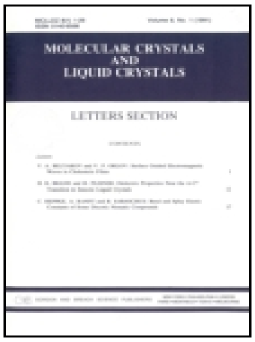

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Homeotropic Alignment of a Linear Polyacrylate Having a Side Chain Consisting of a 1st Generation Polypropyleneimine Dendron with Peripheral Cyclohexylphenyl Mesogens

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Dendronized LC polyacrylate (PA-G1-6PC5) was prepared by the radical polymerization of the 1st generation polypropyleneimine dendron (A-G1-6PC5) having a focal acryloyl and peripheral mesogenic groups. The PA-G1-6PC5 polymer was a thermotropic liquid crystal with a focal conic fan texture in polarizing optical microgram (POM) observations, indicating the formation of a smectic phase. Upon slow cooling, POM images of PA-G1-6PC5 on a native glass substrate showed a dark field with a crossed isogyre in a conoscopic image indicating the homeotropic orientation. Furthermore, a small amount of PA-G1-6PC5 could induce a nematic liquid crystal (NLC) to vertically align.

Keywords dendronized polymer; homeotropic alignment; polyacrylate; dendrimer

Introduction

Liquid crystal (LC) molecules with a dipole respond to an electric field to align along the field, but the director without the electric field generally can not be determined. During LC display production, the orientation without the electric field is especially important because this determines the switching properties of the LC molecules. Alignment layers are widely used today to determine the orientation of the alignment without the electric field. They

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are mainly polyimide wrinkled by a rubbing process which has a negative influence on the integrated circuits of the LCDs and cleanliness of the clean rooms.

We have reported the syntheses and properties of polypropyleneimine dendrimers (PPIDs) having peripheral mesogenic units. The dendrimers, especially exhibiting a stable smectic A phase, tended to exhibit spontaneous alignment in the vertical direction toward a native glass surface. [1–3] When a small amount (typically below 1wt%) of LC dendrimers is dissolved in a nematic LC, the entire LC spontaneously exhibited a vertical alignment property between the bare glass substrates. We have already reported the development of an LC cell without a polyimide alignment layer using this dendrimer-induced vertical alignment. [4, 5] The positive nematic LCs and a comb-like electrode were combined in the cell, in which the LC vertically aligned by the LC dendrimer in the off-state and tilted in the on-state.

Dendronized polymers are one class of branched polymers which is a linear polymer having a side chain consisting of a dendron. For their synthesis, three methods are known, i.e., 1) the reaction of a linear polymer having functional groups which reacts with a focal unit of the dendron, 2) synthesis of a dendron from the functional groups on a linear polymer as a focal unit, and 3) the polymerization of a dendron having a polymerizable focal functional group. [6] The third method has the advantage of quantitative introduction of the dendron. Even though the lower generation of the dendron is used, many mesogens are gathered in one branched molecule by the polymerization. Although the reason for the homeotropic orientation of the LC dendrimers is still obscure, the polymerized dendron should work if the dendrimer architecture gathering the mesogens is effective. We now report the syntheses of a 1st generation LC dendron having a focal acrylate group (A-G1-6PC5) and of a polyacrylate having the dendron (PA-G1-6PC5) through the radical polymerization of A-G1-6PC5. The thermal properties and alignment behaviors of A-G1-6PC5 and PA-G1-6PC5 will also be reported.

Experimental Section

Measurements

The NMR spectra was measured as a 0.5% $CDCl_3$ solution by a JEOL JNM-ECX 400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer. Tetramethylsilane (0.0 ppm) and the solvent peak (77.0 ppm) were used for the internal reference peak for the ^1H and ^{13}C NMR measurements, respectively. Differential scanning calorimetry (DSC) was recorded by a Q200 instrument (TA instruments) at the heating/cooling rate of 10°C/min in nitrogen. Optical textures of the samples were examined using a polarizing optical microscope (POM) equipped with a hot stage (Linkam Co., TH-600RMS).

Materials

4-(*Trans*-4-pentylcyclohexyl)phenol (Kanto Chemicals), 6–bromohexanol (TCI), acryloyl chloride (Aldrich), and Amberlyst 15 ion-exchange resin (Aldrich) were purchased and used as received. A fluoride-type nematic liquid crystal mixture, ZLI-4792 (nematic to isotropic transition temperature: 93°C), was purchased from Merck. 2,2′-Azobis(2-methylpropanenitrile) (AIBN) was purchased from Kanto Chemicals and recrystallized from methanol. Tetrahydrofuran (THF) was distilled from sodium – benzophenone ketyl just before use. *N*,*N*-Bis(3-aminopropyl)-*N*-2-hydroxyethylamine (HO-G1-NH_2)

was prepared according to the procedure reported by Hahn et al. [7] 6-[4-(*Trans*-4-pentylcyclohexyl)phenoxy]hexyl acrylate (A-6PC5) was prepared by a previously reported method. [8] Unless otherwise noted, all other chemicals were commercially available and used without further purification.

The first generation LC dendron having a focal hydroxy group (HO-G1-6PC5). A mixture of HO-G1-NH_2 (0.10 g, 0.58 mmol), A-6PC5 (1.1 g, 2.8 mmol) and Amberlyst 15 (0.33 g) was stirred for 6 h at 60°C under a nitrogen atmosphere. Dichloromethane was added and the insoluble material was filtered off. The filtrate was concentrated under reduced pressure. The residue was purified by preparative SEC using $CHCl_3$ as the eluent to give a yellowish viscous oil. Yield 0.35 g (0.20 mmol, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.12–6.80 (m, 16H, Ph), 4.07 (t, $J = 6.9$ Hz, 8H, $-COOCH_2-$), 3.92 (t, $J = 6.4$ Hz, 8H, $-CH_2OAr$), 3.55 (t, $J = 5.3$ Hz, 2H, $HOCH_2$–), 2.77 (t, $J = 7.1$ Hz, 8H, $-NCH_2CH_2COO-$), 2.55 (t, $J = 5.0$ Hz, 2H, $HOCH_2CH_2N-$), 2.50-2.35 (m, 20H, $OCO-CH_2$– and Ar$-$CH<), 1.92-0.86 (m, 116H, CH_2).^{13}C NMR (100 MHz, $CDCl_3$) : δ (ppm) = 173 (C=O), 157, 140, 127, 114 (Ar), 68 ($-CH_2OAr$), 64 (CH_2COO-), 59 ($HOCH_2$), 56 ($HOCH_2CH_2$), 49 (NCH_2CH_2COO), 44 (OPhCH), 52, 37, 35, 34, 32, 28, 27, 26, 25, 22, 14.

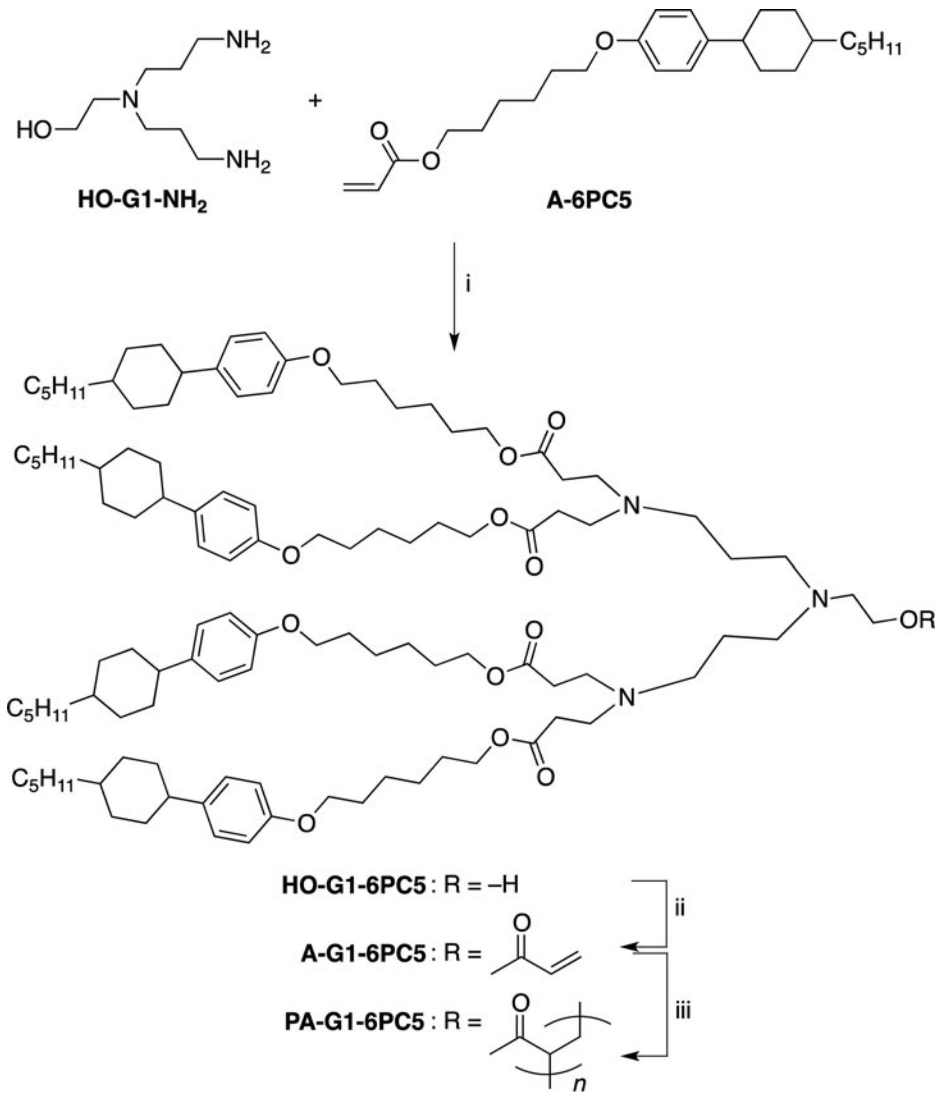
The first generation LC dendron having a focal acryloyl group (A-G1-6PC5). A solution of HO-G1-6PC5 (0.20 g, 0.11 mmol) and triethylamine (0.024 ml, 0.17 mmol) in THF (4.0 mL) was stirred for 30 min at room temperature. The mixture was cooled in an ice bath and acryloyl chloride (0.028 ml, 0.34 mmol) was dropwise added. The mixture was stirred for 3 days at room temperature, then concentrated under reduced pressure. The residue was dissolved in 50 mL of $CHCl_3$, and washed with saturated aqueous $NaHCO_3$ (20 mL × 2), water (20 mL × 3) and brine (20 mL × 2). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by a preparative SEC eluted using $CHCl_3$ to give a yellow viscous oil. Yield 98 mg (0.054 mmol, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) : δ (ppm) = 7.12–6.81 (m, 16H, Ph), 6.41 (d, $J = 17.4$ Hz, 1H, $CH_2 = CH-$), 6.14 (dd, $J = 17.8$ 10.5 Hz, 1H, $CH_2{=}CH-$), 5.81 (d, $J = 10.6$ Hz, 1H, $CH_2{=}CH-$), 4.21 (s, 2H, $-OCH_2CH_2N-$), 4.07 (t, $J = 6.6$ Hz, 8H, $-OCH_2-$), 3.92 (t, $J = 6.2$ Hz, 8H, $-CH_2OPh$-), 2.79–0.89 (m). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 173 (C=O), 160 ($CH_2{=}CHCOO$), 157, 140, 127, 114 (Ph), 131 ($CH_2{=}CH$), 128 ($CH_2{=}CH$), 68 (CH_2OPh), 64 (CH_2COO), 49 (NCH_2CH_2COO), 44 (OPhCH), 52, 51, 37, 35, 34, 32, 29, 28, 27, 26, 25, 22, 14.

Radical polymerization of A-G1-6PC5 (PA-G1-6PC5). A solution of A-G1-6PC5 (78 mg, 0.043 mmol) and AIBN (0.80 mg, 0.0049 mmol) in THF (0.40 mL) was stirred for 12 h at 60°C under a nitrogen atmosphere. The solvent was removed by a rotary evaporator and the residue was purified by preparative SEC eluted using $CHCl_3$ to give a pale yellow powder. Yield, 19 mg (24%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.09–6.79 (m, Ph), 4.03 (m), 3.89 (m), 2.75–0.79 (m).

Results and Discussion

Synthesis of PA-G1-6PC5

The synthetic procedure of PA-G1-6PC5 is shown in Scheme 1. In our previous report, the introduction of mesogenic groups into PPID was carried out by the aza-Michael reaction between the amino groups of PPID and acrylate having mesogenic units through the spacer alkyl chain. If we use a similar methodology for the polymerizable LC dendron, we require a focal functional group which does not affect the aza-Michael reaction and can easily



Scheme 1. Synthesis of PA-G1-6PC5. Conditions: i) Amberlyst 15, THF, 40°C, ii) $CH_2{=}CH{-}COCl$, Et_3N, THF, RT, iii) AIBN, THF, 60°C.

convert to the polymerizable functional group. We selected the hydroxyl group as such a focal unit. Syntheses of the polypropyleneimine dendron having a focal OH group have already been reported by Hahn and his co-workers. [7] According to them, we prepared the 1st generation polypropyleneimine dendron (HO-G1-NH_2), which was reacted with 6-[4-(trans-4-pentylcyclohexyl)phenoxy]hexyl acrylate (A-6PC5) [8], to produce the LC dendron HO-G1-6PC5 in a manner similar to the syntheses of the LC dendrimers. The aza-Michael was successfully achieved in the presence of an acid-type ion-exchange resin. The focal OH group of HO-G1-6PC5 was acrylated by a conventional esterification reaction with acryloyl chloride in the presence of triethylamine to give the acrylated dendron (A-G1-6PC5). The dendrons were purified by a preparative size-exclusion chromatograph (SEC)

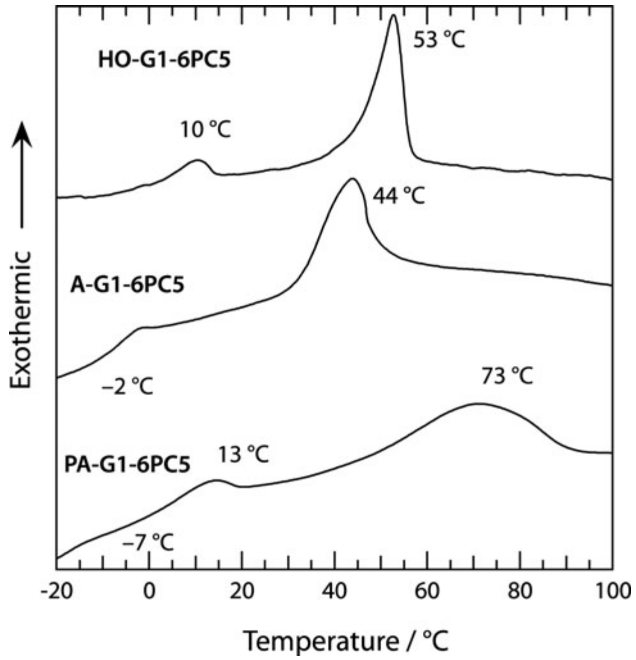


Figure 1. DSC traces of HO-G1-6PC5, A-G1-6PC5 and PA-G1-6PC5 on 2nd cooling scan. $\Delta T = 10^{\circ}\mathrm{C}\ \mathrm{min}^{-1}$.

equipped with a polystyrene-gel column. The structures of the dendrons were confirmed by ^{1}H and ^{13}C NMR and IR spectra, in which the signals and peaks could be assigned without any inconsistency. The polyacrylate PA-G1-6PC5 was synthesized by the free radical polymerization of A-G1-6PC5, which was carried out with 10 mol% of 2,2′-azobis(2-methylpropanenitrile) (AIBN) as the initiator in THF at 60°C for 12 h. The resulting product after purifying by a separative SEC was obtained in 27% yield and had an Mn of 7700 with an Mw/Mn of 1.38.

Thermal Properties

Figure 1 shows the differential scanning calorimetry (DSC) traces of the products in the second cooling process. The OH-bearing dendron HO-G1-6PC5 showed two exothermic peaks at 10°C and 53°C, while A-G1-6PC5 showed a single peak at 44°C and a baseline shift due to the glass transition at –2°C. PA-G1-6PC5 showed two exothermic peaks at 13 and 73°C and a glass transition at –7°C. The optical textures of the dendrons were observed under a polarized optical microgram (POM) with crossed polarizers to explore the liquid crystalline phases. Dark isotropic melts were observed at 75°C for all compounds, therefore, the phase transitions at the higher temperature are due to a clearing point. Figure 2 shows typical optical textures at temperatures below the clearing point. Both samples showed a tiny focalconic fan shape texture indicating the smectic phase, therefore, they exhibit a thermotropic liquid crystalline nature. The mesophase-isotropic transition temperature rose during the polymerization from A-G1-6PC5 to PA-G1-6PC5. The melting point of the latter at 73°C is comparable to the corresponding dendrimer ($T_{\mathrm{SI}} = 69.4^{\circ}\mathrm{C}$) [3], and thus the polymerization should be effective to stabilize the mesophase.

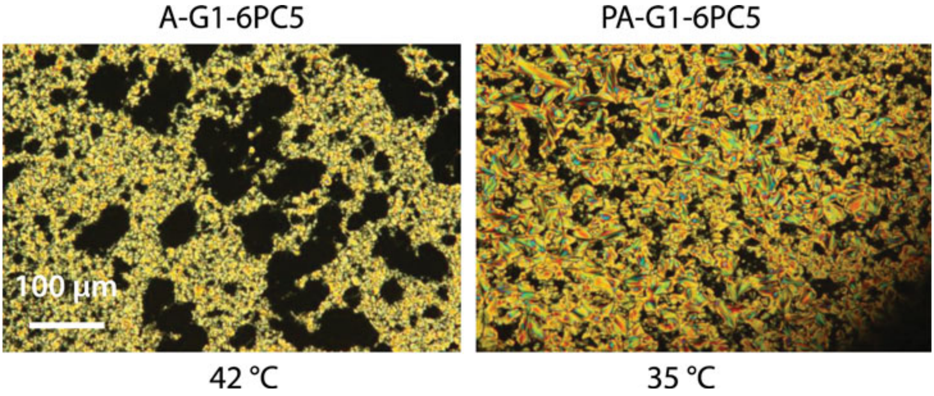


Figure 2. Typical POM images of A-G1-6PC5 and PA-G1-6PC5 below the clearing point.

Homeotropic Alignment of A-G1-6PC5 and PA-G1-6PC5

Figure 3 shows POM images of A-G1-6PC5 and PA-G1-6PC5 during slow cooling (–1.0°C min^{-1}) from the isotropic melt on the native glass surface. For both compounds, the focalconic fan texture disappeared and the dark field area gradually expanded. The typical cross isogyre was observed in the dark field by conoscopic observation under a polarizing optical microscope. This suggests that the dendrons exhibit a spontaneous homeotropic orientation on the native glass surface like the LC dendrimers.

In order to examine the abilities of PA-G1-6PC5 to induce the homeotropic alignment of the low-molecular weight nematic LC, PA-G1-6PC5 was mixed with a commercial nematic LC mixture, ZLI-4792 (Merck), at a 1wt% content. PA-G1-6PC5 completely dissolved in the ZLI-4792 to produce a homogeneous mixture. Figure 4 shows the POM images of the mixture during slow cooling from the isotropic melt. At 98°C, the schlieren texture due to the nematic phase appeared. This immediately disappeared with cooling, and the homogeneous dark field appeared at 91°C was maintained until the temperature reached room temperature. The cross isogyre was also observed by conoscopic observation at room temperature, therefore, it was confirmed that PA-G1-6PC5 can induce the homeotropic

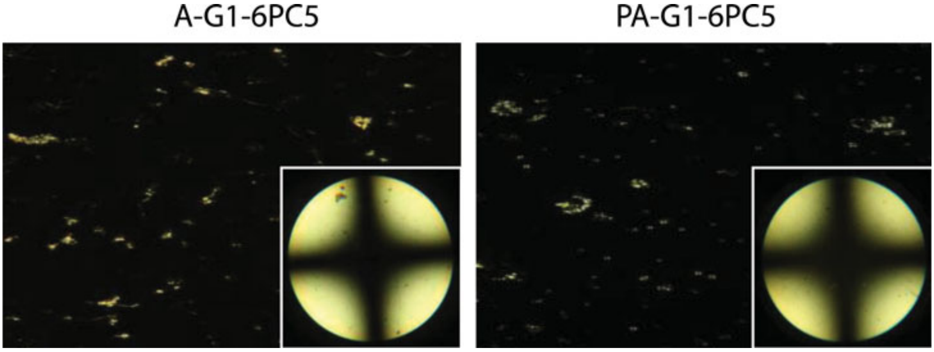


Figure 3. POM and conoscopic (insets) images of A-G1-6PC5 and PA-G1-6PC5 at room temperature after slow cooling (–1°C min^{-1}) from the isotropic melt.

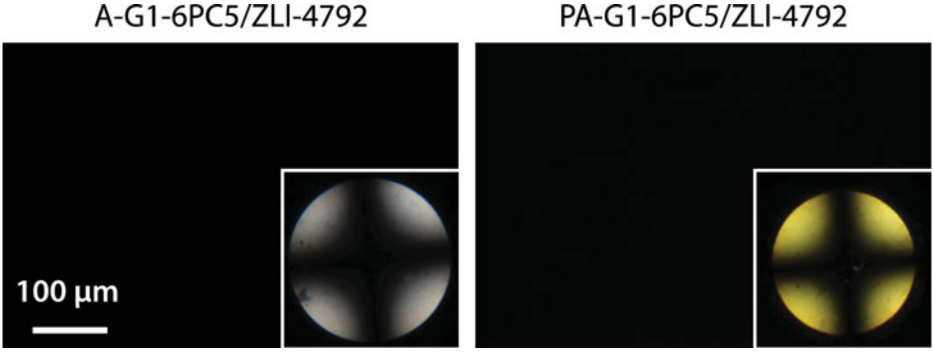


Figure 4. POM and conoscopic (insets) images of ZLI-4792/A-G1-6PC5 and ZLI-4792/PA-G1-6PC5 (99/1, wt/wt) mixtures at room temperature after slow cooling (–1°C min^{-1}) from the isotropic melt.

orientation of the low-molecular weight nematic LC by simply dissolving a small amount of the polymer into the nematic LC.

Summary

A dendronized LC polyacrylate (PA-G1-6PC5) was prepared by the radical polymerization of the 1st generation polypropyleneimine dendron (A-G1-6PC5) having focal acryloyl and peripheral mesogenic groups. Both the dendron and the polymer exhibited homeotropic alignment on a native grass surface upon slow cooling. Furthermore, they could induce the homeotropic alignment of nematic LCs simply by dissolving. The melting point of PA-G1-6PC5 was higher than that of A-G1-6PC5 and comparable to that of the corresponding dendrimer. Because the dendronized polymer could be easily synthesized compared to the dendrimers, they should have advantages as the alignment agent.

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