SHORT COMMUNICATIONS

An Odd-Even Effect in the Mesophasic Behavior of Dimer Liquid Crystals Due to the Bond Orientation of a Phenylene Unit Incorporated in the Flexible Spacer

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Main-chain liquid crystalline polymers such as $[X-mesogenic core-X(CH_2)_m]_x$ (X = an ether or ester group) often form a thermotropic nematic mesophase.¹⁻⁴ The isotropization temperature T_{NI} , and the associated transition enthalpy $\Delta H_{\rm NI}$ and entropy $\Delta S_{\rm NI}$ are known to exhibit an odd-even oscillation with the number of intervening methylene units $m.^{1-4}$ As have been demonstrated in many examples,⁵⁻¹¹ dimer model compounds, composed of two mesogenic cores and a flexible spacer, also exhibit a very similar transition behavior. The conformational analysis of the spacer indicates that the angular correlation between the neighboring mesogenic cores varies largely with the parity of m.¹² When the number (m) of methylene units in the flexible spacer is even, the parallel orientation of successive mesogenic cores are allowed. Thus, it should be easy for these polymers to adopt the nematic order in the mesophase. For the m = odd system, however, two successive cores are inevitably inclined with each other at some angle in the range 50 to 90 degrees. These results suggest that the orientational order of the mesogenic core may be lower for polymers of the m = oddseries. In fact, the order parameter of the mesogenic core, as revealed by the D-NMR

studies on some representative dimer models, is substantially lower for $m = \text{odd.}^{13,14}$ The odd-even oscillation observed in the orientational characteristics of the nematic mesophase mainly arises from the tetrahedral nature of the methylene carbon.^{12,15} The results of D-NMR studies on polyesters, polyethers as well as their model compounds having deuterated spacers were reported by Samulski et al.¹⁶ and Yoon et al.¹⁷ Although the actual procedures are quite different between these two research groups, both reached a conclusion that under the anisotropic environment, internal rotations around the C-C bonds are largely restricted to give highly extended conformations.

In an interest to pursue the role of the flexible spacer in determining thermodynamic properties of these molecules, we synthesized a series of compounds, 1,4-bis((ω -4,4'-cyanobiphenyloxy)alkoxy)benzene:



We designate this series as Pn. From the geometrical point of view, the O- ϕ -O group

situated in the middle of the molecule can be replaced by a virtual bond spanning the $O \cdots O$ distance. Since the axial ratio of this group is small (less than 2), it should be regarded as a part of the flexible spacer. In the Pn series, the spacer joining the two cyanobiphenyl groups comprises 2n methylene units. As may be shown by a simple manipulation, the two mesogenic groups located on both terminals can be arranged parallel to each other without assuming any high energy conformations of rare occurrence. This holds true regardless of the parity of n. The orientation of the O- ϕ -O group, as represented by a virtual bond, varies alternately with n: the alignment of this bond can be parallel to those of the terminal mesogenes only when n =even. If the orientation of such a sub-mesogenic unit (*i.e.*, O- ϕ -O) incorporated in the flexible spacer is unimportant, we should expect a monotonous change in thermodynamic quantities such as $T_{\rm NI}$, $\Delta H_{\rm NI}$, and $\Delta S_{\rm NI}$ when plotted as a function of n.

For comparison, we also prepared trimer liquid crystals, 4,4'-bis((ω -4,4'-cyanobiphen-yloxy)alkoxy)biphenyl (abbreviated as Bn):



They differ from the aforementioned Pn series by incorporation of a biphenylene group in place of phenylene. The O- ϕ - ϕ -O group located in the middle of the chain is sufficiently anisotropic to take part in the formation of mesophase. For this series of compounds, a distinct odd-even oscillation of thermodynamic quantities at the nematic-isotropic transition is anticipated.^{8,9}

RESULTS AND DISCUSSION

The two series of compounds, Pn and Bn, were prepared according to a conventional method.^{8,9,18,19} All the compounds obtained were characterized by using NMR and IR spectroscopy.

Thermodynamic data obtained by DSC are summarized in Table I. The temperatures listed here are those recorded on the cooling cycles. Somewhat surprisingly, Pn's of n= odd do not show any stable mesophase. These results were consistent with observations under the polarizing microscope. Accordingly, transition temperatures $T_{\rm KI}$ for the crystalisotropic transformation are listed for these compounds. For the rest of the samples, including those of Bn, an enantiotropic nematic mesophase was detected by the microscopic examination. In the DSC measurements, the transition ($T_{\rm NI}$) between the nematic and iso-

Compound	$\frac{T_{\rm KN}(T_{\rm KI})^{\rm b}}{\rm deg}$	T _{NI} deg	$\frac{\Delta H_{\rm KN} (\Delta H_{\rm KI})^{\rm b}}{\rm kcalmol^{-1}}$	$\frac{\Delta H_{\rm NI}}{\rm kcalmol^{-1}}$	$\frac{\Delta S_{\rm KN} (\Delta S_{\rm KI})^{\rm b}}{{\rm cal}{\rm mol}^{-1}{\rm deg}^{-1}}$	$\frac{\Delta S_{\rm NI}}{{\rm cal}{\rm mol}^{-1}{\rm deg}^{-1}}$
B 6	187.7	249.5	10.50	2.85	22.8	5.45
P4	164.3	222.9	8.06	3.05	18.4	6.16
P5	(160.5)		(15.20)		(35.1)	
P6	149.7	191.8	7.19	3.21	17.0	6.90
P 7	(141.0)		(17.20)		(41.5)	
P8	138.4	168.9	15.40	3.41	37.4	7.72

Table I. Summary of thermodynamic data for two series of compounds, Bn and Pn^a

^a Values are from DSC measurements at a cooling rate of 10 deg min⁻¹: symbols K, N, and I represent solid, nematic, and isotropic phase, respectively.

^b Values in parentheses are those for the crystal-isotropic transition.



Figure 1. Variation of the phase transition temperature as a function of $n: T_{NI}(\bigcirc)$ and $T_{NK}(\bigcirc)$ for Pn with $n = \text{even}; T_{KI}(\bigtriangleup)$ for Pn with $n = \text{odd}; T_{NI}(\blacksquare)$ and $T_{NK}(\Box)$ for Bn. The solid and broken lines indicate the oddeven oscillation of T_{NI} expected for the Bn series.

tropic phase was clearly observed in addition to the one $(T_{\rm KN})$ for the crystallization.

In Figure 1, the nematic-isotropic transition temperatures $T_{\rm NI}$ are plotted as a function of n. The experimental data for the Pn and Bn series are indicated by filled circles and respectively. The isotropization squares. temperature $T_{\rm NI}$ of trimer compound B6 lies above that of P6. That is, replacement of the biphenylene group by a phenylene in the middle of the chain amounts to a decrease of ca. 50°C in T_{NI} . As indicated in Table I, the value of $\Delta H_{\rm NI}$ observed for P6 is comparable to that of B6. In general, values of $\Delta H_{\rm NI}$ are closely related to the orientational order of mesogenic cores in the mesophase.^{17,20} A preliminary study on the order parameter of the nematic phase of P6 was performed by dissolving a small amount of anthracene- d_{10} as a probe. The quadrupolar splitting Δv observed in the D-NMR spectra gave an estimate of the major orientational order parameter $S_{zz} = 0.58$ for the probe near the N \rightarrow I transition. The value of S_{zz} thus obtained is considerably high as compared to those reported for dimer liquid crystals having a comparable chain length.²¹ These results are consistent with the aforementioned observations on $\Delta H_{\rm NI}$. The observed decrease in $T_{\rm NI}$ from B6 to P6 is mainly attributable to the $\Delta S_{\rm NI}$ term (cf. Table I).

A more profound effect was found in the n = odd system. While B5 forms a stable nematic liquid crystalline phase, P5 exhibits no mesophase. As demonstrated by Emsley et al.8 and Griffin et al.,9 a series of dimer model compounds $NC\phi\phi - O(CH_2)_m O - \phi\phi CN$ are known to form a stable nematic mesophase regardless of the parity of m in the range m = 4 to 12. The role of the O- ϕ -O unit situated in the middle of P5 is somewhat peculiar. As stated in the introductory part, P5 may be regarded as a dimer liquid crystal in consideration of the size of a phenylene group. When n = odd, reduction of the central core size $(O-\phi-\phi-O)$ to a sub-mesogenic unit (O- ϕ -O) should facilitate alignment of the terminal mesogenes in the nematic mesophase (compare B5 with P5). Stability of the mesophase may then be reinforced by such a modification. The observed suppression of mesophase is at variance with what would be expected for P5 from the above-mentioned consideration. At present, we can not offer any plausible explanation for these experimental observations. Further investigations are under way.

Crystallization temperature, $T_{\rm KN}$ or $T_{\rm KI}$, are also indicated in Figure 1. Crystallization of P6 takes place at a considerably lower temperature than that of B6. It may be interesting to note that $T_{\rm KI}$ of P5 is located above $T_{\rm KN}$ of B5. In Figure 1, $T_{\rm KI}$'s of P5 and P7 fall close to the curve connecting $T_{\rm KN}$'s of P4, P6, and P8. This is perhaps a mere coincidence. In fact, the values of $\Delta H_{\rm KI}$ and $\Delta S_{\rm KI}$ for the n=odd system are sizeably greater than those of $\Delta H_{\rm NK}$ and $\Delta S_{\rm NK}$, respectively, for the n= even sample (cf. Table I).

Finally, we would like to emphasize that the

orientation of a phenylene group incorporated in the flexible spacer is critically important in determining the stability of the mesophase. In the examples described above, the odd-even effect in the mesophasic behavior is apparently enhanced as the size of the central mesogenic core is reduced from the $O-\phi-\phi-O$ to the $O-\phi-O$ group.

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