

# INFLUENCE OF SUPERCRITICAL CO<sub>2</sub> OR N<sub>2</sub> ON SELF-ORGANIZED NANO-STRUCTURES IN DI-BLOCK COPOLYMERS

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## ABSTRACT

The effects of high-pressures carbon dioxide (CO<sub>2</sub>) and nitrogen (N<sub>2</sub>) on amphiphilic di-block copolymer (PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub>) have been investigated by scanning transmittometry (ST). Under CO<sub>2</sub> pressures, the isotropic transition temperature decreases with the increase of pressure up to 30 MPa due to CO<sub>2</sub> sorption. Above 40MPa, the transition temperature increases when pressure increases as a consequence of the hydrostatic effect. Under nitrogen which develops weaker interactions with the PMA(Az) domain than CO<sub>2</sub>, increasing pressure induces a smaller decrease of the isotropic transition temperature. The hydrostatic pressure effects of both gases, evaluated by the Clapeyron equation, are smaller than under mercury pressures because the gas sorption decreases the volume change on the isotropic transition.

*Keywords: supercritical carbon dioxide, supercritical nitrogen, high-pressures, amphiphilic di-block copolymers, self-organization*

## INTRODUCTION

High-pressure technology using gases plays an important role in materials nucleation. Particularly interesting are current developments and applications in soft matter science with typical modifications and tailoring of liquid crystals, colloids and polymers including block copolymers, by means of supercritical gases [1-6]. Liquid crystal amphiphilic PEO<sub>m</sub>-*b*-PMA(Az)<sub>n</sub> copolymers, where "m" and "n" are degrees of polymerization of the hydrophilic semi-crystalline poly(ethylene oxide) PEO domain and of the hydrophobic sequences of polymethacrylate derivative (containing mesogen azobenzene units) PMA(Az) domain respectively, form highly ordered PEO hexagonal packed cylinder structures in a wide range of volume fractions and give rise to four kinds of phase transitions [7-10]. These four phase transitions correspond to melting of PEO crystal, glassy -> smectic C phase (SmC), SmC -> smectic A phase (SmA) and isotropic transition of azobenzene moieties PMA(Az) [8]. The effects of CO<sub>2</sub> pressures on structural organization of di-block copolymers have been reported [11, 12]. However, there are no reports on effects of CO<sub>2</sub> pressures on phase transitions of side-chain liquid crystal copolymers and liquid crystals. Similarly, the effects of N<sub>2</sub> pressures on such transitions have not been reported.

We have developed the scanning transitionometry (ST) technique for high-pressure experiments [13-15]. The basic setup, the transitionometer, consists of a calorimetric detector in which one the three thermodynamic variables,  $P$ ,  $V$  or  $T$ , can be scanned independently while a second one is kept constant; four different thermodynamic modes are then possible for which two outputs are obtained during a given scan. By combination of the thermal output and of the mechanical output (*i.e.*, the change of the dependent third variable) and making use of the appropriate Maxwell relations, a complete thermodynamic investigation of the system under study is possible through the determination of the different thermophysical properties, including the enthalpies and volumes of the different transitions undergone by the system. A striking advantage of the technique is the possibility to use various pressure transmitting fluids. For example, mercury, which is a typical “inert” pressure medium was used to investigate the purely hydrostatic pressure effects on the isotropic transitions of PEO<sub>114</sub>-*b*-PMA(Az)<sub>20</sub>. The transition temperature increases with increase of pressure; whereas, the transition entropy decreases with increase of pressure because the molecular motions of the isotropic state are restricted [16].

In the present study, the effects of polar carbon dioxide (CO<sub>2</sub>) and “neutral” nitrogen (N<sub>2</sub>) pressures on the isotropic transition of PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub> have been studied by scanning transitionometry under constant pressure. The results have been compared with those obtained with mercury (Hg).

## SAMPLES AND EXPERIMENTS

The amphiphilic di-block copolymer PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub>, having the general structure shown in Figure 1, was synthesized by the atom transfer radical polymerization as described elsewhere [7]. The molecular dispersion index determined by the gel permission chromatography was 1.13.

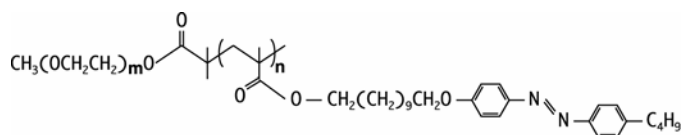


Figure 1: General structure of amphiphilic PEO<sub>m</sub>-*b*-PMA(Az)<sub>n</sub> di-block copolymers.

Transitionometry measurements were performed with a transitionometer (BGR-TECH, Poland) under constant pressure [13-15]. Scanning temperature range was from 330 K to 420 K at 0.2 K min<sup>-1</sup>. The temperature was calibrated with the melting temperature  $T_m$  of standard materials; *p*-bromochloro benzene ( $T_m = 337.73$  K), *p*-dibromo benzene ( $T_m = 360.45$  K) and benzoic acid ( $T_m = 395.55$  K). The enthalpy was calibrated with enthalpy of melting  $\Delta H_m$  of the standard materials; *p*-dibromo benzene ( $\Delta H_m = 87.03$  J g<sup>-1</sup>) and benzoic acid ( $\Delta H_m = 147.9$  J g<sup>-1</sup>). Pressure range was from 0.1 MPa to 150 MPa. PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub> copolymer (a sample of the order of 320 mg), was put into a glass tube, seating in the measuring transitionometric cell, and annealed at 419 K for 6 hrs under vacuum. Before filling gases into the high-pressure line, the whole system was vacuumed.

## RESULTS AND DISCUSSION

Typical transitionometric signals under CO<sub>2</sub> pressures [20] are shown in Figure 2a. The isotropic transition is observed at every pressure. The onset temperatures of the isotropic transition ( $T_{iso}$ ), the transition enthalpies  $\Delta H_{iso}$  and the transition entropies  $\Delta S_{iso}$ , are plotted *versus* pressure in Figure 2b. The  $T_{iso}$  decreases with increase of pressure up to 30 MPa. Above 40MPa, the  $T_{iso}$  increases with

increase of pressure. The transition entropy is constant up to 15 MPa and increases 1.5 times more than under 0.1 MPa above 30 MPa then remains constant. The quadrupole moment of CO<sub>2</sub> interacts with dipole moments of both PMMA chains and azobenzene moieties in PMA(Az) domains. The quadrupole-dipole interactions favour the dissolution of CO<sub>2</sub> into the PMA(Az) domain, then decreases the isotropic transition temperature. The hydrostatic effect by CO<sub>2</sub> overcomes above 40MPa. The increase of entropy and enthalpy are also explained by the CO<sub>2</sub> dissolution into PMA(Az) domain. It was reported that the dissolved amount into amorphous polymers, like PMMA, PS and PVDF, increases with increase of pressure and decreases with increase of temperature [12, 17, 19]. As expected, molecular motions increase with temperature; this is also observed with CO<sub>2</sub> into the PMA(Az) domain. In the case of PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub>, the molecular motions of PMA(Az) domain in the SmA phase are less active than in the isotropic liquid state because the SmA phase is immobilized by  $\pi$ -bounds with azobenzene moieties. The large variations of molecular motions occur at the isotropic transition upon the disruption of  $\pi$ -bounds, inducing the CO<sub>2</sub> desorption. Since the desorption is endothermic, the transition enthalpy and entropy increase with the increase of pressure.

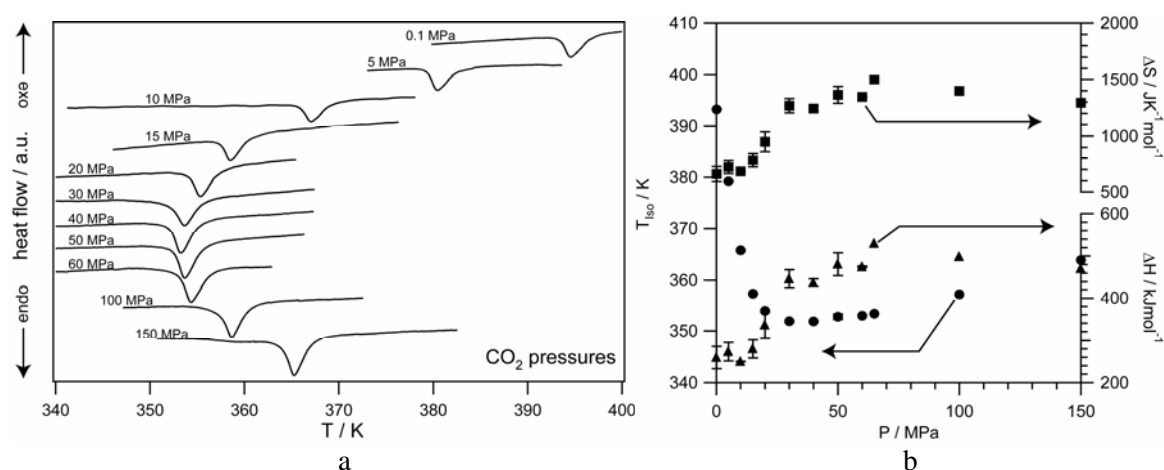


Figure 2a: Transitiometric signals showing the isotropic transition of PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub>, under CO<sub>2</sub> pressures in the range from 0.1 MPa to 150 MPa. Figure 1b: Corresponding isotropic temperatures  $T_{iso}$  (filled circles), isotropic enthalpies  $\Delta H_{iso}$  (filled triangles), and isotropic entropies  $\Delta S_{iso}$  (filled squares).

Figure 3a shows transitiometric signals under N<sub>2</sub> pressures [21]. The  $T_{iso}$  temperatures, the corresponding transition enthalpies  $\Delta H_{iso}$  and transition entropies  $\Delta S_{iso}$  are shown in Figure 3b. The effects of N<sub>2</sub> pressures show different trends. The isotropic transition temperature at 10MPa is nearly the same as under 0.1 MPa. Above 20 MPa, the isotropic transition temperature increases with pressure. The transition entropy remains constant. Since N<sub>2</sub> is non polar, the interaction with the PMA(Az) domain is weaker than with CO<sub>2</sub>. Because the  $\pi$ -bounds of azobenzene moieties do not interact with N<sub>2</sub>, the temperature slightly increases and the hydrostatic effect becomes predominant at a lower pressure, 20 MPa, than under CO<sub>2</sub>. The dissolved amount of N<sub>2</sub> into the PMA(Az) domain is also smaller than for CO<sub>2</sub> because of the weak interaction and therefore the transition enthalpy slightly increases.

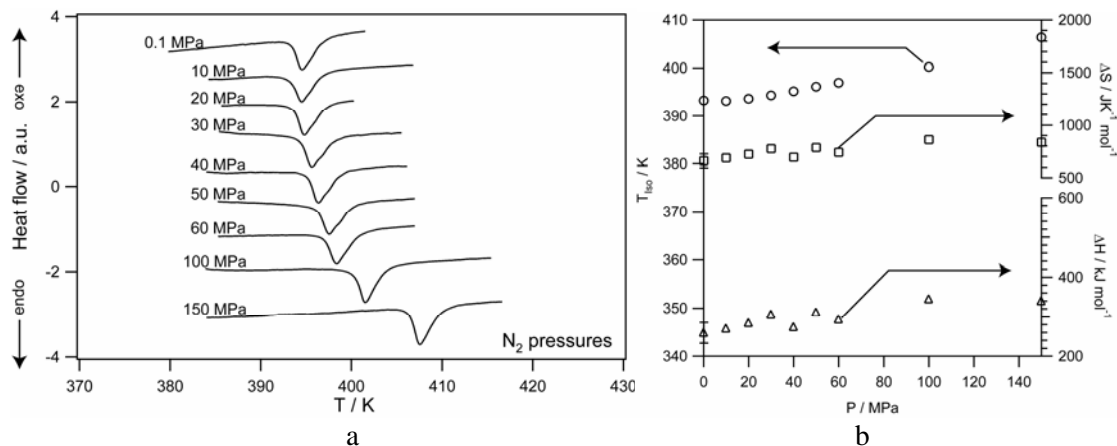


Figure 3a: Transitiometric signals showing the isotropic transition of PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub>, under N<sub>2</sub> pressures in the range from 0.1 MPa to 150 MPa. Figure 3b: Corresponding isotropic temperatures  $T_{\text{iso}}$  (open circles), isotropic enthalpies  $\Delta H_{\text{iso}}$  (open triangles), and isotropic entropies  $\Delta S_{\text{iso}}$  (open squares).

Figure 4 represents the relationship between pressure and the isotropic transition temperatures. The values of Clapeyron slope  $dP/dT$  under CO<sub>2</sub> and N<sub>2</sub> pressures in the high-pressure region, where the hydrostatic effect is dominant, are 8.9 MPa K<sup>-1</sup> and 10.2 MPa K<sup>-1</sup>, respectively. These values are much larger than under mercury pressures,  $dP/dT = 2.85$  MPa K<sup>-1</sup>, for PEO<sub>114</sub>-*b*-PMA(Az)<sub>20</sub> [16].

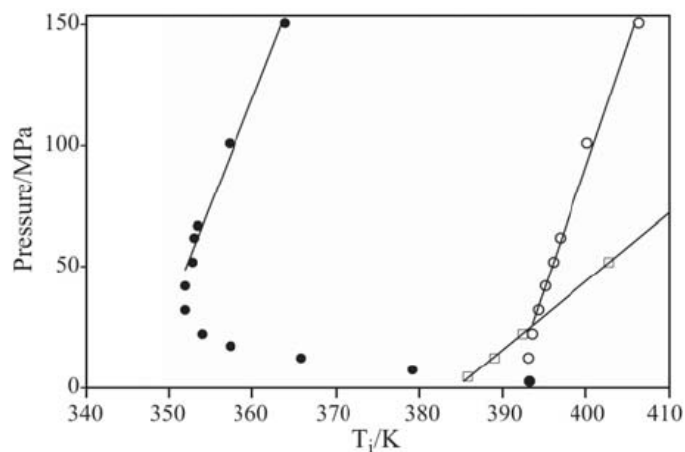


Figure 4: Plot of pressure vs the isotropic temperature  $T_{\text{iso}}$  for PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub>, under pressures of either CO<sub>2</sub> (filled circles) or N<sub>2</sub> (open circles), and for Hg (open squares) for PEO<sub>114</sub>-*b*-PMA(Az)<sub>20</sub> [16].

These results clearly show that the hydrostatic effects of gases are smaller than the hydrostatic effects of mercury, as explicitly explained by the Clapeyron relation (1)

$$\frac{dP}{dT} = \frac{\Delta S_{iso}}{\Delta V_{iso}} \quad (1)$$

Large  $dP/dT$  values are associated with small volume changes, while the corresponding entropy changes are almost constant. The pressure dependency of the transition entropy and temperature (Figures 2b and 3b) suggests that both CO<sub>2</sub> and N<sub>2</sub> are adsorbed into the PMA(Az) domain. The dissolved gases prevent changes in the co-polymer free volume because the gas molecules are not compressed. Consequently, volume changes at the isotropic transition under gas pressures are smaller than under mercury pressures because in the latter case the hydrostatic effect which predominates induces a decrease of the free volume. The scanning transitiometer allows to measure volume variations however, the relatively weak volume change of the isotropic transition was not detected because the expansion of the gas is much larger than the volume change of the PMA(Az) domain [21].

## CONCLUSION

The effects of CO<sub>2</sub> and N<sub>2</sub> pressures on the isotropic transition of the di-block copolymer PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub> were investigated by scanning transitiometry. Under CO<sub>2</sub> pressures, the isotropic transition temperature decreases with the increase of pressure up to 30 MPa because CO<sub>2</sub> is dissolved into the PMA(Az) domain. Above 40 MPa, the isotropic transition temperature increases with pressure because the hydrostatic effect becomes predominant. The pressure dependency of the transition entropy reveals that desorption of the gas occurs at the isotropic transition. Under N<sub>2</sub> pressures, the decrease of the transition temperature is smaller because the interaction between N<sub>2</sub> and PMA(Az) domain is much weaker than with CO<sub>2</sub>. The hydrostatic effect overcomes at a lower pressure, 20 MPa, than under CO<sub>2</sub> pressures (*i.e.* 40 MPa). The transition entropy remains almost constant which means that desorption of N<sub>2</sub> also occurs under N<sub>2</sub> pressures. The hydrostatic effects of both CO<sub>2</sub> and N<sub>2</sub> pressures evaluated by Clapeyron relation appear indeed smaller than in the case of mercury pressures. Finally, it is shown that the adsorbed gases induce smaller volume changes on the isotropic transition than the mercury pressure due to the low compressibility of the dissolved gas molecules.

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