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Anomalous thermotropic liquid crystalline phase behaviour in poly[*n*-decyl-(*RS*)-2-methylbutylsilane]s with narrow molecular weight distributions

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The thermotropic liquid crystalline (LC) phase behaviour of a rod-like polymer, poly[*n*-decyl-(*RS*)-2-methylbutylsilane], with narrow molecular weight distributions, was studied by optical microscopic observations and X-ray diffraction measurements. This polymer exhibited a very unusual LC phase sequence of smectic A (SmA)–reentrant isotropic (I_{re})–nematic (N). Upon heating, the I_{re} phase prevails in the SmA phase, and then the N phase goes over into the I_{re} phase, while upon cooling, the I_{re} phase enantiotropically grows in the N phase. Moreover, the orientation of the polymer and smectic layer reflection simultaneously disappeared during the transition to the I_{re} phase, so that the anchoring transition to the pseudo-isotropic homeotropic alignment can be ruled out. To the best of our knowledge, this is the first example of a rod-like LC polymer exhibiting a reentrant isotropic phase without a drastic conformational change, although the exact molecular origin of the I_{re} phase is still unclear.

Keywords: polysilane; phase behaviour; liquid crystalline polymer (LCP); smectic phase; reentrant isotropic phase

1. Introduction

Reentrant isotropic phases have contradictory phase behaviour, where apparently more symmetric isotropic phases are formed as the temperature decreases. These interesting phenomena have attracted researchers through the years because they appear to be an apparent violation of the natural law that a decrease in temperature should be followed by an increase in molecular order. The existence of a reentrant isotropic phase was first confirmed in a lyotropic liquid crystalline (LC) system of amphiphilic molecules [1], and in the binary mixtures and pure discotic LC compounds [2, 3]. The latter group of molecules occasionally show a rather complex polymorphism with an inverted phase sequence and one or more reentrant phases. Although these reentrant isotropic phases are a well-established research field, there is still no general explanation for the molecular origin of these phenomena.

A reentrant isotropic phase has also been reported for the synthetic polypeptide poly(γ-benzyl-L-glutamate) in a denaturant solvent mixture [4]. The low-temperature reentrant isotropic phase was induced by halogenated organic acids, such as trifluoroacetic acid, which disrupt the intramolecular hydrogen bonding network of the α-helix and convert it into a random coil that is totally incompatible with liquid crystallinity. Upon heating, the polymer chains are desolvated from the denaturing solvent, restored to the α-helix and then form the liquid crystal again. On further heating, they turn into an isotropic liquid due to thermal disruption of the long-range orientational order of polymers. Therefore, this polymer may form both low and high-temperature isotropic phases, which is fundamentally different from the previously reported reentrant isotropic phase.

Recently, we reported the columnar-smectic-cholesteric LC phase sequence in the thermotropic LC systems of a chiral rod-like polymer, poly[*n*-decyl-(*S*)-2-methylbutylsilane] (PD(*S*)MB), with narrow molecular weight distributions [5–8]. This step-by-step development of the LC order in PD(*S*)MB precisely reproduced the theoretical predictions of the phase behaviour of rod-like particles interacting through an excluded-volume effect using a computer simulation technique [9], even though the columnar and smectic LC phases were separately reported for the lyotropic and thermotropic LCs of synthetic polypeptides [10–13], DNA [14, 15], and some viruses [16–18]. PD(*S*)MB could be considered as an ideal molecule to verify the theoretical predictions, because the electrostatic interactions between molecules can be reduced due to its non-polar property. The non-polar nature of the polymer is also advantageous for the preparation of samples with narrow molecular weight distributions by a simple fractional precipitation method, due to the lack of polymer aggregation in solution.

In this article, we report the experimental observations of the unusual smectic A (SmA)–reentrant isotropic (I_{re})–nematic (N) LC phase transition sequence (Figure 1) observed in poly[*n*-decyl-(*RS*)-2-methylbutylsilane] (PD(*RS*)MB), the racemic counterpart of PD(*S*)MB, having the structure shown in Scheme 1.

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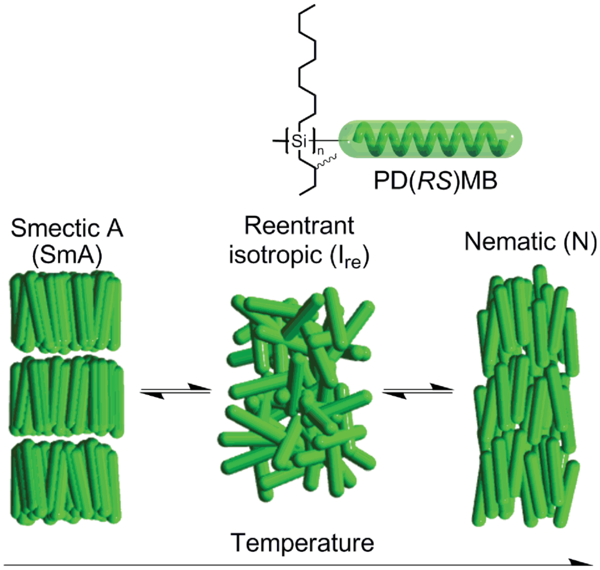
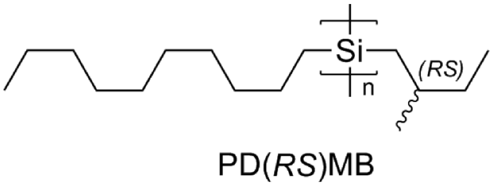


Figure 1. Schematic illustration of anomalous thermotropic phase behaviour in PD(*RS*)MB. The I_{re} phase is drawn as an isotropic liquid for descriptive purposes even though the exact molecular arrangement is still unclear (colour version online).



Scheme 1.

The possible reason for the formation of the I_{re} phase is also discussed based on the optical microscopic observations and X-ray diffraction measurements of PD(*RS*)MB over the entire temperature range of the LC phase transition.

2. Experimental details

2.1 Materials

Chloroform was used as the eluent for the size exclusion chromatography (SEC) measurements and was of high-performance liquid chromatography (HPLC) grade (Wako, Osaka, Japan). Anhydrous chloroform (water content < 30 ppm) was purchased from Wako and used for the preparation of the small-angle X-ray scattering (SAXS) samples. PD(*RS*)MB was synthesised using the optically inactive dichlorosilane monomer bearing (*RS*)-2-methylbutyl and *n*-decyl substituents by a Wurtz-type condensation and then fractionated into samples with different molecular weights and narrow molecular weight distributions according to the previously reported methods [19]. The molecular weights (M_w) and the molecular weight distributions (M_w/M_n) of the samples were determined by SEC measurements.

2.2 Instruments

The SEC measurements were performed using an LC-2000plus HPLC system (Jasco, Tokyo, Japan) equipped with a GPC K-805L column (Showa Denko, Tokyo, Japan). Chloroform was used as the eluent at 40°C and a flow rate of 0.5 mL min^{-1}. The molecular weight calibration curve was obtained using standard polystyrenes (Showa Denko). The polarising optical microscopic observations were carried out with an Olympus BH-2 polarising microscope (Olympus, Tokyo, Japan) equipped with a Mettler FP82 hot stage (Mettler-Toledo, Greifensee, Switzerland). The sample was placed on a glass plate covered by a cover glass to develop the planar structure in the Mettler hot stage at a specific temperature. Wide-angle X-ray diffraction (WAXD) and SAXS measurements were carried out using a Rigaku RINT RAPID-R X-ray diffractometer (Rigaku, Tokyo, Japan) and a rotating-anode generator with graphite monochromated CuKα radiation (0.15418 nm) focused through a 0.3 mm pinhole collimator, which was supplied at 45 kV voltage and 60 mA current, equipped with a flat imaging plate having a specimen-to-plate distance of 120 mm and 899 mm for the WAXD and SAXS, respectively. The samples were kept in glass capillary tubes set in a Mettler FP82 hot stage at a specific temperature during the X-ray exposure. The absorption spectra were obtained using a Jasco V570 spectrophotometer.

3. Results and discussion

In the X-ray diffraction pattern of the uniaxially oriented PD(*RS*)MB, quasi-meridional and meridional reflections with spacings of 4.6 Å and 1.96 Å were observed in the wide-angle region (see Figure S1 in the supplementary material, available via the multimedia link on the online article webpage). These are attributed to the third layer line that is the turn layer line and the seventh layer line of the 7-residue 3-turn (7_3) helical conformation [20]. The rigid-rod nature of PD(*RS*)MB comes from this 7_3 helical structure, even though racemic helical polymers apparently have a number of helical reversals between the interconverting right- and left-handed helical segments because the molecule is not chiral, which may destabilise the rigidity of the polymer backbone. Thus the cholesteric phase observed in the chiral PD(*S*)MB should be converted into the nematic phase in PD(*RS*)MB.

Figure 2 shows the LC phase transition behaviour of PD(*RS*)MB with $M_n = 14.4 \times 10^3$ and $M_w/M_n = 1.07$ observed by polarising optical microscopy. The sample was prepared on a glass plate, covered by a cover glass and allowed to equilibrate at each temperature for about 20 min before the observations. Upon heating, the isotropic area began to grow into the SmA phase at 130°C (Figure 2(b)), and then the whole field of view turned into the optically isotropic phase (I_{re}) at 140°C (Figure 2(c)). The SmA phase was assigned based on the smectic layer reflections in the SAXS patterns in the direction perpendicular to the reflections for the lateral molecular packing of the polymer (see Figure 4). No birefringence could be observed by rotating the sample in the isotropic area, and even the shear-induced birefringence became isotropic immediately after moving the upper glass slide at this temperature. However, upon further heating, an N phase arose (Figure 2(d)) in the I_{re} phase, spread through the whole area (Figure 2(f)) and transformed again in an isotropic liquid (IL) at 200°C. The SmA–I_{re} transition slowly proceeds upon heating. However, the I_{re} phase did not completely recover the birefringence upon cooling even after annealing for a long time, although the I_{re}–N transition occurs quickly and reversibly.

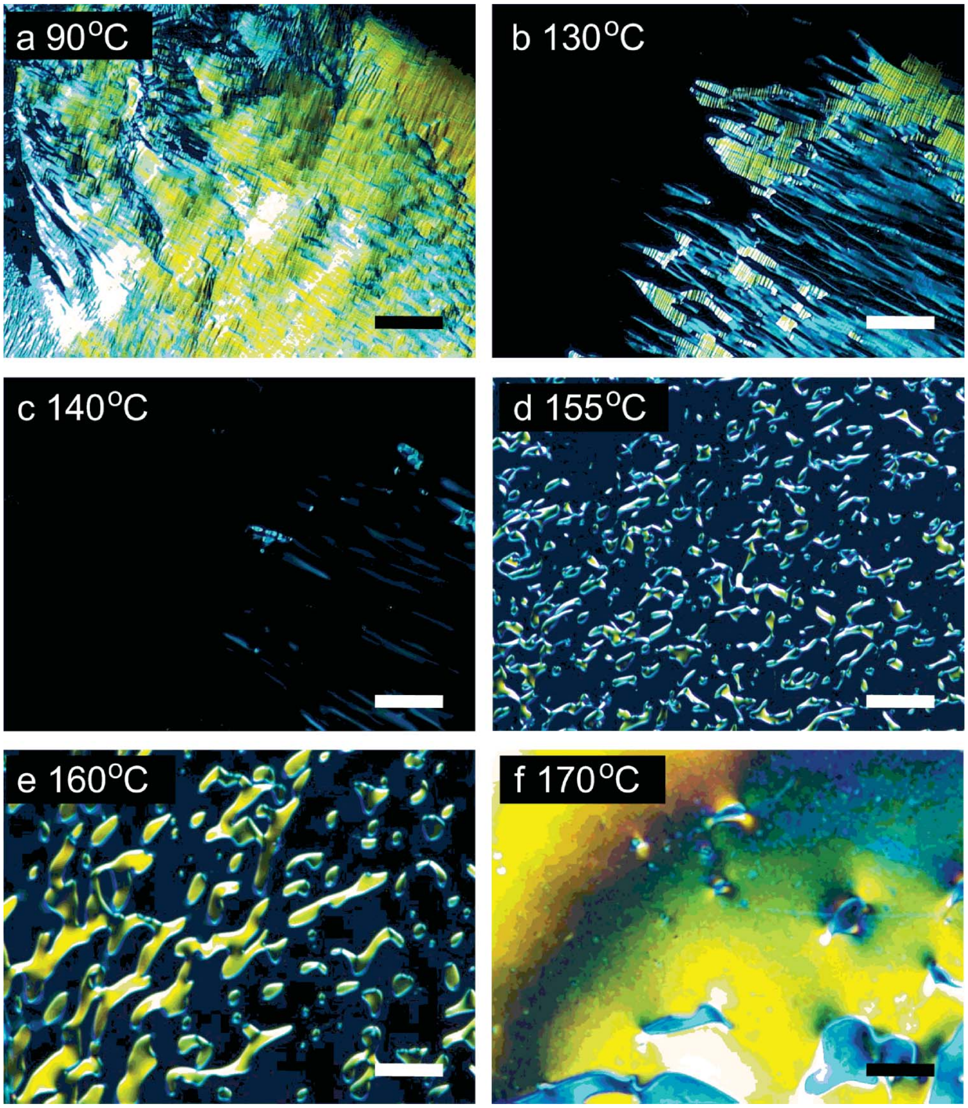


Figure 2. Polarised optical micrographs of PD(*RS*)MB ($M_n = 14.4 \times 10^3$, $M_w/M_n = 1.07$) under crossed polarisers taken at (a) 90°C, (b) 135°C, (c) 140°C, (d) 155°C, (e) 160°C, and (f) 170°C, in a parallel glass cell with the polarising microscope equipped with a hot stage. The I_{re} phase is separating the low-temperature SmA and the high-temperature N phases. Scale bars: 200 μm.

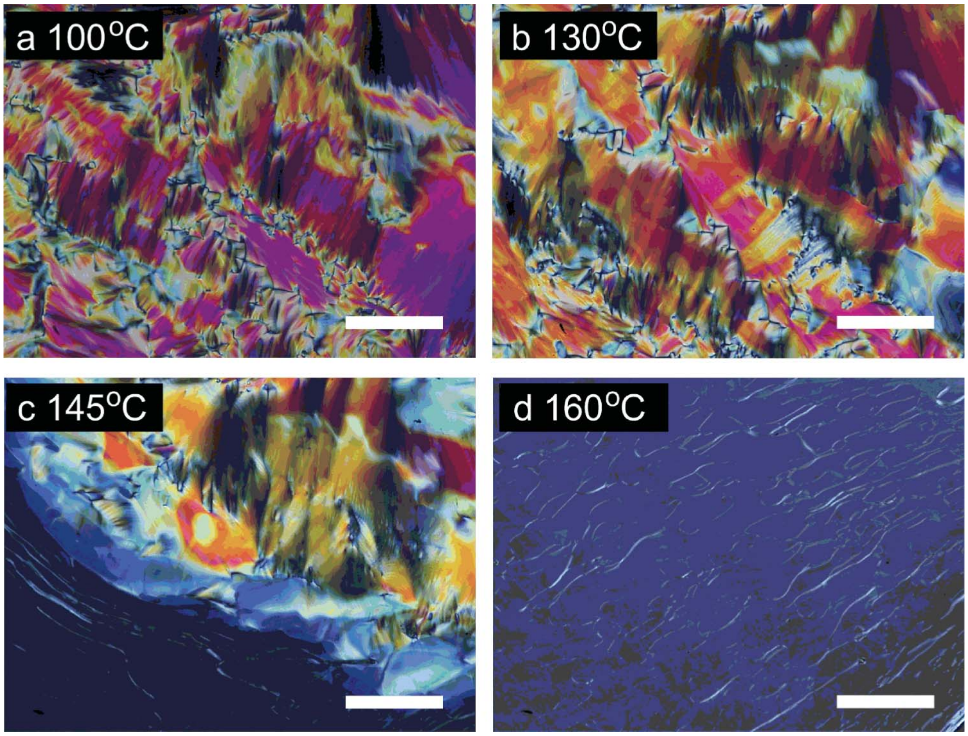


Figure 3. Polarised optical micrographs of PD(*S*)MB ($M_n = 13.3 \times 10^3$, $M_w/M_n = 1.10$) under crossed polarisers taken at (a) 100°C, (b) 130°C, (c) 145°C, and (d) 160°C, in a parallel glass cell with the polarising microscope equipped with a hot stage. The SmA phase was directly transformed into the cholesteric phase without passing through the I_{re} phase upon heating. Scale bars: 200 μm.

In contrast, chiral PD(*S*)MB with similar molecular weight and molecular weight distribution ($M_n = 13.3 \times 10^3$ and $M_w/M_n = 1.10$) was directly transformed from the SmA phase into the cholesteric phase at around 145°C upon heating without showing the isotropic texture (Figure 3). The phase transition took place across a wide temperature range of coexistence and was completed at around 160°C [7]. Even upon further heating the cholesteric phase did not transform in an isotropic melt, probably due to the stiffer polymer backbone which presumably raised the isotropisation temperature.

The observed complete extinction between crossed polars in PD(*RS*)MB may be attributed either to the complete loss of the long-range orientational order of the polymers or the anchoring transition of the polymer into the homeotropic alignment. The isotropic liquid and homeotropic alignments are difficult to distinguish because both states are optically isotropic and therefore dark between crossed polarisers. Thus we employed the X-ray diffraction technique of the magnetically aligned PD(*RS*)MB as a function of temperature in addition to the polarising optical microscopic observations. We found that the orientation of PD(*RS*)MB in a capillary tube is easily achieved by applying a magnetic field (5 T) through the transformation from the isotropic liquid at 190°C to the smectic and columnar phases upon slow cooling at the rate of 0.5°C min^{-1} in the same manner as described elsewhere [21].

Figure 4 shows the WAXD and SAXS patterns of the oriented PD(*RS*)MB upon heating. At 30°C, an almost perfect orientation can be seen in both the WAXD and SAXS patterns (Figure 4(a), (b)). The WAXD pattern shows several higher-order reflections on the equatorial line with spacings of 16.2, 12.4 and 8.7 Å, similar to the previously reported PD(*S*)MB (Figure 4(a)) [5]. The SAXS pattern shows a sharp smectic layer reflection with a spacing of 120.9 Å accompanying the higher-order reflections (Figure 4(b)). Upon heating, the equatorial reflections in the WAXD pattern became diffuse and united into a broad reflection with a spacing of 15.8 Å, while the smectic layer reflection was significantly weakened and blurred, showing that the smectic layers had lost their long range correlation. Upon further heating, the orientation of the polymer and the smectic layer structure disappeared at the same time at 140°C, whereas the outer 4.6 Å reflection characteristic of the 7_3 helical conformation still remained. On the other hand, with the temperature jump from 130°C (SmA phase) to 170°C (N phase),

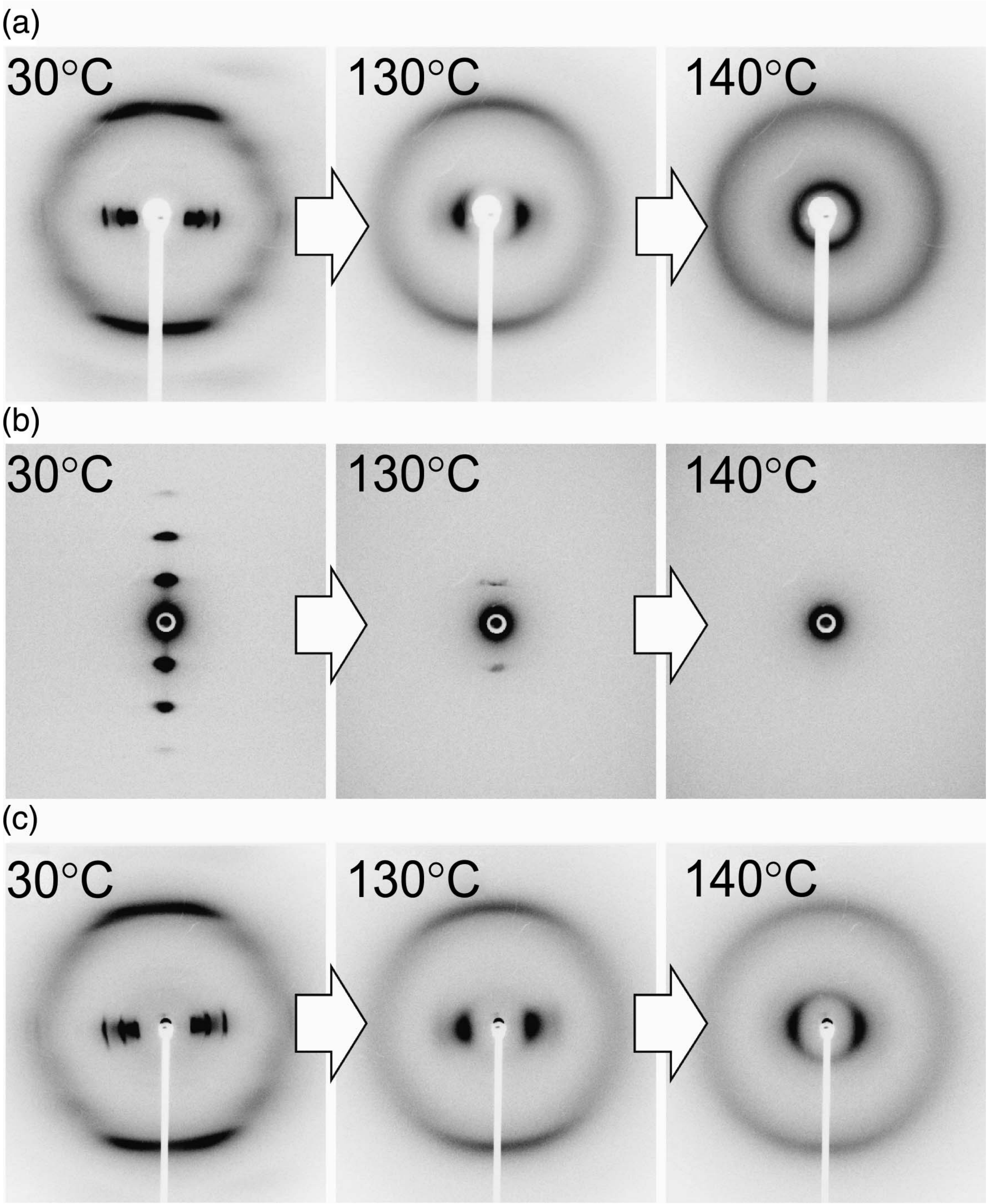


Figure 4. Wide-angle X-ray diffraction (a, c) and small-angle X-ray scattering (b) patterns observed for the magnetically aligned PD(*RS*)MB ($M_n = 14.4 \times 10^3$, $M_w/M_n = 1.07$) in glass capillary tubes, which were taken at specific temperatures with the sequence indicated by the white arrows upon heating. (a, b) The orientation of the polymer and the smectic layer structure disappeared at the same time at 140°C. (c) The orientation of the polymer was retained on the temperature jump from 130°C to 170°C. The magnetic field direction is vertical and along the glass capillary tube.

the orientation of the polymer was retained even after annealing for 3 h (Figure 4(c)).

If the SmA–I_{re} phase transition is an anchoring transition to the pseudo-isotropic homeotropic alignment, the smectic layer reflection should remain and the orientation should be transformed into one perpendicular to the glass wall of the capillary tube at 140°C, because the smectic phase should realign its orientation with the smectic layers retained in the anchoring transition, according to the only report on the anchoring transition of the smectic phase [22]. These observations suggest that we are more likely to be dealing with a normal isotropic liquid.

Furthermore, we found that the darkness spread through the entire area, including its edge, in a droplet of the polymer on a glass substrate between crossed polarisers at 140°C, which seems inconsistent with the existence of a mesophase, even though the exact mechanism of the I_{re} phase formation is still unclear.

Polarised optical micrographs of PD(*RS*)MB with a higher molecular weight showed the further variety of the LC polymorphism in Figure 5. The I_{re} phase slowly grew into the SmA phase at around 145°C upon heating; however, the transition was very slow and the SmA phase remained even after annealing for a long time. Upon further heating, the I_{re} phase was converted back to the smectic fan-shaped texture at around 180°C and then covered the entire area, showing that the I_{re} phase appears in almost the same temperature range regardless of the molecular weight. This transition was relatively fast and the liquid crystal droplets with Maltese crosses, but not bâtonnets, appeared at the onset of the transition. Careful observations revealed that nematic droplets first appeared and immediately transformed into a smectic fan, although the smectic (Sm) phase was directly converted into the I_{re} phase upon cooling. However, the smectic layer reflection of the higher-temperature Sm phase has not yet been observed despite all efforts.

One of the easy-to-follow theories reported as the molecular origin of the I_{re} phase is the thermal variation in the shape anisotropy of microscopic objects [23, 24], including the conformational transition or association/dissociation of the molecules [4, 25].

The conformational transitions of polysilanes have been extensively studied for many years. It has been reported that polysilanes with a long alkyl side chain show a transition of the polymer backbone from a planar zigzag to a helical conformation upon heating, which can be clearly observed as a remarkable blue shift in the electronic spectrum [26, 27]. Because the reentrancy could be attributable to such a conformational change in the polymer backbone, the solid-state variable-temperature UV spectrum of PD(*RS*)MB ($M_n = 14.4 \times 10^3$, $M_w/M_n = 1.07$) was taken at a temperature around the SmA–I_{re} phase transition (Figure 6). However, a sharp peak at 315 nm, which is assignable to the 7_3 helical conformation of the polymer backbone, slightly shifted to 325 nm with its decreasing absorbance upon heating from 40°C to 150°C. Thus the helical conformation of PD(*RS*)MB is stable over the temperature range of the I_{re} phase.

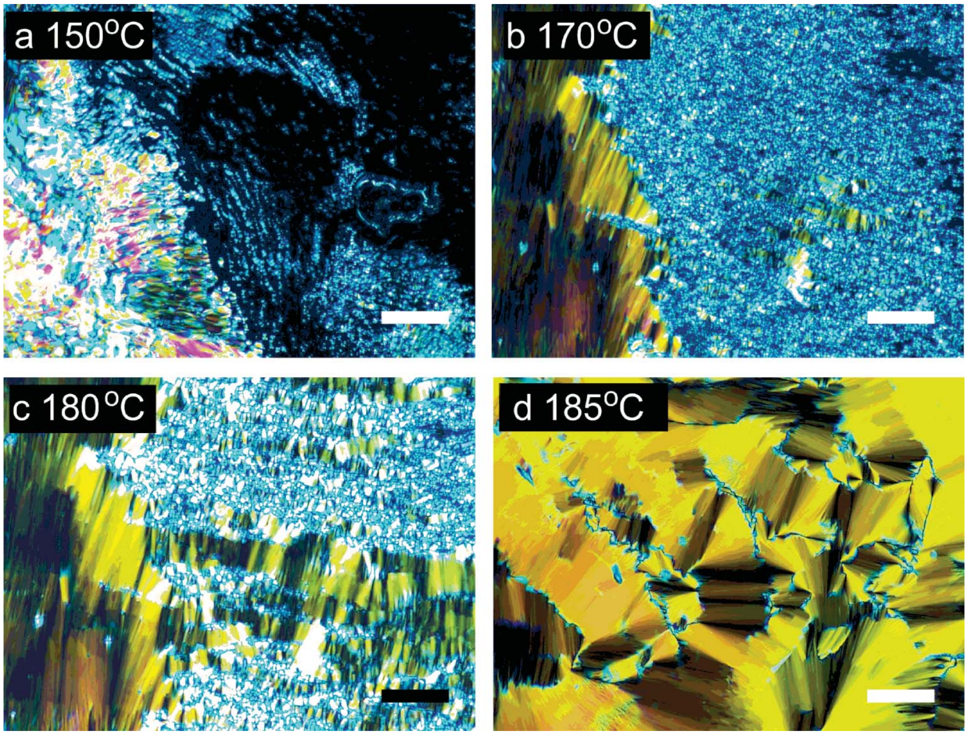


Figure 5. Polarised optical micrographs of PD(*RS*)MB ($M_n = 34.2 \times 10^3$, $M_w/M_n = 1.10$) under crossed polarisers taken at (a) 150°C, (b) 170°C, (c) 180°C, and (d) 185°C in a parallel glass cell. The smectic fan-shaped texture emerged from the optically isotropic phase at around 180°C upon heating with an enantiotropic reversibility. Scale bars: 200 μm (colour version online).

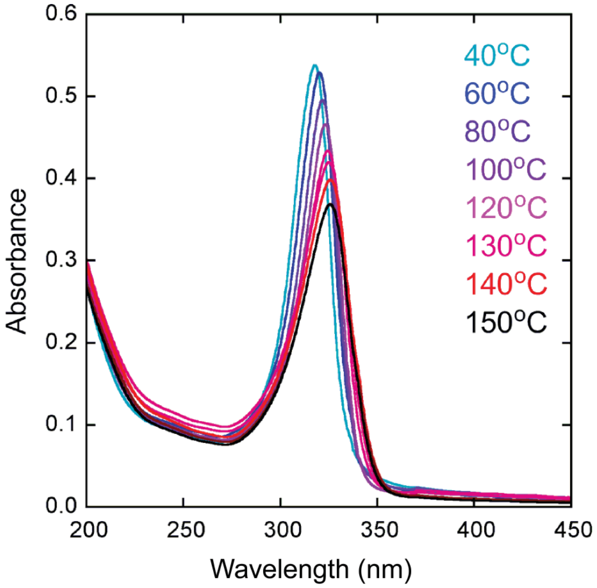


Figure 6. Variable-temperature solid-state UV spectra of PD(*RS*)MB ($M_n = 14.4 \times 10^3$, $M_w/M_n = 1.07$) at around the reentrant isotropic phase between 40°C and 150°C. No conformational change in the polymer backbone could be observed over the SmA–I_{re} phase transition. The sample was cast on a glass substrate and annealed at the designated temperature for 30 min before the measurements (colour version online).

The same association of the α-helical polypeptide might be possible for polysilanes. It has been reported that the supercoiling of two or three α-helices was stabilised by the regular interlocking of the side chains in some groups of fibrous proteins [28]. The chains coiled about each other increase their diameter, thus decreasing the length/diameter ratio, which works against the LC formation. The dissociation of the helical coiled coil of polysilane upon heating evidently increases the length/diameter ratio, possibly leading to the reentrant LC phase. However, its X-ray pattern exhibited no features expected for the coiled-coil conformation although our effort is continuing.

More importantly, the I_{re} phase can be observed only in PD(*RS*)MB with a narrow molecular weight distribution which shows the SmA phase. No such disappearance of the birefringence in the polarising optical microscopy image and the polymer orientation in the WAXD pattern was observed up to 170°C in the samples with wide molecular weight distributions, which form only the nematic phase. This implies that the smectic layer structure might play a role in the reentrant phenomenon, which provides a clue to answering the question regarding the exact origin of the reentrance of the isotropic phase. Initially, we considered that the I_{re} phase corresponded to a certain type of cubic phase analogous to the smectic D phase, which may have a jointed-rod structure made up of cylinders. In the present study, the component molecules have a cylindrical shape, therefore a similar structure could be proposed, even though the cylinders are composed of aggregations of molecules in the reported studies. However, the observed X-ray patterns showed no distinctive features for this structure and the circular shape of the air bubbles in the I_{re} phase indicated that the viscosity is significantly lower than that of the lower-temperature smectic phase. Thus we have no decisive evidence as a basis for identifying the possible structure. The question still remains unanswered.

4. Conclusion

In conclusion, we have demonstrated the very unusual thermotropic LC phase behaviour including the I_{re} phase observed in PD(*RS*)MB with narrow molecular weight distributions. Although both the polarising optical microscopic observations and X-ray diffraction measurements support the existence of the I_{re} phase, a question still remains regarding the molecular origin of the reentrance of the isotropic phase. As a possible mechanism of the I_{re} phase formation, an anchoring transition to the pseudo-isotropic homeotropic alignment as well as a cubic phase does not explain the following features: (i) the I_{re} phase could not be observed in the corresponding chiral counterpart, PD(*S*)MB; (ii) the orientation of the polymer and the smectic layer structure disappear simultaneously at the SmA–I_{re} phase transition; (iii) the I_{re} phase could not be observed in PD(*RS*)MB with wide molecular weight distributions; (iv) no conformational change in the polymer backbone takes place in the SmA–I_{re} phase transition; (v) the fluidity of the I_{re} phase is far greater than that of the lower-temperature SmA phase. Therefore, it is very likely that we are dealing with an isotropic liquid, although the exact molecular origin of the I_{re} phase is still unclear.

This study is not only the first example of a reentrant isotropic phase observed in rigid-rod polymers without an intramolecular conformational change, to the best of our knowledge, but it also provides a key to solve the general mechanism of the reentrant phenomena in liquid crystals. In particular, the studies of the lyotropic LC phase behaviour of PD(*RS*)MB might be worth implementing for the purpose of understanding the reentrant phenomena, and will be a subject of a future investigation.

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