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Phase Transitions of Pure Long-Chain α,ω-Alkanediols from C_{13} to C_{24}

Yoshihiro Ogawa* and Naotake Nakamura†

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami, Kumamoto 860-8555

†Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University,
Nojihigashi, Kusatsu, Shiga 525-8577

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A series of pure α,ω-alkanediols HO-$(CH_2)_n$-OH (n = 13—24) was prepared and the effects of chain length and parity on their thermal properties were investigated. Crystal structures of odd α,ω-alkanediols were orthorhombic, while those of even α,ω-alkanediols were monoclinic. α,ω-Alkanediols with n = 13—24 showed solid–solid transitions except for n = 14. The solid–solid transition was found to be reversible. Transition temperatures from the crystal to the high-temperature phase indicated distinctive and regular odd-even effects, while from the high-temperature phase to the liquid, slightly odd–even effects were noted. The average enthalpy increment per methylene unit from the crystal to liquid for odd α,ω-alkanediols was 4.0 kJ mol^{-1}. Enthalpies of transition from crystal to high-temperature phases considerably exceeded those of n-alkanes. $HOC_{13}H_{26}OH$ lost 62% total enthalpy at the solid–solid transition and only 38% at melting. High-temperature phases of α,ω-alkanediols may possibly be liquid crystal phases.

Normal alkanes CH_3–$(CH_2)_{n-2}$–CH_3 are very simple long-chain compounds with repeating units –CH_2– and two terminal methyl groups, but their crystal structures and thermal behavior are quite complex. The crystal structures at room temperature of odd n-alkanes are orthorhombic and those of even n-alkanes, triclinic or monoclinic, depending on $n < 26$ or $n \geq 26$, respectively.[1] Those of impure or metastable even n-alkanes are orthorhombic at $n \geq 36$.[2—4] Alkanes have many solid–solid transitions before melting. Two solid–solid phase transitions were found in n-$C_{33}H_{68}$ in addition to the highest-temperature solid–solid transition ("rotator phase" transition).[5]

A study was done to observe the effects of different terminal groups on phase transition. The thermal properties of α,ω-bis{4-(4-biphenylyloxycarbonyl)phenyl}alkanedioates formed by a sequence of mesogen—methylene units—mesogen were studied,[6,7] and a liquid crystal phase (nematic phase) after melting from n = 8 to n = 18 was noted. These compounds are called dimeric liquid crystals, and they have been studied widely as model compounds of liquid crystal polymers.[8,9]

Long-chain α,ω-alkanediols HO–$(CH_2)_n$–OH are used as raw materials for the synthesis of liquid crystal polymers or biodegradable polyesters.[10,11] The crystal structures and thermal properties of long-chain α,ω-alkanediols have been studied only sparingly. Physical data on α,ω-alkanediols of higher molecular weight are particularly few. Long-chain α,ω-alkanediols are simple compounds similar to n-alkanes. Normal alkanes and α,ω-alkanediols have the same repeating unit, –CH_2–. The basal surfaces of n-alkane lamellae are composed of methyl groups, but alkanediols have terminal hydroxy groups which form a network of H-bonds. The effects of –OH end groups on crystallization and phase transitions of α,ω-alkanediols should thus be different from those of n-alkanes. α,ω-alkanediols with n = 16 were previously shown to have solid–solid phase transitions.[12] The transition subsequently was found to be rotator phases reported for n-alkanes.

Some structure and thermodynamic properties of long-chain compounds are sensitive to parity and chain length. Twelve α,ω-alkanediols, from $HOC_{13}H_{26}OH$ to $HOC_{24}H_{48}OH$, including odd-number carbon members were prepared in this study and the effects of chain length and parity on thermal behavior of α,ω-alkanediols were investigated.

Experimental

Materials. α,ω-Alkanedioic acids $HOOC(CH_2)_{n-2}COOH$ were obtained from Tokyo Kasei (n = 9—16, 18, 20) and Aldrich (n = 22). Diacids with n = 17, 19, 21, and 23 were obtained from short-chain diacids by ketene dimerization synthesis.[13] The diacid with n = 24 was prepared by the Wolff–Kishner reduction of 7,18-dioxotetracosanedioic acid formed by reaction of 1-morpholino-1-cyclohexene and dodecanedioyl chloride.[14] Diacids with n = 9—24 were converted to methyl esters by conventional procedures. The pure compounds were obtained through fractional distillation and recrystallization, and purity was 99.9% or more according to capillary gas chromatography.

The pure dimethy esters were further reduced to α,ω-alkanediols by $LiAlH_4$. Crystalline α,ω-alkanediols were obtained by slow crystallization from toluene solution.

Measurements. The α,ω-alkanediols were examined at room temperature by X-rays using powder methods. 2θ could be read directly from traces at an accuracy exceeding ±0.02 from 1° to 40°. D-spacings were calibrated using silicon powder with a 200 mesh, which provides a 2θ angle of 28.46°.

Melting points were measured in capillary tubes by the usual method. Transition temperatures and enthalpies of these α,ω-alkanediols were measured on a Seiko DSC SSC560 differential scanning calorimeter at 1 $\mathrm{K\,min^{-1}}$. Solid–solid transition temperatures were measured from the positions of peak maxima. Heat quantity was computed from the peak area of DSC using indium as the standard. Value accuracy was within 3%.

Results and Discussion

Crystal Structure. Figure 1 shows plots of long periods L of crystalline α,ω-alkanediols HO–$(CH_2)_n$–OH obtained by X-ray powder diffraction versus the number n of methylene units. For the odd number series (line A), the linear equation was,

$$L = 1.277n + 2.33 \ (\text{Å}). \tag{1}$$

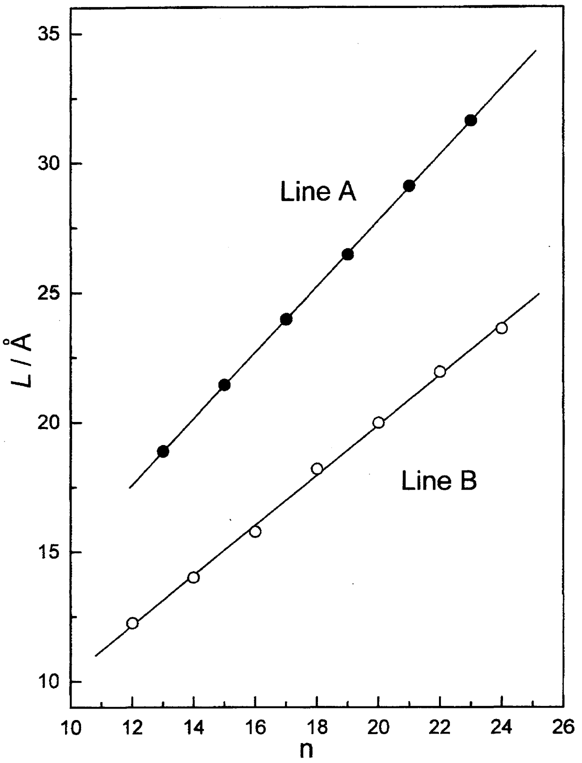

Fig. 1. Long periods L of crystalline α,ω-alkanediols versus the number n of methylene units. Line A: odd, Line B: even α,ω-alkanediols.

This equation demonstrates the additivity of contributions from polymethylene and terminal hydroxy groups and is essentially the same as the relation $L = 1.270n + 1.98$ (Å) proposed by Broadhurst for orthorhombic crystals of n-alkanes.[1] 1.277 Å of the first term in formula (1) agrees almost with that of n-alkanes; that is, α,ω-alkanediols and n-alkanes have the same length per methylene unit. The 2.33 Å of the second term in formula (1) is somewhat longer than the 1.98 Å of n-alkanes since the terminal groups differ. The crystal structure of $HOC_{13}H_{26}OH$ has been analyzed from single crystal X-ray diffractometry and shown to be orthorhombic; the skeleton of the molecule is completely in the *trans*-conformation.[15] The long period of $HOC_{13}H_{26}OH$ in this study is 18.93 Å as shown in Table 1, which is consistent with the 18.78 Å of single crystal $HOC_{13}H_{26}OH$. Odd α,ω-alkanediols may possibly have the same orthorhombic form as $HOC_{13}H_{26}OH$ in consideration of the linearity of L vs. n.

There are two reports on the crystal structures of even α,ω-alkanediols. The structures of single crystal $HOC_{12}H_{24}OH$ ($a = 4.964$, $b = 5.190$, $c = 24.497$ Å, $\beta = 90.75°$) and $HOC_{16}H_{32}OH$ ($a = 4.980$, $b = 5.207$, $c = 31.396$ Å, $\beta = 91.71°$) are monoclinic with all-*trans* conformation skeletons.[16,17] Structural features show the herring-motif with different β, but differences are not significant. Should even α,ω-alkanediols be similar in monoclinic form, the following linear equation will apply for the even number series (line B).

$$L = 0.967n + 0.565 \ (\text{Å}). \tag{2}$$

Polymethylene in a molecule of an α,ω-alkanediol is assumed to have an extended zigzag structure of length 1.27 Å per methylene. The angle θ between the polymethylene chain and the planes of ends by equation $\sin\theta = 0.967/1.27$ was found to be 50°.

The crystal structures of even α,ω-alkanediols depend on crystallization conditions. The crystallization of even α,ω-

Table 1. Long Periods L and Thermodynamic Properties of Crystalline α,ω-Alkanediols HO–C_n–OH

HO–C_n–OH	L/Å	L/Å	T_t/°C	T_m/°C	ΔH_t / kJ mol^{-1}	ΔH_m / kJ mol^{-1}	ΔH_{sum} / kJ mol^{-1}	$\Delta H_t/\Delta H_{sum}$
C_{13}	18.93		69.8	77.8	28.9	17.8	46.7	0.619
C_{14}		14.03	—	87.2		61.9	61.9	
C_{15}	21.51		76.2	88.2	35.1	23.6	58.7	0.598
C_{16}	(22.75)[a]	15.71	89.9	92.2	[b]	64.2	64.2	
C_{17}	24.04		81.4	94.1	34.9	30.8	65.7	0.531
C_{18}	(25.34)	18.27	92.9	98.3	38.7	33.6	72.3	0.535
C_{19}	26.53		85.7	100.7	37.1	35.7	72.8	0.510
C_{20}	(27.82)	19.98	95.4	102.9	37.0	39.7	76.7	0.482
C_{21}	29.18		86.8	104.3	38.8	41.7	80.5	0.482
C_{22}	(30.48)	22.10	96.5	106.2	39.8	46.5	86.3	0.461
C_{23}	31.71		93.1	107.5	41.8	46.5	88.3	0.473
C_{24}	(32.97)	23.64	99.5	108.3	42.7	51.2	93.9	0.455

a) L given in parentheses are the values of metastable crystals. b) Transition temperature too close to melting point for ΔH_t to be determined.

alkanediols by rapid crystallization from benzene or ethanol solution resulted in the orthorhombic form (parentheses in Table 1) and from slow crystallization, in monoclinic unit cells, respectively. This is essentially in agreement with the results by Takamizawa et al. for n-$C_{48}H_{98}$.[3)]

Thermal Properties. Typical DSC heating and cooling curves of a solution recrystallized $HOC_{24}H_{48}OH$ sample are shown in Fig. 2. In addition to the solid–liquid transition at 108.5 °C, a solid–solid transition was observed at 99.5 °C on heating and noted to be reversible. $HOC_{14}H_{28}OH$ showed no solid–solid transition. The other α,ω-alkanediols displayed solid–solid transitions. Kobayashi et al. showed the high-temperature phase of $HOC_{16}H_{32}OH$ to be a smectic G liquid crystal by X-ray diffraction, and a rotator type by the dielectric constant measurement.[12)] It is also considered that the angle of the molecular axes between the alternate layers increase to about 180° to enable the molecule to rotate easily for even alkanediols.

Figure 3 presents the crystal–high-temperature phase (T_t) and high-temperature phase–liquid (T_m) transition temperatures as a function of n. T_t and T_m were found to increase with n. T_m showed a slight odd–even effect, while T_t had a distinctive and regular odd–even effect. T_t of even members are laid on the upper curve. Normal alkanes[18)] and primary alcohols[19)] showed the same thermal behavior as α,ω-alkanediols. The effects of parity on melting and solid–solid transition behavior may be explained based on structure. The crystal structures of n-alkanes, n-primary alcohols, and α,ω-alkanediols having even-numbered methylene units were noted to be monoclinic and those for odd-numbered methylene units, orthorhombic. Tilted structures appeared more stable than vertical structures at low temperature. Parity had no effect on the melting of n-alkanes, primary n-alcohols, or α,ω-alkanediols. Differences in structures of the odd and even members thus apparently do not exist in the high-temperature phase. The temperature range over which high-temperature phases of even α,ω-alkanediols exist becomes

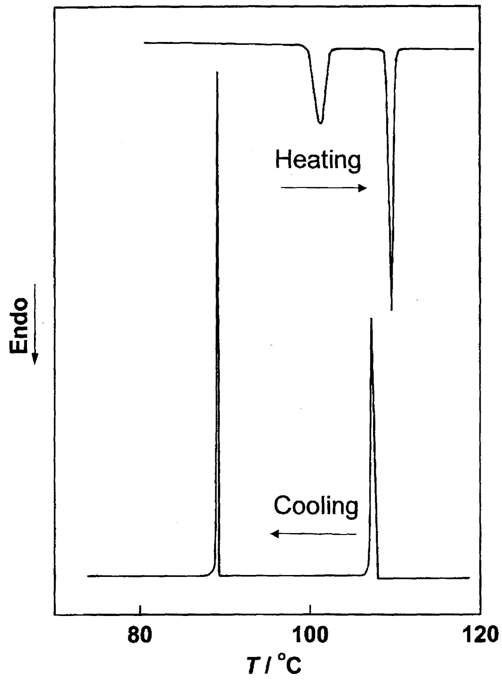

Fig. 2. DSC heating and cooling curves of $HOC_{24}H_{48}OH$.

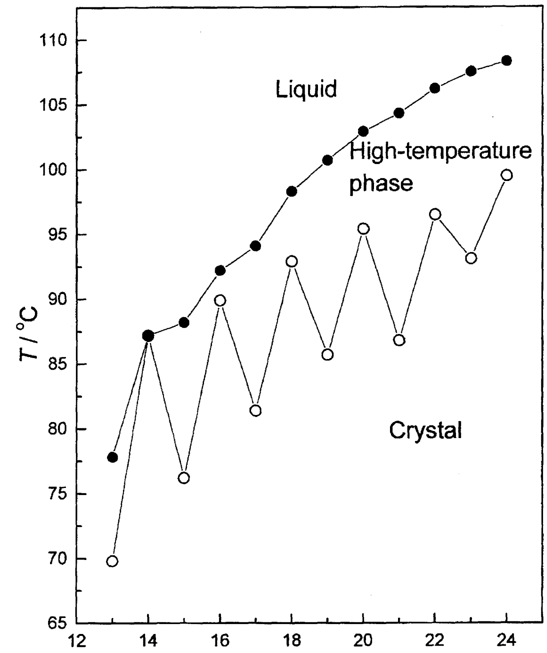

Fig. 3. Dependence of melting, T_m (●), and solid–solid transition, T_t (○) temperatures of α,ω-alkanediols on n.

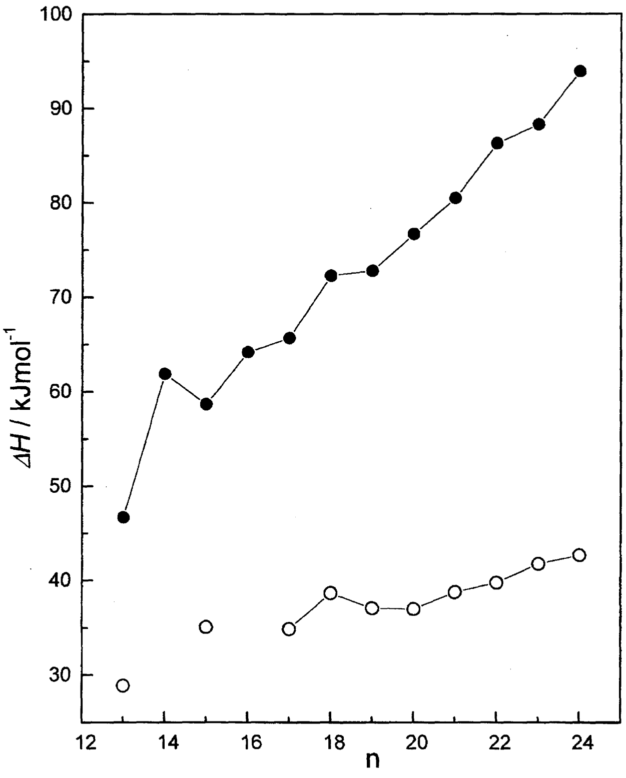

Fig. 4. Dependence of crystal–liquid, ΔH_{sum} (●), and solid–solid, ΔH_t (○), transition enthalpies of α,ω-alkanediols on n.

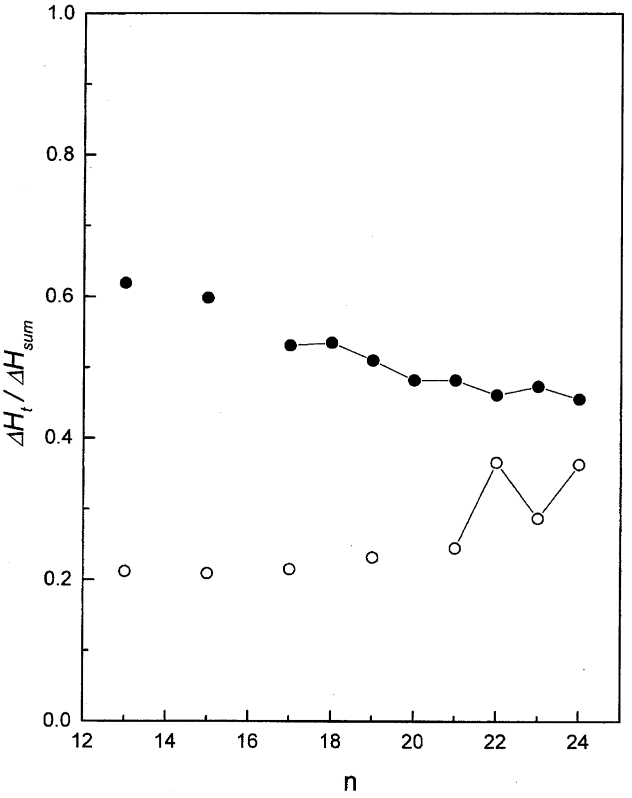

Fig. 5. Dependence of $\Delta H_t/\Delta H_{sum}$ of α,ω-alkanediols (●) and n-alkanes (○) with n = 13—24 on n.

smaller with decreases in n, and finally at $n = 14$ no high-temperature phase is detectable, while the temperature range for odd α,ω-alkanediols remains almost constant independent of n between $n = 13$ and 23. These results of α,ω-alkanediols are analogous to those of n-alkanes. Normal alkanes with only carbon number $9 \leq n_{odd} \leq 43$ or $20 \leq n_{even} \leq 42$ show the high-temperature phase (rotator-phase).$^{1)}$

The enthalpies of solid–solid transitions ΔH_t and melting ΔH_m on heating are listed in Table 1. ΔH_{sum} was computed as the sum of ΔH_t and ΔH_m. ΔH_t and ΔH_{sum} are plotted in Fig. 4 as a function of n. A solid–solid transition temperature of $HOC_{16}H_{32}OH$ was too close to melting point for ΔH_t to be measured. Odd-even effects for ΔH_t and ΔH_{sum} were apparent and decreased with increase in n. For n = 13—23, ΔH_{sum} of odd α,ω-alkanediols was noted to increase almost linearly as a function of n. Increase for the odd series was, on the average, $[\Delta(\Delta H_{sum})]$ of 4.0 kJ mol^{-1} per methylene unit, which is essentially 3.8 kJ mol^{-1} per methylene unit of odd n-alkanes with n = 13—23.$^{1)}$ In the crystal state, odd α,ω-alkanediols and n-alkanes would thus appear to have the same methylene packing.

$\Delta H_t/\Delta H_{sum}$ as representative of the order in the high-temperature phase relative to that of the crystal phase was measured. $\Delta H_t/\Delta H_{sum}$ data are listed in Table 1. Figure 5 shows $\Delta H_t/\Delta H_{sum}$ of α,ω-alkanediols and n-alkanes with n = 13—24 as a function of n. All odd n-alkanes with n = 9—23 and even n-alkanes with n = 22, 24 underwent one solid–solid transition. The high-temperature phase is often termed the "rotator" or "hexagonal phase". No even n-alkanes with $n \leq 20$ showed a solid–solid transition. For shorter members of this series, $\Delta H_t/\Delta H_{sum}$ of α,ω-alkanediols was much larger than that of n-alkanes, being 0.62 for $HOC_{13}H_{26}OH$, while for $C_{13}H_{28}$ it was only 0.21. The former value is quite large. $HOC_{13}H_{26}OH$ loses 62% of ΔH_{sum} at the solid–solid transition and only 38% at melting. The high-temperature phases of α,ω-alkanediols may possibly be liquid crystal phases. Differences in $\Delta H_t/\Delta H_{sum}$ for α,ω-alkanediols and for n-alkanes become smaller and smaller with increases in n.

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