

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

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### Introduction

Di-block copolymers form the nano-scale ordered structure due to phase separation as an equilibrium state. We have reported the phase transitions and the nano-scale order structure of amphiphilic di-block copolymers consisted of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(methacrylate) derivatives PMA(R) containing liquid crystalline mesogen unit (R) as an ester [1-3]. In the case of di-block 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, the nano-scale structure and liquid crystalline state of amphiphilic di-block copolymer having stilbene moieties as mesogenic unit, PEO<sub>114</sub>-*b*-PMA(Stb)<sub>n</sub>.

### Experiments

#### Materials

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

#### Methods

The simultaneous DSC-XRD 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-scale structure

The SAXS profile change of PEO<sub>114</sub>-*b*-PMA(Stb)<sub>45</sub> obtained by DSC-SAXS on heating was shown in Fig.1. DSC indicated three endothermic peaks at 40, 140 and 160 °C, the endothermic peak at 40 °C was assigned to the melting of PEO segment. The SAXS profiles of PEO<sub>114</sub>-*b*-PMA(Stb)<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\*, q\*<sup>1/2</sup>, 3q\*<sup>1/3</sup>, and 2q\*) indicated the hexagonal packed cylinder structure for PEO<sub>114</sub>-*b*-PMA(Stb)<sub>n</sub> with n = 26 – 75, however, PEO<sub>114</sub>-*b*-PMA(Stb)<sub>4</sub> formed the lamellar structure. The scattering peaks at q\*<sup>1/2</sup>, 3q\*<sup>1/3</sup>, and 2q\* became weak above the melting of PEO, and the peaks at q\*<sup>1/2</sup>, and 3q\*<sup>1/3</sup> appeared again at 170 °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 azobenene moieties as liquid crystalline mesogenic units [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(Stb) domain. The q value of smectic layer was constant below the melting temperature of PEO, and increased in the temperature range from 100 to 140 °C. The q value and its intensity of smectic layer decreased in the temperature range from 140 to 160 °C, and this scattering peak disappeared at the endothermic DSC peak at 160 °C. From this result, the endothermic DSC peak at 160 °C was assigned as the isotropic transition of PEO<sub>114</sub>-*b*-PMA(Stb)<sub>45</sub>. In the case of PEO<sub>114</sub>-*b*-PMA(Az)<sub>n</sub>, two types of smectic phase, S<sub>C</sub> and S<sub>A</sub> were observed and the transition between S<sub>C</sub> and S<sub>A</sub> was measured thermo-reversibly. Furthermore investigations are proceeding to assign the type of liquid crystalline state of PEO<sub>114</sub>-*b*-PMA(Stb)<sub>n</sub>.

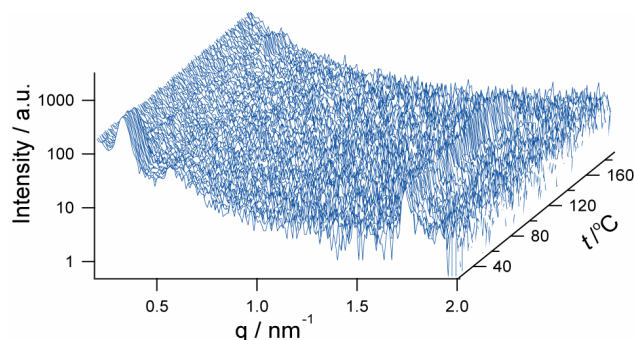


Fig.1 SAXS profile change of PEO<sub>114</sub>-*b*-PMA(Stb)<sub>45</sub> on heating

### References

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