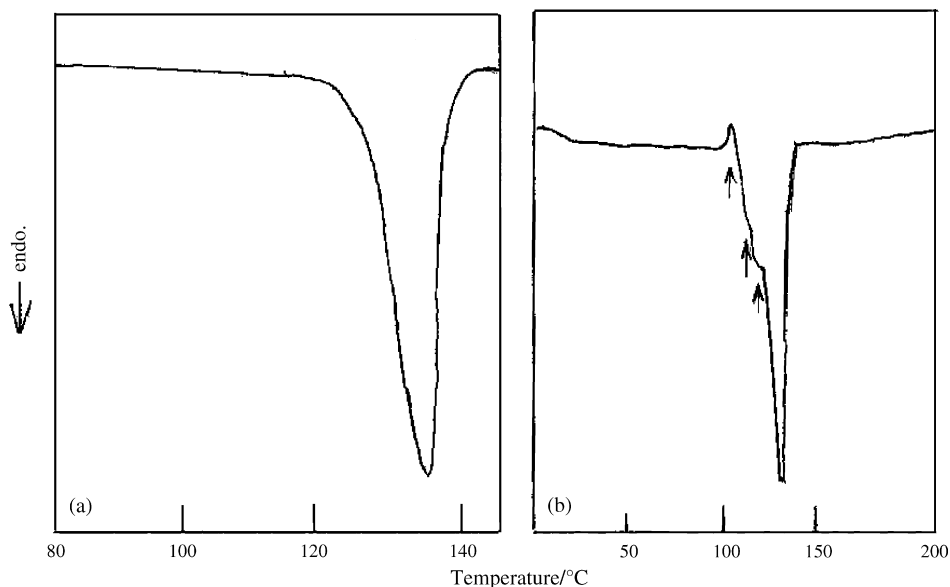(T. Ishioka).

Fig. 1. DSC traces for (a) unannealed and (b) annealed specimens. Trace (a) has one endothermic peak at 134 °C. Trace (b) has one exothermic peak at 103 °C, and endothermic shoulders at 118, 124 °C and a peak at 131 °C.

Fig. 2 shows infrared spectra of (a) the unannealed specimen and (b) the annealed specimen in the 400–1500 cm^{-1} region at room temperature. This infrared region is sensitive to the conformational change of the alkyl chain and the COO group. All bands that appeared in Fig. 2(a) are ascribed to the all-trans conformation of the alkyl chain, as confirmed by normal mode analysis [1]. Almost all bands that appear in Fig. 2(b) are also ascribed to the all-trans conformation, but several new bands appear at 858, 823, 793, 766, 688, and 604 cm^{-1}. Fig. 2(b) indicates that in the annealed specimen, almost all molecules take the all-trans conformation but partial molecules have some conformational defects.

We want to clarify what kind of conformational disorder appeared in the annealed specimen. Maroncelli et al. have investigated thermal structural transitions of a series of odd n-alkanes whose carbon numbers from 17 to 29 by the CH$_2$ progressive region [3]. The structural transition temperatures depend on the carbon number. As a result, they found that in the low temperature phase I, n-alkanes take all-trans form, but in the high temperature phase II, n-alkanes have disorder at the mainly methyl end such as end-gauche, kink, and double gauche conformations. This case of n-alkanes, conformation disordered bands appeared in the wide frequency region from 700 to 1400^{-1}, But in the case of zinc stearate, conformational disordered bands appear mainly in the methylene rocking progressive region from 858 to 604 cm^{-1}. Some normal fatty acids have a polymorphism having the gauche conformation at Cα–Cβ position where α and β means O$_2$C–Cα–Cβ [4]. We postulate that the conformational disorder in the annealed specimen of zinc stearate also occurs at the COO end. In order to confirm this idea, we carried out normal mode analyses of the molecules having conformational disorder around the COO group as follows.

We carried out normal mode analyses for an all-trans molecule and three molecules having conformational defects at COO end where O$_2$C–Cα–Cβ–Cγ. The detail of the calculation has been reported [1]. We used two sets of force constants for the alkyl chain: one is for all-trans [5] and the other is for disordered molecule [6]. The all-trans molecule is represented as TTT. This means O$_2$C–Cα, Cα–Cβ, and Cβ–Cγ are all-trans conformation. The second molecule is indicated as CTT. It means the OOC group is rotated by 90° around O2C–Cα bond, and Cα–Cβ and Cβ–Cγ are trans. The third model TGT means Cα–Cβ taking gauche conformation, and OOC–Cα, Cβ–Cγ are trans. The forth model is CGT. This means the COO group is rotated by 90°, Cα–Cβ bond takes gauche, and Cβ–Cγ is trans. We will discuss these four models, TTT, CTT, TGT, and CGT as follows. All models are shown in Fig. 3.

Table 1 lists the observed frequencies (cm^{-1}) and the calculated frequencies for the TTT, CTT, TGT, and CGT models in the CH$_2$ wagging progressive region from 1180 to 1370 cm^{-1}. All calculated frequencies for the four models agree with the
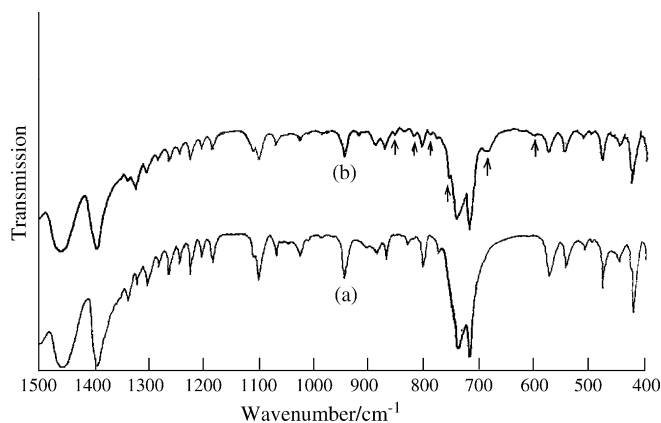

Fig. 2. IR spectrum of zinc stearate of (a) unannealed and (b) annealed specimen in the 400–1500 cm^{-1} region. In the annealed spectrum, defect bands appear at 858, 823, 793, 766, 688, and 604 cm^{-1} as shown by arrows.
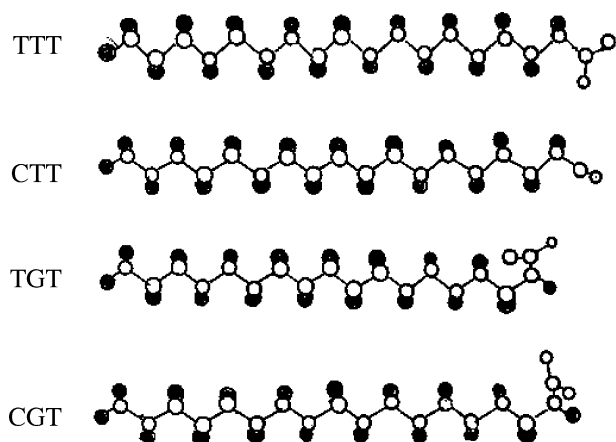
Fig. 3. TTT, CTT, TGT, and CGT molecular models where open circles are ascribed carbon or oxygen, and filled circles are hydrogen atom. They have conformational disorder at the COO end.

observed frequencies within $10\,\mathrm{cm}^{-1}$. This means the all models explain the observed wagging frequencies.

Table 2 shows the observed frequencies (cm^{-1}) and calculated frequencies for the four models in the C–C stretching region from 960 to $1130\,\mathrm{cm}^{-1}$. In this region, the observed frequencies also agree with the calculated frequencies for all models within $12\,\mathrm{cm}^{-1}$. This result indicates that we cannot identify which model corresponds to the observed disordered conformation bands for the annealed specimen. So, we carry out a comparison of the frequencies in the CH_2 rocking region from 700 to $950\,\mathrm{cm}^{-1}$, where the new bands appeared at 858, 823, 793, and $766\,\mathrm{cm}^{-1}$ of the annealed zinc stearate specimen.

Table 3 shows the result of the observed frequencies in the CH_2 rocking region from 700 to $920\,\mathrm{cm}^{-1}$, where ν_{all} corresponds to all-trans conformation, $\nu_{annealed}$ represents the defect bands. The calculated frequencies (cm^{-1}) are also shown as TTT, CTT, TGT, and CGT. The observed new frequencies (cm^{-1}) that appeared of the annealed specimen at 858, 823, 793, and $766\,\mathrm{cm}^{-1}$. These frequencies of new bands correspond fairly well to those of the CGT and TGT models. Based on the results described above, partial disordered state expected from the observed infrared spectrum of the annealed specimen may be assigned to the TGT or CGT conformation at the COO end. In order to distinguish between the TGT and CGT models, we

Table 1
Observed ν_{obs} and calculated frequencies (cm^{-1}) in the CH_2 wagging region where TTT, CTT, TGT, and CGT, see the text

ν_{obs}	TTT	CTT	TGT	CGT
1360	1364	1364	1361	1361
1340	1348	1349	1344	1344
1326	1331	1331	1325	1325
1306	1314	1315	1308	1308
1287	1282	1284	1290	1291
1266	1266	1268	1273	1262
1247	1248	1250	1255	1252
1228	1227	1229	1231	1231
1208	1203	1205	1206	1207
1188	1178	1180	1180	1180

Table 2
Onserved ν_{obs} and calculated frequencies (cm^{-1}) in the C–C stretching region

ν_{obs}	TTT	CTT	TGT	CGT
1116	1127	1127	1126	1126
	1097	1096	1091	1092
1074	1073	1071	1084	1077
	1071	1070	1071	1071
	1069	1068	1070	1070
	1066	1066	1067	1067
1063	1063	1064	1065	1065
	1062	1061	1062	1061
	1061	1056	1057	1056
1052	1048	1049	1045	1045
1032	1038	1032	1035	1032
	1019	1016	1016	1014
	1010	1011	1005	1005
993	992	989	989	983
	975	976	973	973
972	969	968	963	960

For the TTT, CTT, TGT, and CGT, see the text.

Table 3
Observed and calculated frequencies (cm^{-1}) in the CH_2 rocking region

ν_{all}	$\nu_{annealed}$	TTT	CTT	TGT	CGT
		913	910	919	900
875		878	875	898	885
840	858	844	840	861	861
808	823	810	807	825	824
780	793	778	775	790	790
758	766	750	746	758	758
744		724	722	730	730
		703	701	707	707

For the TTT, CTT, TGT, and CGT, see the text.

use the observed new band at 688 and $604\,\mathrm{cm}^{-1}$ of the annealed specimen.

Table 4 shows the results of the observed frequencies of the COO group vibrations. That is, the COO bending, the COO out-of-plane and the COO rocking. Observed bands ascribed to all-trans conformation are ν_{all}, and defect band is designated as $\nu_{annealed}$ as in the case of Table 3. ν_{all} corresponds well to TTT conformation. The $\nu_{annealed}$ at $688\,\mathrm{cm}^{-1}$ can be ascribed to both TGT or CGT models, but $604\,\mathrm{cm}^{-1}$ band should be ascribed only to TGT.

In conclusion, zinc stearate have the all-trans conformation at room temperature, but its annealed specimen has almost all-trans

Table 4
Observed ν_{all} and $\nu_{annealed}$ (cm^{-1}), and calculated frequency region in the COO bending, the COO out-of-plane, and the COO rocking region

Description	ν_{all}	$\nu_{annealed}$	TTT	CTT	TGT	CGT
COO bending	722	688	712	717	695	688
COO out-of-plane	580	604	579	652	584	652
COO rocking	550		548	526	561	572

For the TTT, CTT, TGT, and CGT, see the text.

conformation but partially disordered conformation of TGT at the COO end.

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