Factor Analysis of Phase Transitions and Conformational Changes in Pentaerythritol Tetrastearate

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The phase transitions and conformational changes of pentaerythritol tetrastearate (n-C$_{17}$H$_{35}$COOCH$_2$)$_4$C have been studied by applying factor analysis (FA) to the examination of Fourier transform infrared spectra (FTIR) at different temperatures. The FA indicates the presence of three phase transitions and four conformational changes, which are substantiated, respectively, by differential scanning calorimetry (DSC) and FTIR. The study reveals that FA of the phase transitions and conformational changes may be applied to esters and other organic compounds which can be tested by infrared spectroscopy (IR).

INTRODUCTION

A multivariate statistical analysis method called factor analysis (FA), originally developed by psychologists and sociologists,[1,2] has been found to be useful in the interpretation of data by yielding the number of independently contributing entities. In recent years, this method has been applied to infrared spectra, ultraviolet/visible spectra, Raman spectra, mass spectroscopy, nuclear magnetic resonance, chromatography, polarography, biological activity, solution qualities (equilibrium constant, stability constant, and thermodynamic parameters), etc. as reviewed by Weiner and He et al.[3,4] In infrared spectroscopy, factor analysis has found application to the spectral identification of unknown mixtures,[5] the determination of the number of components contributing to a chemical system,[6,7] the reduction of noise in Fourier transform infrared spectra (FTIR),[8] the separation of pure component spectra from mixture spectra,[9] and the compression of IR data for storage in spectral libraries.[10,11] The analyses of these systems have focused on infrared spectra at ambient temperature; however, little attention has been paid to applying factor analysis to infrared spectra at varied temperature.[12]

In order to understand temperature-induced phase transitions and conformational changes of (n-C$_{17}$H$_{35}$COOCH$_2$)$_4$C, we are interested in applying factor analysis to its FTIR spectra at different temperatures. Satisfactory results are obtained as shown in this paper.

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(2) Harman, H. H. *Modern Factor Analysis*; University of Chicago: Chicago, 1967.
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Table I. Criteria of Factor Analysis

$$(1) \quad RE = \left[\frac{\sum_{p+1}^{n} \lambda_j}{m(n-p)} \right]^{1/2} \quad \text{real error}$$

$$(2) \quad IND = \frac{RE}{(n-p)^2} \quad \text{indicator function}$$

$$(3) \quad IE = \left[\frac{p\sum_{p+1}^{n} \lambda_j}{mn(n-p)} \right]^{1/2} = RE\left(\frac{p}{n}\right)^{1/2} \quad \text{imbedded error}$$

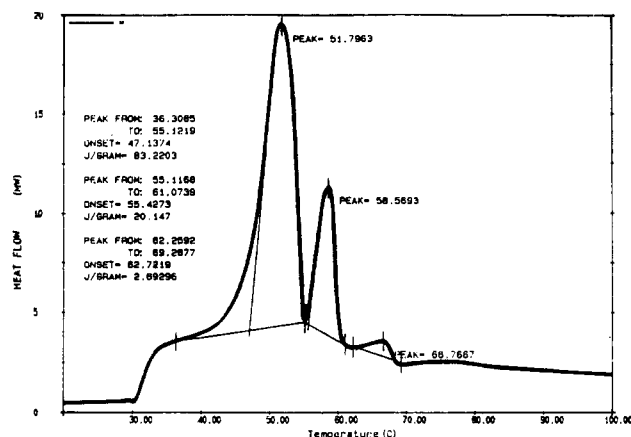$$(4) \quad ER = \frac{\lambda_p}{\lambda_{p+1}} \quad \text{eigenvalue ratio}$$

Figure 1. The DSC thermogram of (n-C$_{17}$H$_{35}$COOCH$_2$)$_4$C.

The theory of factor analysis has been described elsewhere in detail,[5-9,13-16] so only a short summary relating to some criteria is given here. Malinowski[14] developed a theory of error in factor analysis that leads to three types of errors: (1) real error (RE), the difference between exact data and raw experimental data, which contain experimental error; (2) imbedded error (IE), the difference between the factor analysis regenerated data and the exact data; (3) extracted error (XE), the amount of error that is removed by factor analysis regenerated data from the raw data. The first approach developed by Malinowski[14] utilizes the concept of imbedded error (IE). The second approach, an empirical function called the indicator function (IND), utilizes the concept of real error

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Table II. Criteria of the FA of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ in the Frequency Range 1080–1300 cm^{-1}

no.	T (°C)	IND	ER	IE × 10^5	no.	T (°C)	IND	ER	IE × 10^5
				Set 1 (62–67 °C)					
1	62	0.641E–05^a	6580.291	0.99	4	65	0.117E–04	3.372	0.37
2	63	0.707E–05	1.973	0.89	5	66	0.459E–04	1.090	0.29
3	64	0.706E–05	5.034	0.53	6	67	0.000E+00	0.000	0.00
				Set 2 (62–68 °C)					
1	62	0.433E–05	7157.856	0.98	5	66	0.113E–04	1.651	0.37
2	63	0.448E–05	1.818	0.91	6	67	0.427E–04	1.236	0.27
3	64	0.406E–05	5.037	0.58	7	68	0.000E+00	0.000	0.00
4	65	0.566E–05	2.446	0.45					
				Set 3 (62–69 °C)					
1	62	0.451E–05	3368.285	1.40	5	66	0.566E–05	2.442	0.48
2	63	0.424E–05	2.512	1.27	6	67	0.113E–04	1.652	0.38
3	64	0.435E–05	1.901	1.01	7	68	0.427E–04	1.235	0.27
4	65	0.406E–05	4.681	0.62	8	69	0.000E+00	0.000	0.00
				Set 4 (62–70 °C)					
1	62	0.337E–05	3804.085	1.37	6	67	0.563E–05	1.869	0.49
2	63	0.318E–05	2.264	1.32	7	68	0.112E–04	1.648	0.38
3	64	0.322E–05	1.607	1.11	8	69	0.420E–04	1.271	0.27
4	65	0.282E–05	5.417	0.72	9	70	0.000E+00	0.000	0.00
5	66	0.378E–05	1.487	0.61					
				Set 5 (62–72 °C)					
1	62	0.262E–05	4238.906	1.36	6	67	0.335E–05	1.866	0.57
2	63	0.248E–05	1.860	1.36	7	68	0.549E–05	1.158	0.49
3	64	0.235E–05	1.726	1.13	8	69	0.108E–04	1.594	0.38
4	65	0.195E–05	6.134	0.74	9	70	0.390E–04	1.475	0.25
5	66	0.248E–05	1.334	0.67	10	72	0.000E+00	0.000	0.00

^{a} This is read as 0.641×10^{-5}.

Table III. Criteria of the FA of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ in the Frequency Range 1080–1300 cm^{-1}

no.	T (°C)	IND	ER	IE × 10^5	no.	T (°C)	IND	ER	IE × 10^5
				Set 1 (95–150 °C)					
1	95	0.140E–04^a	1307.132	2.16	4	130	0.128E–04	2.063	0.40
2	100	0.149E–04	1.824	1.86	5	140	0.408E–04	2.170	0.25
3	120	0.724E–05	28.598	0.54	6	150	0.000E+00	0.000	0.00
				Set 2 (70–150 °C)					
1	70	0.385E–05	487.386	3.01	7	95	0.177E–05	1.355	0.52
2	72	0.160E–05	9.913	1.39	8	100	0.255E–05	1.143	0.46
3	75	0.820E–06	16.552	0.68	9	120	0.401E–05	1.494	0.37
4	80	0.904E–06	1.636	0.64	10	130	0.805E–05	1.515	0.29
5	85	0.106E–05	1.644	0.60	11	140	0.298E–04	1.391	0.20
6	90	0.134E–05	1.139	0.57	12	150	0.000E+00	0.000	0.00
				Set 3 (69–150 °C)					
1	69	0.342E–05	449.849	3.20	8	95	0.176E–05	1.351	0.53
2	70	0.161E–05	11.565	1.72	9	100	0.254E–05	1.159	0.46
3	72	0.142E–05	1.340	1.46	10	120	0.400E–05	1.496	0.38
4	75	0.820E–06	12.433	0.75	11	130	0.805E–05	1.513	0.29
5	80	0.902E–06	1.640	0.69	12	140	0.296E–04	1.361	0.20
6	85	0.106E–05	1.640	0.64	13	150	0.000E+00	0.000	0.00
7	90	0.134E–05	1.139	0.59					
				Set 4 (68–150 °C)					
1	68	0.295E–05	434.625	3.24	8	90	0.132E–05	1.017	0.60
2	69	0.132E–05	12.903	1.68	9	95	0.172E–05	1.417	0.53
3	70	0.116E–05	1.278	1.46	10	100	0.248E–05	1.172	0.46
4	72	0.686E–06	11.181	0.79	11	120	0.394E–05	1.408	0.38
5	75	0.735E–06	1.627	0.73	12	130	0.785E–05	1.601	0.28
6	80	0.831E–06	1.927	0.67	13	140	0.291E–04	1.333	0.19
7	85	0.103E–05	1.126	0.65	14	150	0.000E+00	0.000	0.00

^{a} This is read as 0.140×10^{-4}.

(RE). He et al.[16] put forward a practical criterion called the eigenvalue ratio (ER), which is the ratio between two adjacent eigenvalues. The mathematical expressions of the different criteria used in this paper are listed in Table I where n = number of spectra, p = number of pure components, m = number of points/spectrum, and λ_i = eigenvalues.

EXPERIMENTAL SECTION

The FTIR spectra of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ were collected as a function of temperature from 1540 to 650 cm^{-1} on a Nicolet FTIR-5DX spectrometer using 10 scans of sample and reference at a resolution of 4 cm^{-1}. On the FTIR spectrometer, the heating

Table IV. Criteria of the FA of $(n\text{-}C_{17}H_{35}COOCH_2)_4$ in the Frequency Range 1080–1300 cm^{-1}

no.	T (°C)	IND	ER	IE × 10^5	no.	T (°C)	IND	ER	IE × 10^5
				Set 1 (60–68 °C)					
1	60	0.250E–05[a]	7641.472	1.02	6	65	0.503E–05	1.064	0.44
2	61	0.251E–05	1.202	1.04	7	66	0.987E–05	1.745	0.34
3	62	0.171E–05	9.108	0.59	8	67	0.371E–04	1.261	0.24
4	63	0.210E–05	2.072	0.53	9	68	0.000E+00	0.000	0.00
5	64	0.303E–05	1.359	0.49					
				Set 2 (59–68 °C)					
1	59	0.249E–05	3437.131	1.29	6	64	0.295E–05	1.412	0.50
2	60	0.194E–05	2.945	1.06	7	65	0.490E–05	1.066	0.44
3	61	0.154E–05	4.746	0.74	8	66	0.955E–05	1.687	0.33
4	62	0.170E–05	1.920	0.64	9	67	0.345E–04	1.445	0.23
5	63	0.206E–05	2.082	0.56	10	68	0.000E+00	0.000	0.00
				Set 3 (58–68 °C)					
1	58	0.280E–05	1461.834	1.80	7	64	0.283E–05	1.079	0.50
2	59	0.162E–05	7.565	1.14	8	65	0.458E–05	1.335	0.42
3	60	0.149E–05	1.745	0.96	9	66	0.934E–05	1.339	0.33
4	61	0.122E–05	5.221	0.65	10	67	0.325E–04	1.636	0.21
5	62	0.143E–05	2.083	0.58	11	68	0.000E+00	0.000	0.00
6	63	0.192E–05	1.311	0.54					
				Set 4 (57–68 °C)					
1	57	0.345E–05	575.765	2.70	7	63	0.187E–05	1.019	0.55
2	58	0.135E–05	20.749	1.18	8	64	0.272E–05	1.232	0.49
3	59	0.130E–05	1.616	1.07	9	65	0.447E–05	1.309	0.42
4	60	0.923E–06	7.843	0.66	10	66	0.933E–05	1.189	0.33
5	61	0.106E–05	2.045	0.60	11	67	0.324E–04	1.651	0.21
6	62	0.135E–05	1.321	0.58	12	68	0.000E+00	0.000	0.00

[a] This reads as 0.25 × 10^{-5}.

Table V. Criteria of the FA of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ in the Frequency Range 1080–1300 cm^{-1}

no.	T (°C)	IND	ER	IE × 10^5	no.	T (°C)	IND	ER	IE × 10^5
				Set 1 (51–56 °C)					
1	51	0.356E–04[a]	127.019	5.49	4	54	0.114E–04	2.913	0.36
2	52	0.114E–04	31.285	1.43	5	55	0.399E–04	1.596	0.25
3	53	0.668E–05	16.584	0.51	6	56	0.000E+00	0.000	0.00
				Set 2 (51–57 °C)					
1	51	0.292E–04	86.964	6.58	5	55	0.108E–04	1.557	0.35
2	52	0.719E–05	45.956	1.45	6	56	0.393E–04	1.400	0.25
3	53	0.449E–05	10.371	0.64	7	57	0.000E+00	0.000	0.00
4	54	0.540E–05	4.027	0.43					
				Set 3 (51–58 °C)					
1	51	0.246E–04	63.846	7.62	5	55	0.494E–05	1.614	0.41
2	52	0.497E–05	62.900	1.48	6	56	0.104E–04	1.180	0.35
3	53	0.325E–05	5.895	0.75	7	57	0.372E–04	1.506	0.24
4	54	0.311E–05	6.804	0.48	8	58	0.000E+00	0.000	0.00
				Set 4 (51–59 °C)					
1	51	0.208E–04	51.310	8.46	6	56	0.454E–05	1.381	0.39
2	52	0.355E–05	80.710	1.47	7	57	0.955E–05	1.238	0.33
3	53	0.226E–05	6.199	0.78	8	58	0.351E–04	1.362	0.23
4	54	0.195E–05	6.972	0.49	9	59	0.000E+00	0.000	0.00
5	55	0.277E–05	1.386	0.45					
				Set 5 (51–61 °C)					
1	51	0.148E–04	40.290	9.53	7	57	0.258E–05	1.238	0.45
2	52	0.216E–05	106.647	1.51	8	58	0.437E–05	1.038	0.40
3	53	0.148E–05	3.949	0.95	9	59	0.898E–05	1.508	0.32
4	54	0.111E–05	6.649	0.59	10	60	0.347E–04	1.137	0.23
5	55	0.130E–05	2.147	0.53	11	61	0.000E+00	0.000	0.00
6	56	0.174E–05	1.353	0.49					

[a] This reads as 0.356 × 10^{-4}.

process was continuous at a properly chosen rate. Temperature was continuously measured with a thermistor thermograph and controlled to within ±0.1 °C. The spectra were stored by computer.

The spectra were manually digitized at 1-cm^{-1} intervals as described previously,[17] giving a total of 221 data points between 1300 and 1080 cm^{-1} for each spectrum. All spectral data were transferred to a DEC MICRO VAX-II computer for factor analysis. Factor analysis was done initially using self-programs at a minimum (or maximum) number of spectra in their corresponding temperature range. Then the procedure was repeated by increasing (or decreasing) the number of spectra

(17) Bulmer, J. T.; Shurvell, H. F. *Can. Spectrosc.* 1971, *16*, 94–99.

Table VI. Criteria of the FA of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ in the Frequency Range 1080–1300 cm^{-1}

no.	T (°C)	IND	ER	IE × 10^5	no.	T (°C)	IND	ER	IE × 10^5
				Set 1 (54–62 °C)					
1	54	0.163E–04[a]	82.412	6.65	6	59	0.454E–05	1.346	0.39
2	55	0.168E–05	273.782	0.70	7	60	0.960E–05	1.174	0.33
3	56	0.143E–05	6.500	0.49	8	61	0.347E–04	1.453	0.22
4	57	0.188E–05	1.482	0.48	9	62	0.000E+00	0.000	0.00
5	58	0.275E–05	1.193	0.45					
				Set 2 (52–62 °C)					
1	52	0.137E–04	46.605	8.84	7	58	0.251E–05	1.161	0.44
2	53	0.132E–05	241.740	0.93	8	59	0.421E–05	1.124	0.38
3	54	0.889E–06	8.412	0.57	9	60	0.864E–05	1.551	0.30
4	55	0.997E–06	2.129	0.53	10	61	0.340E–04	1.068	0.22
5	56	0.126E–05	1.263	0.51	11	62	0.000E+00	0.000	0.00
6	57	0.169E–05	1.371	0.48					
				Set 3 (51–62 °C)					
1	51	0.124E–04	38.692	9.73	7	57	0.169E–05	1.369	0.49
2	52	0.171E–05	116.478	1.50	8	58	0.251E–05	1.164	0.45
3	53	0.118E–05	3.690	0.98	9	59	0.420E–05	1.121	0.39
4	54	0.881E–06	6.526	0.63	10	60	0.861E–05	1.564	0.31
5	55	0.996E–06	2.029	0.57	11	61	0.338E–04	1.070	0.22
6	56	0.126E–05	1.262	0.54	12	62	0.000E+00	0.000	0.00

[a] This reads as 0.163 × 10^{-4}.

**Table VII. Criteria of the FA of $(n\text{-}C_{17}H_{35}COOCH_2)_4$ in the Frequency Range 1080–1300 cm^{-1}**

no.	T (°C)	IND	ER	no.	T (°C)	IND	ER
			Set 1 (33–45 °C)				
1	33	0.298E–04[a]	222.600	4	41	0.195E–04	4.694
2	37	0.210E–04	5.787	5	43	0.630E–04	2.072
3	39	0.145E–04	10.419	6	45	0.000E+00	0.000
			Set 2 (33–46 °C)				
1	33	0.325E–04	80.817	5	43	0.189E–04	4.660
2	37	0.179E–04	9.414	6	45	0.568E–04	2.546
3	39	0.154E–04	3.983	7	46	0.000E+00	0.000
4	41	0.143E–04	5.002				
			Set 3 (33–47 °C)				
1	33	0.296E–04	50.927	5	43	0.138E–04	1.801
2	37	0.158E–04	12.020	6	45	0.178E–04	5.109
3	39	0.167E–04	1.401	7	46	0.548E–04	2.365
4	41	0.104E–04	11.618	8	47	0.000E+00	0.000
			Set 4 (33–48 °C)				
1	33	0.292E–04	28.348	6	45	0.123E–04	1.965
2	37	0.124E–04	18.858	7	46	0.164E–04	4.752
3	39	0.126E–04	1.747	8	47	0.512E–04	2.280
4	41	0.121E–04	2.100	9	48	0.000E+00	0.000
5	43	0.952E–05	6.555				
			Set 5 (33–49 °C)				
1	33	0.274E–04	18.999	6	45	0.947E–05	2.398
2	37	0.936E–05	28.208	7	46	0.122E–04	2.000
3	39	0.915E–05	1.865	8	47	0.159E–04	4.934
4	41	0.893E–05	1.991	9	48	0.499E–04	2.268
5	43	0.849E–05	2.954	10	49	0.000E+00	0.000

[a] This reads as 0.298 × 10^{-4}.

gradually for factor analysis. A series of error criteria were obtained finally.

The calorimetric measurements of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ were performed with a Perkin-Elmer DSC 7 differential scanning calorimeter (DSC) equipped with a Perkin-Elmer 3700 data station.

The $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ sample was synthesized by a previous method[18] and purified by column chromatography. pH measurements and hydroxy value titrations gave chemical purity estimated at >99%.

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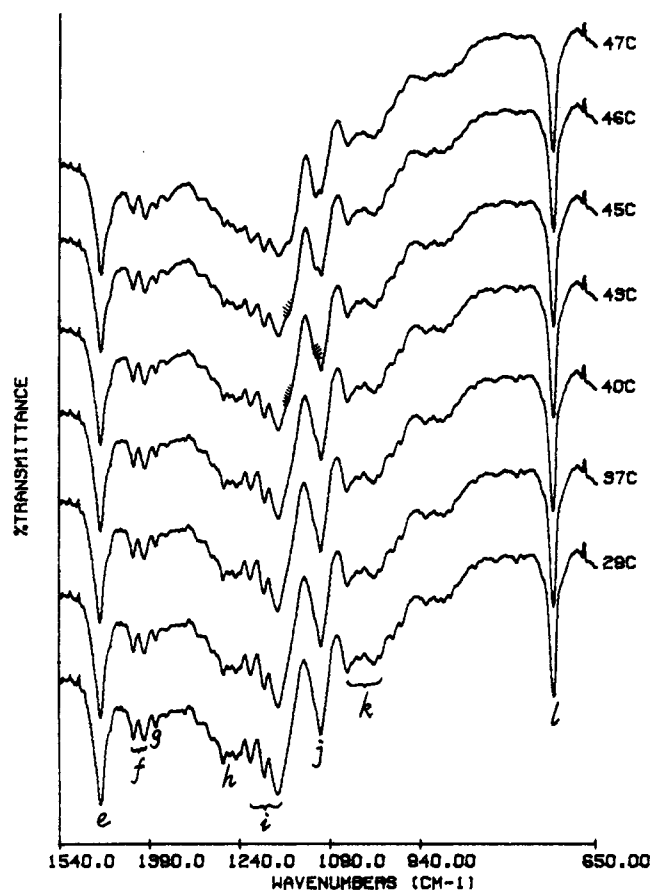
Figure 2. The FTIR spectra of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ from 29 to 47 °C.

RESULTS AND DISCUSSION

A. Solid–Liquid Phase Transition. In the frequency range 1080–1300 cm^{-1}, the factor analysis of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ was done initially with six spectra recorded at 62, 63, 64, 65, 66, and 67 °C. Later, the number of spectra included in the analysis was increased one at a time. Five sets of error criteria were obtained in turn, shown in Table II. It can be seen from this table that $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ is a three-component system for set 1 as the indicator function
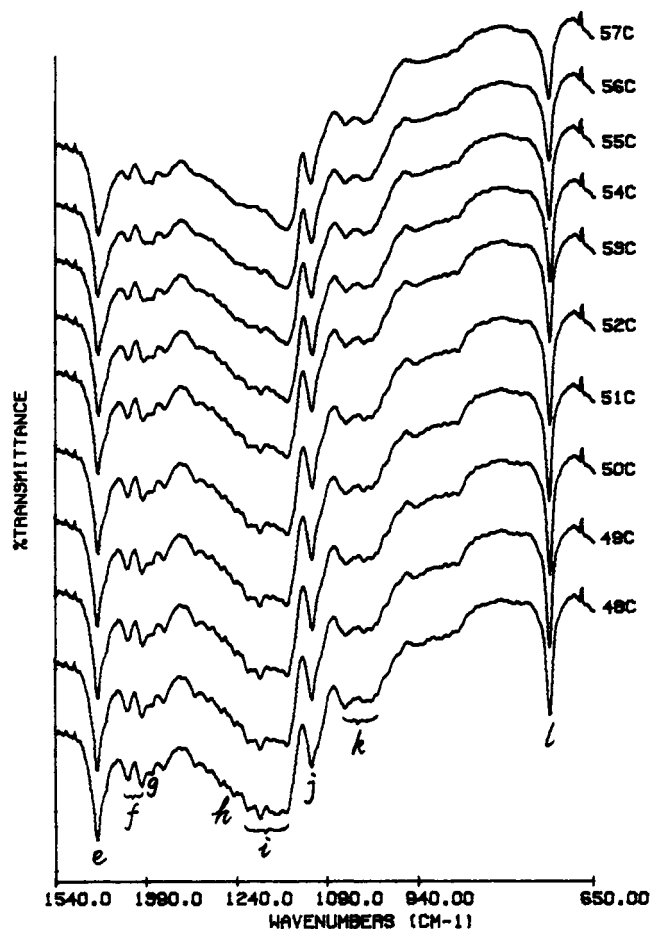
Figure 3. The FTIR spectra of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ from 48 to 57 °C.

Figure 4. The FTIR spectra of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ from 58 to 150 °C.

(IND) is a minimum at no. = 3. This conclusion is substantiated by the eigenvalue ratio (ER) reaching a maximum at no. = 3 and by the imbedded error (IE) not decreasing appreciably beyond no. = 3. When the spectrum at 68 °C is included in the analysis, the number of components is still three (see set 2). For set 3, the IND at no. = 4 reaches a minimum, giving an evidence for four components. The conclusion is substantiated by the ER reaching a maximum at no. = 4 and by the IE not decreasing appreciably beyond no. = 4. This indicates that a fourth independent component enters the system between 68 and 69 °C. When the number of spectra included in the analysis is increased, $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ is still a four-component system until 72 °C (see set 4 and set 5).

To sum up, when the temperature range is extended from 62–68 °C to 62–69 °C, the number of components of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ increases from 3 to 4. Namely, a solid–liquid phase transition occurs between 68 and 69 °C. It is in good agreement with the results of differential scanning calorimetry (DSC) of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ (see Figure 1). The figure demonstrates that there is a endothermic peak at 68.8 °C, with no other peaks above the temperature.

In order to confirm the above-mentioned conclusion and explore the sensitivity of factor analysis, we change the temperature range of factor analysis with results shown in Table III. We find from this table that $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ is a three-component system for set 1 or set 2 because IND reaches a minimum at no. = 3 and the ER is a maximum at no. = 3 and the IE does not decrease appreciably beyond no. = 3. When the spectrum at 69 °C is included in the analysis, the number of components become four (see set 3). When the spectrum at 68 °C is included in the analysis, the number of components is still four (see set 4).
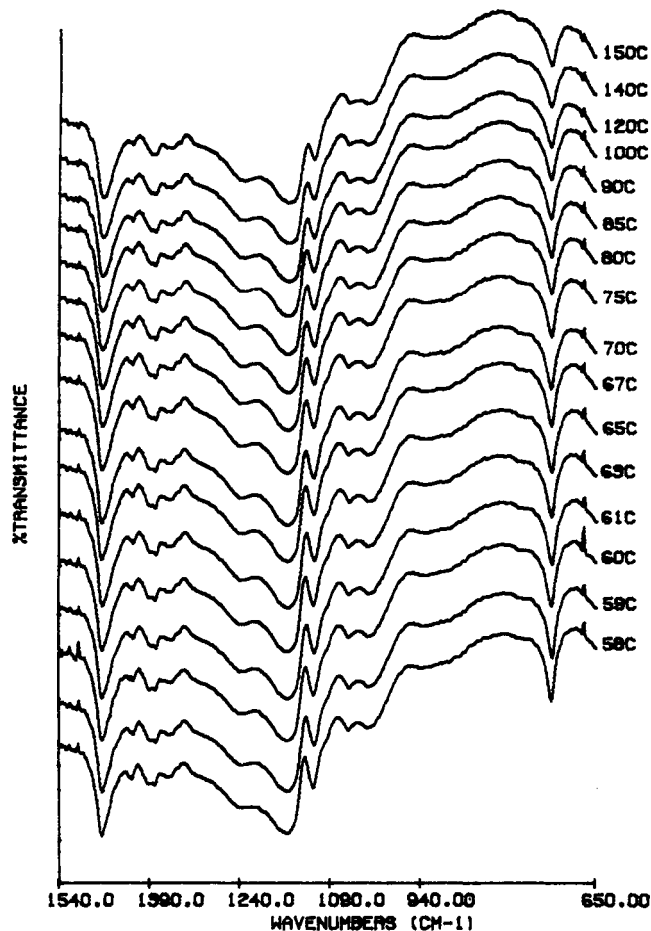
To sum up, when the temperature range is extended from 70–150 °C to 69–150 °C, the number of components of $(n\text{-}C_{17}H_{35}COOH_2)_4C$ increases from 3 to 4. This result agrees substantially with the conclusion of Table II.

It is noteworthy that Table II differs somewhat from Table III at the temperature of phase transitions; the former is between 68 and 69 °C and the latter between 69 and 70 °C. This is explained as in the process of solid–liquid phase transition from 62.3 to 69.3 °C (see Figure 1), where there are both solid and liquid components. During the gradual melting of the solid, the liquid component is initially minor and not found by factor analysis until 68 °C (see Table II). When the quantity of liquid become measurable above 68 °C, the liquid is detected by factor analysis as a component, so the temperature of the phase transition in Table II is between 68 and 69 °C. For Table III, because there is only a liquid above 70 °C, no solid component is found by factor analysis, whereas when solid become measurable at 69 °C or lower, the solid component is detected by factor analysis. Therefore, the temperature of the phase transition in Table III is between 69 and 70 °C. Though the conclusions of factor analysis are slightly different at two temperature ranges, the same phase transition is substantiated.

B. Solid–Solid Phase Transitions. Some error criteria of factor analysis of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ are listed in Table IV in the frequency range 1080–1300 cm^{-1}. Table IV shows that in set 1 or 2 $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ is a three-component system, as indicated by the minimum data of the IND, further supported by the ER reaching a maximum at no. = 3 and by the IE not decreasing obviously beyond no. = 3. When the spectrum at 58 °C is included in the analysis, the number of components become 4 for set 3. When the number of spectra included in the analysis is increased, $(n\text{-}C_{17}H_{35}COOCH_2)_4C$

Table VIII. Criteria of the FA of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ in the Frequency Range 1080–1300 cm^{-1}

no.	T (°C)	IND	ER	IE × 10^5	no.	T (°C)	IND	ER	IE × 10^5
				Set 1 (49–62 °C)					
1	49	0.994E–05[a]	30.661	10.94	8	56	0.123E–05	1.066	0.56
2	50	0.136E–05	159.010	1.74	9	57	0.164E–05	1.536	0.51
3	51	0.120E–05	1.419	1.52	10	58	0.246E–05	1.030	0.46
4	52	0.853E–06	3.394	0.98	11	59	0.411E–05	1.210	0.39
5	53	0.656E–06	8.563	0.65	12	60	0.859E–05	1.436	0.31
6	54	0.780E–06	1.199	0.63	13	61	0.338E–04	1.065	0.23
7	55	0.954E–06	1.291	0.60	14	62	0.000E+00	0.000	0.00
				Set 2 (50–62 °C)					
1	50	0.112E–04	33.658	10.43	8	57	0.165E–05	1.528	0.50
2	51	0.149E–05	144.258	1.59	9	58	0.249E–05	1.028	0.46
3	52	0.122E–05	2.170	1.25	10	59	0.417E–05	1.138	0.39
4	53	0.919E–06	3.370	0.84	11	60	0.858E–05	1.550	0.31
5	54	0.798E–06	6.214	0.61	12	61	0.338E–04	1.057	0.23
6	55	0.982E–06	1.085	0.59	13	62	0.000E+00	0.000	0.00
7	56	0.124E–05	1.284	0.55					
				Set 3 (51–62 °C)					
1	51	0.124E–04	38.692	9.73	7	57	0.169E–05	1.369	0.49
2	52	0.171E–05	116.478	1.50	8	58	0.251E–05	1.164	0.45
3	53	0.118E–05	3.690	0.98	9	59	0.420E–05	1.121	0.39
4	54	0.881E–06	6.526	0.63	10	560	0.861E–05	1.564	0.31
5	55	0.996E–06	2.029	0.57	11	61	0.338E–04	1.070	0.22
6	56	0.126E–05	1.262	0.54	12	62	0.000E+00	0.000	0.00
				Set 4 (53–62 °C)					
1	53	0.150E–04	59.883	7.80	6	58	0.259E–05	1.325	0.44
2	54	0.148E–05	253.015	0.81	7	59	0.424E–05	1.271	0.38
3	55	0.108E–05	9.087	0.52	8	60	0.869E–05	1.586	0.30
4	56	0.134E–05	1.508	0.51	9	61	0.344E–04	1.041	0.22
5	57	0.180E–05	1.163	0.49	10	62	0.000E+00	0.000	0.00
				Set 5 (54–62 °C)					
1	54	0.163E–04	82.412	6.65	6	59	0.454E–05	1.346	0.39
2	55	0.168E–05	273.782	0.70	7	60	0.960E–05	1.174	0.33
3	56	0.143E–05	6.500	0.49	8	61	0.347E–04	1.453	0.22
4	57	0.188E–05	1.482	0.48	9	62	0.000E+00	0.000	0.00
5	58	0.275E–05	1.193	0.45					
				Set 6 (55–62 °C)					
1	55	0.171E–04	130.422	5.30	5	59	0.480E–05	1.398	0.40
2	56	0.196E–05	291.773	0.58	6	60	0.101E–04	1.138	0.34
3	57	0.204E–05	4.101	0.47	7	61	0.348E–04	1.695	0.22
4	58	0.294E–05	1.252	0.45	8	62	0.000E+00	0.000	0.00
				Set 7 (56–62 °C)					
1	56	0.182E–04	220.359	4.09	5	60	0.108E–04	1.395	0.35
2	57	0.273E–05	201.448	0.55	6	61	0.397E–04	1.374	0.25
3	58	0.321E–05	3.305	0.46	7	62	0.000E+00	0.000	0.00
4	59	0.527E–05	1.267	0.42					

[a] This reads as 0.994 × 10^{-5}.

Table IX. Summary of the FA of Phase Transitions and Conformational Changes in $(n\text{-}C_{17}H_{35}COOCH_2)_4C$

change of temperature range, °C	change of component number	change of temperature, °C	change type[a]	substantiation
33–45 to 33–46	3 to 4	45–46	conformational change	FTIR
33–47 to 33–48	4 to 5	47–48	conformational change	FTIR
51–62 to 50–62	4 to 5	50–51	conformational change	FTIR
52–62 to 51–62	3 to 4	51–52	S–S phase transition	DSC
55–62 to 54–62	2 to 3	54–55	conformational change	FTIR
51–57 to 51–58	3 to 4	57–59	S–S phase transition	DSC
59–68 to 58–68	3 to 4			
62–68 to 62–69	3 to 4	68–70	S–L phase transition	DSC
70–150 to 69–150	3 to 4			

[a] S, solid; L, liquid.

is still a four-component system (see set 4).

To sum up, when the temperature range is extended from 59–68 °C to 58–68 °C, the number of components of $(n\text{-}C_{17}H_{35}\text{-}COOCH_2)_4C$ increases from 3 to 4. Namely, a solid–solid phase transition occurs between 58 and 59 °C as substantiated

by the DSC of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ (see Figure 1, indicating an endothermic peak at 58.6 °C).

This conclusion is also seen in Table V in that the number of components of $(n\text{-}C_{17}H_{35}COOCH_2)_4C$ increases from 3 to 4 when the temperature range is extended from 51–57 °C to

51–58 °C. Namely, a solid–solid phase transition occurs between 57 and 58 °C. For Tables IV and V, the conclusions of factor analysis are slightly different at two temperature ranges, too. They are similar to Tables II and III.

Some results of factor analysis of $(n$-$C_{17}H_{35}COOCH_2)_4C$ in the frequency range 1080–1300 cm^{-1} are shown in Table VI, which indicates that the number of components of $(n$-$C_{17}H_{35}$-$COOCH_2)_4C$ increases from 3 to 4 when the temperature range is extended from 52–62 °C to 51–62 °C. Namely, a solid-solid phase transition occurs between 51 and 52 °C, which is again substantiated by DSC results for $(n$-$C_{17}H_{35}COOCH_2)_4C$. Figure 1 shows a endothermic peak at 51.8 °C.

According to the papers of Maroncelli et al.,[19] Snyder et al.,[20] and Strobl et al.,[21] below the melting point the crystals of long-chain n-alkanes showed a remarkable series of solid-solid phase transitions, which were studied by DSC and substantiated by X-ray scattering experiments.[21] This suggests that $(n$-$C_{17}H_{35}COOCH_2)_4C$ passes through three crystal states before melting, which are denoted X, Y, and Z. X crystal exists below 51.8 °C, where a solid–solid phase transition to Y crystal occurs. The second solid–solid phase transition occurs from Y to Z crystal at 58.6 °C, and a solid-liquid phase transition occurs at 68.8 °C where Z crystal melts.

C. Conformational Changes. Some error criteria of factor analysis of $(n$-$C_{27}H_{35}COOCH_2)_4C$, in the frequency range 1080–1300 cm^{-1}, are listed in Table VII. The number of components of $(n$-$C_{17}H_{35}COOCH_2)_4C$ increases from 3 to 4 when the temperature range is extended from 33–45 °C to 33–46 °C. Namely, a conformational change occurs between 45 and 46 °C and the number of components of $(n$-$C_{17}H_{35}$-$COOCH_2)_4C$ increases from 4 to 5 when the temperature range is extended from 33–47 °C to 33–48 °C. Namely, the second conformational change occurs between 47 and 48 °C. The above-mentioned conformational changes can be substantiated by Fourier transform infrared spectra (FTIR) of $(n$-$C_{17}H_{35}COOCH_2)_4C$ in Figures 2 and 3. Figure 2 manifests that the four spectra at 29, 37, 40, and 43 °C are almost the same. In the spectrum at 45 °C, the right side of the i peaks crooks and so does the left side of the j peak (the oblique lines in the spectra). When the temperature increases to 46 °C, the right side of the i peaks bends obviously, and the j single peak becomes double peaks. This indicates that a conformational change occurs between 45 and 46 °C. The right side of the i peaks bends more, and the j double peaks still exist at 47 °C.

When the temperature increased from 47 to 48 °C, the i peaks change from triple to quadruplet peaks and the j peaks change from double peaks to a single peak (see Figure 3). This indicates that the second conformational change occurs between 47 and 48 °C. Two conformational changes are in good agreement with the conclusions of factor analysis about 45.5 and 47.5 °C.

Some error criteria of factor analysis of $(n$-$C_{17}H_{35}$-$COOCH_2)_4C$ in the frequency range 1080–1300 cm^{-1} are shown in Table VIII where the number of components of $(n$-$C_{17}H_{35}$-$COOCH_2)_4C$ changes from 5 to 4 when the temperature range is decreased from 50–62 °C to 51–62 °C. The third conformational change occurs between 50 and 51 °C. When the temperature range is decreased from 54–62 °C to 55–62 °C, the number of components of $(n$-$C_{17}H_{35}COOCH_2)_4C$ changes from 3 to 2. (The ER also reaches a maximum at no. = 3 besides the maximum at no. = 2, and the value at no. = 2 is much more than one at no. = 3, so we infer the number of components on the basis of the IND and the IE. The ER was only a reference.) The fourth conformational change occurs between 54 and 55 °C. Because at higher temperature the conformational changes are faster, the latter two conformational changes are not seen clearly in the FTIR, but there are still some changes in the i peaks between 50 and 55 °C (see Figure 3).

The above four conformational changes indicate that the energy provided by temperature is not enough to generate conformational changes below 45 °C, where $(n$-$C_{17}H_{35}$-$COOCH_2)_4C$ exists in a stable, dominant conformation. The energy provided by temperature allows conformations to quickly and freely transform between each other above 55 °C; thus the conformational changes of $(n$-$C_{17}H_{35}COOCH_2)_4C$ are not determined by factor analysis and FTIR (see Figures 3 and 4, Tables II–VI). So a temperature range where conformational changes not only occur but are also determined by factor analysis and FTIR is limited to between 45 and 55 °C.

The conclusions of factor analysis of phase transitions and conformational changes in $(n$-$C_{17}H_{35}COOCH_2)_4C$ are summarized in Table IX.

ACKNOWLEDGMENT

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