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First observation of a smectic A–cholesteric phase transition in a thermotropic liquid crystal consisting of a rigid-rod helical polysilane

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A smectic A–cholesteric phase transition for a rigid-rod helical polymer, poly[*n*-decyl-(*S*)-2-methylbutylsilane] (PD2MBS), with a narrow molecular weight distribution, has been observed for the first time. Polarizing optical microscopy showed that the fan-shaped texture of the smectic A phase turned into the characteristic planar texture of the cholesteric phase upon heating. The positive CD band, which corresponds to the reflection band of the cholesteric phase, gradually decreased in intensity within a range 30°C below the transition temperature on cooling, while the peak maximum shifted towards shorter wavelengths. It was concluded that the system has a very wide temperature region over which the cholesteric–smectic A phase transition occurs and in which the cholesteric pitch varies with temperature.

1. Introduction

Numerous attempts have been made in the last decade to study theoretically the formation of liquid crystal phases by rigid-rod molecules using the computer simulation technique employing a reduced molecular model in which intermolecular interactions were taken into consideration.

In the early studies, Hoshino *et al*. provided the first evidence that the smectic A–nematic phase transition can take place in systems consisting of completely aligned cylindrical molecules interacting only through an excluded volume effect [1–3]. Frenkel *et al.* elucidated the complete phase diagram of hard parallel spherocylinders as a function of the axial ratio and volume density using computational simulations and reported a columnar–smectic–nematic phase sequence with volume density if the axial ratio was sufficiently high [4–7].

Recently, and for the purpose of describing the liquid crystalline behaviour of synthetic polymers or biopolymers such as DNA, the phase behaviour of molecules having polydisperse lengths have been investigated theoretically by Sluckin [8] and Bates and Frenkel [9]. It was found that the phase behaviour of the polydisperse system remained unchanged from that expected for a monodispersed system when the polydispersity was small. However, with increasing polydispersity, the smectic phase became increasingly destabilized relative to the nematic phase.

Experimentally, this has been studied mainly using lyotropic liquid crystal phases formed by rod-like helical biopolymers [10–15]. Smectic liquid crystal phases have been reported in lyotropic systems containing synthetic polypeptides [16, 17] and some viruses [18, 19] with monodisperse molecular weight distributions. The phase transition behaviour however has never been clarified, mainly because of the difficulties of treating lyotropic systems.

Very recently, we have reported the columnar–smectic A–cholesteric phase sequence, which exactly coincides with theoretical predictions for thermotropic systems consisting of rigid-rod helical polysilanes and polypeptides with extremely narrow molecular mass distributions [20, 21]. A typical polysilane which shows

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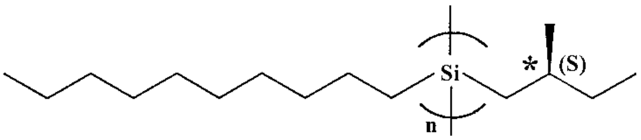
the phase sequence is poly[*n*-decyl-(*S*)-2-methylbuthylsilane] (PD2MBS):



The polymer backbone adopts a rigid helical conformation due to the steric demands of neighbouring chiral side chains and has a persistent length of around 85 nm, which is amongst the largest for this kind of polymer [22, 23].

Although the smectic A–cholesteric liquid crystal phase transition is one of the most intensely studied of the liquid crystalline phase transitions from both theoretical and experimental points of view, a smectic A–cholesteric phase transition for a rigid-rod polymer has never been experimentally reported. Here we report the first observation of this transition for a rigid-rod polymer.

2. Experimental

2.1. *Sample preparation*

A detailed procedure for the synthesis of PD2MBS has been described elsewhere [24]. The polymers were fractionated repeatedly in toluene solution with 2-propanol, ethanol and methanol as precipitants to prepare samples having narrow molecular mass distributions. The resulting samples were characterized by GPC (Jasco CO1560) with Shodex K-200K, at 40°C in chloroform (Nacalai Tesque, Kyoto, Japan) as an eluent, based on a calibration by polystyrene standards. The fractionated sample with $M_w = 14\,900$, $M_w/M_n = 1.12$, shows a columnar (80°C)–smectic A (150°C)–cholesteric phase sequence, and was used in the present study.

2.2. *Measurements*

Polarizing optical microscopy (POM), small angle X ray scattering (SR-SAXS), using synchrotron radiation and circular dichroism were employed to characterize the liquid crystalline phase transition behaviour. POM was carried out with an Olympus BX50 polarizing optical microscope equipped with an Olympus CCD camera connected to a computer and a Mettler FP82 hot stage. The sample was placed on a glass plate, covered by a cover glass, sheared to develop the planar structure and annealed in the hot stage at the designated temperature for 30 min before observation.

The SR-SAXS experiment was carried out at the Institute of Materials Structure Science Tsukuba, Japan (Photon Factory) with small angle X-ray equipment installed on beam line BL10C, under the approval of the Photon Factory Program Advisory Committee (No.2001G277). Details of the optics and the instrumentation are described elsewhere [25]. The sample was annealed at the designated temperature for 30 min in a copper heat-block with an optical window fixed on the beam line, in which the temperature was regulated to within ±1°C, to remove the previous thermal history before measurement. The SR-SAXS intensity was collected with point focusing optics as an accumulation of the scattered intensity during 600 s using a one-dimensional position sensitive proportional counter (PSPC) with an effective length of 200 mm. The scattering profiles measured by SR-SAXS were normalized for a minor decrease in the ring current during the measurement, which was continuously monitored by an ionization chamber placed just before the sample, and then was corrected with the calibration using the 6th reflection of collagen standard samples, and corrected for background scattering and Lorentz factor.

Circular dichroism measurements were performed using a Jasco J730 CD spectropolarimeter calibrated with sodium camphor sulphonate standard solution. The sample was prepared as in the case for microscopy.

3. Results and discussion

Although the fractionated sample was similar to a sticky wax in appearance and texture, its viscosity drastically decreased at around 150°C upon heating. Figure 1 shows the POM texture after annealing at the designated temperature for 30 min to ensure equilibrium had been attained. The well developed fan-shaped texture of the smectic A phase, figure 1 (*a*), was retained at 130°C while slightly changing its colour on heating. Figure 1 (*b*) shows the change of the texture recorded at 145°C after 30 min annealing which almost seemed to reach equilibrium. Half of the texture was found to be similar to that of the planar texture, with oily streaks indicative of a cholesteric phase. At this temperature, smectic A and cholesteric phases coexist, at least according to the microscopy observations. At 160°C, the whole area was occupied by the cholesteric planar texture as shown in figure 1 (*c*).

Although the same experiment on cooling was performed, the development of the fan-shaped texture was observed only around the air interface and never in the entire field of view after annealing for 30 min.

For the purpose of evaluating the smectic volume evolution, corrected SR-SAXS intensity profiles of the same sample obtained in the designated temperature region around the smectic A–cholesteric phase transition are shown in figure 2. The measurement was carried out after 30 min annealing at the designated temperature in the manner already described. The spacing of the observed peak is 137 Å which nearly coincides with the molecular length 121 Å calculated for $M_w = 14\,900$ and a translational unit length per residue of 1.96 Å, and thus can be assigned to the layer reflection of the smectic A phase.

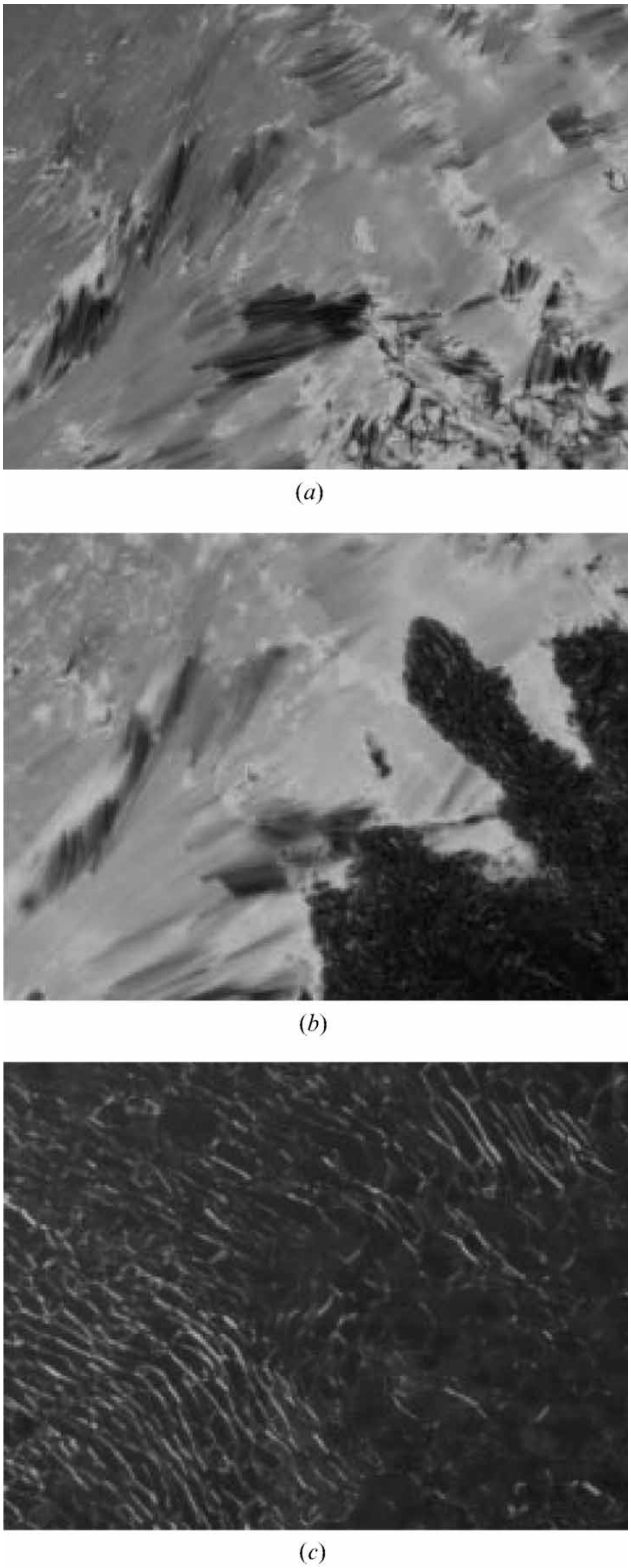


Figure 1. Polarizing optical micrographs for PD2MBS with $M_w = 14\,900$ and $M_w/M_n = 1.12$. (*a*) Fan-shaped texture (130°C); (*b*) fan-shaped texture in coexistence with a cholesteric Grandjean texture (145°C); (*c*) typical cholesteric texture with oily streaks over the whole area, (160°C). Each micrograph has the same area and was taken after 30 min annealing at the designated temperature during heating.

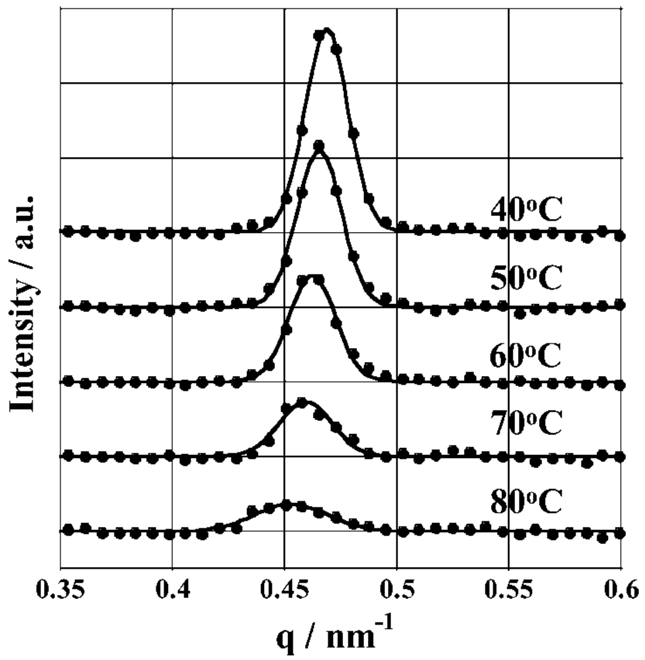


Figure 2. SR-SAXS profiles taken at designated temperatures on heating over the smectic A–cholesteric liquid crystal phase transition temperature for PD2MBS with $M_w = 14\,900$ and $M_w/M_n = 1.12$. The intensity was normalized and corrected.

The reflection became weak and diffuse even at 60°C, shifting to the small angle region on heating, and almost vanished at around 130°C, also indicating the coexistence of the smectic A and cholesteric phases. The reflection did not show reversibility after annealing for 30 min, as was also the case for the microscopy observations, which again indicated that a long time is needed to organize the layer structure. The reason for the large transition temperature difference between the SR-SAXS and microscopy observations is not clear.

The broadening and shifting of the smectic layer reflection at the phase transition is usually not observed for low molecular mass smectic liquid crystals [26, 27]. It is presumably attributable to the change in correlation length due to the thermal motion of rod-like molecules with a polydisperse length, and will be discussed elsewhere in detail.

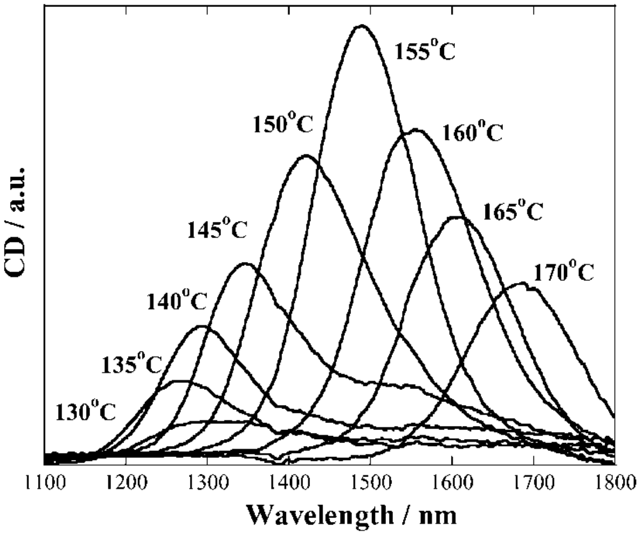


Figure 3. Circular dichroism spectra taken at 130, 135, 140, 145, 150, 155, 160, 165 and 170°C over the smectic A–cholesteric liquid crystal phase transition temperature for PD2MBS with $M_w = 14900$ and $M_w/M_n = 1.12$.

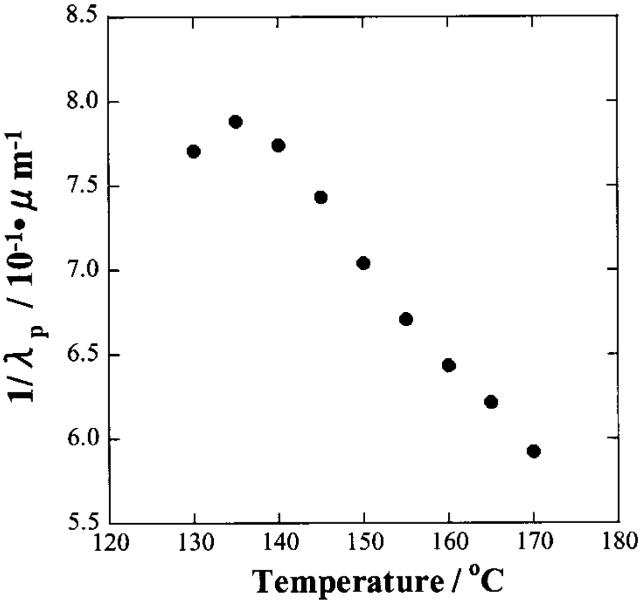


Figure 4. Reciprocal plot of peak wavelength of the circular dichroism spectra in figure 3 against temperature.

As for the cholesteric volume fraction variation, circular dicroism of the same sample has been taken at the corresponding temperature region, as shown in figure 3. The peak wavelength (λ_p) shifted upon cooling even though its intensity started to decrease noticeably around 150°C, which corresponds to the smectic A–cholesteric phase transition temperature. These results also suggested the coexistence of smectic A and cholesteric phases.

It can be assumed that the fractionated segregation of different molecular mass species occurs by analogy with the partitioning of solutes in binary mixtures of lyotropic liquid crystal systems [27, 28]. However this assumption needs to be tested by further theoretical and experimental studies which are currently in progress.

Theoretical studies and conventional low molecular mass liquid crystals show divergence of the helical pitch at the smectic–cholesteric transition; however, this is inconsistent with the present study. The shoulder of the CD spectrum in the longer wavelength region, which increases below the transition temperature, possibly indicates the reported helical pitch divergence, which may be concealed by the very wide coexistence region and the long relaxation time of the polymer.

Figure 4 shows the reciprocal peak wavelength, which is proportional to its twisting angle, as a function of sample temperature. The linear relationship over the transition temperature range indicates that the cholesteric phase, which coexists with the smectic phase, evolves its helical pitch in the usual manner and in accord with theory [29]. The deviation from linearity just before it vanishes in the lower temperature region may be attributed to the theoretically predicted and experimentally reported helical pitch divergence.

4. Conclusion

The first observation of a smectic A–cholesteric transition for a rod-like polymer is reported. All the measurements made showed the smectic A/cholesteric two-phase coexistence on heating over a wide temperature range, which has never been observed for conventional low molecular mass liquid crystals. The transition could not be observed on cooling using microscopy or SR-SAXS, indicating that the organization of the higher order structures takes a long time due to the long relaxation time of polymer systems. The reason for the large transition temperature difference between SR-SAXS and the other measurements is not clear.

The coexisting cholesteric phase showed a typical evolution of the helical pitch over essentially the entire range of the phase transition. It was also observed that the helical pitch increased just as the cholesteric phase was extinguished, which may possibly be attributed to the helical pitch divergence which was theoretically predicted and experimentally reported for conventional low molecular mass liquid crystal systems.

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