# Effect of $CO_2$ and $N_2$ Pressures on Isotropic transition of Amphiphilic Liquid Crystal Di-block Copolymer

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## Introduction

We have reported phase transitions and nano-scale ordered structures of amphiphilic liquid crystal di-block copolymers consisting of hydrophilic poly ethylene oxide (PEO) and hydrophobic poly methacrylate derivatives having liquid crystal side-chains in which mesogen was azobenzene moiety (PMA(Az)) ($PEO_m$-*b*-$PMA(Az)_n$, where "m" and "n" are degrees of polymerisation of each domain) [1,2]. The $PEO_m$-*b*-$PMA(Az)_n$ copolymers exhibit upon heating four successive phase transitions corresponding to melting of the PEO domain, melting of azobenzene moieties, liquid crystal phase transition from smectic C phase to smectic A phase and the isotropic transition respectively. The $PEO_m$-*b*-$PMA(Az)_n$ copolymers form the highly ordered hexagonal packed PEO cylinder structures in a wide volume fraction range because the liquid crystal phase compensates the entropy loss of the interface between PEO domain and PMA(Az) domain [2].

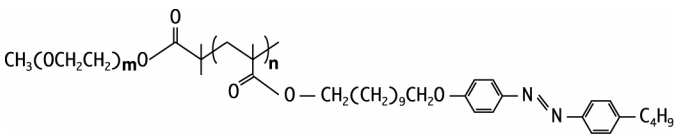

**Figure 1.** Chemical structure of $PEO_{114}$-*b*-$PMA(Az)_{40}$.

The highly ordered PEO cylinder structures have a great potential as nano-templates for nano objects. We have investigated the possibility to modify the nano-scale structures to form nano-composites with gold nano-particles by using super critical carbon dioxide, which is one of the environment respectful solvents [3]. It is important for super critical fluids processing to understand effects of carbon dioxide ($CO_2$) on phase transition. In this study, effects of $CO_2$ pressure on the isotropic transition were investigated by scanning transitiometry. A comparative study was done under nitrogen ($N_2$) pressure.

## Samples and Experiments

$PEO_{114}$-*b*-$PMA(Az)_{40}$ block copolymer and $PMA(Az)_{30}$ were synthesized by atom transfer radical polymerisation. The degree of polymerisation and molecular index were decided by $^1$H-NMR and GPC. The molecular index of both $PEO_{114}$-*b*-$PMA(Az)_{40}$ and $PMA(Az)_{30}$ were 1.13 and 1.19 respectively. The scanning transitiometry measurements were performed with the transitiometer (BGR-TECH, Poland) [4]. The pressure range was from 0.1 MPa to 150 MPa. The temperature range was between 330 K and 430K with 0.2 K min$^{-1}$ scanning rate. The sample weight was about 300 mg.

## Results and Discussions

Figure 2 shows calorimetric signals of $PEO_{114}$-*b*-$PMA(Az)_{40}$ under $CO_2$ pressure. An endothermic peak corresponding to the isotropic transition was observed at 0.1 MPa. The peak shifted to the lower temperature side up to 30 MPa and to the higher temperature side above 40 MPa. Figure 3 shows the transition temperature ($T_{Iso}$), enthalpy and entropy of the isotropic

transition. The $T_{Iso}$ decreased with increasing pressure up to 30 MPa and slightly increased with increase of pressure above 40 MPa. The transition entropy and enthalpy were almost constant up to 15 MPa and increased with increasing pressure up to 50 MPa. Eventually the transition entropy and enthalpy levelled off to a constant value, which was 1.5 times larger than under 0.1 MPa. The change of the $T_{Iso}$ suggests that the $CO_2$ acted as both a plasticizer and hydrostatic pressure medium. $CO_2$ has a quadrupole moment which interacts with the dipole moments in the PMA(Az) domain like carbonyl groups in the methacrylate main chain and azobenzene moieties in the side-chain. The plasticization effect was predominant up to 30 MPa. On the other hand, the hydrostatic effect became predominant above 40 MPa.

The transition entropy under mercury pressures, which is usual hydrostatic medium, decreases with increasing pressure because the molecular motion in the isotropic state is restricted [5]. However the transition entropy under $CO_2$ pressures does not decrease. This result indicates that not only phase transition but also gas sorption or adsorption occurred during phase transition because the molecular motion became easier. The active molecular motion decreases the adsorption of the poly methacrylate chain, but favours the adsorption by the side chain since disappearance of the π-stacking of azobenzene moieties increases the adsorption site of the side-chain.

Figure 4 shows the pressure dependency of the $T_{Iso}$ under both $CO_2$ and $N_2$ pressures. Under $N_2$ pressure, the decrease of $T_{Iso}$ was smaller than under $CO_2$ pressure and the hydrostatic effect became predominant above 20 MPa, which was lower than under $CO_2$ pressure, because nitrogen has neither dipole nor quadrupole moment. These results indicate that chemical interactions between gases and PMA(Az) domain play an important role in plasticization .

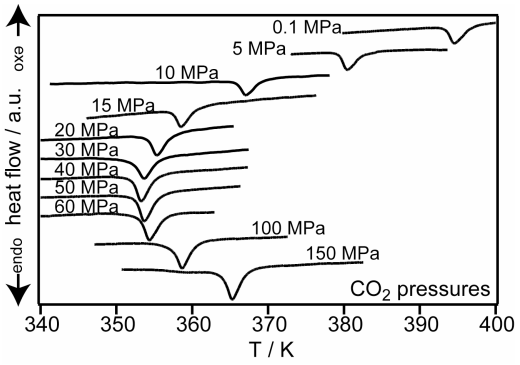


**Figure 2.** Calorimetric signals of $PEO_{114}$ -*b*-$PMA(Az)_{40}$ under $CO_2$ pressures.

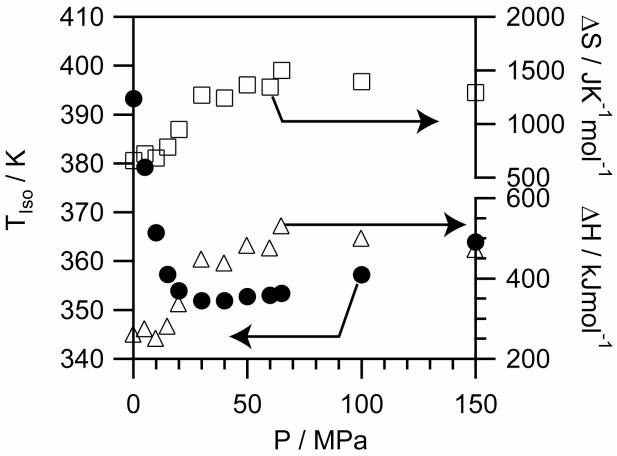


**Figure 3.** Plot of transition temperature (filled circle), enthalpy (open triangle) and entropy of the isotropic transition (open square) to the pressure under $CO_2$ pressure.

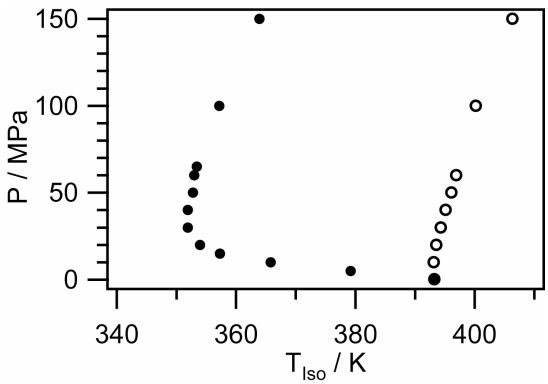


**Figure 4.** Plot of pressure to the isotropic transition temperature. Filled circle; $CO_2$ pressures, open circle; $N_2$ pressures.

**References**

[1] Tian et. al, *Macromolecules*, **2002**, 35, 3739. [2] Yoshida et. al, *Trans. Mat. Res. Sci. Jpn.*, **2004**, 29, 861. [3] Iwamoto et. al. *Polym. Prepr. Jpn.* [4] Randzio, Chem. Soc. Rev. **1996**, 25, 383. [5] Boyer et. al, *Polymer,* submitted