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Ferroelectric liquid crystalline phase transition of (*S*)-hexakis(4-(4′-(6-methyl)octyloxy)biphenoxy) cyclotriphosphazene

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(*S*)-Hexakis(4-(4′-(6-methyl)octyloxy)biphenoxy)cyclotriphosphazene (SMOCP) was synthesized in a search for new ferroelectric liquid crystalline compounds. We found an enantiotropic ferroelectric smectic C* phase between 419 and 441 K in SMOCP by using polarizing microscopy and DSC measurements. The spontaneous polarization was estimated to be $-130{\cdot}5\,\mu\mathrm{C\,m^{-2}}$ at 437·6 K, several times larger than that of DOBAMBC ((*S*)-2-methylbutyl 4-(4′-decyloxybenzylidene)aminocinnamate.

Several cyclotriphosphazene compounds in which six mesogenic side groups are linked to a cyclotriphosphazene ring [1–3], have been reported to show a liquid crystalline phase. In particular, we recently found that hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphosphazenes show a smectic C phase, although these side groups have no flexible spacer link to the cyclotriphosphazene ring [4–6]. This finding attracted us to study how 4-alkyloxybiphenyl side groups arrange themselves to form a smectic C phase and moreover, whether these compounds produce smectic C* phases showing ferroelectricity when chiral side groups are used. This communication reports that (*S*)-hexakis(4-(4′-(6-methyl)octyloxy)biphenoxy) cyclotriphosphazene (SMOCP) does show a ferroelectric smectic C* state.

Synthesis of (*S*)-*hexakis*(*4-*(*4′-*(*6-methyl*)*octyloxy*)*biphenoxy*)*cyclotriphosphazene* (*SMOCP*). (*S*)-1-bromo-6-methyloctane (SMOP) was synthesized from the Grignard reagents of (*S*)-1-chloro-2-methylbutane (20·0 g, 0·19 mol) and 1,2-dibromoethane (26·0 g, 0·12 mol) in the presence of dilithium tetrachlorocuprate in THF (100 ml) [7, 8]. The crude products were separated by distilling at 343 K at 8 mmHg; $[\alpha]_{\mathrm{D}}^{28} = +7{\cdot}7°$. (*S*)-4-(6-methyloctyloxy)biphenyl-4′-ol (SMOBP) was synthesized from SMOP (12·0 g, 58 mmol), 4,4′-dihydroxybiphenyl (16·2 g, 87 mmol) and potassium hydroxide (5·0 g, 90 mmol) in ethanol (300 ml); $[\alpha]_{\mathrm{D}}^{26} = +7{\cdot}3°$. Finally, SMOCP was synthesized from the sodium salt of SMOBP (10·0 g, 32 mmol), hexachlorocyclotriphosphazene (1·55 g, 4·4 mmol) and tetra-*n*-butylammonium bromide (1·0 g, 3·2 mmol) in dioxane (45 ml) by heating under reflux for 24 h. The crude crystals obtained were purified by recrystallizing from hexane/THF (20:1) solution after chromatography on a silica gel column (eluant: chloroform); $[\alpha]_{\mathrm{D}}^{27} = +5{\cdot}9°$. Samples were judged to be fully purified using TLC, GC, IR, ^{1}H NMR and ^{31}P NMR. ^{31}P NMR spectra were measured using THF solutions whose surroundings were locked by D_2O and using H_3PO_4 as a standard. The data showed only one singlet peak near 20·0 ppm for hexachlorocyclotriphosphazene and only one singlet peak at 10·6 ppm for SMOCP, suggesting that all six chlorine atoms in the hexachlorocyclotriphosphazene had been replaced by the side groups.

Phase transition temperatures and their entropy changes were measured by differential scanning calorimetry (Seiko Electronics DSC 210) and texture observations were made using a Nikon Optiphotopol XTP-11 optical polarizing microscope equipped with a Mettler FP 82 hot stage, at a heating/cooling rate of 5 K min^{-1}. Spontaneous polarization was measured by a triangular wave method [9–11] using a homogeneously oriented liquid crystalline sample in a cell with 12 μm thick spacers.

For SMOCP, DSC data showed endothermic peaks near 384, 411, 419 and 441 K on the first heating and at 441, 403 and 352 K on the first cooling. Based on microscope observations with crossed polarizers, SMOCP melted at

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419 K and showed simultaneously a schlieren texture with disclinations having $s = \pm 1$ and a broken fan texture between 419 and 441 K. The broken fan texture also had striped pattern (pitch lines) as shown in figure 1. This indicates the existence of smectic C*. The width of the stripes corresponds to a full pitch of the S_C^* phase and the full pitch was estimated to be about 15 μm at 433 K. This large pitch suggests that the twisting power in SMOCP is relatively weak. The spontaneous polarization of the S_C^* phase in SMOCP was measured in a homogeneously aligned cell of 12 μm thickness. The alignment was obtained by rubbing the surface of the ITO electrodes, which were coated by a polyimide, PSI-A-X044-CF1 of Chisso Co., Ltd., with velvet. A racemic composition of hexakis(4-(4′-(6-methyl)octyloxy)biphenoxy)cyclotriphosphazene (MCOP), which was synthesized separately by the same procedure as that for SMOCP, was used to determine the base line of the signal [12].

Figure 1. Photomicrograph (× 100) at 433 K (crossed polarizers) for the S_C^* phase of SMOCP in the first cooling process.

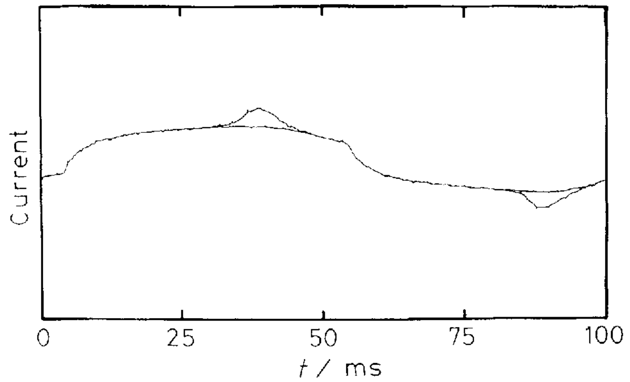

Figure 2. Typical signal for the spontaneous polarization measured by a triangular wave method at 437·6 K for the S_C^* phase of SMOCP.

A typical signal for the spontaneous polarization is shown for SMOCP in figure 2; the spontaneous polarization is seen as a hump on a base line which is the signal provided by the racemic composition of MOCP. The spontaneous polarization was estimated to be $-130{\cdot}5\,\mu\mathrm{C\,m^{-2}}$ at 437·6 K, and the sign of the polarization was determined by applying the d.c. electric field in a normal direction to the cells. The P_S value is about 5 times larger than that of (*S*)-2-methylbutyl (4-(4′-decyloxybenzylidene)aminocinnamate (DOBAMBC) ($P_S = 30\,\mu\mathrm{C\,m^{-2}}$, at $T_c - T = 2$ K) [13].

In conclusion , we confirm the existence of a ferroelectric smectic C* state for SMOCP. In SMOCP, six chiral (*S*)-(4-(4′-(6-methyl)octyloxy)biphenoxy (SMO) groups are linked to the cyclotriphosphazene ring with no flexible chain spacer. The chiral SMO groups could be perpendicular to the cyclotriphosphazene ring, in 2 sets of three (*S*)-4-(6-methyloctyloxy)biphenoxy side chains, one above and one below as found in hexabiphenoxycyclotriphosphazene [14]. Therefore the ferroelectricity of SMOCP is a very interesting and unusual property. Studies of the relationship between the ferroelectricity and the structure are progressing in our laboratories.

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