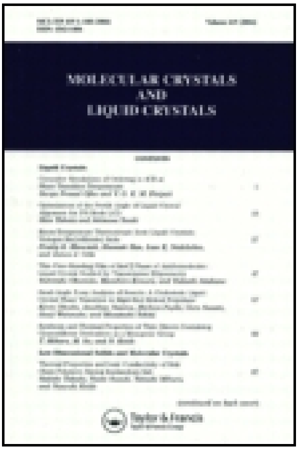

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Thermal Properties and Order Parameter for Model Compounds of Liquid Crystalline Polymers

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THERMAL PROPERTIES AND ORDER PARAMETER FOR MODEL COMPOUNDS OF LIQUID CRYSTALLINE POLYMERS

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Abstract The thermal behavior and order parameter of two kinds of model compounds for liquid crystalline polyesters were studied by DSC and ESR spin probe methods, respectively. The transition temperatures for the twin model compounds which composed of structural sequences with a mesogen-flexible chain-mesogen demonstrated a dramatic odd-even alternation as increasing the number of methylene unit in the central flexible part. Both melting(Tm) and isotropization(Ti) temperatures for the twin model compounds with an even number of methylene lengths were higher than those with an odd number of methylene lengths. The strong alternation in the isotropization entropy change(ΔSi) and in the order parameter(S) were also observed in these twin compounds with variable spacer lengths. However, an inverse alternation regarding with the number of methylene length was found in Si and S for the azobenzene type of twin models which are composed of the inverse order of atoms in the ester linkage comparing with that of the cyanostilbene type of twin models.

INTRODUCTION

There has been extensive interests in the thermotropic polymer liquid crystals composed of alternating a rigid mesogenic moiety and a flexible spacer group. The structure-property relationships of thermotropic main-chain type polyesters have been studied extensively in terms of the effect of the structure of their repeating units.[1] The flexible spacer group plays an important role to the thermal properties exhibiting an odd-even oscillation of the melting (Tm) or the isotropization(Ti) temperature and lowering the transition temperature with an increase in flexible spacer units. Recently Abe[2]has reported a theoretical investigation about the role of a flexible spacer on the thermotropic polymeric liquid crystals. It is interesting that the polyesters with the bonding sequence of O-CO- are often nematic, while the polyesters with the reverse bonding of  CO-O- are smectic.[3,4] These experimental findings are thought that the bonding order of atoms in the ester linkage would play an important role to the mesomorphic properties.

In the present paper we wish to report the synthesis, thermal properties and molecular ordering on two kinds of model compounds.

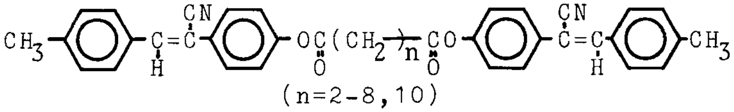
EXPERIMENTAL

The structure of model compounds investigated are shown in Figure 1.

Synthesis of cyanostilbene type twin models

p-Hydroxy-p'-methyl-α-cyanostilbene(HMCS) was obtain by the hydrolysis of p-methoxy-p'-methyl-α-cyanostilbene which was synthesized by the reaction of p-methoxybenzylcyanide with tolualdehyde.

Cyanostilbene type twin models:



Azobenzene type twin models:

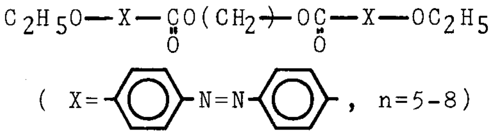


FIGURE 1. Structures of model compounds

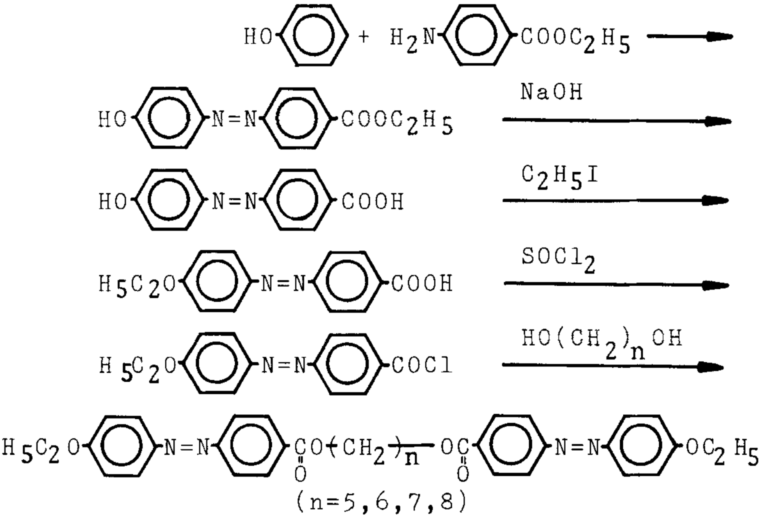
p,p'-Di[(p-methyl)-α-cyanostilbene]alkanoate (DMCSA-n) was synthesized by the reaction of HMCS and α,ω-alkyldiacid chloride in pyridine. DMCSA-n was purified by the recrystallization from the mixed solvent of chloroform-ethanol.

Synthesis of azobenzene type twin models

The azobenzene type twin model compounds were synthesized via the route shown in the following reaction scheme. Only the final two steps will be described as for a representative procedure. Other steps of these reactions were conducted by modified Iida's method of azoxybenzene synthesis.^{5}

4'-Ethoxy azobenzene-4-carboxylic acid

4'-hydroxyazobenzene-4-carboxylic acid(6.1g), potassium hydroxide(6.7g) and small amounts of potassium iodide were dissolved in ethanol(100ml) and



Reaction scheme

then ethyl iodide(7.8g) was added. The mixture stirred under reflux for 20h. After removal ethanol, the mixture was poured into water(1.5 l). The pale orange solid was obtained after acidified by HCl. The pale orange solid was filtered off, washed thoroughly with water and dried. The product was recrystallized from ethanol(yield 50%).

α,ω -Bis(4'-ethoxy azobenzene-4-carbonyloxy)alkane

All other members of the azoxybenzene type twin model compounds were prepared in the following way.

4'-Ethoxyazobenzene-4-carboxylic acid(4.1g) was dissolved in excess thionyl chloride, and the mixture was refluxed for 2h in the presence of dimethylformamide. After removal of unreacted thionyl chloride under vacuum, the product was dissolved in pyridine. α,ω-Alkanediol in pyridine was added to the acid chloride solution with vigorous stirring and the mixture was refluxed for 15h. After cooling the mixture was poured into the dilute hydrochloric acid, and the precipitate collected by filteration. The precipitate was thoroughly washed with water. The product was recrystallized from chloroform. The product was purified by passing through silica gel column using chloroform as eluent. After evaporation of the solvent, the product was obtained as a reddish crystal.

CHARACTERIZATION

All of the compounds were characterized by measuring NMR and IR spectra. The thermal transition behavior of each compound was studied on Mettler TA 3000 instrument. The DSC thermograms were obtained under a nitrogen atmosphere at scanning rates of 10°C/min. Thermodynamic parameters for the transitions were obtained from the area ratio of transition peaks in the DSC thermograms to that of indium peak using as a standard.

The order parameter was measured by a ESR method using vanadyl acetylacetonate instead of conventional nitroxy radical used as a spin probe, because cyano group would react with the nitroxy radical.

Optical textures of the melts were examined on a polarizing microscope(Nikon) equipped with the hot-stage (Mettler FP-5) with a thermal controller (Mettler FP-52).

RESULTS AND DISCUSSION

The phase transition temperature of the cyanostilbene type twin models, DMCSA-n, is shown in Figure 2. DMCSA-n exhibited nematic phase regardless with the number of methylene units in the central alkyl chain. The monotropic nature observed for the cyanostilbene type twin model having the methylene chain length of 2, 3 and 5, while those with longer methylene chain showed an enantiotropic phase. The *Tm* and *Ti* showed the regular odd-even oscillation.

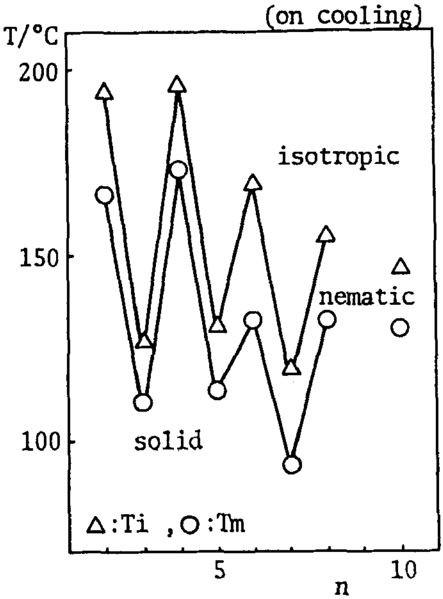


FIGURE 2. Phase transition temperature of cyanostilbene type twin model obtained by DSC curves on cooling runs.

With increasing the methylene chain length, as shown in Figure 3, the ΔSi increased with a pronounced an odd-even alternation with the higher values for n=even (from 6.73 to 15.17 J $mol^{-1}K^{-1}$), than those for n=odd(from 2.68 to 3.97J $mol^{-1}K^{-1}$). This phenomenon can be explained by the conformational factors of the methylene chain, that is, the even-numbered molecule has a more extended and stable conformation. Thermal transition behaviors of these cyanostilbene type twin model compounds are similar to those of homopolyesters having the same mesogenic group.[6]

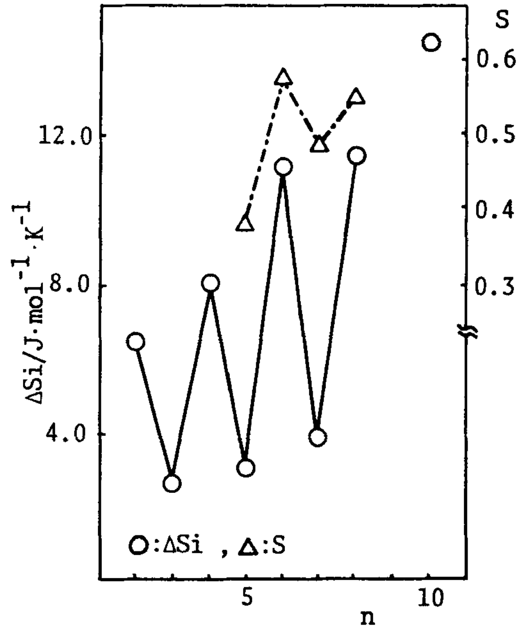


FIGURE 3. Oscillation of isotropization entropy(ΔSi) and order parameter (S) of cyanostilbene type twin model.

The azo type twin model compounds of methylene length(n) of n=5,6,7 and 8 are designated as D5,D6, D7 and D8,respectively. The D5 and D7 show a monotropic mesophase, while D6 and D8 show an enantiotropic mesophase.

The optical textures observed with the polarizing microscope were different depending upon the methylene length of the central chain. A schlieren texture was easily observed for D6 and D8, while a fan-shaped texture was observed for D5 and D7.

However, we could not detected the typical smectic or nematic texture for homopolyesters having same mesogenic group of azobenzene.[7]

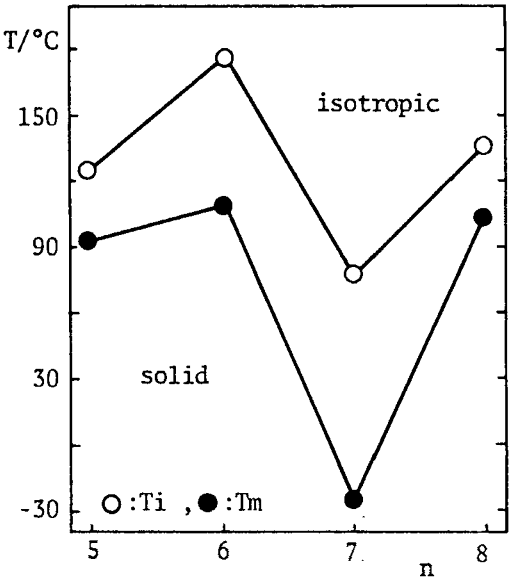


FIGURE 4. Phase transition temperatures of azobenzene type twin model.

The transition temperatures(Tm and Ti) plotted against the number of methylene unit in the central n-alkane chain are shown in Figure 4. The transition temperatures demonstrate a dramatic odd-even alternation as increasing the number of methylene unit in the flexible chain. Both Tm and Ti for these azobenzene type twin compounds with an even number of methylene group are higher than those with an odd number of methylene group.

The ΔSi and order parameter (S) of azobenzene type twin model are shown in Figure 5. Both ΔSi and S fall similarly as the length of the central alkyl chain increases. In this experiment, we could not observed the odd-even oscillation of

ΔSi as usually observed for the conventional low mass liquid crystals.

The temperature dependence of order parameter are shown in Figure 6. The S decreases with increasing temperature. The S of the twin compounds with odd-numbered methylene length are higher values than that with the even-numbered methylene length.

However, we have found an abnormal odd-even oscillation for the azobenzene type twin model compounds. As shown in Figure 4, the Tm and Ti exhibit a normal odd-even

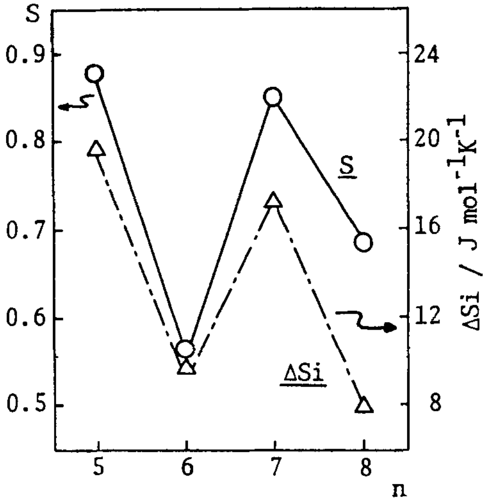


Figure 5. Oscillation of isotropization entropy(ΔSi) and order parameter of azobenzene type twin model.

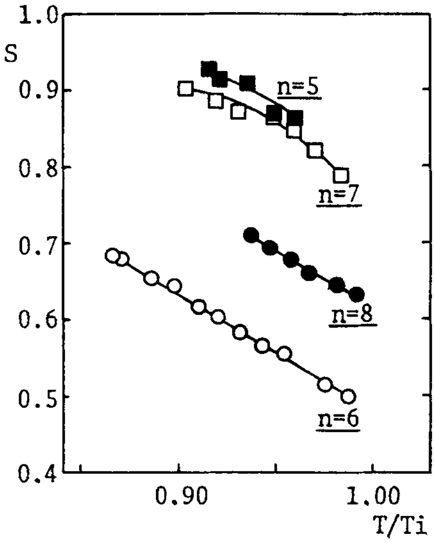


FIGURE 6. Temperature dependence of order parameter of azobenzene

effect concerning to the number of methylene unit in the soft segment, that is, the transition temperatures of the twin compounds with the even number of methylene group are higher than those with the odd number of methylene group. However the odd-even effect with the ΔSi was found to be opposite. This difference could arise from their mesomorphic structure. The D6 and D8 compounds give a nematic phase, whereas D5 and D7 compounds exhibit a smectic phase. These liquid crystalline phases were also confirmed by measuring both the optical texture and small angle X-ray scattering.

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