Poly(diphenylacetylene) Bearing Long Alkyl Side Chain via Silylene Linkage: Its Lyotropic Liquid Crystallinity and Optical Anisotropy

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The liquid crystalline properties and optical anisotropy of poly(diphenylacetylene) bearing an *n*-octadecylsilane moiety in the side chain, poly(1-phenyl-2-*p*-{dimethyl-*n*-octadecylsilylphenyl}acetylene) (C18-PDPA), were investigated in detail. C18-PDPA exhibited unexpected smectic phase liquid crystallinity in highly concentrated aromatic organic solvents such as toluene, despite its extremely high molecular weight of 4.18×10^6 g/mol and a fairly wide polydispersity index of 2.5. This lyotropic liquid crystallinity was derived from: a high molecular stiffness (expected from the high viscosity index of $\alpha \approx 1.03$), a high degree of intermolecular packing (the fractional free volume ≈ 0.16), and ultrahigh molecular weight. The two major absorption bands, located at 430 and 370 nm, are attributed to the $\pi-\pi^*$ transition parallel to the main chain and the localized $\pi-\pi^*$ transition with a charge-transfer characteristic among mesogenic repeating units perpendicular to the main chain axis, respectively. C18-PDPA exhibited highly polarized absorption and fluorescence bands in a sheared film. The main chain axis of the polymer was aligned parallel to the shearing direction, whereas the long axis of the stilbene-like side group was perpendicular to the shearing direction.

Introduction

Fluorescent conjugated polymers have attracted much attention because of practical applications in photo- and electroluminescence devices due to a controllable optical band gap and good processability.[1] However, their films, obtained by traditional processing such as electrospraying and spin-coating, inevitably emit unpolarized light due to randomly oriented main chains. Recently, considerable synthetic and processing efforts directed toward highly polarized fluorescence materials, such as liquid crystalline conjugated polymers, have been intensively performed in the field of light-emitting device (LED) materials.[2]

Highly anisotropic solid films and fibers may be obtained by carefully controlling the solid-state morphology via molecular design and material processing. To accomplish the uniaxial molecular alignment in a polymer film, a promising method would be to add a liquid crystalline (LC) nature to individual polymer chains and then apply external forces, such as shear stress, an electric field, and magnetic field to align the LC material.

Disubstituted acetylene polymers exhibit a very intense fluorescence in the blue and green region due to the main chain conjugation, whereas most monosubstituted acetylene polymers absolutely do not.[3] If LC nature could be added to the polymers, their optical applications would be greatly extended due to highly emissive quantum efficiencies. Recently, Tang and colleagues have developed synthetic routes for various fluorescence, disubstituted polyacetylenes with LC properties.[1a,1b,4] Certain disubstituted polyacetylenes

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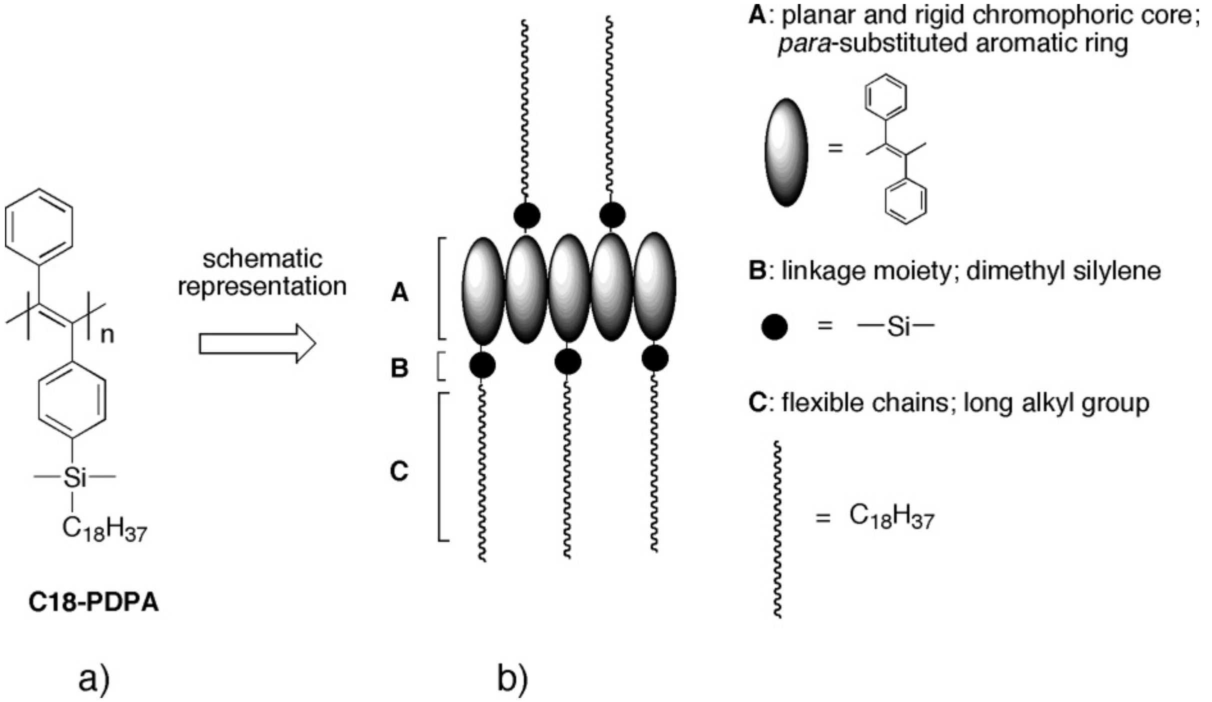

Figure 1. (a) Chemical structure and (b) schematic molecular structure of C18-PDPA required for LC crystallinity. Note that its actual structure may be either trans-form or head-to-tail coupling because its stereo- and regio-regularity have not been determined yet. Details will be given in the main text with Figure 10.

among these showed unique optical properties due to well-defined molecular structures as well as excellent thermal and mechanical stabilities. Their approaches may, however, have some synthetic difficulties when dealing with mesogenic monomers. Group 5 transition-metal catalysts are used to polymerize the acetylene monomers, and these LC monomers include ester and nitrile groups in polar side chains.[1b] As for the LC polyacetylenes, the optical anisotropy in the UV−vis absorption and fluorescence spectra has not been reported thus far.

Masuda and co-workers have long investigated the chemistry and potential applications of poly(diphenylacetylene)s bearing various alkylsilyl groups from the early stage of catalytic polymerization of disubstituted acetylene derivatives.[5] Compared to mesogenic monomers with ester and nitrile groups, diphenylacetylenes with an alkylsilyl group can be polymerized with group 5 transition-metal catalysts due to the absence of polar groups that can poison the catalyst. Silicon-containing diphenylacetylenes with group 5 transition metal catalysts, thus, readily afford the corresponding polymers with high molecular weights up to 1.0 × 10^6 in high yields. The resulting poly(diphenylacetylene)s with an alkylsilyl group are highly soluble in common organic solvents such as chloroform and toluene, and easily processed to make various functional films and fibers with excellent mechanical strength and thermal stability. Yoshino et al. pointed out that poly(diphenylacetylene)s are recognized as intensely emissive polymeric materials because of effective exciton confinement within the main chain due to the steric hindrance and/or intramolecular electron interactions of bulky aromatic substituents such as a phenyl ring.[3a,3b]

It is widely accepted that thermotropic LC molecule is composed of three fundamental parts: The first is a hard core, the second a linkage moiety, and the third a flexible long chain. Polymer chain stiffness closely correlates to liquid crystallinity. It is well-known that soluble rigid shape persistent macromolecules usually exhibit a wormlike chain conformation in solution, so they will self-assemble into an ordered state, namely, a lyotropic liquid crystal phase when the polymer concentration gradually raises to a critical concentration.[6] Recently, the authors synthesized a unique poly(diphenylacetylene) with a long alkyl side chain, which is linked to a silyl moiety, poly(1-phenyl-2-*p*-{dimethyl-*n*-octadecylsilylphenyl}acetylene) (abbreviated C18-PDPA), as shown in Figure 1.[5b] Although C18-PDPA was already known as a useful polymer for gas-permeable membranes, its monomer repeating structure (shown in Figure 1) completely satisfies the structural requirements for thermotropic LC compounds, except for its inherent wide polydispersity index. It should be noted that C18-PDPA is regarded as a collection of stiff, planar *p*-substituted phenylenevinylene-phenylene (stilbene) repeating units (hard core part) bearing a flexible long alkyl chain and dimethylsilane linkage with rotational freedom. The C18-PDPA has an extremely high

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molecular weight of >1.0 × 10^6 g/mol and its backbone is thus expected to adopt a considerably stiff main chain structure due to bulky phenyl rings with strictly limited rotational freedom. The high molecular weight and the inherent chain stiffness may allow lyotropic liquid crystallinity.

In this paper, the authors demonstrate lyotropic LC behavior and unique optical anisotropy of C18-PDPA. C18-PDPA in sheared films shows highly polarized absorption and fluorescence characteristics in the UV−vis region, because C18-PDPA adopts a highly aligned rodlike polymeric molecule dispersed in aromatic solvents. The main chain axis of the polymer was aligned parallel to the shearing direction, whereas the long axis of the stilbene-like side group was aligned perpendicular to the shearing direction.

Experimental Section

The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of C18-PDPA were evaluated using gel permeation chromatography (GPC, Shimadzu A10 instruments, Polymer Laboratories, PLgel Mixed-B (300 mm in length) as a column, and HPLC-grade tetrahydrofuran as eluent at 40 °C), based on a calibration with polystyrene standards. The intrinsic viscosity−molecular weight relationship was obtained using an in-line configured viscometer (Viscotek T60A) and SEC instrument.

Polarizing microscopic photographs were taken with an Olympus BX50 polarizing optical microscope equipped with an Olympus CCD camera. All variable-temperature measurements were carried out on a Mettler Toledo FP82HT hot stage equipped with a Mettler Toledo FP90 central processor.

UV−vis absorption spectra were measured on a JASCO UV-550 spectrophotometer, and photoluminescence spectra were recorded on a JASCO FP-6500 spectrofluorometer. Polarized UV−vis absorption and photoluminescence spectra were obtained using these spectrometers with the corresponding JASCO polarizer/analyzer units, respectively.

Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature using a MacScience (MXP18) X-ray diffracter. A flat sample was mounted directly into the diffracter. The experiment was carried out using CuK_α radiation operating at 40 kV and 120 mA. The two-dimensional wide-angle X-ray diffraction (2D-WAXD) pattern was taken by the Rigaku out-of-plane system for a thin film equipped with an X-ray generator (ultraX18/R-AXIS IV) emitting Ni-filtered Cu Kα radiation (λ = 0.154 nm, 45 kV, 50 mA).

The density of each sample was determined using a Mettler Toledo AX205 analytic balance coupled with a Mettler Toledo density determination kit at room temperature. The density determinations were performed by Archimedes' principle and methanol was used as an auxiliary liquid. Thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were performed under pure nitrogen gas using a Seiko EXSTR6200 TG-DTA and a Seiko EXSTRA6000/DSC6200, respectively.

The fractional free volume (FFV) was defined as $(\upsilon_{sp} - \upsilon_0)/\upsilon_{sp} \approx (\upsilon_{sp} - 1.3\upsilon_W)/\upsilon_{sp}$, where υ_{sp} is the specific volume of the polymer and υ_0 the occupied volume (or zero-point volume at 0 K) of the polymer. The occupied volume was typically estimated to be 1.3 times of the van der Waals volume (υ_W) calculated from the group contribution method.[7] The factor of 1.3 was a universal packing parameter introduced by Bondi.[8]

Results and Discussion

The synthesis of C18-PDPA was already reported in previous papers.[5b] The polymer used in this study has a high weight-average molecular weight (M_w) of 4.18 × 10^6 g/mol and a polydispersity index (PDI = M_w/M_n) of 2.5.

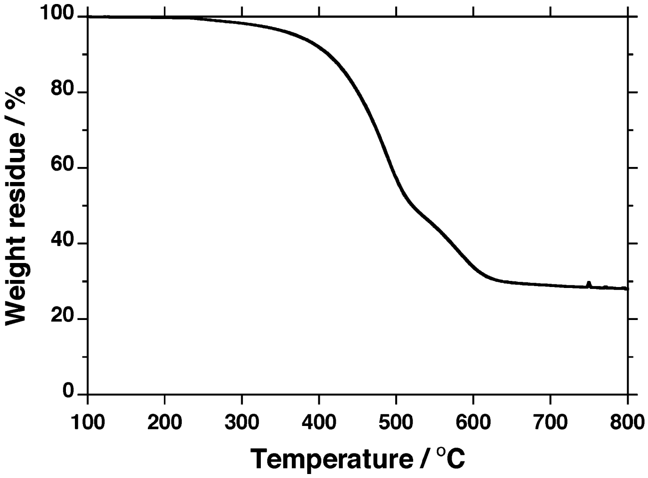

Figure 2. TG thermogram of C18-PDPA under nitrogen at a heating rate of 10 °C/min.

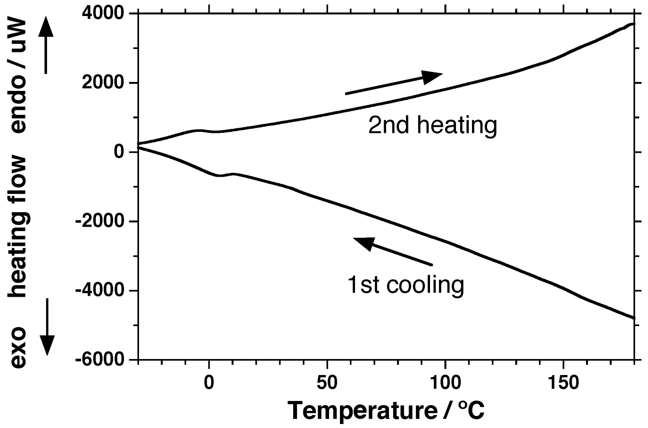

Figure 3. DSC thermogram (heating and cooling runs) of C18-PDPA under nitrogen at a scan rate of 10 °C/min.

Figure 2 shows the TGA curve of C18-PDPA. The polymer begins to degrade around 250 °C. A conversion point is then observed around 480 °C, to leave 30 wt % to reside as ash at 800 °C. This indicates that the alkyl group initially begins to degrade at a relatively low temperature, and the diphenylacetylene backbone decomposes at a higher temperature. The long alkyl chain linked by silyl may thus significantly affect the thermal stability of C18-PDPA.

Figure 3 shows the DSC curve of C18-PDPA. The polymer showed an endothermic signal around 5 °C, due to a glass transition, whereas any significant exothermic signals due to melting and isotropization transitions were not seen in the range from −50 to 200 °C.

From polarizing optical microscope (POM) studies, neat C18-PDPA forms no birefringent texture in the range of 25−200 °C. Although this agrees with the DSC result that indicated no thermotropic LC behavior, this polymer was expected to exhibit a lyotropic LC in concentrated solutions,

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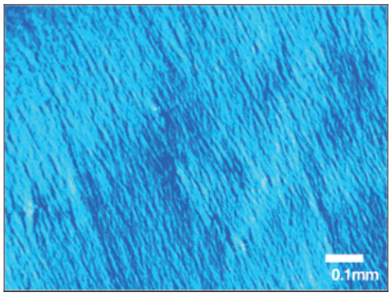

Figure 4. Polarized optical microscope (POM) photographs of a film sheared from highly concentrated C18-PDPA solution (conc. > 5 wt % in toluene).

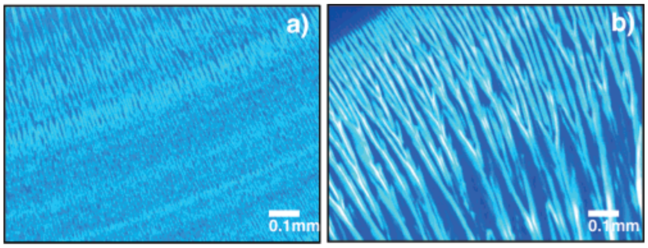

Figure 5. POM photographs of films cast from C18-PDPA solutions with different concentrations: (a) conc. = 0.05 wt %, (b) conc. = 0.5 wt % in toluene).

resulting from both the comblike structure of the stiff backbone and the flexible long alkyl chain connected through a silane linkage.

Figure 4 shows the POM photograph of C18-PDPA in a concentrated solution of toluene. A typical texture with parallel striations, characteristic of a hexagonal phase, was seen in the sheared solution. The existence of the parallel striations may be ascribed to the defects of the curvature of certain highly ordered aggregates lying with their long axis parallel to the shearing direction.[9] Noticeably, the LC property of C18-PDPA significantly depends on solvent used. Although this microscopic texture was clearly observed in concentrated solutions of aromatic solvents, such as toluene, benzene, and *o*-dichlorobenzene, the texture was scarcely observed in alkane solvents such as *n*-hexane and *n*-decane. This led to the idea that this liquid crystallinity may be driven by intermolecular packing of long alkyl chains through hydrophobic interactions with hampering the $\pi-\pi$ stacking of main chains and/or weak CH/π interaction between aromatic solvent and long alkyl chains.

Alternatively, Figure 5 shows the POM photograph of C18-PDPA films obtained by the solvent casting technique. The polymer solution formed textures with chevron morphology on the surface of the cast films by simply evaporating the solvent, regardless of the initial concentration. These optical textures are characteristic of a lamellar lyotropic LC phase, indicating that a certain highly ordered structure was spontaneously formed during the process of solvent evaporation.

Figure 6 shows the WAXD pattern of C18-PDPA. A broad scattering signal is seen in a wide range of 15−30°, indicating the isotropic liquidlike order of the polymer. On the other hand, a signal at a small angle of 4° is clearly seen. This is assumed to be an interlayer spacing of ∼22 Å, which is almost the same as the octadecyl length (22.5 Å), indicating a lamellar layer structure. This indicates that the lyotropic planar phase is either a monolayer phase, or it could be a bilayer lamellar phase with lots of side chain interdigitation or side chain tilt to get an effective repeat distance equivalent to ca. 1 side chain length. Figure 7 shows the possible monolayer smectic structure, and highly interdigitated or tilted bilayer lamellar lyotropic phase. As for liquid crystalline monosubstituted polyacetylenes, Tang et al. have already reported that longer spacer effectively promotes monolayer arrangement rather than bilayer packing.[10] For comparison with C18-PDPA, WAXD measurement was also conducted for C8-PDPA which has an *n*-octyl group in place of *n*-octadecyl group. A sharp signal at the higher angle of 5.92° was clearly seen for C8-PDPA, indicating an interlayer spacing of 14.9 Å, which is much longer than the *n*-octyl length (10 Å). The C8-PDPA is thus considered to be packed in an interdigitated bilayer and/or end-to-end bilayer mode. The chain length of *n*-octadecyl group is assumed to be long enough to induce monolayer arrangement in the smectic phase. From the 2D-WAXD pattern of the sheared C18-PDPA film shown in the inset, it is evident that intense signals at smaller angles of diffraction appear on the equator, which is perpendicular to the shearing direction. This indicates that the smectic layer is perpendicular to the shearing direction.

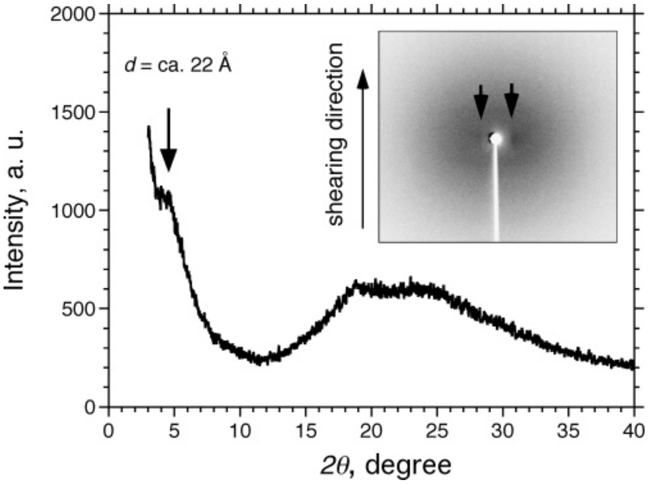

Figure 6. Wide-angle X-ray diffraction (WAXD) patterns of C18-PDPA (inset: two-dimensional (2D)-WAXD pattern of the sheared film).

As demonstrated previously, the present polymer seems to self-assemble into a hierarchical structure with a smectic phase in the concentrated solution, even though they have extremely high molecular weights (greater than 1.0 × 10^6) with a relatively wide polydispersity. This result may be contrast to the traditional idea that it was long believed that a high-molecular-weight polymer with a wide polydispersity hardly forms highly ordered structures like a smectic or lamellar LC phase due to high packing entropy energy, compared to a well-defined low molecular weight LC compounds with no molecular weight dispersity.

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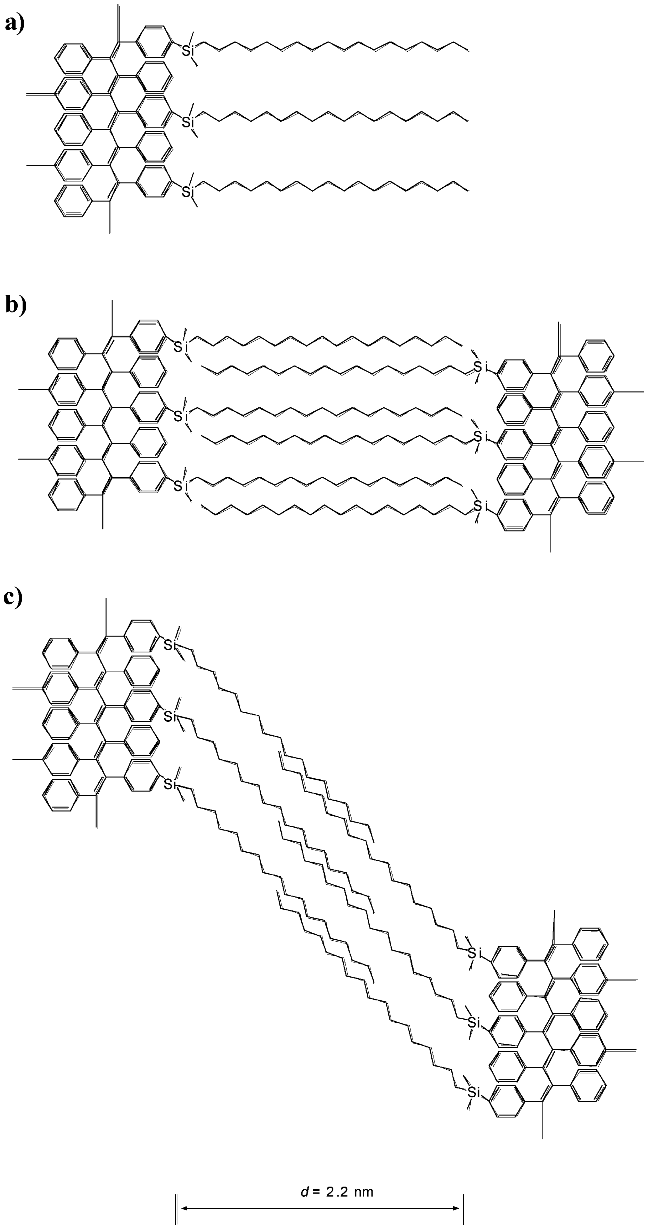

Figure 7. Possible layer structures of C18-PDPA. (a) Smectic monolayer, (b) highly interdigitated, and (c) tilted bilayer lamellar phases.

Table 1. Properties of C18-PDPA

molecular weight, M_w	polydispersity index (M_w/M_n)	viscosity index, α	density, d	fractional free volume, FFV
4.18×10^6	2.5	1.03	0.96	0.16

The open question is why the present polymer shows lyotropic LC properties. According to Flory's theory, following conditions should be satisfied in order to show lyotropic liquid crystallinity.[6] First, the polymer concentration being higher than the critical concentration. Second, a high-molecular-weight polymer being a rigid rodlike molecule.

Table 1 gives several physical properties of C18-PDPA. The stiff nature of this polymer is evident from the high viscosity index of α = 1.03 (in THF at 40 °C). The value was obtained by $[\eta] = KM^{\alpha}$ from the Mark−Houwink−Sakurada plot on the basis of the universal calibration curve, where $[\eta]$ is the intrinsic viscosity and M is the absolute molecular weight. The high α value, which is a typical for a stiff chain, is much higher than that of random coiled polystyrene (α = 0.69). Thus, the lyotropic LC property of C18-PDPA can be explained by the idea that the polymer backbone is sufficiently stiff to act as a mesogen itself, and that the inherent stiffness of main chain significantly lowers the isotropic LC transition entropy energy. In particular, the flexible long alkyl side chain may behave like solvent molecules even in a solid state to effectively lower the molecular entropic energy by intermolecular packing. Accordingly, the packing can minimize the amount of free volume of C18-PDPA.

To confirm these ideas, the value of fractional free volume (FFV), which indicates the degree of intermolecular chain packing, was estimated from the density of C18-PDPA was 0.96 (Table 1). Indeed, the FFV value of C18-PDPA was estimated to be 0.16, and was much lower than that of the corresponding, no-LC-ability polymer without any long alkyl chains, poly(1-phenyl-2-{*p*-trimethylsilylphenyl}acetylene) (FFV = 0.26).[11] Thus, it is concluded that both the molecular packing of long *n*-alkyl chains and the stiffness of the main chain are responsible for the lyotropic LC nature of C18-PDPA.

The above results led to the idea that C18-PDPA with lyotropic LC behavior can easily be aligned into a desired direction by applying a shear force. In this case, the polymer backbone may be aligned with its molecular axis in the direction parallel to the external force, and then organized into a layered structure of smectic phase. On the other hand, the LC mesogenic units, which are regarded as a collection of repeat units, may be perpendicular to the polymer backbone. Intense UV−vis absorption and fluorescence bands due to a delocalized photoexcited $e-h$ pair along with the main chain should thus appear in the direction parallel to the shearing direction rather than in the perpendicular one.

Although poly(diphenylacetylene) derivatives are already known to exhibit two absorption bands located at ca. 370 and 430 nm, the origin of the two bands and their spectroscopic assignment was not clarified. It remains unclear whether the 370 nm absorption band is due to the main chain or aromatic side chain and whether the 370 nm absorption is due to the cis-transoid structure of the main chain or helical structure.

Figure 8 shows the polarized absorption spectra of C18-PDPA in a sheared film as a function of the polarizer angle. It is noted that the parallel and perpendicular components in the absorptions are significantly different from each other. When the angle of the polarizer to the shearing direction was changed from 0 to 90° with an interval of 10°, the 430 nm absorption band gradually decreased, whereas the 370 nm absorption band increased. For comparison, UV−vis absorption spectra of an extremely dilute solution and a spin-coated film of C18-PDPA were measured. Indeed, this polymer in such isotropic states exhibited both the 370 and 430 nm absorption bands and no change in intensity and peak wavelengths of the bands, regardless of the polarizer angle. The 370 and 430 nm absorption bands are thus a collection of $\pi-\pi^*$ transitions in mesogenic repeat units and

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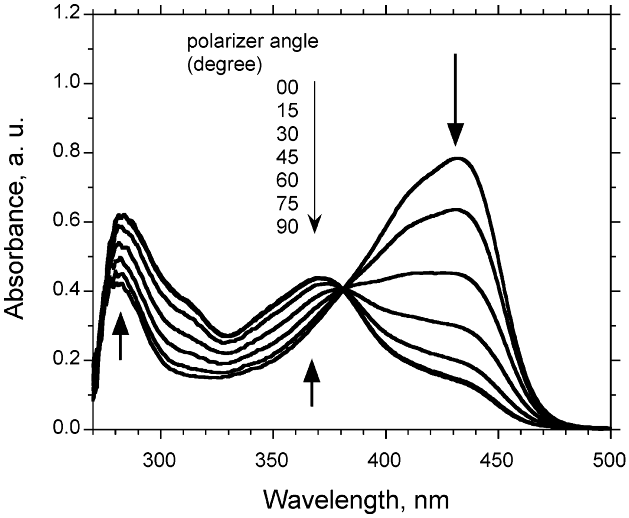

Figure 8. Polarized UV−vis absorption spectra of the C18-PDPA sheared film as a function of the polarizer angle against shearing direction.

the $\pi-\pi^*$ transition of the polymer backbone, respectively. The polarized UV−vis absorption and the 2D-WAXD experiments of the aligned C18-PDPA film clearly proved that the 430 nm absorption band originates from the lowest $\pi-\pi^*$ transition parallel to the main chain axis of poly(diphenylacetylene) derivatives.

The apparent dichroic ratio with absorption (D_{abs}) at 430 nm was evaluated to be 5.56 from the polarized absorption spectra. The optical order parameter (S) defined as $S = (D_{\mathrm{abs}} - 1)/(D_{\mathrm{abs}} + 2)$ is usually used to evaluate the degree of LC alignment. If the molecular axes are ideally parallel and perpendicular to the shearing directions, the S values will be 1.0 and −0.5, respectively. In the present case, the S value is evaluated to 0.60, which is very close to the ideal value of 1.0 rather than −0.5, confirming that the polymer main chain prefers to align in the direction parallel to the shearing direction.

To confirm our idea, we carried out polarized fluorescence and photoexcitation experiments. Polarized fluorescence spectra gives information for relatively local photoexcited states of various polymer chains due to photoexcited energy migration, whereas polarized absorption spectra may give averaged absorption bands from various polymer chains even in highly oriented film states.

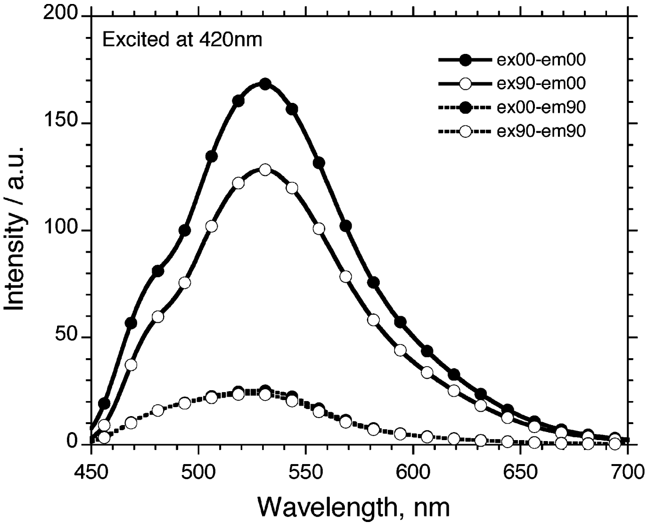

Figure 9. Polarized fluorescence spectra of the C18-PDPA sheared film with changing angles of the polarizers in the excitation and emission sides against shearing direction. The indexes of ex00, ex90, em00, and em90 refer to the parallel excitation, perpendicular excitation, parallel emission, and perpendicular emission, respectively.

Figure 9 shows the polarized fluorescence spectra of C18-PDPA in the sheared film when excited at 0 and 90° excitation (ex00 and ex90) and monitored at 0 and 90° emission (em00 and em90). The fluorescence in the parallel direction (em00) appears yellowish green at ca. 525 nm with a shoulder at ca. 485 nm, whereas the fluorescence in the perpendicular direction (em90) did not clearly show the 485 nm band. Although the shoulder band is assumed to be due to the lowest photoexcited $\pi-\pi^*(0-0)$ transition state without a vibration phonon side parallel to the main-chain axis, the intense 525 nm bands may be from a vibrational phonon side $\pi-\pi^*(0-1)$ band coupled with C=C stretching vibrations parallel to the main chain axis. This is because the estimated energy difference between the 525 nm band and 485 nm bands is ca. 1570 cm^{-1}. Also, when the monitored wavelength was varied in the range of 450−650 nm, the excitation spectrum of C18-PDPA was essentially identical to the corresponding absorption spectrum, without any changes in the spectral shape. From the change in polarized fluorescence intensity of C18-PDPA in the sheared film (Figure 9), the maximum dichroic ratio with emission (D_{em}) was evaluated to be ca. 8.5, which is greater than the D_{abs} value of 5.56, indicating the existence of highly aligned photoluminous main-chain domains.

A long-standing question on asymmetrically substituted poly(diarylacetylene)s may be their stereochemistry. C18-PDPA, a model of these poly(diarylacetylene)s, may have two types of configurations (trans-transoid and cis-transoid) and two types of dyad structures (head-to-tail and head-to-head), as illustrated in Figure 10. Although it is widely accepted that monosubstituted acetylene polymer derivatives made by some late transition-metal catalysts afford the almost pure 100% cis-transoid polymers, it remains unclear whether asymmetrically substituted poly(diarylacetylene)s adopt trans-transoid or cis-transoid sequence. The C18-PDPA may prefer to adopt a trans-transoid structure with a head-to-head (tail-to-tail) dyad because it is less sterically bulky and less polar at the ground state as compared to the head-to-tail structure. C18-PDPA appears not to adopt the cis-transoid form due to sterically overcrowded diaryl groups, even though the head-to-head (tail-to-tail) configuration is less polar.

The two aryl side groups in the trans-transoid form are similar to trans-stilbene like structures, whereas those in the cis-transoid are similar to cis-stilbene like structures. The trans-stilbene like diaryl structures perpendicular to the main chain axis might be responsible for the 370 nm band, because the trans-stilbene absorbs at a longer wavelength at ∼ 325 nm, whereas the cis-stilbene absorbs at ∼300 nm as the shoulder.[12] The difference between the 370 and 325 nm bands could result from the charge-transfer characteristics in the

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(12) Lewis, G. N.; Magel, T. T.; Lipkin, D. *J. Am. Chem. Soc.* **1940**, *62*, 2973−2980.

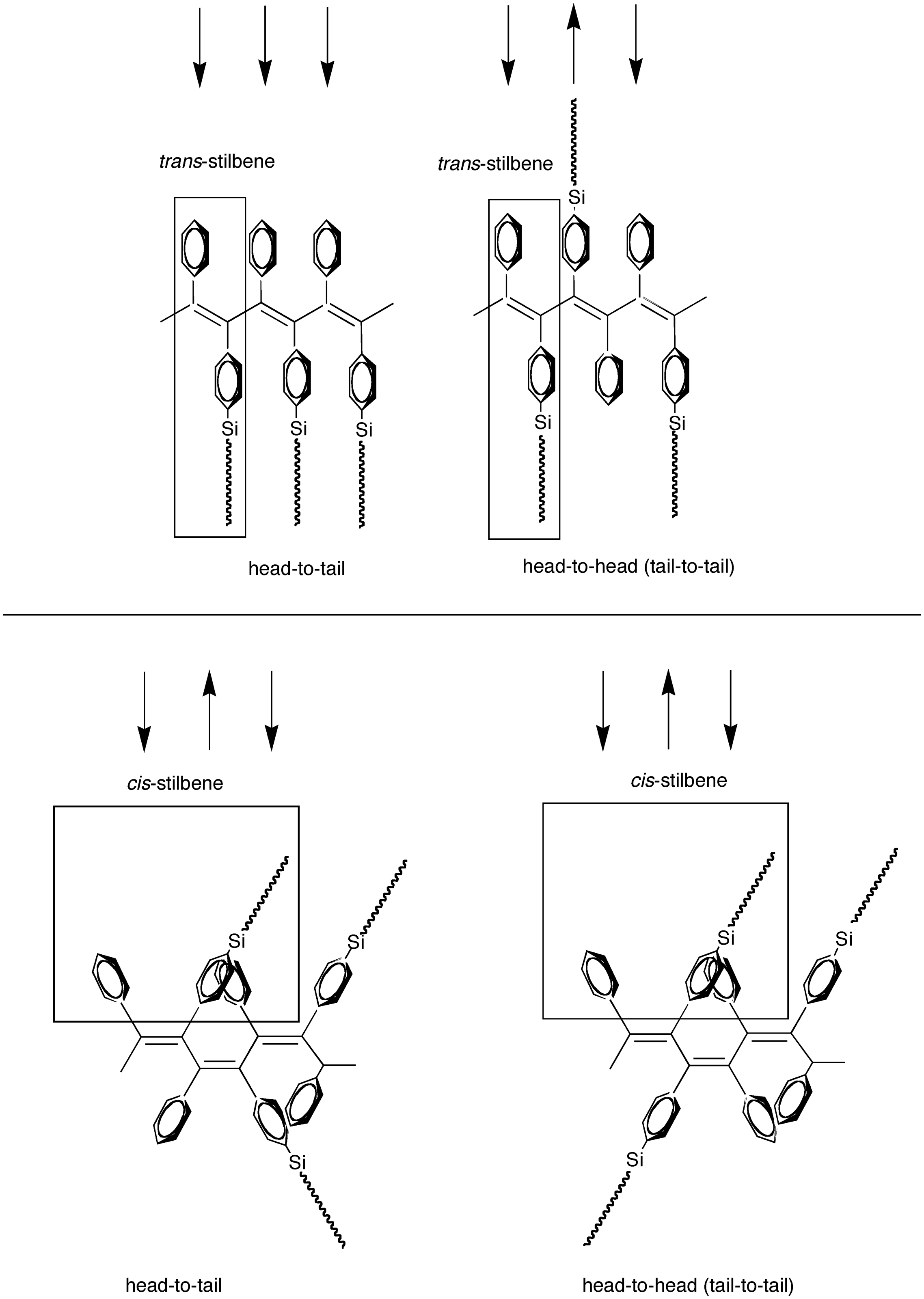

Figure 10. Hypothetical stereochemistry of C18-PDPA. Top illustrates trans-transoid structures and bottom illustrates cis-transoid structures. Left refers to head-to-tail and right refers to head-to-head (tail-to-tail). Arrow means dipole moment vector at the ground state.

ground and/or excited states and come from partial band mixing between $\pi-\pi^*$ orbitals of stilbene-like moieties and $\pi-\pi^*$ orbitals of trans-transoid polyene structure. Hypothetical cis-transoid structures incorporated in the trans-transoid polyene structure may act as block sites of photoexcited energy migration, leading to effective quantum confinement along the whole main chain, due to a wider optical band gap relative to the trans-transoid structure.

Conclusion

The present paper demonstrates the thermal degradation and phase transition properties, liquid crystalline behavior, unpolarized and polarized UV−vis absorption, and polarized fluorescence properties of high-molecular-weight C18-PDPA. This polymer is thermally stable and exhibits hierarchical structures with smectic phase lyotropic liquid crystallinity in highly concentrated aromatic organic solvents such as toluene, regardless of high molecular weight and wide polydispersity, although there was no thermotropic liquid crystalline property. The lyotropic liquid crystalline nature of C18-PDPA was due to a stiff main chain structure and intermolecular packing of flexible long *n*-alkyl side groups. The C18-PDPA exhibited strongly polarized absorption in the sheared film, reaching the maximum dichroic ratio at 430 nm of ca. 5.56. The 430 and 370 nm absorptions were found to be ascribed to the $\pi-\pi^*$ transition parallel to the main chain and the localized $\pi-\pi^*$ transition with a charge-transfer characteristic among mesogenic repeating units perpendicular to the main chain axis, respectively. The C18-PDPA in the sheared film also exhibited strongly polarized fluorescence band at 525 nm parallel to the main chain, showing the maximum dichroic ratio of ca. 8.5. This polymer is thus very promising as a highly polarized fluorescence material in liquid crystalline display and sensory device applications in near future.

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