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Phase Transitions in Cyclotriphosphazenes Bearing Different Types of Mesogenic Side Groups

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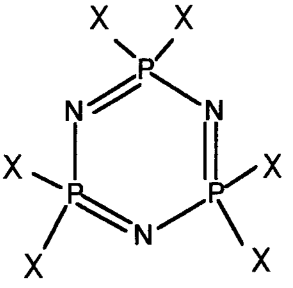
Cyclotriphosphazenes with three different types of mesogens of hexakis(4-dodecyloxyphenoxy)cyclotriphosphazene(1), hexakis(4-(4'-dodecyloxy)biphenoxy)cyclotriphosphazene(2) and hexakis(3, 4-didodecyloxybenzyloxy)cyclotriphosphazene(3) were synthesized and their phase transitions and mesogenicities were studied using calorimetry and optical microscopy. The enantiotropic smectic C and columnar phases were observed for compounds 2 and 3, respectively. No mesomorphic phase was observed for compound 1. The appearance of the mesomorphic phase was attributed to the molecular shape and the molecular structure in the cyclotriphosphazenes.

Key words: liquid crystals, cyclotriphosphazene, phase transition

1. INTRODUCTION

The phase transitions of the cyclotriphosphazenes with mesogenic side groups are quite interesting because they have peculiar molecular shapes which consist of six-membered cycloptriphosphazene rings and mesogenic side chains.[1-3] The rings are made of alternating N and four coordinated P atoms and the side chains are attached to each of the P atoms.[4] Therefore, each cyclotriphosphazene molecule has six mesogenic side chains. The role in which the cyclotriphosphazene rings and mesogenic side chains act in the mesomorphic phase transitions is also interesting. Recently, we found several mesomorphic phases in some cyclotriphosphazene derivatives.[5-16] For example, in hexakis(4-(4'-octyloxy)biphenoxy)cyclotriphosphazene, an enantiotropic smectic C phase was observed.[11,12] This fact was explained as follows. Each of the three mesogenic side chains of this compound bend at the P-O-C linkage upwards and downwards from the cyclotriphosphazene rings and six mesogenic side chains line up parallel in the molecule. Such large cyclotriphosphazene molecules are easy to form a layer structure which helps the formation of the smectic phase.[12]

In this paper, we synthesized three different types of the cyclotriphosphazene derivatives of hexakis(4-dodecyloxyphenoxy)cyclotriphospahzene(1), hexakis(4-(4'-dodecyloxy)biphenoxy)cyclotriphosphazene(2) and hexakis(3, 4-didodecyloxybenzyloxy)cyclotriphosphazene(3) and studied their phase transitions and mesogenicities using differential scanning calorimetry(DSC) and polarizing microscopy based on their molecular shapes and structures. The synthesized molecules are shown in Fig.1.



X= $OC_6H_4OC_{12}H_{25}$(1), $OC_6H_4C_6H_4OC_{12}H_{25}$(2), $OCH_2C_6H_3(OC_{12}H_{25})_2$(3)

Fig. 1 Chemical fomulas of hexakis(4-dodecyloxyphe-noxy)cyclotriphosphazene(1), hexakis(4-(4'-dodecyloxy)biphenoxy)cyclotriphosphazene(2) and hexakis(3, 4-didodecyloxybenzyloxy)cyclotriphosphazene(3).

2. EXPERIMENTAL

2.1 Synthesis

2.1.1 Synthesis of hexakis(4-dodecyloxyphenoxy)-cyclotriphosphazene(1)

4-Dodecyloxyphenol(4) was prepared from hydroquinone(50.0 g, 0.454 mol), 1-bromododecane(94.2 g, 0.378 mol) and KOH(29.9 g, 0.454 mol) in ethanol(500 ml) under reflux for 12 h. The crude crystals were recrystallized twice from hexane after being column chromatographed(SiO_2, $CHCl_3$). The sodium salt of compound 4 was prepared from compound 4(7.00 g, 25.2 mmol) in THF(50 ml) and a NaH(1.00 g, 25.0 mmol) suspension in THF(10 ml) under reflux for 2 h. Compound 2 was prepared by dropwise adding hexachlorocyclotriphosphazene(HClCP) (1.00 g, 2.88 mmol) in THF(10 ml) to the sodium salt of compound 4 in THF(50 ml) at room temperature and further refluxed for 15 h. The obtained crude crystals were column chromatographed(SiO_2, $CHCl_3$) and recrystallized twice from ethanol. The identification and purity of compound 1 were confirmed by TLC (SiO_2, $CHCl_3$), ^1H and ^{31}P NMR, IR and elemental analyses. The analytical results for compound 1 are as follows: mp 348 K; IR (KBr) 2921, 1506, 1476, 1253, 1197, 1171, 956 cm^{-1}; ^1H NMR δ 0.9(t, 6.6 Hz, 3H), 1.3-1.8(m, 20H), 3.9(m, 6.6 Hz, 2H), 6.6(d, 9.2 Hz, 2H), 6.8(d, 9.2 Hz, 2H); ^{31}P NMR δ 11.1 (s); Calcd for $C_{108}H_{174}O_{12}N_3P_3$: C, 72.11; H, 9.75; N, 2.34. Anal. Found: C, 71.96; H, 9.84; N, 2.38 %.

2.1.2 Synthesis of hexakis(4-(4'-dodecyloxy)-biphenoxy)cyclotriphosphazene(2)

4-Dodecyloxy(4'-hydroxy)biphenyl(5) was prepared from 4,4'-dihydroxybiphenyl(90 g, 0.48 mol), 1-bromododecane(80.0 g, 0.321 mol) and KOH(2.70 g, 0.48 mol) in ethanol(1300 ml). Compound 2 was prepared from compound 5(24.8 g, 70.0 mmol) with a NaH(1.85 g, 77.0 mmol) suspension in dioxane(400 ml), HClCP (2.7 g, 8.0 mmol) in dioxane(60 ml) and tetrabutylammonium bromide(TBAB)(1.40 g, 4.4 mmol) under reflux for 12 h. The obtained crude products of compound 2 were column chromato-graphed(SiO_2,$CHCl_3$) followed by the recrystallization twice from a hexane/THF(20:1) mixed solvent. The sample was judged to be thoroughly purified by TLC(SiO_2, CCl_4), ^1H and ^{31}P NMR, IR and elemental analyses. The analytical results for compound 2 are as follows: mp 425 K, cp 453 K; IR (KBr) 2956, 1608, 1500, 1242, 1178, 977, 826 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9(t, 3H), 1.3-1.8(m, 20H), 4.0(t, 2H), 6.8-7.3 (m, 8H); ^{31}P NMR δ 10.6 (s); Calcd. for $C_{144}H_{198}N_3O_{12}P_3$: C, 76.66; H, 8.85; N, 1.86 %. Anal. found: C, 75.62; H, 8.88; N, 1.90 %.

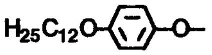
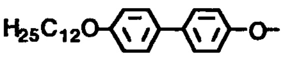
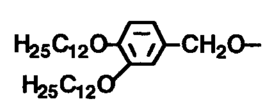
2.1.3 Synthesis of hexakis(3, 4-didodecyloxy-benzyloxy)cyclotriphosphazene(3)

Ethyl 3,4-didodecycloxybenzoate(6) was prepared from ethyl 3,4-dihydroxybenzoate (8.03 g 44.0 mmol), 1-bromododecane (32.8 g, 132 mmol) and potassium carbonate(48.5 g, 350 mmol) in DMF(90ml) by reacting at 80 °C for 8 h. The reaction mixture was cooled to room temperature and extracted twice from ether(400 ml) after adding water(350 ml). The extracted solution was washed with a small amount of saturated NaCl solution. The obtained crude crystals were recrystallized three times from ethanol. 3,4-Didodecyloxybenzylalcohol(7) was prepared from compound 6(19.0 g, 37.0 mmol) and lithium aluminum hydride(4.21 g, 111 mmol) in ether(300 ml) by refluxing at 50 °C for 5 h after stirring the solution 15 min at room temperature. After the temperature of the solution was cooled to 0 °C, a small amount of ethyl acetate and then water was added. The obtained crude crystals were recrystallized twice from ethanol. The sodium salt of compound 7 was prepared from compound 7(73.6 g, 154 mmol) and NaH(3.72 g, 150 mmol) in THF(400 ml) by reacting at 75 °C for 3 h. After the solution was cooled to room temperature, HClCP(6.40 g, 12.8 mmol) and TBAB(4.90 g, 15.4 mmol) were added and further reacted by refluxing for 21 h. The reaction mixture was column chromatographed(SiO_2, $CHCl_3$) and the crude crystals of compound 3 were recrystallized three times from ethyl acetate. The identification of the sample was performed by ^1H and ^{31}P NMR, IR and elemental analyses. The analytical results for the compound 3 are as follows: IR 2959, 2899, 1593, 1236, 998 cm^{-1}; ^{31}P NMR δ 18.53(s); ^1H NMR δ 0.9(t,6.8 Hz, 6H), 1.3-1.8(m, 40 H), 3.9(t, 6.7 Hz, 4H), 4.8(s, 2H), 6.7(d, 8.1 Hz, 1H), 6.8 Hz(d, 8.3 Hz, 1H), 6.9(s, 1H). Calcd for $C_{186}H_{330}O_{18}N_3P_3$: C, 74.73; H, 11.13; N, 1.40; P, 3.11; Anal. found: C, 74.95; H, 11.28; N, 1.43; P, 3.28.

2.2 Analytical techniques and instruments

The phase transition temperatures and phase transition entropies were measured using a differential scanning calorimeter (Seiko Instruments DSC 210 and SSC 5500 system) at a heating/cooling rate of 5 $Kmin^{-1}$ between room temperature and to over the melting or the clearing point. The apparatus was calibrated by the melting of indium(T_m; 429.6 K, ΔH ; 28.5 Jg^{-1}) and tin(T_m; 505.1 K, ΔH ; 59.5 Jg^{-1}). Texture observations of the mesomorphic phases were performed using an optical polarizing microscope (Nikon Optiphot-pol XTP-11) equipped with a Mettler FP 82 hot stage at a heating/cooling rate of 5 $Kmin^{-1}$ between room temperature and to over the clearing

Table I Phase transition temperature / entropy and chemical shift of ^{31}P NMR in $(PNX_2)_3$

Compound	X	phase transition temperature / K / transition entropy / JK^{-1} mol^{-1}				^{31}P NMR chemical shift / ppm
		Cr	SmC	Columnar	I	
1		■ 348/393	—	—	■	11.1
2		■ 425/136	■ 453/37	—	■	10.6
3		■ 305/520	—	■ 328/27	■	18.5

point. ^{1}H NMR (solvent $CDCl_3$) and ^{31}P NMR (solvent THF) were recorded on a JEOL JNM-GX 270 spectrometer using TMS as the internal standard for the former and 85% H_3PO_4 as the external standard for the latter. The lock signal for the ^{31}P NMR was provided by the external D_2O inserts. IR spectra were measured in KBr disks using a Perkin Elmer FT-IR 1600.

3. RESULTS AND DISCUSSION

In the DSC thermograms of compound 1 for the first cooling process, only one exothermic peak at 337 K was observed and on the polarizing microscope observations, the eye-piece became from black to the texture of the crystal with birifringence at this temperature. Therefore, this exothermic peak corresponds to the freezing point from an isotropic liquid to a crystal phase. In the second heating process of the DSC thermograms for compound 1, only one endothermic peak corresponding to the melting from a crystal to an isotropic liquid, which was ascertained by the polarizing microscope observation, was observed at 348 K. No mesomorphic phase appeared in compound 1.

In the DSC thermograms of compound 2 for the first cooling process, three exothermic peaks were seen between at 378, 453 and 418 K. Upon cooling from the isotropic liquid on the polarizing microscope, a schlieren of discrination lines with s = ±1 and a simultaneous broken-fan texture was observed between 418 and 453 K, showing the existence of the smectic C(SmC) phase.[17] Compound 2 froze at 418 K into a crystal on the polarizing microscope observation. The exothermic peak at 378 K corresponds to a crystal-crystal phase transition. In the second heating process, four endothermic peaks were observed at 374, 392, 425 and 453 K. The endothermic peaks at 374 and 392 K corresponded to a crystal-crystal phase transition from the polarizing microscopy. Compound 2 melted at 425 K. Between 425 and 453 K a mesomorphic texture similar to the first cooling process was observed, suggesting the existence of the SmC phase. Consequently, an enantiotropic SmC phase appeared in compound 2.

In the DSC thermograms of compound 3 for the first cooling process, two exothermic peaks were seen at 327 and 296 K. Upon cooling from the isotropic liquid on the polarizing microscopy, the growth of the pseudo focal conic fan texture was observed around 327 K which implies that this phase corresponds to a discotic columnar phase. This phase has not yet been identified. For the identification of this phase, more detailed experimental results, for example, x-ray measurements, are needed. At 296 K the textures became those in a crystal with a birefringence. In the second heating process, two endothermic peaks were observed at 305 and 328 K. Between these temperatures, a similar mesomorphic texture to the first cooling process was observed. Therefore, an enantiotropic columnar mesophase appeared in compound 3.

The mesomophic phase transition temperatures and mesomorphic phase transition entropies with the chemical structure of the rigid core of the mesogens in cyclotriphosphazenes and the chemical shifts of the ^{31}P NMR for compounds 1, 2 and 3 are shown in Table I. The thermodynamic data were taken from the second heating process of the DSC thermograms. All ^{31}P spectra of these samples show only one singlet and these results suggest almost complete substitution of the side groups in the cyclotriphosphazenes. The difference in the chemical shift in the ^{31}P NMR shows their different electron circumstances and molecular shapes. In compound 1, no mesomorphic phase was observed. In compound 2, a smectic C phase was observed between 425 and 453 K. In compound 3, the discotic columnar phase was observed between 305 and 328 K. Compared with the side chains of compounds 1, 2 and 3, the outer end tails are similar dodecyloxy groups. However, in compounds 1 and 2, only one dodecyloxy group is attached to the para position of the phenyl rings and in compound 3, two dodecyloxy groups are attached to the 3 and 4 positions of the phenyl rings. The difference in the compounds 1 and 2 is that in the compound 1 the side chains have only shorter phenyl rings but in compound 2 they have longer biphenyl rings as a rigid part of the side chains in the cyclotriphosphazenes. Compound 3 has very different mesomorphic side chains from compounds 1 and 2 which include soft spacer CH_2 groups between the P and O atoms and two dodecyloxy groups at the 3 and 4 positions of the phenyl rings as the end groups in the side chains. Porbably, in compound 1, the rigid part of the mesogen may be too short to form the mesomorphic phase and melted to the isotropic liquid before attaining the mesomorphic transition region. In compound 2, the dodecyloxybiphenoxy side groups are situated perpendicular to the cyclotriphosphazene rings as in the hexakis(4-biphenoxy)cyclotriphosphazene whose structure was determined by the x-ray single crystal structure analysis[18] and such a molecular shape helps the formation of the layer structure of the smectic C phase. In compound 3, the introduction of a biforked mesogen of two dodecyloxy groups at the end and methylene groups between the P and O atoms into the side chains expand the mesomorphic side chains of the cyclotriphosphazene molecules and the molecular shape of the cyclotriphoshazene may become closer to that of discotic. As a result, the discotic phase is thought to appear in compound 3. The entropy of the phase transitions from the mesomorphic phase to the isotropic liquid phase is 37 and 27 $JK^{-1}mol^{-1}$ for compounds 2 and 3, respectively. The value of the former is larger than that of the latter and this suggests that the mesomorphic phase in compound 3 is more disorderd tha compound 2, and its disorder is closer to the isotopic liquid phase than that in compound 2.

In conclusion, in the cyclotriphosphazenes, the molecular shapes and structure of the side chains strongly affect the molecular shapes of the cyclotriphosphazenes which results in the formation of different mesomophic phases of smectic and columnar phases in compounds 2 and 3 and non-existence of the mesomorphic phase in compound 1.

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