

## Simultaneous DSC-SAXS measurement of PEO-*b*-PMA(Bza) copolymers

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### Introduction

Side-chain type liquid crystal-amphiphilic di-block copolymers form nano-scale phase separation at an equilibrium state. We have reported the phase transitions and the nano-scale order structure of di-block copolymer consisted of hydrophilic poly (ethylene oxide) (PEO) and hydrophobic poly (methacrylate) derivatives (PMA(R)) containing liquid crystalline mesogen unit (R) as an ester group [1-3]. In the case of copolymer having azobenzene as a mesogenic unit, both smectic C and A were observed on heating by the simultaneous DSC-SAXS measurement. In this study, we have investigated the nano-scale structure and liquid crystalline phase of amphiphilic di-block copolymer having benzylideneamine (Bza), besides azobenzene and styrene, PEO<sub>114</sub>-*b*-PMA(Bza)<sub>n</sub>.

### Experiments

#### Materials

PEO<sub>114</sub>-*b*-PMA(Bza)<sub>n</sub> used through the experiments was prepared by the atom transfer radical polymerization. The degree of polymerization of PMA(Bza), *n*, was determined by <sup>1</sup>H-MNR, and the molecular weight disparity determined by GPC was less than 1.1.

#### Experiments

The simultaneous DSC-SAXS measurements [4] were performed by SAXS optics at BL-10C, PF, KEK. The wavelength of X-ray and the measurement range of scattering vector were 0.1488 nm and 0.06 nm<sup>-1</sup> < *q* (=4πsinθ/λ) < 3 nm<sup>-1</sup>, respectively. DSC scanning rate and XRD time resolution were 2 K min<sup>-1</sup> and 30 sec, respectively.

### Results

#### Nano phase separation structure

The SAXS profile changes of PEO<sub>114</sub>-*b*-PMA(Bza)<sub>73</sub> obtained by DSC-SAXS on heating was shown in Fig.1. DSC indicated three endothermic peaks at 38.5, 78.5 and 127.3 °C, the endothermic peak at 38.5 °C was assigned to the melting of PEO segment. The SAXS profiles of PEO<sub>114</sub>-*b*-PMA(Bza)<sub>n</sub> showed the scattering peaks in the *q* range from 0.3 to 1.0 nm<sup>-1</sup>, these peaks (at *q*\*, 3<sup>1/2</sup>*q*\* and 2*q*\*) indicated the hexagonal packed cylinder structure for PEO<sub>114</sub>-*b*-PMA(Bza)<sub>n</sub> with *n* = 38 – 73. The scattering peaks at *q*\*, 3<sup>1/2</sup>*q*\* and 2*q*\* became weak above the melting of PEO, and the peaks at *q*\*, 3<sup>1/2</sup>*q*\* and 2*q*\* appeared again at 120 °C. These nano-scale structures observed at various temperatures were almost the same with those of PEO<sub>114</sub>-*b*-PMA(Az)<sub>n</sub>, which contained azobenzene moieties as liquid crystalline mesogen [2, 3].

#### Liquid crystalline phase

In Fig.1, the scattering peak at 1.8 nm<sup>-1</sup> was corresponded to the smectic layer of hydrophobic PMA(Bza) domain. The smectic layer distance (*d*<sub>L</sub>) was constant below the melting temperature of PEO, and decreased in the temperature range from 70 to 120 °C, and this scattering peak disappeared at the endothermic DSC peak at 127.3 °C. From this result, the endothermic DSC peak at 127.3 °C was assigned as the isotropic transition of PEO<sub>114</sub>-*b*-PMA(Bza)<sub>73</sub>. In the case of azobenzene as liquid crystalline mesogen, two types of smectic phase, S<sub>m</sub>C and S<sub>m</sub>A were observed and the transition between S<sub>m</sub>C and S<sub>m</sub>A was measured thermo-reversibly. However, PEO<sub>114</sub>-*b*-PMA(Bza)<sub>73</sub> showed only S<sub>m</sub>A phase, because the *d*<sub>L</sub> was matched with the molecular length [5]. Moreover we will investigate the effect on liquid crystal phase by the difference from liquid crystalline mesogens.

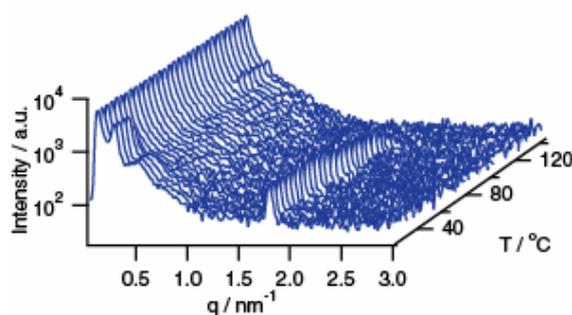


Fig.1 SAXS profile change of PEO<sub>114</sub>-*b*-PMA(Bza)<sub>73</sub> on heating

### References

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