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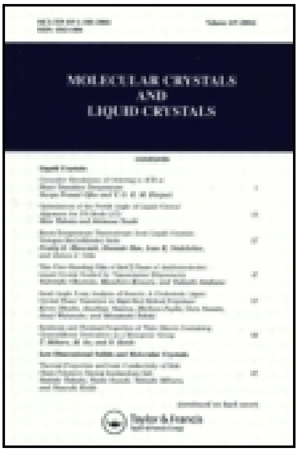

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Synthesis and Characterization of Polypropyleneimine Dendrimers Having Peripheral Mesogenic Groups: Homeotropic Orientation and Mesogen Structure

O. Haba [a] , D. Hiratsuka [a] , T. Shiraiwa [a] , T. Koda [a] , K. Yonetake [a] , Y. Momoi [b] & K. Furuta [b]

[a] Graduate School of Science and Engineering, Yamagata University Yonezawa , Yamagata , Japan

[b] LG Display Japan Laboratory, Glass Cube Shinagawa , Shinagawa-ku , Tokyo , Japan

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Synthesis and Characterization of Polypropyleneimine Dendrimers Having Peripheral Mesogenic Groups: Homeotropic Orientation and Mesogen Structure

O. HABA,[1,*] D. HIRATSUKA,[1] T. SHIRAIWA,[1] T. KODA,[1]
K. YONETAKE,[1] Y. MOMOI,[2] AND K. FURUTA[2]

[1]Graduate School of Science and Engineering, Yamagata University Yonezawa, Yamagata, Japan
[2]LG Display Japan Laboratory, Glass Cube Shinagawa, Shinagawa-ku, Tokyo, Japan

In order to estimate the effectiveness of mesogenic structure on the spontaneous homeotropic orientation of side-chain type liquid crystalline dendrimers, five mesogens, 4′-methoxybiphenyl (PPO1), 4-methoxyphenyl benzoate (BPO1), trans-4-(4-pentylcyclohexyl)phenyl (PC5), 4′-fluorobiphenyl (PPF), and 3′,4′,5′-trifluorobiphenyl (PPF_3), were introduced to the terminal amino groups of a second-generation polypropyleneimine dendrimer. Among them, the PC5 mesogen exhibited superior homeotropic orientation during the slow cooling process from the isotropic melt. Using the PC5 mesogen, the effect of the spacer length (n) was also examined. Homeotropic orientation was observed only for n = 3 and 6, which exhibited a stable smectic A phase in a wide temperature range.

Keywords DSC; homeotropic orientation; polypropyleneimine dendrimer; POM; smectic phase; XRD

Introduction

Dendrimer-based liquid crystalline (LC) materials are seeking great attention due to their unique structures and properties. Numerous LC dendrimers, including side chain, main chain, and dendron types, have been reported [1–5]. Side-chain LC dendrimers consisting of peripheral mesogenic groups with dendritic cores, including polyamidoamine, polypropyleneimine, polycarbosilane, polysiloxane, and so on, have been reported. The relationship between their liquid crystallinity and the structure of LC dendrimers, such as generation, mesogenic unit, length of spacer between the dendritic core and the mesogenic units, has been also studied. According to the reports, side-chain LC dendrimers tend to form smectic or discotic columnar phases depending on the mesogenic structure. Mesogens having one terminal alkyl group tend to cause the smectic phase, and those with two or more alkyl groups favor the discotic phase.

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[*] Address correspondence to Osamu Haba, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan. Tel.: +81-238-26-3091. E-mail: haba@yz.yamagata-u.ac.jp

We have also reported syntheses and characterizations of poly(amidoamine)-based and polypropyleneimine-based side-chain LC dendrimers possessing rigid 4′-cyanobiphenyl [6–8], 2,3-dicyanophenyl [9], or 2,3-difluorophenyl [10] mesogens. Among them, the polypropyleneimine dendrimer with mesogenic groups coupled through ester linkage exhibited a thermotropic LC nature showing the smectic A phase. Furthermore, spontaneous homeotropic orientation took place in LC dendrimers with a second-generation scaffold, when it was slowly cooled or kept in the smectic A phase on an untreated glass surface [8–10]. Such homeotropic orientation has been observed in some LC dendrimers having cholesteryl mesogenic groups [11–13] or dodecyloxy groups [12,14] on a mica, carbon, or glass surface, but has not been reported for other numerous dendrimers. Thus, there are still some questions as to why spontaneous homeotropic orientation occurred, and what type of LC dendrimers aligns homeotropically on a native glass surface.

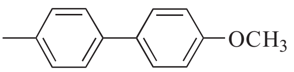
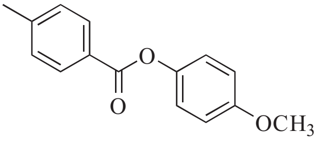
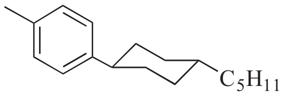
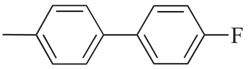
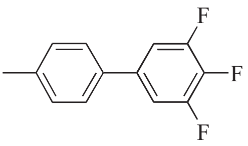
For the spontaneous homeotropic orientation of LC dendrimers between two glass substrates, we have assumed that the dendrimers form a cylindrical shape by gathering together the mesogenic groups in their smectic phase [10]. The tail of the mesogenic groups in such structural contact with the glass surface, and therefore the affinity of the mesogenic groups to the glass surface, may play an important role for such an orientation. In this paper, we prepared and characterized second-generation polypropyleneimine-based LC dendrimers having five different types of mesogens with C_6 spacers, and investigate the relationship between the mesogenic structure and the homeotropicity. In addition, the effect of the spacer length was also examined.

Results and Discussion

Synthesis and Characterization of LC Dendrimers

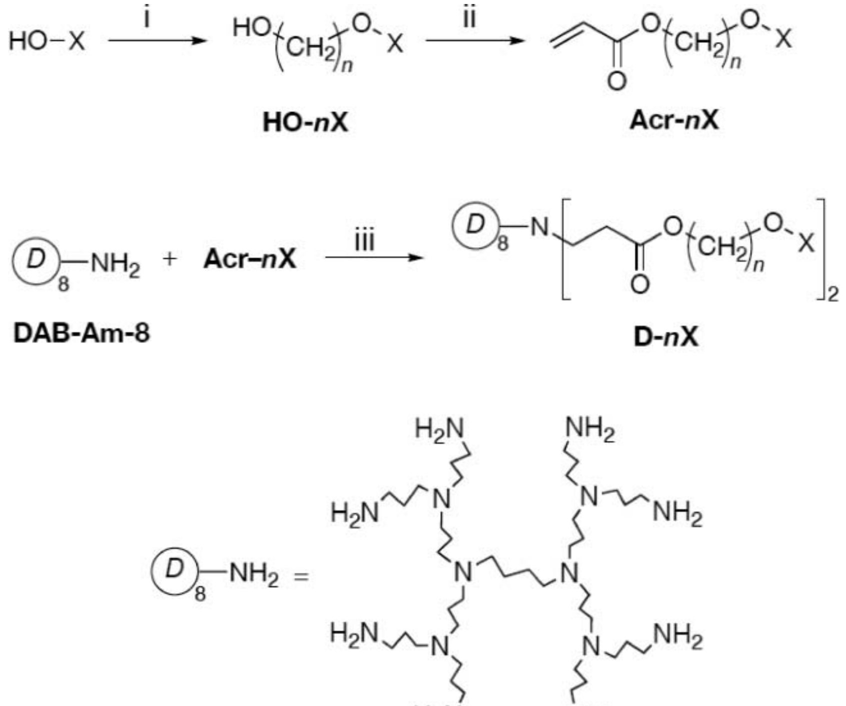
Our previous dendrimers possess cyano and butoxy groups in the termini, and these seem to be sufficient for homeotropic orientation. In order to estimate the affinity, we selected

Table 1. Abbreviations for the mesogenic units

X	Structure
PPO1	
BPO1	
PC5	
PPF	
PPF_3	

five mesogens, 4′-methoxybiphenyl (PPO1), 4-methoxyphenyl benzoate (BPO1), *trans*-4-(4-pentylcyclohexyl)phenyl (PC5), 4′-fluorobiphenyl (PPF), and 3′,4′,5′-trifluorobiphenyl (PPF$_3$) shown in Table 1, considering their availability. PPO1 and BPO1 have shorter alkyl groups than the butoxy group, whereas the 4-pentylcyclohexyl group of PC5 can be regarded as a longer alkyl chain. PPF and PPF$_3$ have one and three hydrophobic fluorine atoms, respectively, and many F atoms should cause much repulsion toward the glass surface.

We prepared eight second-generation polypropyleneimine dendrimers peripherally modified with the mesogenic groups as shown in Table 1. We named the dendrimers "D-*n*X," where *n* is the number of carbons in the spacer chain, and X stands for the mesogenic groups. D-*n*Xs were prepared by our previously reported procedure, starting from the corresponding phenols, as shown in Scheme 1. The phenols react with ω-bromoalkanols to give alcohols (HO-*n*X) having the mesogen, which was converted to an acrylate (Acr-*n*X). The introduction of Acr-*n*X to the commercial second-generation polypropyleneimine dendrimer (DAB-Am-8) was achieved by Michael addition of the peripheral amino groups to the acrylate. The reaction was conducted by heating the DAB-Am-8 and Acr-*n*X at 50°C in tetrahydrofuran (THF) for 1 week monitoring a disappearance of the primary and secondary amino groups due to incomplete additions by ^{1}H NMR spectroscopy. The reaction mixture was poured into methanol and the precipitate was filtered and washed with methanol several times. The target dendrimers were obtained as a white or pale yellow sticky solid except for D-6P$_2$F$_3$, which was colorless viscous oil at room temperature.



Scheme 1. Preparation of D-*n*Xs[a]. a) Conditions: (i) HO—(CH$_2$)$_n$—Br, K$_2$CO$_3$, 2-butanone, reflux, 60 h; (ii) CH$_2$=CH—COCl, Et$_3$N, THF, 60°C, RT, 24 h; (iii) THF, 60°C, 7 days.

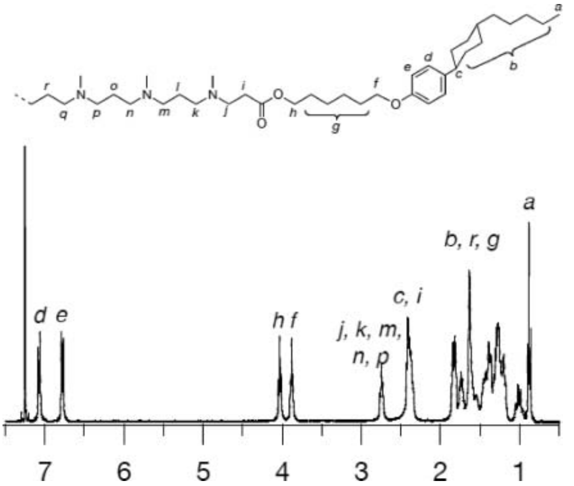


Figure 1. ^{1}H NMR spectra of D-6PC5 measured in $CDCl_3$ at room temperature.

The infrared (IR) spectra of all dendrimers showed characteristic ester carbonyl bands at 1730 cm^{-1}, and no peaks at 3290–3300 cm^{-1} due to the presence of primary amino groups. Figure 1 shows the ^{1}H NMR spectrum for D-6PC5, which has 16 cyclohexylphenyl units at the chain ends. Some distinct features are apparent. All protons in the structure were identified. All assignments are inset in Fig. 1. Other dendrimers also showed similar ^{1}H NMR spectra.

The molecular weights of D-6Xs were estimated by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. The dendrimers show one signal that is clearly due to the formation of the desired dendrimers with 16 mesogens. The obtained *m/z* values of the signal corresponded to the calculated value. The results are also listed in Table 2. These results clearly indicate the formation of the desired dendrimers modified with terminal mesogenic groups.

Phase Transition of D-6Xs

Figure 2 shows differential scanning calorimetry (DSC) traces of D-6Xs, having C_6 spacers, in the second cooling process. The dendrimers showed exothermic peaks except for D-6PPF$_3$, which is viscous oil at room temperature. D-6PPO1 and D-6PC5 showed two

Table 2. Results of MALDI-TOF MS measurements[a]

	Molecular weight (M+Na$^+$) (Da)	
LC dendrimer	Theoretical	Observed
D-6PC5	7205.57	7209.03
D-6PPO1	6466.74	6468.07
D-6PBO1	7170.57	7172.48
D-6PPF	6274.42	6273.65
D-6PPF$_3$		—

[a] Measured using DHBA as the matrix.

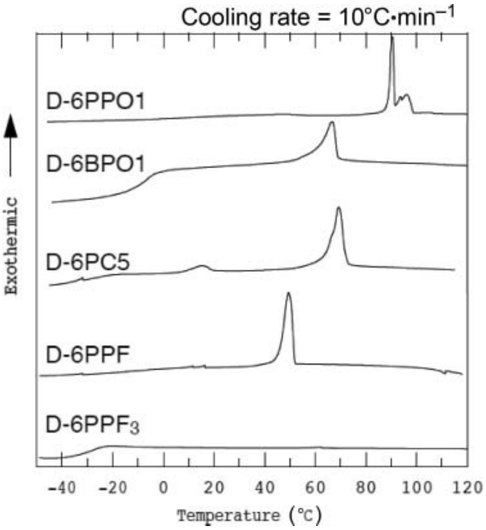


Figure 2. DSC thermograms of D-6Xs in the second cooling cycle. Cooling rate=10°C·min^{-1}.

distinct peaks, which indicate they form two kinds of mesophase. The optical textures of D-6Xs were observed under polarizing optical microscope (POM) with crossed polarizers to explore the LC phases. D-6PPF$_3$ showed a dark field within the whole temperature range due to the isotropic phase, and did not form a LC phase. Similar dark isotropic melts were observed at 100°C for the other D-6Xs, and therefore phase transition at a higher temperature is due to a clearing point. Figure 3 shows typical optical textures at temperatures below the clearing point. D-6PPO1 shows a schlieren texture, D-6PBO1 and D-6PC5 a focalconic fan texture, and D-6PPF a tiny schlieren texture. Thus, all samples exhibit an LC nature. X-ray diffraction (XRD) measurements were carried out to determine

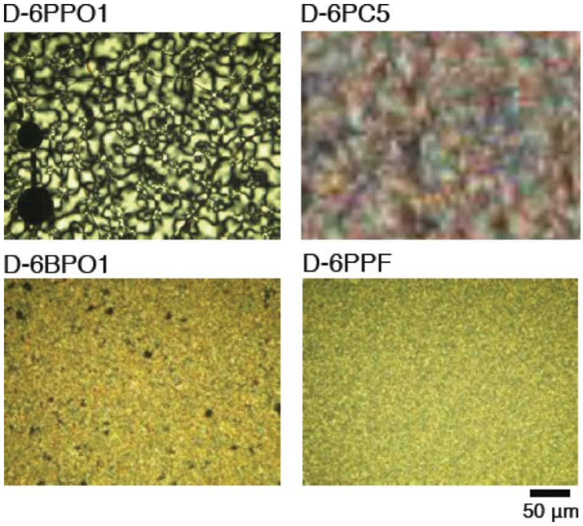


Figure 3. Polarizing optical micrographs of D-6Xs.

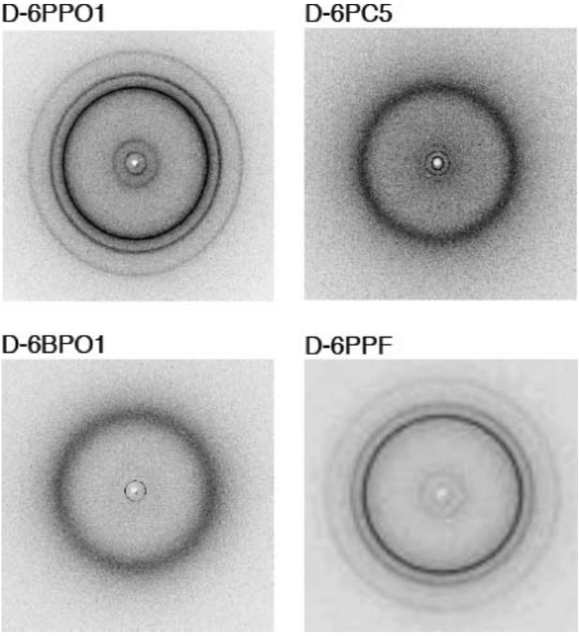


Figure 4. X-ray diffraction patterns of D-6Xs.

the liquid crystal phases. The XRD patterns and intensity curves are shown in Figs. 4 and 5, respectively. The XRD patterns of all samples show Debye–Sherrer rings at the small-angle area. The reflections are due to smectic layer structure. D-6PPO1 and D-6PPF show comparatively sharp rings at the wide-angle area. The three reflections at the wide-angle area could be assigned to (110), (200), and (210) reflections of an orthorhombic packing mode. Thus, their LC phases are smectic E (SmE). The lattice parameters, *a* and *b*, of D-6PPO1 and D-6PPF were estimated from the *d* values of the three reflections as shown in Table 3. In contrast, a diffuse halo at the wide-angle area was observed in D-6PBO1 and D-6PC5. The diffuse reflection at the wide-angle area was obtained at approximately 0.45 nm, which corresponds to the lateral distance between the mesogens. These results confirmed that their LC phases were smectic A (SmA).

Figure 6 shows POM images of the D-6Xs during slow cooling (cooling rate = 1.0°C·min^{-1}) from isotropic melt on the native glass surface. The textures of D-6PPO1 and D-6BPO1 below the clearing point were unchanged until the temperature reached T_g. On the other hand, the focalconic fan texture of D-6PC5 disappeared and the area of dark field gradually expanded. The typical cross isogyre was observed in the dark field by conoscopic

Table 3. Lattice parameters *a* and *b* of SmE phase for D-6PPO1 and D-6PPF

	Lattice parameter (nm)	
Sample	*a*	*b*
D-6PPO1	0.74	0.55
D-6PPF	0.78	0.53

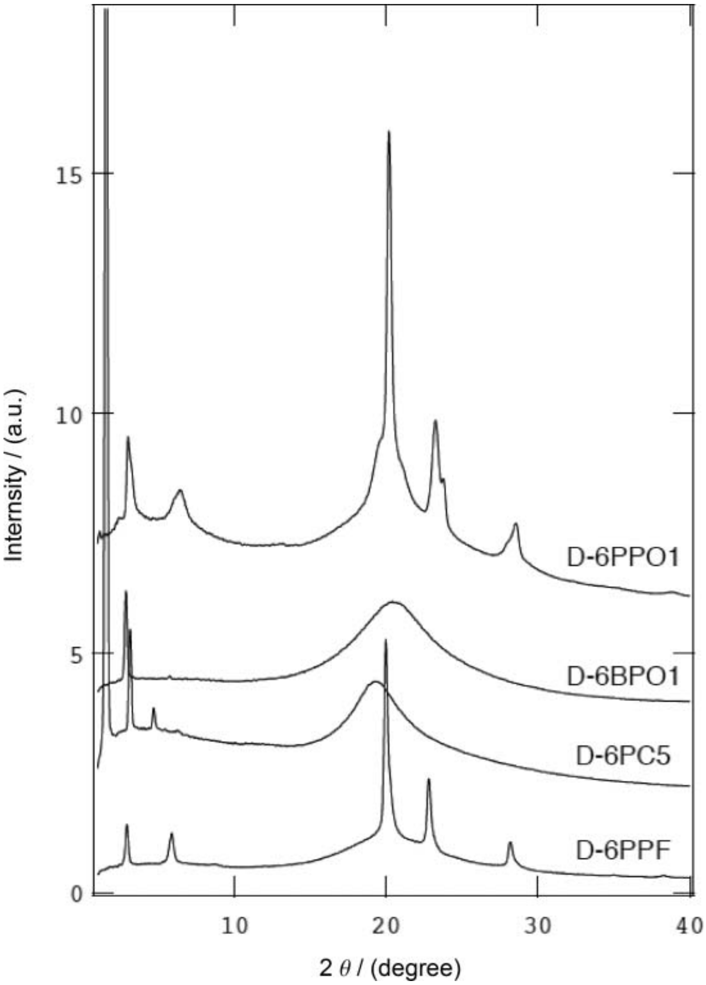


Figure 5. X-ray diffraction intensity curves of D-6Xs.

observation under a polarizing optical microscope. This suggests spontaneous homeotropic orientation on the native glass surface.

Changes in Phase Transition of D-nPC5s With Spacer Length

As mentioned above, the PC5 mesogen showed superior homeotropicity compared to the other four mesogens. Then we prepared D-3PC5 and D-12PC5, which have C_3 and C_{12} spacers, respectively, with the PC5 mesogen, in order to examine the effect of spacer length on the homeotropicity. Table 4 summarizes the phase transition behavior of the D-*n*PC5s. D-3PC5 and D-12PC5 showed two-phase transition temperatures above T_g in their DSC measurements as well as D-6PC5. From POM observations and XRD measurements, they exhibited smectic B and smectic A phases at the lower and the higher temperature region, respectively, as shown in D-6PC5. Figure 7 shows the effect of the spacer length (*n*) of D-*n*PC5 on the phase transition temperature. It was clearly seen that the longer alkyl spacer makes the SmB phase thermodynamically stable.

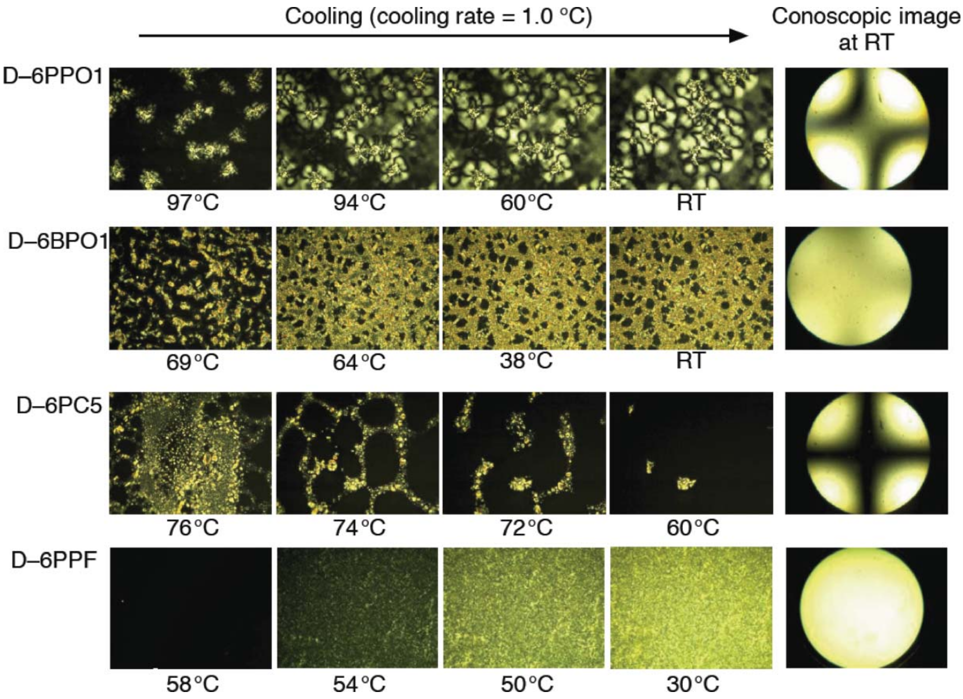


Figure 6. Polarizing optical micrographs of D-6Xs under cooling at 1°C×min^{-1} from melt.

Figure 8 shows the optical textures of D-*n*PC5s ($n = 3$ and 12) slowly cooled at 1°C·min^{-1} from isotropic melt on the native glass surface. Similar to D-6PC5, the optical texture of D-3PC5 disappeared and the area of dark field gradually expanded with cooling. D-3PC5 also showed the typical conoscopic pattern, which suggests that D-3PC5 can spontaneously aligned homeotropically on the native glass surface. On the other hand, when D-12PC5 was cooled slowly, the fan shape texture did not disappear until reaching the glass transition temperature. The temperature range showing the smectic A phase was much narrower for D-12PC5 compared to D-3PC5 and D-6PC5. Therefore, spontaneous homeotropic orientation, observed for D-3PC5 and D-6PC5 should occur in their smectic

Table 4. Phase transition behavior of D-*n*PC5s[a]

	Phase transition temperature (°C) (Δ*H* (J g^{-1}))	
	Heating	Cooling
D-3PC5	G –8.1 S_B 16.9 (0.79) S_A 77.9 (9.24) I	I 74.3 (8.49) S_A 15.5 (0.64) S_B –14.1 G
D-6PC5	G –15.2 S_B 20.2 (1.18) S_A 73 (9.70) I	I 69.4 (10.0) S_A 16.7 (1.40) S_B –20.6 G
D-12PC5	G 8.6 SB 74.2 (11.2) SA 81.8 (9.60) I	I 79.8 (9.6) S_A 72.6 (9.80) S_B 5.2 G

[a] G: glassy, S_B: smectic B, S_A: smectic A, I: isotropic.

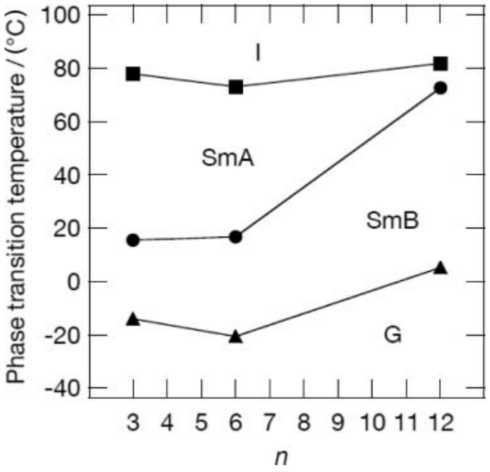


Figure 7. Plots of the phase transition temperatures of D-*n*PC5s versus the number of carbon atoms in the spacer (*n*), measured in second cooling scan.

A phase, and such rearrangement of the mesogenic units hardly occurs in the higher order smectic B phase.

Effect of the Mesogen Structure on the Homeotropic Orientation

From the results about D-*n*PC5s, it is suggested that the homeotropic orientation should occur in the smectic A phase. This is supported by the results that PPO1 and PPF mesogens, which exhibited smectic B phase, also did not show the homeotropic orientation. However, the BPO1 mesogen did not show homeotropic orientation although that exhibited stable smectic A phase as well as PC5. Thus, the alkyl chain in termini of PC5 might be effective for the homeotropic orientation. This should be supported by the results in our previous works (butoxy termini) and in literature (dodecyloxy termini). Unfortunately, the affinity of mesogen toward the glass surface still remains unclear, because the both fluorinated mesogens, PPF and PPF_3, did not orient homeotropically. Therefore, further works should

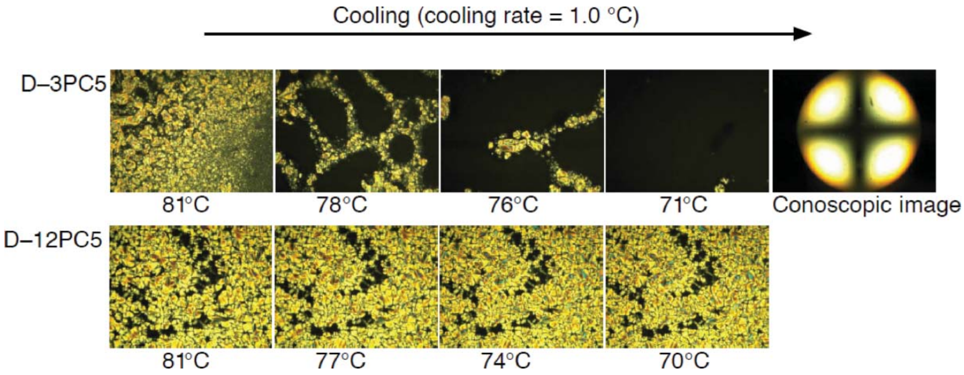


Figure 8. Polarizing optical micrographs of D-*n*PC5s under cooling at 1°C×min^{-1} from melt.

be necessary to clear the effect of polar terminal groups and length of the alkyl termini in the future.

Summary

As described above, five mosogens were introduced to second-generation polypropyleneimine dendrimers to examine the effectiveness of the mesogenic structure on the spontaneous homeotropic orientation of LC dendrimers on a native glass surface. Among them, the PC5 mesogen exhibited superior homeotropic orientation during the slow cooling process from isotropic melt. Using the PC5 mesogen, the effect of the spacer length (n) was also examined. The LC dendrimers with $n = 3$ and 6 exhibited a stable smectic A phase in a wide temperature range, whereas the smectic B phase was stable with $n = 12$. Homeotropic orientation was not observed with $n = 12$, and therefore the stable smectic A phase seems to be necessary during the slow cooling process in order to homeotropically rearrange the mesogenic units.

Experimental Section

Measurements

The IR spectra were recorded on a HORIBA FT-210 spectrometer, and the NMR spectra on a JEOL JNM-ECX 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer. MALDI-TOF ultraviolet mass spectroscopy was performed on a PE Biosystems Voyager-DE Pro spectrometer using 2,4-dihydroxybenzoic acid (DHBA) as the matrix. DSC was recorded on a TA instrument Q200 instrument at a heating/cooling rate of 10°C·min^{-1} in nitrogen. Optical textures of the samples were examined using a POM (Olympus Co. Ltd.) equipped with a hot stage (Linkam Co., TH-600RMS) under nitrogen. XRD experiments were carried out on a RAD-rA diffractometer (Rigaku Denki Co. Ltd.) equipped with a heating device. Nickel-filtered CuKα radiation was employed. XRD traces were recorded by a scintillation counter system with a 1.0-mm diameter pinhole collimator and $1^\circ \times 1^\circ$ receiving slit. Diffractometry was performed in transmission. The XRD traces were obtained by a step-scanning method: step width and fixed time were programmed for steps of 0.05° every 10 s. XRD photographs were taken with a flat Laue camera with a 0.5-mm diameter pinhole collimator.

Materials

4-(*trans*-4-Pentylcyclohexyl)phenol (PC5) (Kanto Chemicals), 6-bromohexanol (TCI), 12-bromodecanol (TCI), 3-bromopropanol (TCI), acryloyl chloride (Ardrich), and second-generation polypropyleneimine dendrimer (DAB-Am-8, Ardrich) were purchased and used as received. 6-[4-(4-Methoxyphenyl)phenyloxy]hexyl acrylate (Acr-6PPO1), 6-[4-(methoxyphenyloxycarbonyl-phenyl]hexyl acrylate (Acr-6BPO1), 6-[4-(4-fluorophenyl) phenyloxy]hexyl acrylate (Acr-6PPF), and 6-[4-(3,4,5-trifluorophenyl)phenyloxy]hexyl acrylate (Acr-6PPF$_3$) were obtained from Koyo Chemical Industry Inc. 6-[4-(*trans*-4-Pentylcyclohexyl)phenoxy]alkyl acrylates (Acr-*n*PC5) were prepared by a previously reported method [15]. THF was distilled from sodium–benzophenone ketyl just before use. Unless otherwise noted, the other chemicals were commercially available and used without further purification.

General Procedure for Peripherally Modified Propyleneimine Dendrimers (D-nX)

A solution of DAB-Am-8 dendrimer, Acr-*n*X, in THF (2.0 mol × L^{-1} for Acr-*n*X) was stirred at 50°C for 72 h under an N_2 atmosphere. The solution was concentrated under reduced pressure. The residue was dissolved to a minimal volume of $CHCl_3$ and the resulting solution was poured into an excess of CH_3OH. The precipitated sticky solid or viscous oil were separated from the solvents by decantation. This operation was repeated further two times and dried in vacuo to give D-*n*X.

D-6PPO1 was prepared from 0.33 g of DAB-Am-8 dendrimer (0.43 mmol) and 7.0 g of Acr-6PPO1 (19 mmol). Yield: 1.3 g (47%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.43 (q, J = 6.4 Hz, 64H, ArH), 6.89 (t, J = 11 Hz, 64H, ArCH), 4.03 (t, J = 6.4 Hz, 32H, OCH_2), 3.91 (t, J = 6.9 Hz, 32H, $PhOCH_2$), 3.79 (s, 48H, OCH_3), 2.75 (t, J = 7.3 Hz, 32H, $N{-}CH_2$), 2.41 (t, J = 7.3 Hz, 84H, $N{-}CH_2$ and $CH_2C{=}O$), 1.85–1.29 (m, 284H, CH_2).

D-6BPO1 was prepared from 0.28 g of DAB-Am-8 dendrimer (0.31 mmol) and 6.0 g of Acr-6BPO1 (15 mmol). Yield: 1.7 g (76%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.07 (d, J = 9.2 Hz, 32H, ArH), 7.08 (d, J = 9.2 Hz, 32H, ArH), 6.92 (t, J = 8.7 Hz, 64H, ArCH), 4.12 (t, J = 6.4 Hz, 32H, OCH_2), 3.98 (t, J = 6.4 Hz, 32H, $PhOCH_2$), 3.78 (s, 48H, OCH_3), 2.74 (t, J = 7.3 Hz, 32H, $N{-}CH_2$), 2.42 (t, J = 6.9 Hz, 84H, $N{-}CH_2$ and $CH_2C{=}O$), 1.91–1.31 (m, 284H, CH_2).

D-6PPF was prepared from 0.33 g of DAB-Am-8 dendrimer (0.43 mmol) and 7.0 g of Acr-6PPF (20 mmol). Yield: 1.9 g (72%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.43 (m, 64H, ArH), 7.05 (t, J = 8.7 Hz, 32H, ArH), 6.88 (d, J = 8.2 Hz, 32H, ArCH), 4.04 (t, J = 6.4 Hz, 32H, OCH_2), 3.91 (t, J = 6.4 Hz, 32H, $PhOCH_2$), 2.74 (t, J = 6.4 Hz, 32H, $N{-}CH_2$), 2.39 (t, J = 6.9 Hz, 84H, $N{-}CH_2$ and $CH_2C{=}O$), 1.84–1.31 (m, 284H, CH_2).

D-6PPF$_3$ was prepared from 0.25 g of DAB-Am-8 dendrimer (0.32 mmol) and 6.0 g of Acr-6PPF$_3$ (15 mmol). Yield: 1.3 g (59%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.37 (d, J = 7.8 Hz, 32H, ArH), 7.08 (t, J = 6.4 Hz, 32H, ArH), 6.89 (d, J = 7.7 Hz, 32H, ArCH), 4.06 (t, J = 6.4 Hz, 32H, OCH_2), 3.94 (t, J = 5.5 Hz, 32H, $PhOCH_2$), 2.74 (t, J = 6.4 Hz, 32H, $N{-}CH_2$), 2.41 (t, J = 6.8 Hz, 84H, $N{-}CH_2$ and $CH_2C{=}O$), 1.86–1.30 (m, 284H, CH_2).

D-3PC5 was prepared from 0.44 g of DAB-Am-8 dendrimer (0.57 mmol) and 6.5 g of Acr-3PC5 (18 mmol). Yield: 2.1 g (57%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.08 (d, J = 8.6 Hz, 32H, Ar–H), 6.78 (d, J = 8.6 Hz, 32H, Ar–H), 4.21 (t, J = 6.3 Hz, 32H, $C\underline{H}_2$–OCO), 3.97 (t, J = 5.9 Hz, 32H, CH_2–O–Ar), 2.74 (t, J = 6.8 Hz, 32H, CH_2–COO), 2.30–2.50 (m, 100H, CH_2–N and Ar–CH), 1.95–2.15 (m, 32H, O–$CH_2C\underline{H}_2CH_2$–O), 1.83 (d, J = 10.9 Hz, 64H, cyclohexyl CH_{2eq}), 1.60–1.73 (br, 4H, N–$CH_2C\underline{H}_2C\underline{H}_2CH_2$–N), 1.47–1.60 (br, 16H, cyclohexyl $C\underline{H}$–CH_2), 1.10–1.47 (m, 184H, alkyl CH_2 and cyclohexyl CH_{2ax}), 0.95–1.10 (m, 32H, $C\underline{H}_2CH_3$), 0.89 (t, J = 7.3 Hz, 48H, CH_3).

D-6PC5 was prepared from 0.48 g of DAB-Am-8 dendrimer (0.62 mmol) and 12 g of Acr-6PC5 (30 mmol). Yield: 2.5 g (56%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.08 (d, J = 8.6 Hz, 32H, Ar–H), 6.79 (d, J = 8.6 Hz, 32H, Ar–H), 4.04 (t, J = 6.8 Hz, 32H, $C\underline{H}_2$–OCO), 3.89 (t, J = 6.3 Hz, 32H, CH_2–O–Ar), 2.76 (t, J = 7.3 Hz, 32H, CH_2–COO), 2.30–2.50 (m, 100H, CH_2–N and Ar–CH), 1.12–1.90 (m, 396H, alkyl CH and CH_2), 0.94–1.10 (m, 32H, $C\underline{H}_2CH_3$), 0.89 (t, J = 7.3 Hz, 48H, CH_3).

D-12PC5 was prepared from 0.26 g of DAB-Am-8 dendrimer (0.34 mmol) and 8.0 g of Acr-12PC5 (17 mmol). Yield: 1.1 g (38%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.09 (d, J = 8.6 Hz, 32H, Ar–H), 6.80 (d, J = 8.6 Hz, 32H, Ar–H), 4.03 (t, J = 6.8 Hz, 32H, $C\underline{H}_2$–OCO), 3.90 (t, J = 6.3 Hz, 32H, CH_2–O–Ar), 2.76 (t, J = 7.2 Hz, 32H, CH_2–COO), 2.30–2.50 (m, 100H, CH_2–N and Ar–CH), 1.17–1.98 (m, 588H, alkyl CH and CH_2), 0.94–1.10 (m, 32H, $C\underline{H}_2CH_3$), 0.89 (t, J = 7.2 Hz, 48H, CH_3).

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