Supporting Information

Discrete and Sequential Formation of Helical Nanofilaments in Mixtures Consisting of Bent- and Rod-shaped Molecules

Hiroki Nagayama, Yuji Sasaki,[#] Fumito Araoka, Kenji Ema,[#] Ken Ishikawa, and Hideo Takezoe*

Department of Organic and Polymeric Materials
Tokyo Institute of Technology
O-Okayama, Meguro-ku, Tokyo, 152-8552 (Japan)
*E-mail: takezoe.h.aa@m.titech.ac.jp
[#]Department of Physics
Tokyo Institute of Technology
O-Okayama, Meguro-ku, Tokyo, 152-8551, Japan

Contents

1. Full data using commercial DSC in five mixtures

In the measurement of pure P8, the Iso-B2-B4 transition was observed and B3 phase is missing, because of thermally unstable phase. In P8/5CB (0.8/0.2), the heat capacity anomaly peak becomes broader on heating run. The peak broadening develops when 5CB content increases even on cooling run. The transition temperature to the Iso phase decreases with increasing 5CB content. P8/5CB (B4/Iso) to (B4/N) transition becomes visible when 5CB content is more than 50% (see e.g. (d)). Broad peaks are observable around 80 °C. This is related to a glass transition in P8 (see Fig. S3).

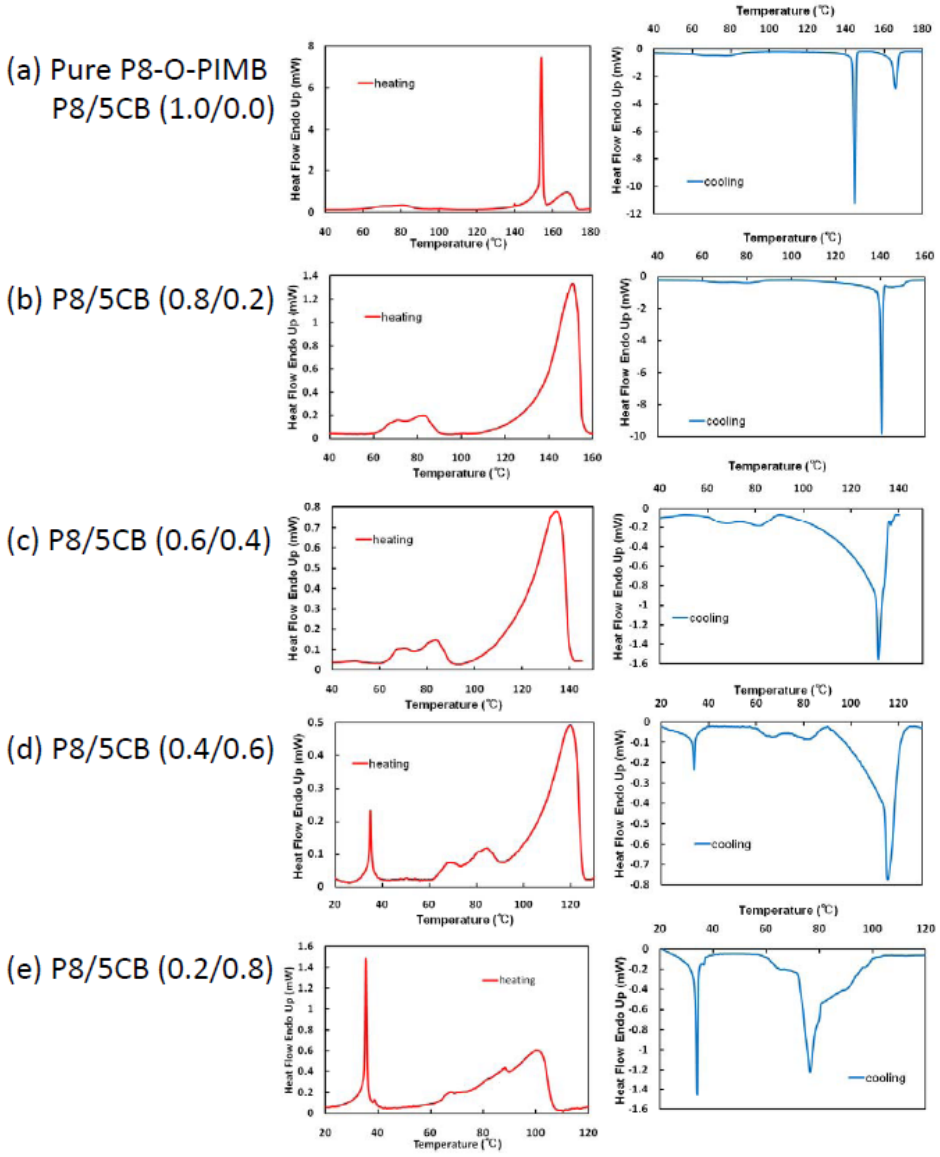

Fig. S1. DSC data of both on cooling and heating in (a) pure P8, (b) P8/5CB (0.8/0.2), (c) P8/5CB (0.6/0.4), (d) P8/5CB (0.4/0.6), (e) P8/5CB (0.2/0.8). The heating and cooling rate was 10 °C/min.

2. Highly sensitive DSC data using a sandwich cell

In order to examine whether the discrete and sequential heat anomalies can be seen even in conventional sandwich cells, we conducted HS-DSC measurements, where glass substrates of 120~170 μm and a cell gap of 16 μm were used. The sample used was P8/5CB (0.4/0.6). The cooling rate was 0.1 °C/min. Because of thermal conductivity difference in aluminum, which was used for normal HS-DSC, and glass, the peak positions are quite different. However, we confirmed the existence of many discrete sharp peaks. Thus we learned that optical spectroscopy using sandwich cells is useful to investigate the phenomenon for the discrete and sequential transitions using sandwich cells.

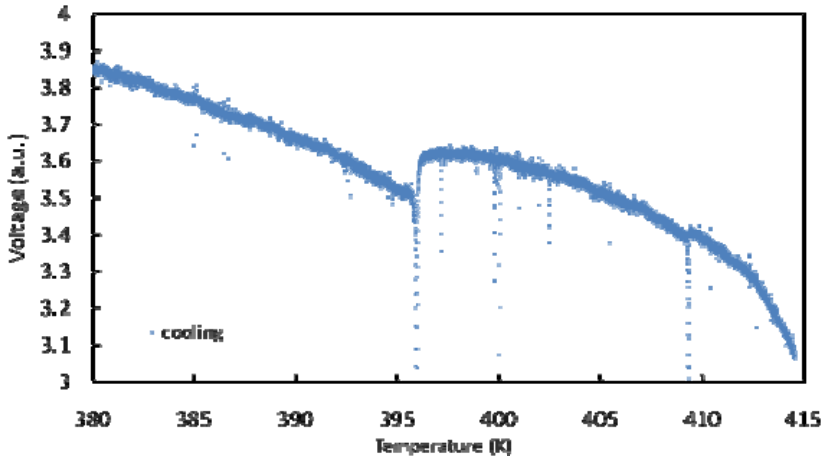

Fig. S2. HS-DSC data on cooling in P8/5CB (0.4/0.6) sandwiched by thin glass substrates.

3. DSC over a wide temperature range showing a glass transition

Figure S3(a) shows DSC data for pure P8. If we closely look at 60~90 °C, there are two peaks, as shown in Figure S3(b).

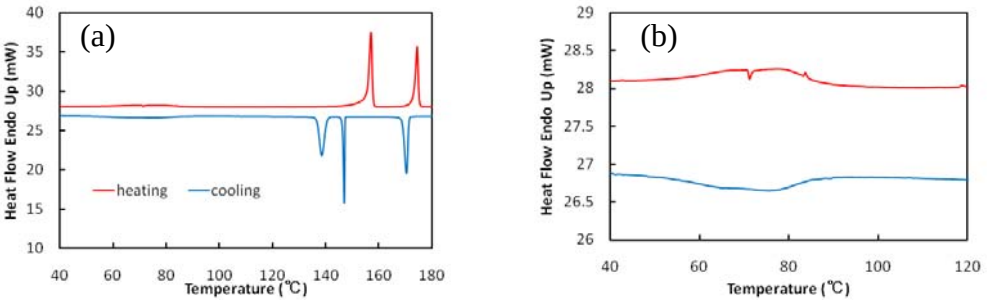

Fig. S3. (a) DSC data for pure P8. (b) Close up of the peaks around 60~90 °C.

We can observe not a sharp but a gradual distinct change around this broad heat anomaly peaks. We can also observe some changes, for instance, in texture observation, IR and UV-Vis absorptions, and even vibrational CD spectra. Similar observation was made in some liquid crystals and was assigned to glass transition, where layer undulation is frozen.[S1,S2] The existence of glass transition was also pointed out by Chen et al.[S3] without mentioning any details.

4. IR absorption spectra in the mixture of P8/5CB=0.4/0.6

Figure S4 shows IR spectra for three mixtures P8/5CB; (a) 0.8/0.2, (b) 0.6/0.4, and (c) 0.4/0.6. Here we focus only a peak at 1280 cm^{-1}. This peak is observable only in the B_4 phase, as shown in Figure 2(a); i.e., no peaks are observed at this wavelength in Iso and B_2, and the absorbance of this peak shows only a negligible change once it appears in the B_4 phase. Hence we can use this IR absorption peak for examining the existence of the B_4 phase and even for estimating the growth of helical nanofilament domains. Contrary to the sample P8/5CB (0.8/0.2), the IR intensity of the 1280 cm^{-1} peak gradually increases in the B_4 phase in P8/5CB (0.6/0.4). The behavior is essentially the same in P8/5CB (0.4/0.6), although the data points are not as much as in P8/5CB (0.6/0.4). This gradual increase of the IR intensity at 1280 cm^{-1} is attributed to the increase of the B_4 (helical nanofilament) domains.

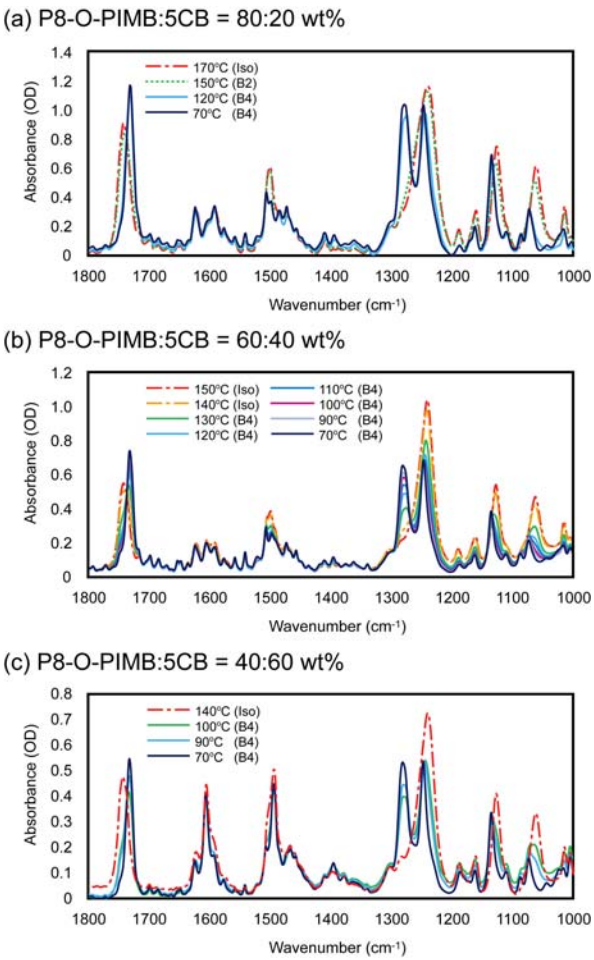

Fig. S4. IR spectra for three mixtures P8/5CB; (a) 0.8/0.2, (b) 0.6/0.4, and (c) 0.4/0.6.

5. Full data of UV-Vis absorption spectra

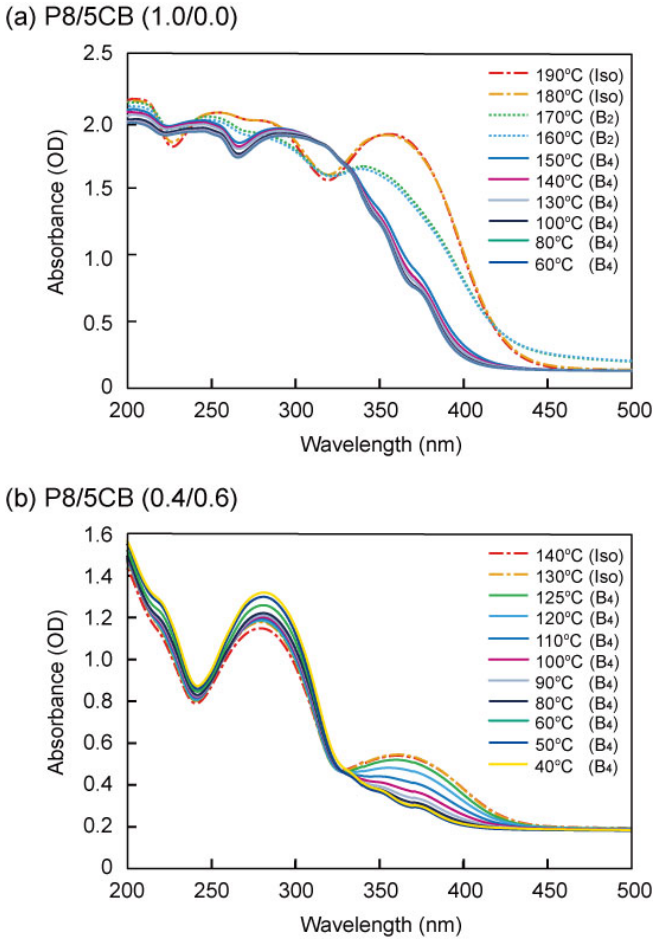

Fig. S5. Temperature dependence of UV-Vis absorption spectra in (a) pure P8 and the mixture of P8/5CB (0.4/0.6).

References

S1. H. Yoshioka et al. *Mol. Cryst. Liq. Cryst.*, 1983, **95**, 11.

S2. M. Sorai, S. Seki, *Mol. Cryst. Liq. Cryst.*, 1973, **23**, 299.

S3. D. Chen et al. *Langmuir,* 2010, **26**, 15541.