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LIQUID-CRYSTALLINE BRANCHED POLYMERS HAVING IONIC MOIETIES

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Ionic LC-dendrimers were obtained by proton-transfer reaction of alkanoic acid and primary amino groups of poly(amidoamine) dendrimer in a 1:1 molar ratio. The ion complexes containing stearate, palmitate or myristate ions showed a smectic A phase. However, the ion complexes containing laurate and decanoate ions exhibited no liquid-crystalline phase. Oilystreak, maltese, and homeotropic textures were observed in the smectic A phase. The formation of the homeotropic structure is characterized by conoscopic observation. The X-ray diffraction pattern in the smectic A temperatures consists of sharp inner reflections at the small angles and the wide-angle diffuse halo. Mixtures of the dendrimer and stearic acid [a molar ratio (x) of stearic acid against the primary amino groups of the dendrimer] were prepared; mixtures with $x = 0.11$–1.5 showed a smectic A phase. However, the mixture with $x = 2.33$ formed a disordered hexagonal columnar mesophase, characterized by an optical texture and X-ray diffraction measurement.

Keywords: dendrimer, ion complex, ionic interactions, liquid crystal, phase transitions, X-ray diffraction

INTRODUCTION

Ionic interactions effectively act during the complexation of distinct compounds and the formation of liquid crystalline systems [1]. Ion-containing amphiphilic materials can generally form thermotropic LC systems having a layered structure that contains hydrophilic and lipophilic sublayers [2].

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Several ionic liquid crystalline polymers such as ionic side-groups containing main-chain LCPs and side-chain LCPs having ion-containing mesogenic side-chains were synthesized [3]. The ionic interactions are useful to design self–assembly liquid crystalline systems. Polyamines can form self-assembled liquid crystalline systems by ionic complexation with compounds having a carboxyl group [4]. Ion complexes of alkylamine and polyacrylic acid, which do not have aromatic-mesogenic units, show a smectic A phase on self-assembly. A poly(amidoamine) dendrimer is a polyamine with surface primary amino groups and can form an ion complex by reaction with a carboxylic acid. The ion complex of a mesogenic group with a carboxyl group and the dendrimer was reported [5]. In this study, the ion complexes of an alkanoic acid and the poly(amidoamine) dendrimer were synthesized. Their phase transitions and orientational ordering behavior were estimated.

EXPERIMENTALS

Samples

Normal alkanoic acid ($C_nH_{2n}O_2$) and poly(amidoamine) dendrimer (DD) (generation 3.0) was used. DD has 32 surface primary amino groups (Fig. 1). An ion complex consisting of DD and an alkanoic acid was obtained by a proton-transfer reaction. DD and an alkanoic acid were dissolved into methanol at room temperature. The methanol solution was stirred for 24 h and the methanol was evaporated. The ion complex was estimated by IR spectroscopy. The ionic complex showed the absorption of ionized carboxylates at 1580 cm^{-1} and 1405 cm^{-1}. The broad band of the ionic N^+-H stretching vibration was observed at 2670 cm^{-1}.

Measurements

The phase transitions were examined with a Mettler Thermosystem 3000, a Shimadzu differential scanning calorimeter (DSC-50Q), and an Olympus polarizing microscope equipped with a Mettler FP900 system(FP90-FP82). The optical textures of the liquid crystalline phases were observed by polarizing microscopy. The X-ray diffraction measurement was performed with a Rigaku X-ray diffractometer RINT2100 system using

[-CH_2N[CH_2-R-N[CH_2-R-N[CH_2-R-N(CH_2-R-NH_2)$_2$]$_2$]$_2$]$_2$]$_2$

R= -$CH_2CONHCH_2CH_2$-

FIGURE 1 Poly(amidoamine) dendrimer (generation 3.0).

Ni-filtered Cu-Kα radiation. In the X-ray diffraction measurement, the samples were placed on a Linkam hot stage system(TC600PH).

RESULTS AND DISCUSSION

Ionic Dendrimer Complexes by Reaction of Primary Amino Groups and Alkanoic Acid in a 1:1 Ratio

Ionic dendrimer complexes (DD-n) with a long alkanoate ($n = 14, 16, 18$), which were obtained by reaction of alkanoic acid and the primary amino groups of the dendrimer in a 1:1 ratio, showed a thremotropic liquid crystalline phase (Fig. 2). A shorter alkanoate could not lead to the formation of the mesophase for the ionic dendrimer complexes. The isotropization temperature increased with increasing alkyl chain length of alkanoic acid. Oilystreak, maltese, and homeotropic textures were observed in the liquid crystalline phase (Fig. 3a). These optical textures indicate the formation of the smectic A lamellar structure. The homeotropic structure spontaneously formed on the surface of the glass substrate. The formation of the homeotropic structure is characterized by conoscopic observation. A conoscopic figure was obtained for the homeotropic sample of ionic dendrimer complex with stearate ($n = 18$) (Fig. 3b).

The X-ray diffraction pattern consisted of Bragg reflections and a wide-angle diffuse halo. Smectic layer spacings of the ionic dendrimer complexes

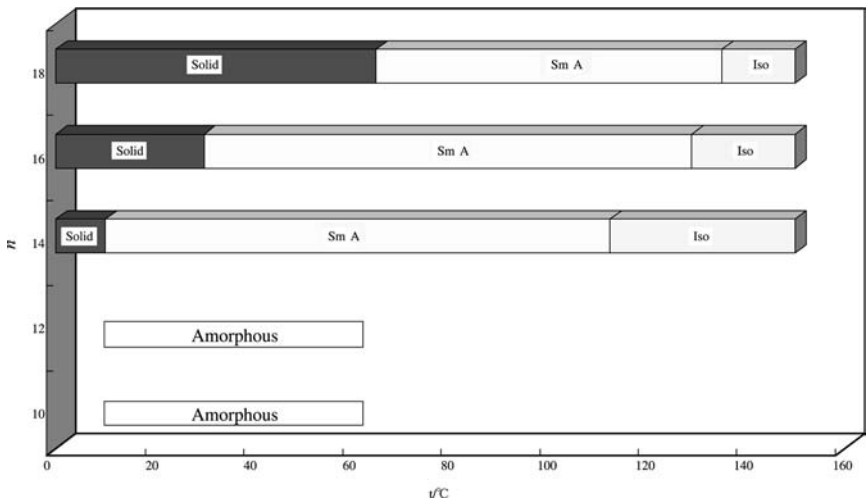

FIGURE 2 Phase transitions of ionic dendrimer complexes: n; carbon numbers of alkanoate.

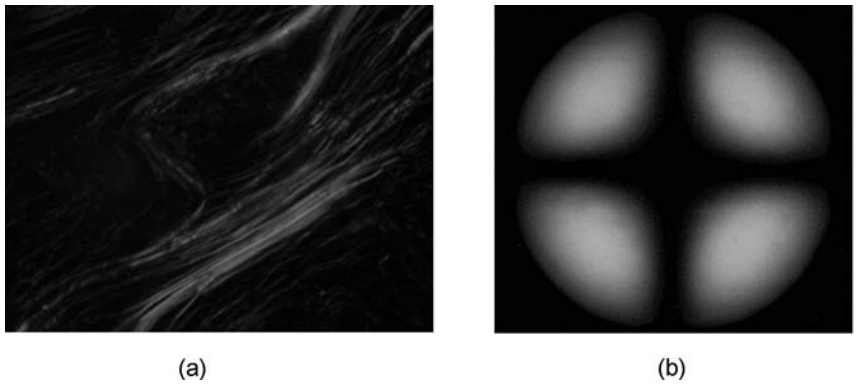

FIGURE 3 Optical textures of ionic dendrimer complex with $n = 18$ at 90°C: a; oilystreak texture: b; conoscopic figure for homeotropic structure.

clearly decreased with increasing temperature (Fig. 4). It is expected that the skeleton of the ionic dendrimer in a solution has a ball-like molecular shape. In this case, the diameter of the dendrimer is about 48 Å. In the bulk state, however, the dendrimer has an ellipse-like shape because the molecular shape of the dendrimer can easily deform [6]. The dendrimer changes the molecular shape depending on the temperature and affects the layer spacing. The alkyl chain of the stearate has a random conformation because the smectic fluid phase is formed at temperatures at which the stearic acid is isotropic.

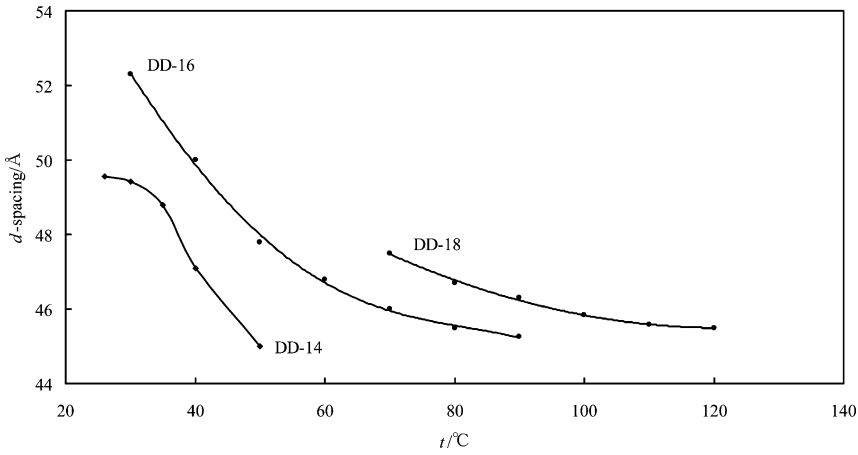

FIGURE 4 Layer spacings of ionic dendrimer complexes at smectic temperatures.

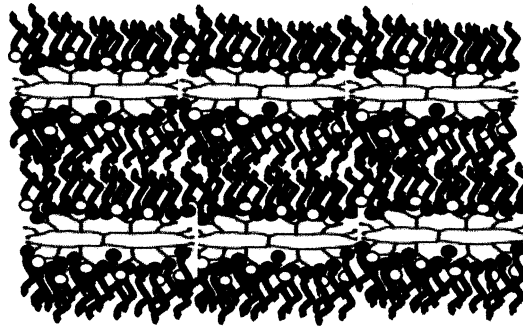

FIGURE 5 Possible packing model of layered structure for ionic dendrimer complex.

Figure 5 shows a packing model of ionic dendrimer complexes. The alkyl chains and dendrimers segregate and form separate sublayers. It is expected that the dendrimer cores were located at random within the layer, because the X-ray diffraction pattern corresponds to the smectic A phase. Also, the conformation of the alkyl chains is at random because the mesomorphic temperatures are higher than melting points of the alkanoic acids.

FORMATION OF COLUMNAR PHASE

Liquid crystalline mixtures [$x =$ molar ratio of stearic acid for the primary amino groups of dendrimer] were prepared by mixing the

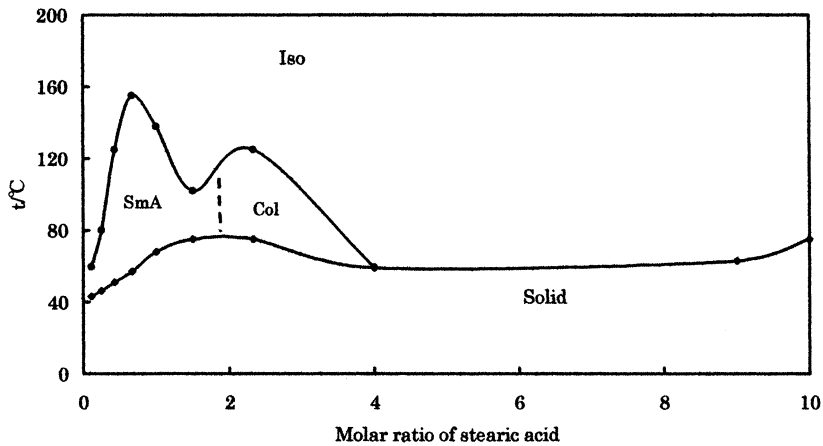

FIGURE 6 Phase diagram of mixture consisting of poly(amidoamine) dendrimer and stearic acid ($n = 18$).

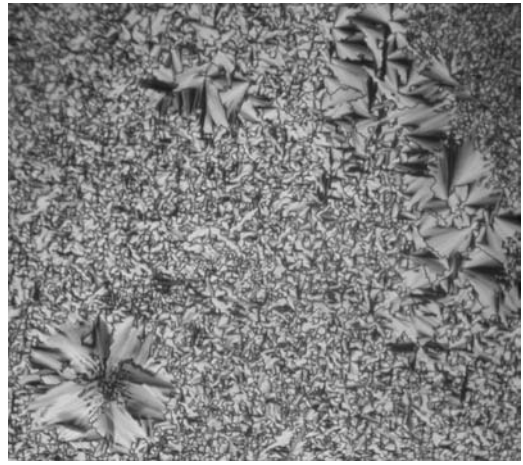

FIGURE 7 Optical texture of columnar phase formed by mixture with $x = 2.33$ at 80°C.

poly(amidoamine) dendrimer and stearic acid. Figure 6 shows a phase diagram of the mixture. The mixture with $x = 0.11$–1.5 exhibites a smectic A phase. The mixture with $x = 2.33$ exhibited a columnar mesophase (Col). In the columnar mesophase, a fan like texture was observed (see Fig. 7).

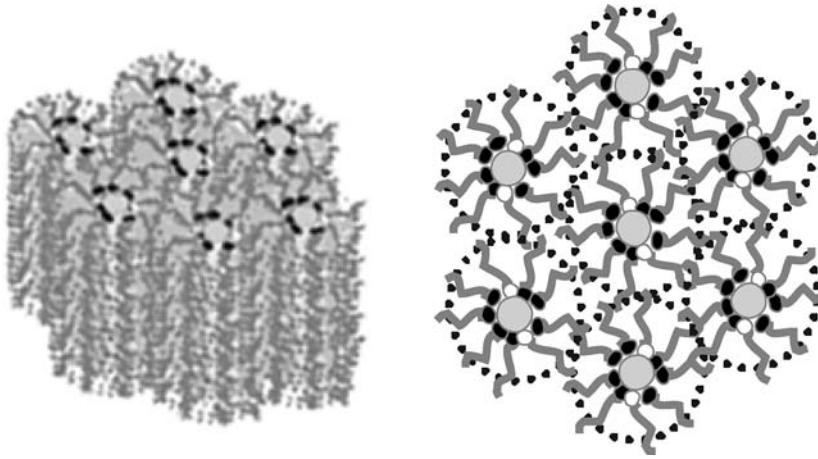

FIGURE 8 Possible packing model of columnar mesophase: ● ionized stearate, ○ stearic acid.

The X-ray diffraction pattern consists of inner reflections [d(100) = 39.2 Å, d(110) = 23.2 Å, d(200) = 19.6 Å] at the small angles and wide-angle diffuse halo (80°C). This indicates the formation of the disordered hexagonal columnar order. A possible packing model is shown in Figure 8. The dendrimers are located on the center of the column. In the mixture with $x = 2.33$, the stearic acid groups reacted with all primary amino groups and the ion complex was formed at a ratio of 1:1. The surplus stearic acid groups formed the ion complex with a part of the tertiary amino groups by proton-transfer reaction and the rest of the stearic acid groups are arranged so that the dendrimers are surrounded in the column.

CONCLUSIONS

The ion complexes composed of ionic poly(amidoamine) dendrimer (generation 3.0) and normal alkanoate showed a smectic A phase with a lamellar structure. Ionic interactions acted effectively for the formation of liquid crystalline systems. The mixture of the ionic complex and stearic acid formed a columnar mesophase. The formation of the lamellar and columnar structures is explained by the fact that the dendrimer skeleton has a high flexibility.

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