

Liquid Crystalline Amphiphilic Materials with Ammonium Unit

Seiji Ujiie*[†], Yumi Yano*, and Akira Mori

*Department of Material Science, Interdisciplinary Faculty of Science and Engineering,

Shimane University, Matsue 690-8504

Fax:81-852-32-6421, [†]e-mail:seujiie@riko.shimane-u.ac.jp

Institute of Advanced Material Study, Kyushu University,

6-1 Kasuga-koen, Kasuga-shi, Fukuoka 816-8580

Thermotropic and lyotropic liquid crystalline properties of new amphiphilic materials were estimated. The amphiphilic molecules (Az6N), in which a polyaziridine unit with hydroxyl side-groups attach to an azobenzene unit through a methylene spacer chain, showed thermotropic and lyotropic mesophases with a smectic A layered structure. The amphiphilic compound (Oxa6N) with a polyoxazoline unit exhibited no thermotropic mesophase. However, the addition of water for Oxa6N led to the formation of a smectic A lyomesophase. The difference in the liquid crystal formation of Az6N and Oxa6N is due to the affinity of the hydrophilic polymer units with the mesogenic units.

Key words: Amphiphilic, Liquid Crystal, Ionic, Phase Transitions, X-Ray

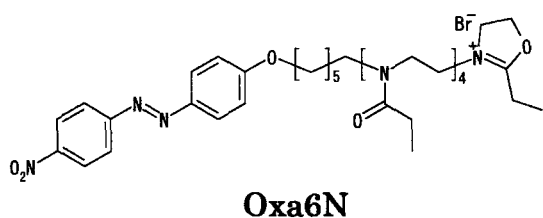
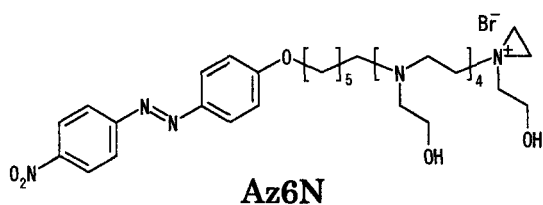
1. INTRODUCTION

Surfactants having aromatic-mesogenic groups can exhibit liquid crystal formation, due to the anisotropy formed by aggregation of the polar head groups and interactions between the aromatic mesogenic cores and the higher anisotropy when compared to the surfactants without the aromatic-mesogenic groups.¹⁾ Moreover, the surfactants can show thermotropic and lyotropic behavior and form various types of liquid crystalline phases such as lamellar, columnar, and cubic mesophases. It is of high importance in the fundamental field to synthesize novel liquid crystalline amphiphilic materials, forming interesting self-assembled arrangements, and estimate their thermotropic and lyotropic properties.

This present paper describes the thermotropic and lyotropic liquid crystalline behavior of an amphiphilic compound in which a polyethyleneimine unit with 2-hydroxyethyl side-chain in the repeating unit attaches to an aromatic-mesogenic moiety through a hexamethylene spacer chain.

2. EXPERIMENTAL SAMPLES

The amphiphilic compounds were synthesized by ring-opening polymerization of an aziridine derivative (or an oxazoline derivative) using 6-bromo-1-(4-(4-nitrophenylazo)phenoxy)hexane as a polymerization initiator.²⁾



MEASUREMENTS

The phase transitions were measured by DSC (a Mettler thermosystem 3000 and a Shimadzu DSC-50Q), polarizing microscopy (an Olympus polarizing microscope equipped with a Mettler hot stage FP82).

The orientational behavior was estimated by X-ray diffraction measurements in the mesomorphic temperature range using Ni-filtered $\text{Cu-K}\alpha$ radiation. The measuring temperatures were controlled with a Linkam hot stage HFS91.

3. RESULTS AND DISCUSSION

The amphiphilic liquid crystal (Az6N) having a hydrophilic polyaziridine unit with 2-hydroxyethyl side-groups showed a thermotropic smectic A phase with fan and oilstreak textures on the heating and cooling processes. The amphiphilic compound (Oxa6N) with a poly(ethyloxazoline) unit did not show a thermotropic liquid crystalline phase. However, Oxa6N displayed an anisotropic state with the weak birefringence on a rapidly cooling process from 100°C (isotropic) to 0°C. This indicates that Oxa6N has a potential forming a liquid

crystalline alignment.

The lyotropic liquid crystalline systems, consisting of Az6N and water, exhibited a smectic A lyomesophase (Fig. 1). In the lyomesophase, fan and oilstreak textures were observed. The addition of water decreased the ability of the liquid crystal formation and the lyotropic system with above 30wt% of water showed no mesophases.

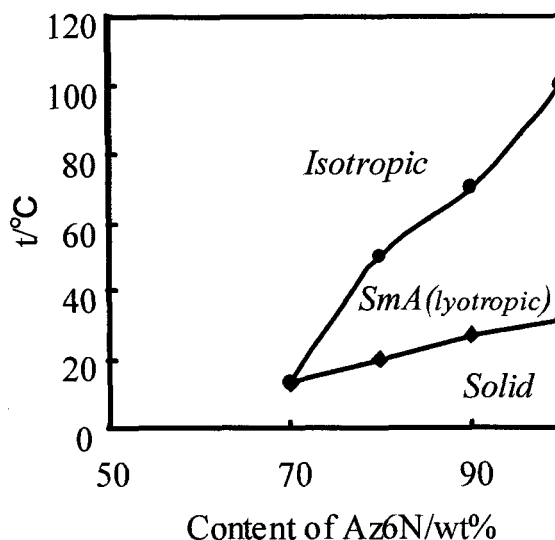


Fig. 1. Phase transitions of lyotropic systems for Az6N

X-Ray diffraction measurements were performed at 30°C. The layer spacings for the thermotropic and lyotropic liquid crystalline systems of Az6N were 41 Å and 43 Å, respectively, while the extended molecular length of Az6N is 37 Å. In this case, the orientational structures of the thermotropic and lyotropic mesophases were proposed as shown in Fig. 2. The hydrophilic and lipophilic units in the molecules of Az6N form sublayer domains, respectively. The nitroazobenzene units overlap each other. The polyaziridine units aggregate by the formation of hydrogen bondings.

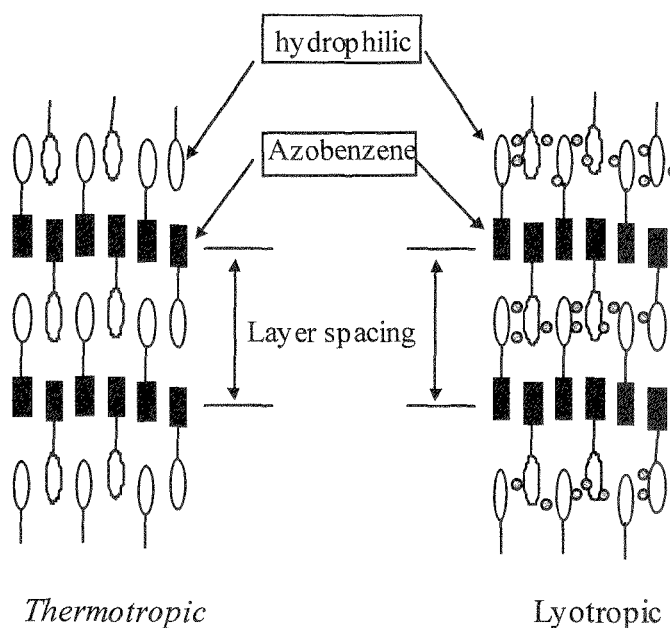


Fig. 2. Possible packing models of thermotropic and lyotropic liquid crystalline systems for Az6N.

The mixture of non-mesomorphic Oxa6N and water showed a smectic A lyomesophase (Figs 3 and 4). The lyotropic system of Oxa6N formed oilstreak and homeotropic textures in the smectic A lyomesophase. Fig. 3 shows the generation of an anisotropic state (bright region) formed by the contact of Oxa6N and water. The appearance of the birefringence shown in Fig. 3 is produced by the formation of the lyotropic liquid crystalline system consisting of Oxa6N (upper right: dark region) and water (bottom left: dark region). The repeating units in the polyoxazoline chain resemble to *N,N*'-dimethylformamide. So it is expected that the polyoxazoline chain has the affinity with the azobenzene units and the azobenzene units can dissolve in the polyoxazoline domains. In this case, it is difficult from Oxa6N to form the thermotropic mesophase because the domains (sublayers) of hydrophilic or lipophilic cannot be produce. The addition of water for

Oxa6N leads to the segregation of the polyoxazoline and azobenzene units. The lyotropic mesophase with the hydrophilic and lipophilic sublayers is formed. The temperatures, at which an isotropic fluid phase form, raised with addition of water. This is due to the effective action of interactions between the azobenzene units in the lipophilic sublayers and the aggregation producing from hydrophilic units and water in the hydrophilic sublayers.

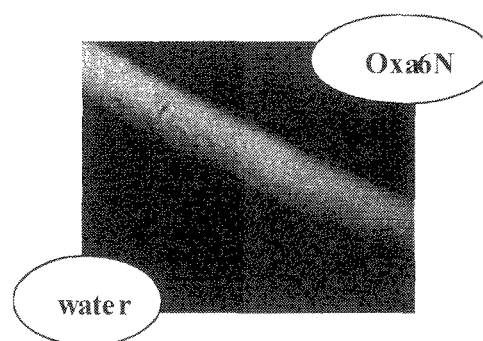


Fig. 3. Contact test of water and Oxa6N.

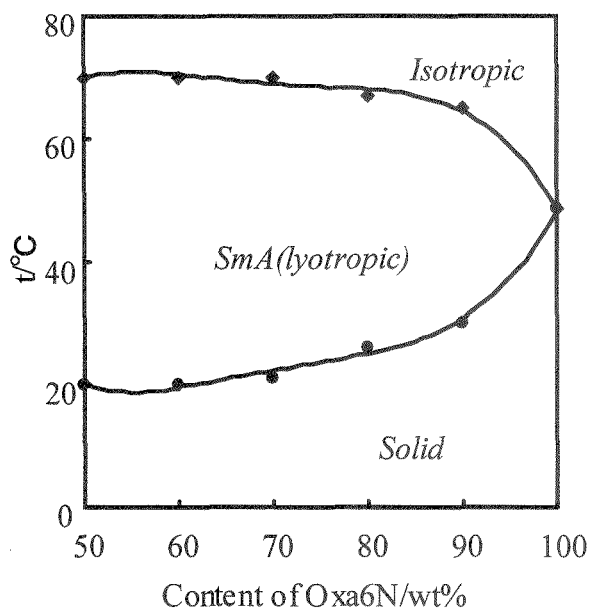


Fig. 3. Phase transitions of lyotropic systems for Oxa6N.

4. CONCLUSIONS

The amphiphilic compound, in which the hydrophilic polyaziridine unit attaches to one aromatic-mesogenic unit, showed the thermotropic and lyotropic liquid crystalline

behavior (amphotropic behavior). The amphiphilic compound (Oxa6N) with the polyoxazoline unit formed no thermotropic mesophase. However, the systems consisting of Oxa6N and water exhibited the lyotropic mesophase. In the liquid crystalline phases formed by the thermotropic and lyotropic systems of the amphiphilic compounds, the hydrophilic and lipophilic units in the molecules form sublayer domains, respectively.

5. REFERENCES

- [1] A. G. Peter, *The Lyotropic State of Mater*, Gordon and Breach Science Publishers (1999); D. Blunk, K. Praefcke, and V. Vill, *Handbook of Liquid Crystals*, Wiley-VCH, 305-340 (1998); S. Ujiie and K. Iimura, *Polym. J.*, **25**, 347(1993); S. Ujiie, Y. Tanaka, and K. Iimura, *Poly. Adv. Technol.*, **11**, 450(2000).
- [2] S. Ujiie and Y. Yano, *Mol. Cryst. Liq. Cryst.*, **347**, 265 (2000).
- [3] S. Ujiie and Y. Yano, *Chem. Comm.*, **79** (2000).

(Received December 7, 2000; Accepted March 23, 2001)