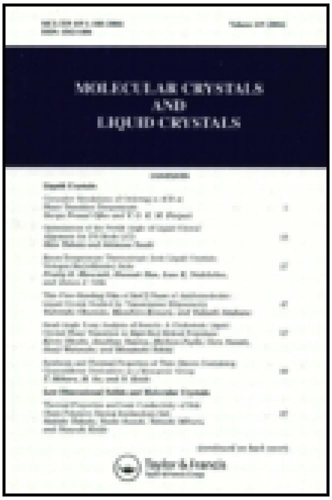

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Liquid Crystalline Properties and Orientational Structure of Binary Systems Built from Poly(Vinylalcohol) and Amphiphilic Compound

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Liquid Crystalline Properties and Orientational Structure of Binary Systems Built from Poly(Vinylalcohol) and Amphiphilic Compound

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Liquid crystalline binary systems, consisting of poly(vinylalcohol) and an amphiphilic compound with hydrophobic nitroazobenzene and hydrophilic ethyleneimine units, were prepared, and their thermal and liquid crystalline properties were estimated. The amphiphilic compound exhibited a smectic A phase with a focal conic fan texture. The liquid crystalline binary systems showed a thermotropic smectic A mesophase. In the smectic A phase, a smectic layer structure with hydrophobic and hydrophilic sublayers was formed.

Keywords: liquid crystalline binary system; amphiphilic; noncovalent interaction; X-ray diffraction; thermal properties

INTRODUCTION

Amphiphilic molecules such as surfactants possess both hydrophilic (polar) and hydrophobic (non-polar) parts in the same molecule. Carboxylate salts with a long alkyl chain, ammonium salts with a long alkyl chain, and poly(oxyethylene) alkyl ethers are amphiphilic molecules and form a lamellar type with a layered structure.$^{1)}$ In the layered structure, the non-polar alkyl chains and the polar groups segregate and produce sublayers. The hydrogen-bonded molecules or ionic molecules can be inserted into the sublayer formed from the polar groups. In the liquid crystalline phase of amphiphilic compounds, noncovalent interactions such as hydrogen bondings and Coulombic force play an important role for liquid crystal formation and the enhancement of liquid crystallinity.$^{2\text{-}5)}$ The use of the noncovalent interactions can lead to the building of novel liquid crystalline systems.$^{6\text{-}11)}$ Moreover, amphiphilic compounds with aromatic-mesogenic groups can form liquid crystalline phases, encompassing interactions between hydrophilic moieties and anisotropy produced by the interactions between the aromatic-mesogenic groups.$^{4,5)}$ Two types of interactions can lead to the formation of functional liquid crystalline systems with self-organization and enhancement of liquid crystallinity

In this work, new liquid crystalline binary systems were built by mixing mesomorphic amphiphilic molecules with an aromatic-mesogenic group and poly(vinylalcohol); their liquid crystalline and thermal properties were estimated.

EXPERIMENTALS

Materials

The amphiphilic compound(5AzN) with an azobenzene mesogenic unit was synthesized by polymerization of 1-(2-hydroxyethyl)ethyleneimine using 6-bromo-1-(4-(4-nitrophenylazo)phenoxy)hexane. The degree of polymerization(n) of the poly(ethyleneimine) unit with a terminal ionic group was examined by ^{1}H NMR. It was estimated that the poly(ethyleneimine) unit was composed of five ethyleneimine units (n=5).

Synthesis of 4-Nitrophenylazophenol

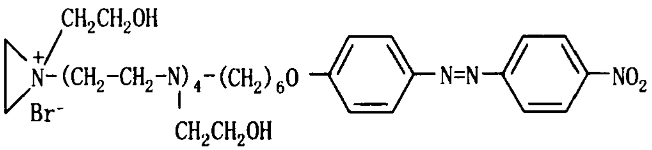
4-Nitroaniline(37mmol) was dissolved in hydrochloric acid(12mol/l, 30ml), and the solution was cooled below 5℃. For the diazotaion, a small amount of sodium nitrite was added at a temperature below 5℃. To the cooled solution, a mixture of sodium of hydroxide solution(37mmol) with phenol(37mmol) was added. The reaction mixture was stirred for 1h about 5℃ and after the reaction acidified with conc. hydrochloric acid. The precipitate was isolated by filtration and dried. Yield, 90%.

Synthesis of 6-bromo-1-(4-(4-nitrophenylazo)phenoxy)hexane(BN)

4-(4-Nitrophenylazo)phenol(19mmol) was dissolved in acetone (100ml), and potassium carbonate and 1,6-dibromohexane (93mmol) were added. The reaction mixture was refluxed for 100h. The precipitated potassium bromide was filtered off, and the filtrate was evaporated under reduced pressure. Chloroform(200ml) was added to the crude product, and the chloroform solution was extracted ten times with water and evaporated. The product was recrystallized from the ethanol solution. Yield, 60%. ^{1}H NMR ($CDCl_3$): 1.5(m, 4H), 1.9(m, 4H), 3.4(t, 2H), 4.0(t, 2H), 7.05(m, 2H), 7.25(m, 4H), 7.85(m, 2H).

Synthesis of amphiphilic compound(5AzN)

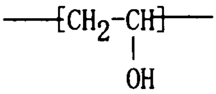
1-(2-Hydroxyethyl)ethyleneimine(50mmol) and BN(10mmol) were dissolved in chloroform(100ml), and the solution was stirred for 300h. After the reaction, the solution was condensed, and the product was precipitated by adding tetrahydrofuran to the condenced solution(50ml). The product was purified by twice reprecipitation from its chloroform solution with THF and dried under reduced pressure. ^{1}H NMR ($CDCl_3$): 1.5(m, 4H), 1.9(m, 4H), 2.66(m, 24H), 3.7(m, 10H), 3.85(m, 8H), 4.0(t, 2H), 7.05(m, 2H), 7.25(m, 4H), 7.85(m, 2H).



5AzN

Preparation of mixtures consisting of 5AzN and PVA

5AzN and poly(vinylalcohol)(PVA: no mesophase) were dissolved separately in distilled water. These solutions were mixed well with a stirrer. After 24h, the water was slowly evaporated, and the mixture of 5AzN and PVA was completely dried under reduced pressure.



$$-\!\!\left[CH_2-\underset{OH}{\underset{|}{CH}}\right]\!\!-$$

PVA

Measurements

The phase transitions were estimated by DSC(a Mettler thermosystem 3000 and a Shimadz DSC-50Q), polarizing microscopy (a Nikon polarizing microscope equipped with a Mettler hot stage FP82), and variable temperature X-ray diffraction. The X-ray diffraction measurements were performed with a Rigaku Rint 2100 system using Ni-filtered Cu-K α radiation. The measuring temperatures of the samples were controlled with a Linkam hot stage HFS91.

RESULTS AND DISCUSSION

The amphiphilic compound (5AzN) with a nitroazobenzene mesogenic unit displayed a thermotropic smectic A phase with a focal conic fan texture on heating and cooling. The transition temperatures of 5AzN and the liquid crystalline binary systems are listed in Table 1. 5AzN showed crystal-smectic A and smectic A-isotropic phase transitions. The liquid crystalline binary systems (PVA/5AzN-*x*, *x*=mole fraction of

5AzN component) consisting of PVA and 5AzN showed an enantiotropic liquid crystalline phase. PVA/5AzN-*x* (x=0.9, 0.85, 0.75, 0.6) exhibited a smectic A mesophase with a fan texture (see Figure 1).

TABLE 1. Phase transition temperatures of 5AzN and liquid crystalline binary systems

Sample	Transition temperatures[1]/℃				
5AzN	K	26.1	SmA	97.2	I
PVA/5AzN-0.9	SmAg	-8.7	SmA	110.1	I
PVA/5AzN-0.85	SmAg	-4.7	SmA	111.9	I
PVA/5AzN-0.75	SmAg	0.9	SmA	115.7	I
PVA/5AzN-0.6	SmAg	1.0	SmA	126.5	I

1) K: solid, SmAg: glassy smectic A, SmA: smectic A, I: isotropic.

5AzN and PVA/5AzN-*x* exhibited a perpendicular alignment. Conoscopic observation indicated that the perpendicular alignment is characterized by an optical uniaxiality. In the DSC measurements of PVA/5AzN-*x*, glassy mesophase-mesophase and mesophase-isotropic phase transitions were obtained. The glass transition in PVA/5AzN-*x* is due to the polymer effect of PVA because 5AzN did not show a glass transition. The transition enthalpies could not be estimated because the DSC peaks at the mesophase-isotropic phase transitions were very weak. PVA showed a melting point at 185℃. However, PVA/5AzN-*x* did not exhibit a DSC peak at 185℃. Also, PVA/5AzN-*x* did not show a phase transition at 55℃ which is the glass transition point of PVA. Moreover, the transition temperatures of PVA/5AzN-*x* increased with increasing PVA content. These indicate that PVA is miscible with 5AzN, and phase separation does not occur.

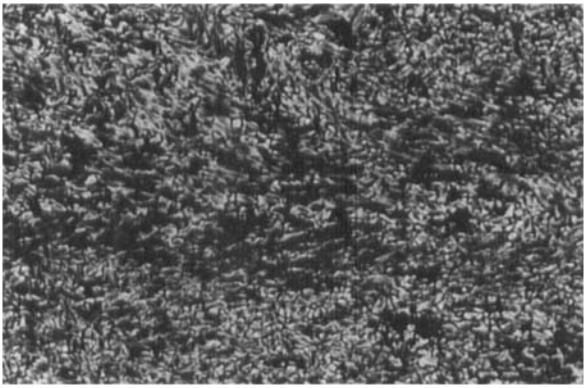


FIGURE 1. Fan texture observed in smectic A phase of PVA/5AzN-0.85 at 80℃.

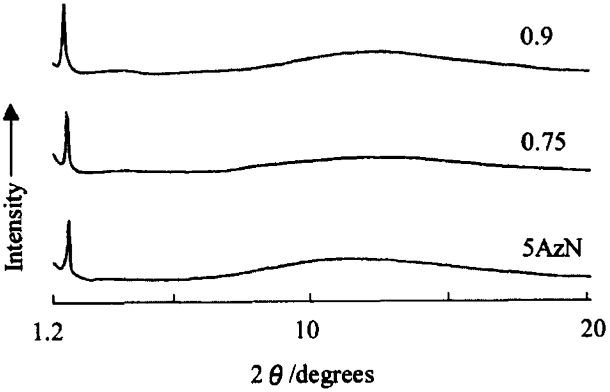


FIGURE 2. X-Ray diffraction patterns of 5AzN, PVA/5AzN-0.75, and PVA/5AzN-0.9.

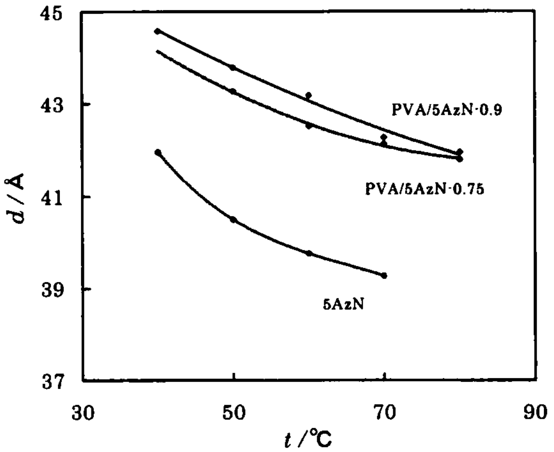


FIGURE 3. Smectic layer spacings(*d*) of 5AzN, PVA/5AzN-0.9, and PVA/5AzN-0.75.

Both 5AzN and PVA/5AzN-*x* exhibited sharp reflections at X-ray small-angles and a broad reflection in the X-ray wide-angle region (see Figure 2). In both 5AzN and PVA/5AzN-*x*, the smectic A layer spacings increased with decreasing temperature, as shown in Figure 3. The possible packing models of 5AzN and PVA/5AzN-*x* in the smectic A phase are illustrated in Figure 4. 5AzN has a hydrophobic azobenzene unit and a hydrophilic poly(ethyleneimine) chain. In the thermotropic smectic A layer, the azobenzene units and the poly(ethyleneimine) chains with the ethanol unit segregate, respectively, and the hydrophilic and hydrophobic sublayers are formed, as shown in Figure 4. These sublayers alternate. In PVA/5AzN-0.9 and PVA/5AzN-0.75, PVA, which is a hydrophilic component, is located within an aggregated domain (sublayer) formed from the poly(ethyleneimine) chains and so enhance the thermal stability of the smectic A mesophase. The smectic layer spacing of PVA/5AzN-*x* is longer than for 5AzN (see Figure 3). This indicates that PVA is inserted in the hydrophilic sublayer in which the poly(ethyleneimine) chains are aggregated.

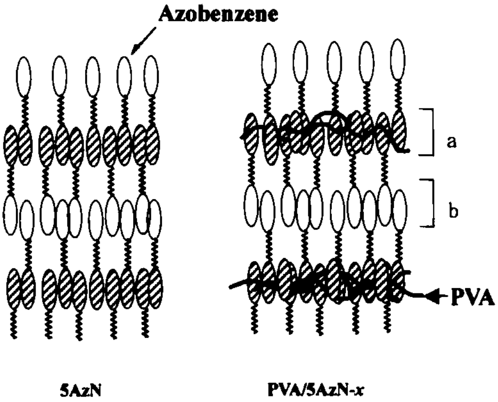


FIGURE 4. Possible packing models proposed for the smectic A phase of 5AzN and PVA/5AzN-*x*: a; hydrophilic sublayer: b; hydrophobic sublayer.

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