

First Observation of Thermotropic Cholesteric Liquid Crystal in Helical Polysilane

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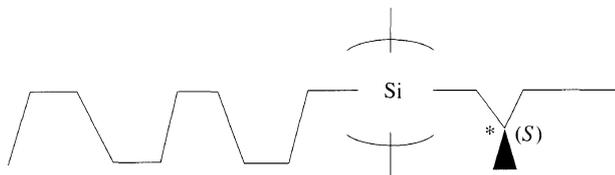
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(Received November 24, 2000; Accepted March 1, 2001)

KEY WORDS Polysilane / Helical Conformation / Thermotropic Liquid Crystal / Cholesteric Phase / Circular Dichroism /

A property of rigid and semi-rigid rodlike helical polymers is the ability to spontaneously form a thermotropic cholesteric liquid crystalline phase (TChLC) under specific conditions as well as a lyotropic liquid crystal. First example of TChLC in rodlike helical polymer was reported in poly(*l*-glutamates) with long alkyl side chains.^{1,2} The long side chains act as solvents in the lyotropic system to attach the TChLC nature to the rodlike helical polymer. By the same idea, TChLC was successfully prepared from cellulose.³ In this paper, we present a third example of TChLC formed from poly[*n*-decyl-(*S*)-2-methylbutylsilane] (**PS-1**) with the following formula,



Whose helical conformation has been well established.⁴ Novel TChLC was proved in a relatively lower molecular weight sample of **PS-1** ($M_w = 11100$, $DP_w = 46$, and $M_w/M_n = 1.19$) in the temperature range above 70°C, by circular dichroism (CD), wide-angle X-Ray and optical microscopy measurements.

PS-1 with bimodal molecular weight distribution was first synthesized according to the patent and literature procedures,^{4e,4f} and the lower molecular weight fraction was isolated by fractional precipitation from a mixed toluene-methanol polymer solution. Molecular weights (M_w and M_n) and the polydispersity index were evaluated by GPC analysis (THF, 30°C) and calibrated against polystyrene standards. Assuming the molecular parameters of helical **PS-1** elucidated later, the average molecular length and diameter of **PS-1** employed here were evaluated to be approximately 90 and 15 Å, respectively, affording an axial ratio of 6. This ratio is sufficiently small as a LC polymer, but large enough as a low molecular weight LC molecule.

PS-1 appears like a milky wax at room temperature. It begins to flow at around 70°C on heating. Optical microscopy measurement elucidated that the fluid phase exhibits strong birefringence, characteristic of a liquid crystal, which is retained at least until 220°C. However, no marked thermal transition around 70°C could be detected by even highly sensitive DSC (Perkin-Elmer, DSC-7) measurement.

Figure 1a shows the X-Ray diffraction pattern of **PS-1** at 30°C. It revealed several strong reflections at smaller angles, which have spacings of 17.9, 14.6, 12.0, 10.0, and 8.5 Å. For uniaxially oriented fibers drawn from the liq-

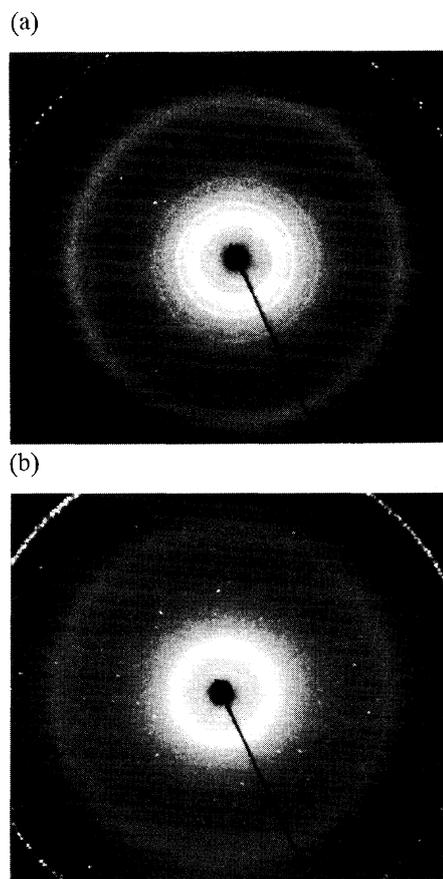


Figure 1. X-Ray diffraction patterns of **PS-1** observed at (a) 30°C and (b) 80°C.

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uid crystalline phase, all these reflections were located on the equator and assigned to orthogonal molecular packing with a two dimensional lattice of $a = 17.9 \text{ \AA}$, $b = 24.0 \text{ \AA}$, and $\gamma = 90^\circ$. In addition, the *quasi*-meridional and meridional reflections with spacings of 4.4 and 1.96 Å were observed in the wide angle region. These are attributed to the 7-residue 3-turn (7_3) helical conformation with a repeat length of 1.96 Å; the 4.4-Å reflection is from a 3rd layer line, that is a turn layer line, and 1.96-Å reflection is a meridional reflection on a 7th layer line.^{5,6} Considering that two **PS-1** chains run through the unit cell, the calculated density is 0.95 g mL^{-1} , whose value is appropriate for this type of molecules with the long side chain groups.^{1b,5b} It is therefore concluded that the room temperature phase should be semicrystalline or columnar liquid crystalline phase.

The sharp X-Ray reflections of the inner region become diffuse on heating to the temperature above 70°C where **PS-1** becomes fluid. As found in Figure 1b, only the broad reflection with the 15-Å spacing is distinguishable whereas the outer 4.4- and 1.96-Å reflections characteristic of the 7_3 helical conformation still remain. These can be expected for a liquid crystal, which does not have positional order, but maintains the orientational order of rodlike polymers.

Because of the lack of positional order associated with the presence of chirality, the liquid crystal of **PS-1** should be a cholesteric phase. This idea is suggested by iridescent colors due to reflection light from randomly aligned textures. If we prepare a specimen less than 50 μm thickness by applying a shear between two glasses, we can observe the Grandjean microscopic texture including partly oily streaks and showing the beautiful reflection colors from blue to red in the temperature range from 70°C to 110°C . This is just indicative of the cholesteric helical phase.

Further decisive evidence for the cholesteric structure is gained by directly observing the variable temperature CD reflection band (JASCO J-725 spectropolarimeter equipped with Mettler FP-82 heat stage). Figure 2 shows the CD spectra at respective temperatures, which are observed for Grandjean textures. The CD reflection spectra are fairly sharp at any temperature, and the wavelength (λ), corresponding to the optical pitch of the cholesteric helix (nP ; P = pitch and n = refractive index), is

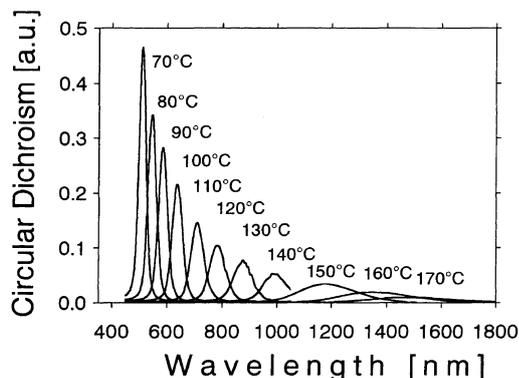


Figure 2. CD reflection bands characteristic of cholesteric phases of **PS-1** observed in the temperature range of 70 to 170°C on heating.

greatly dependent on temperature. The optical pitch decreases progressively with temperature from 500 nm at 70°C to 1500 nm at 170°C . In Figure 3, the reciprocal optical pitch ($1/nP$) proportional to twisting angle is plotted against temperature (T). The linear relationship is elucidated between $1/nP$ (μm^{-1}) and T (K), which can be expressed by the equation

$$1/nP = -1.3 \times 10^{-2} T + 6.6$$

This type of temperature dependence is not similar to that for ordinal small TChLC molecules, but that of the rodlike helical polymers.¹⁻³ The positive sign of the CD reflection band indicates a left-handed helical screw sense of the cholesteric phase.² In the cooling run, the optical pitch becomes insensitive to temperatures below 70°C . If the **PS-1** is kept for a long time at 60 – 70°C , the CD reflection band undergoes the red shift with its intensity decreasing markedly, and finally disappears. These features imply a phase transition from the cholesteric to some ordered phase without helical structure.

As already reported,⁴ molecularly dispersed **PS-1** in dilute *n*-hexane solution shows very sharp UV absorption and CD bands located at 320 nm. These, given in Figure 4a, are assigned to the lowest exciton $\text{Si}\sigma$ - $\text{Si}\sigma^*$ transition confined in a one dimensional 7_3 helical silicon quantum-wire.⁴ On the other hand, bulk **PS-1** in the cholesteric phase at 80°C exhibits a UV absorption band peaking at 318 nm, and a bisignate CD band with equal rotatory strengths, including positive and negative extrema at 313 and 327 nm, respectively (see Figure 4b). The bisignate CD band results from the exciton couplet CD signals⁷ of a chirally ordered motif between two adjacent **PS-1** molecules.^{4e,8} On the basis of the exciton couplet assignment already established,⁷ the chiral motif in this system is assumed to take a left-handed helicity. This is consistent with the assignment of left-handed helicity to the TChLC phase. It should be noted that similar bisigned CD couplet signals have been observed in the solutions of polysilanes in specific solvents and discussed in a relation to the aggregation style of polysilane.^{4e,9,10} The wavelength, intensity, and width of the bisignate CD spectra around 320 nm are less sensitive to the temperatures above 70°C , again indicating that rigid 7_3 helical conformation of **PS-1** is sustained in the cholesteric mesophase.^{5,6,9}

The cholesteric pitch quickly altered in response to the change in temperature with little hysteresis on heating

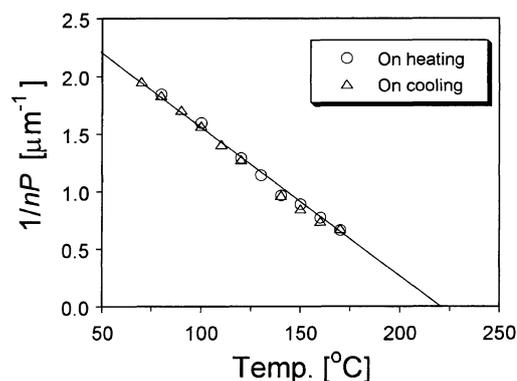


Figure 3. Temperature dependence of the reciprocal optical pitch.

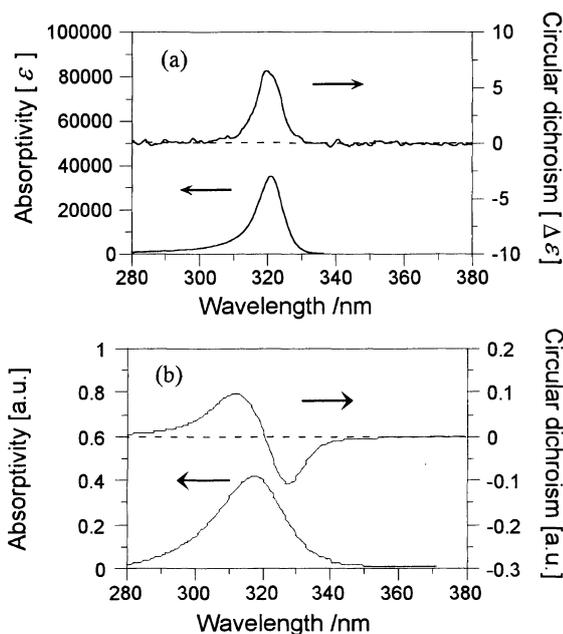


Figure 4. UV absorption (lower trace) and CD spectra (upper trace) due to $\text{Si}\sigma\text{-Si}\sigma^*$ backbone transition for (a) **PS-1** molecularly dissolved in hexane (an order of 10^{-2} g L^{-1}) and (b) **PS-1** in the thermotropic cholesteric phase at 80°C .

and cooling runs. On fast cooling, the recovery time of the pitch was less than *ca.* 1 min. These quick response CD band characteristics in the *visible* and *near infrared* regions may be useful in a practical-level circularly polarizing band-path filter including blue, green and red, and could be applied in the area of display and optical fiber communication technologies. Our finding may bring a new insight for achieving a practical level polysilane-based application, which avoids one of the major problems of polysilanes, Si-Si chain scissoring by intense UV light irradiation.

In conclusion, we found the first thermotropic cholesteric liquid crystal phase of a rigid rodlike 7_3 -helical poly- $[n\text{-decyl-(S)-2-methylbutylsilane}]$ with $M_w=11100$ and $M_w/M_n=1.19$. Selective CD reflection bands in the range from 500 to 1500 nm and Grandjean texture optical image directly proved the cholesteric phase in the temperature range above 70°C . Although several workers have reported the formation of columnar mesophases of more flexible polysilanes so far,^{5b,11-14} this is the first clear evidence proving a well-defined cholesteric (or nematic) mesophase structure based on a polysilane. Finally, it should be noted that in the higher molecular weight **PS-1** with $M_w=1.4\times 10^7$ and $M_w/M_n=2.21$ obtained as one of the fractions, the columnar phase is stable so that no transformation of the columnar phase to cholesteric one takes place until the decomposition temperature around 250°C . This suggests the significant effect of the molecular weight on the thermotropic phase

behavior of **PS-1**. The recent examination, in fact, shows that the transition temperature is gradually increased from 70°C to 180°C with an increase of the molecular weight from 10000 to 40000.¹⁵ Work is now in progress to examine the thermotropic phase behavior as functions of the M_w and M_w/M_n .

Acknowledgment. The authors thank Drs. Masao Morita and Hideaki Takayanagi for support. Drs. Julian R. Koe and Hiroshi Nakashima are acknowledged for fruitful discussion.

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