

Effects of Spacer Length on Thermal Properties of Dimeric Model Compounds for Main Chain Liquid Crystalline Polymers

Yoshihiro OGAWA

Department of Chemistry, Faculty of General Education,
Kumamoto University, Kumamoto 860, Japan

(Received September 1, 1995)

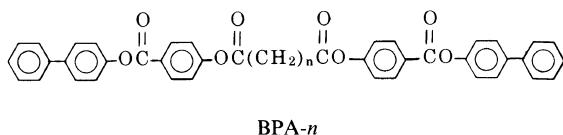
ABSTRACT: The thermal properties of a series of α,ω -bis[4-(4-biphenyloxy)carbonyl]phenyl]alkanedioates (BPA-*n*) dimeric liquid crystals containing even-number methylene spacer from $n=8$ to $n=20$ were studied. All synthesized compounds showed the same crystal form at room temperature. They were all enantiotropic nematic except BPA-20 which was monotropic. The temperature range over which the nematic phase exists becomes smaller with increasing spacer length, and finally at $n=20$ it no longer shows liquid crystal on heating. Thermodynamic quantities were classified as contributions from mesogens and polymethylene spacers. The overall entropies ΔS_{KI} of transition from crystals at room temperature to the isotropic liquid were shown as a linear equation of the number, n , of methylene units as follows, $\Delta S_{KI}=8.50n+95.4\text{ JK}^{-1}\text{ mol}^{-1}$. The coefficient ($8.50\text{ JK}^{-1}\text{ mol}^{-1}$), which means the increase in ΔS_{KI} value per methylene, corresponds well to melting entropy per methylene of n -alkanes. The entropies of transition from nematic to isotropic phase were almost constant ($8.3\text{--}8.9\text{ JK}^{-1}\text{ mol}^{-1}$), independent of the number of methylene units in the flexible spacer.

KEY WORDS Dimer / Liquid Crystal / Nematic Phase / Model Compounds / Spacer Length Effect / Thermotropic Polyester / Long Spacer / Mesogens / Thermal Properties /

Dimeric liquid crystals formed by a sequence of mesogen-spacer-mesogen are low molecules from the standpoint of the degree of polymerization, though these nematic-isotropic transition temperatures and heats of transition depend on odd or even numbers of methylene units in the spacer, very much the same as main chain liquid crystalline polymers with repeated units of mesogen-spacers.^{1–3} This is a quite different character from low molecular mass liquid crystals which have small odd–even oscillation. Therefore dimeric liquid crystals are considered as a proper model of liquid crystalline polymer. There are many reports stating how the thermodynamic quantity of dimeric liquid crystals depends on spacer length,^{4,5} but there is no study that treats such thermodynamic quantity quantitatively with separation of contribution of mesogens and contribution of polymethylene spacer parts respectively.

If spacer length becomes certain large and crystal structures of compounds show same form, then we consider that contribution caused by mesogens and polymethylene spacer would work almost independently for thermodynamic quantity of phase transitions, and then handle dimeric compounds with considerably long polymethylene chain.

In this work, we synthesized and studied dimeric liquid crystals having long polymethylene chain, as shown below:



We designated these dimers BPA-*n*, which consist of both a flexible even-number polymethylene spacer of varying length ($n=8, 10, 12, 14, 16, 18, 20$) and two terminal mesogens. Since the nematic-isotropic transition temperatures of the dimers with even numbers less

than $n=8$ were so high that the precise thermodynamic quantities could not be obtained, they were not dealt with here. The dimers with odd numbers will not be dealt with here, because they have a crystal structure different from that of dimers with even numbers. The main objective of this work was the classification of thermodynamic quantities of dimers in terms of mesogens and polymethylene spacers. We can thereby discuss quantitatively the effects of spacer length and mesogens for generation or regularity of nematic phase of liquid crystals.

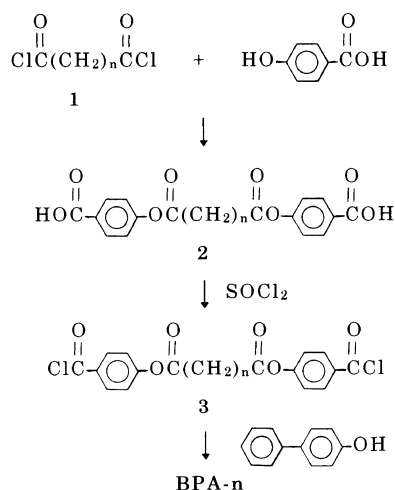
EXPERIMENTAL

Materials

Sebacic acid, dodecanedioic acid, tetradecanedioic acid, hexadecanedioic acid, eicosanedioic acid, *p*-hydroxybenzoic acid, and *p*-phenylphenol manufactured by Tokyo Kasei were used as received. Octadecanedioic acid and docosanedioic acid were obtained by the method of Hünig.⁶ For example, docosanedioic acid was prepared by Wolff–Kishner reduction of 7,16-diketodocosanedioic acid, formed by reaction of 1-morpholino-1-cyclohexene and sebacoyl chloride.

Dimers Synthesis

α,ω -Bis[4-(4-biphenyloxy)carbonyl]phenyl]alkanedioates (BPA-*n*) were prepared according to Scheme 1. 4,4'-(Alkanedioyldioxy)dibenzoic acids **2** were obtained from aliphatic diacyl chloride **1** and *p*-hydroxybenzoic acid by the method of Biligin.⁷ 4,4'-(Alkanedioyldioxy)-dibenzoyl dichlorides **3** were obtained by reaction of **2** with excess thionyl chloride in the presence of **1** drop of dry *N,N*-dimethylformamid. A solution of 0.01 mol of **3** and 0.1 mol of excess *p*-phenylphenol dissolved in 100 ml of dry 4:1 benzene–pyridine was heated to reflux for six hours. The reaction mixture was cooled to room temperature and poured into a methanol to pre-

Scheme 1. Synthetic route of dimers BPA-*n*.Table I. Elemental analysis of BPA-*n*

BPA- <i>n</i>	C%	H%
BPA-8	77.30 (77.19) ^a	5.67 (5.67)
BPA-10	77.33 (77.49)	5.82 (5.98)
BPA-12	77.73 (77.78)	6.27 (6.28)
BPA-14	78.16 (78.05)	6.28 (6.55)
BPA-16	78.05 (78.30)	6.83 (6.81)
BPA-18	78.53 (78.53)	7.02 (7.04)
BPA-20	78.73 (78.74)	7.22 (7.22)

^a Values in parentheses are those calculated.

precipitate the produced crude BPA-*n*. The products were at first purified by column chromatography on silica gel. A mixture of xylene and toluene was used as the developing solvent. Repeated recrystallizations from tetrahydrofuran gave pure BPA-*n*. The results of elemental analysis are in good agreement with the calculated values shown in Table I. All crystalline BPA-*n* used in this study were crystallized from dilute tetrahydrofuran solution.

Measurements

Transition temperatures and enthalpies of BPA-*n* were measured on a Rigaku DSC 8240 differential scanning calorimeter at a heating rate of 3 K min⁻¹. Heat quantity was taken from peak area of DSC based on Indium as the standard. Optical textures were determined using a Olympus BH-2 optical polarizing microscope with heating stage Mettler FP80/82.

Lattice constants were determined with Weissenberg camera using nickel-filtered Cu-*K*_α radiation. Wide-angle X-ray diffraction patterns were recorded with Rigaku diffractometer.

RESULTS AND DISCUSSION

Crystal Structure

The crystal structure of BPA-8 is monoclinic and the space group is P2₁/a (*a* = 5.89 Å, *b* = 7.48 Å, *c* = 42.9 Å, β = 90.8°). There are two molecules in unit cell. So molecules fill the cell without losing central symmetry. The values of *a*-axes and *b*-axes for crystalline BPA-14 and BPA-18 from a rotational photograph were 5.86 Å

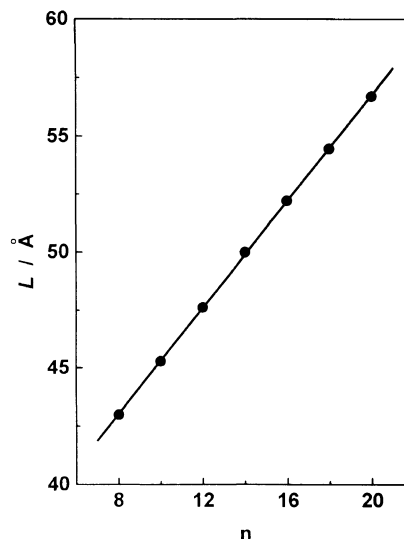


Figure 1. Long period *L* of crystalline BPA-*n* versus the number, *n*, of methylene units in a flexible spacer.

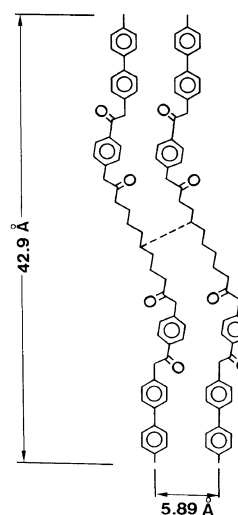


Figure 2. Schematic arrangement of crystalline BPA-8 molecules in the unit cell. Dotted line indicates the cross section of a zigzag chain.

and 7.48 Å, respectively, and almost same as crystalline BPA-8. Considering that a long period is a linear function of the number of methylene units, then an even number of BPA-*n* is considered to have the same crystal form as BPA-8.

Figure 1 shows plots of long period *L* of crystalline BPA-*n* obtained by X-ray powder diffraction versus the number, *n*, of methylene units. For an even number series, a linear equation is,

$$L = 1.14n + 33.9 (\text{Å}) \quad (1)$$

For even number series crystals, a polymethylene spacer in a molecule is assumed to form extending zigzag structure which has the length 1.27 Å per methylene. The angle between the polymethylene chain and the layer thus becomes 64°. Whole a molecule formed extending structure, then molecular length of BPA-8 would be 42.8 Å, and this corresponds well to actual measured *c* axis length 42.9 Å. The calculated value 33.8 Å of the length of two mesogens corresponded nearly to 33.9 Å of the second term in formula (1).

Figure 2 illustrates the approximate molecular ar-

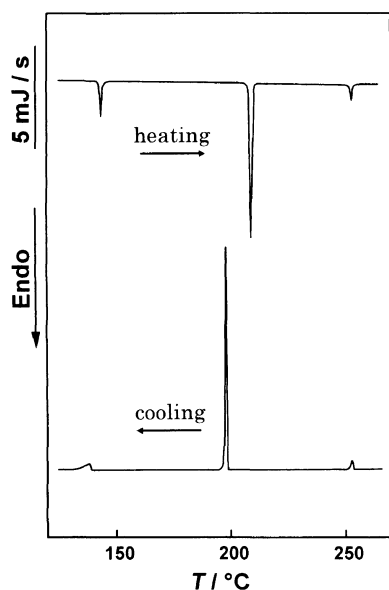


Figure 3. DSC heating and cooling thermograms of BPA-8.

Table II. Long periods L and thermodynamic properties of crystalline BPA- n

BPA- n	L Å	T_{KN} °C	T_{NI} °C	ΔS_{KI} JK ⁻¹ mol ⁻¹	ΔS_{NI} JK ⁻¹ mol ⁻¹
BPA-8	43.0	206	248	163	8.7
BPA-10	45.3	202	230	178	8.8
BPA-12	47.6	197	218	201	8.9
BPA-14	50.0	194	206	214	8.7
BPA-16	52.2	190	196	233	8.6
BPA-18	54.5	187	189	249	8.3
BPA-20	56.7	(184) ^a		262	

^a Value in parentheses is crystal-isotropic transition temperature.

range of BPA-8 in the crystal phase. Cross sectional area in vertical direction to the polymethylene chain, shown as the dotted line in the figure, is 39.6 Å², and this is only 7% larger than that of n -alkane crystals, *e.g.*, hexatriacontane crystal which has a cross sectional area 36.7 Å².⁸ Cohesive energy density of methylene parts is considered to almost correspond to that of n -alkane crystals.

Transition Temperatures

Figure 3 shows DSC heating and cooling thermograms of BPA-8. On heating, three endothermic peaks were found. The sequence of phase transitions is as follows: solid–solid, solid–nematic, nematic–isotropic, because schlieren texture which is characteristic of nematic was observed after melting by optical polarizing microscope.

All synthesized compounds were enantiotropic nematic except BPA-20 which was monotropic nematic. Thermodynamic data for each dimers are given in Table II. Figure 4 shows the dependence of crystal–nematic (T_{KN}) and nematic–isotropic (T_{NI}) transition temperatures *versus* n . Because T_{NI} more closely depends on n than T_{KN} , the temperature range over which the nematic phase exists becomes smaller with increasing spacer length, and finally at $n=20$ it no longer shows liquid crystals on heating. Even when spacer length increases,

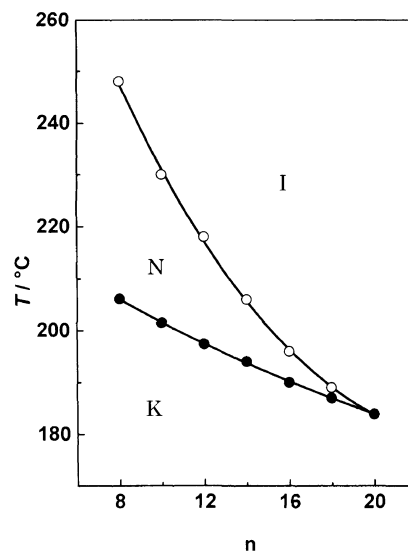


Figure 4. Dependence of crystal–nematic, T_{KN} (●), and nematic–isotropic, T_{NI} (○), transition temperatures of BPA- n versus the number, n , of methylene units in a flexible spacer (K, crystalline; N, nematic; I, isotropic).

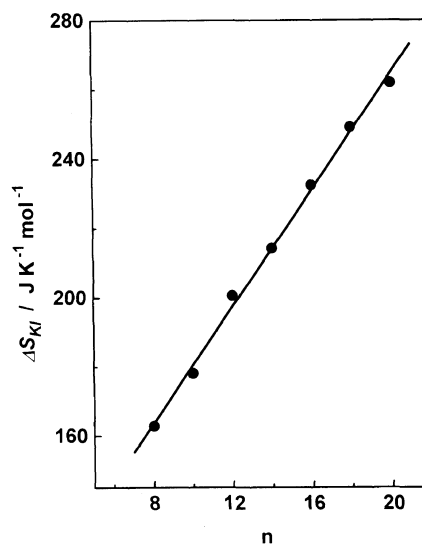


Figure 5. Overall entropy change ΔS_{KI} of transition from crystals at room temperature to the isotropic liquid as a function of the number, n , of methylene units in the flexible spacer.

it does not reveal a smectic phase. These results are characteristic of dimeric crystals and liquid crystalline polymer. Liquid crystals of small molecules tend to be smectic as polymethylene spacer increases in length.⁹

Entropy Change for Crystal–Isotropic Phase Transition

Including solid–solid transition, the overall entropy change ΔS_{KI} of transition from crystals at room temperature to the isotropic liquid is plotted as a function of n as shown in Figure 5. Obtained linear function is expressed as

$$\Delta S_{KI} = 8.50n + 95.4 \quad (\text{JK}^{-1} \text{mol}^{-1}) \quad (2)$$

This equation demonstrates the additivity of contributions from polymethylene spacers and mesogens. Therefore, eq 2 can be rewritten as: $\Delta S_{KI} = \Delta s_{KI}^F n + \Delta S_{KI}^M$. Δs_{KI}^F is the entropy change of methylene unit in the flexible spacer, and ΔS_{KI}^M is the entropy change of

mesogens, at the crystal-isotropic transition. The value $8.50 \text{ J K}^{-1} \text{ mol}^{-1}$ of $\Delta S_{\text{KI}}^{\text{F}}$ nearly corresponds to actual measured melting entropy $9.9 \text{ J K}^{-1} \text{ mol}^{-1}$ per methylene of polyethylene single crystal.¹⁰ This indicates that the polymethylene spacer of BPA- n in isotropic liquid has conformational diversity, as does also polyethylene liquid. As described for crystal structure, cross sectional area of the polymethylene chain of BPA- n is slightly larger than that of n -alkane crystals, and this contributes to the difference in $\Delta S_{\text{KI}}^{\text{F}}$ of BPA- n and melting entropy per methylene of crystalline n -alkanes. In this sense, using $\Delta S_{\text{KI}}^{\text{M}}$ of mesogens from data of other series dimeric compounds, it may be possible to make thermodynamic characterization for various mesogens.

Entropy Change for the Nematic-Isotropic Phase Transition

Nematic-isotropic transition entropies ΔS_{NI} are shown in Table II for BPA- n . When n becomes larger, the ΔS_{NI} decreases a little, but as ΔS_{NI} itself is small, it is possible to consider that the ΔS_{NI} is constant independent of n . This seems in conflict with Abe's report that in the liquid crystalline state of dimeric liquid crystals which have even number methylene chains, they have trans structures at every second methylene chain.^{11,12} But this contradiction is eliminated in consideration of differences in mesogenic groups. Basically n dependence of ΔS_{NI} varies for each kind of liquid crystalline polymer^{2,3} and dimeric liquid crystals^{4,5} containing even-number poly-

methylene spacers. These differences are due to the presence of various mesogens and different linking sequences between mesogens and spacers. These points will be clarified based on additional study on n dependence of ΔS_{NI} for many dimeric compounds which have various mesogens.

Acknowledgment. The author thanks the late Professor K. Takamizawa, Kyushu University, for assistance in crystal structure analysis of BPA-8.

REFERENCES

1. A. Griffin and T. Britt, *J. Am. Chem. Soc.*, **103**, 4957 (1981).
2. A. Blumstein and O. Thomas, *Macromolecules*, **15**, 1264 (1982).
3. A. Roviello and A. Sirigu, *Makromol. Chem.*, **183**, 895 (1982).
4. N. Koide and K. Iimura, *Mol. Cryst. Liq. Cryst.*, **153**, 73 (1987).
5. A. Griffin, S. Vaidya, R. Hung, and S. Gorman, *Mol. Cryst. Liq. Cryst. Lett.*, **1**, 131 (1985).
6. S. Hünig, E. Lücke, and W. Brenninger, *Org. Synth. Coll.*, Vol. **5**, 533 (1973).
7. A. Yu. Bilibin, A. V. Ten'Kovtsev, and S. S. Skorokhodov, *Makromol. Chem., Rapid Commun.*, **6**, 209 (1985).
8. M. Shearer and V. Vand, *Acta Cryst.*, **9**, 379 (1956).
9. G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, London, 1962.
10. B. Wunderlich, "Macromolecular Physics," Vol. 3, "Crystal Melting," Academic Press, New York, N.Y., 1980, p 58.
11. A. Abe and S. Y. Nam, *Macromolecules*, **28**, 90 (1995).
12. A. Abe, H. Furuya, R. N. Shimizu, and S. Y. Nam, *Macromolecules*, **28**, 96 (1995).