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ISOTROPIC TRANSITION OF AMPHIPHILIC SIDE-CHAIN TYPE LIQUID CRYSTALLINE DI-BLOCK COPOLYMERS

Effects of nitrogen pressure

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The effects of nitrogen (N_2) pressure on amphiphilic di-block copolymer, PEO_{114}-*b*-$PMA(Az)_{40}$, were investigated by scanning transitiometry. The isotropic transition temperature increased with the increase of pressure above 20 MPa. The hydrostatic pressure effects evaluated with the Clapeyron equation were smaller than the value obtained by mercury as a pressurizing medium because the amount of absorbed gas decreases the volume change at the isotropic transition.

Keywords: *block copolymer, liquid crystal, nitrogen, pressure effect, transitiometry*

Introduction

High-pressure technology using gases as process intermediates plays an important role in materials nucleation, extrusion, power plants, or oil drillings. In materials science this is illustrated by several applications dealing with soft matter systems like typical modifications of liquid crystals, colloids and polymers, including block copolymers submitted to high pressures transmitted by pressurizing fluids either inert or chemically active [1–6]. High-pressure experiments require special experimental techniques able to work at extreme (as regards the type of material under consideration) conditions of temperature and pressure. Neutron scattering has been widely used for structure analysis of high permeability materials. For example, effects of hydrostatic pressures on the order–disorder transition of block copolymers were reported by using neutron scattering [6, 7]. Thermal properties of liquid crystals and polymers under high-pressure were reported by using special DTA cells [2, 5]. However, with these cells it was difficult to estimate in a single experiment the melting enthalpy and the associated volume change. With a scanning transitiometer it is possible to control one of the three thermodynamic variables p, V or T independently and to obtain heat flow signals with sufficiently low N/S ratio (noise/signal ratio) through the calorimetric detector [8–10]. Then, the transition enthalpy of a phase transition is directly read out and furthermore, when scanning a variable while maintaining one constant, the recording of the change of the (third) dependent variable yields readily access through the high pressure mechanical system to the corresponding different thermophysical properties. As a matter of fact, combination of thermal signal and mechanical signal obtained in a single experiment and using Maxwell relations make transitiometry to be a very versatile technique by excellence to study phase transitions over extended T and P ranges.

Block copolymers connecting incompatible polymers by covalent bonds are currently studied from the viewpoints of both fundamental science and applications [7, 11–13]. Recently, we reported the synthesis of amphiphilic liquid crystal block copolymers consisting of a hydrophilic polyethyleneoxide (PEO) and a polymethacrylate derivative having azobenzene moieties which act as mesogenic groups in side chain liquid crystals (PMA(Az)), e.g. yielding a PEO-*b*-PMA(Az) copolymer [15]. The PEO_m-*b*-$PMA(Az)_n$ copolymers, where m and n are degrees of polymerization of PEO and PMA(Az) sequences respectively, form the highly ordered PEO hexagonal packed cylinder structure in a wide range of volume fraction, and have four kinds of phase transitions [15–18]. These four phase transitions correspond respectively and successively to melting of PEO crystal, melting of azobenzene moieties, liquid crystal transition from smectic C phase (SmC) to

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smectic A phase (SmA), and isotropic transition when increasing temperature [16, 19]. The effect of pressure transmitted by mercury, which is a typical hydrostatic pressure, on the isotropic transition of PEO$_{114}$-*b*-PMA(Az)$_{20}$ has been investigated by scanning transitiometry [20]. Under mercury pressure, the transition temperature increased with the increase of pressure. The transition entropy decreased with the increase of pressure because the molecular motion in the isotropic state was restricted by hydrostatic pressure. These phenomena were well described by the Clapeyron equation.

The focus of this paper was to study the effect of nitrogen as pressurizing fluid, of which critical temperature and pressure are 126.19 K and 3.3978 MPa, respectively [21], on the isotropic transition of PEO$_{114}$-*b*-PMA(Az)$_{40}$ copolymer. Nitrogen can adsorb not only on the surface but also into the free volume of the polymer chain by physical interaction, whereas mercury has no interaction with the substance. In order to compare the difference between ‘mercury pressure’ and ‘nitrogen pressure’, both transition temperature and transition entropy of the isotropic transition of PEO$_{114}$-*b*-PMA(Az)$_{40}$ copolymer were evaluated by scanning transitiometry.

Experimental

Materials and methods

PEO$_{114}$-*b*-PMA(Az)$_{40}$ copolymer shown in Fig. 1 was synthesized by the atom transfer radical polymerization as described elsewhere [15]. The molecular dispersion index determined by the gel permission chromatography was 1.13.

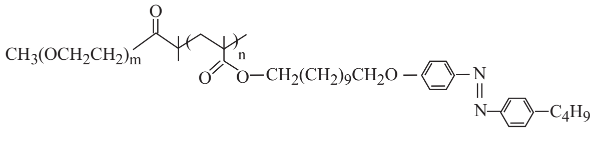

Fig. 1 Chemical structure of PEO$_{114}$-*b*-PMA(Az)$_{40}$

Transitiometry measurements were performed with a scanning transitiometer (BGR-TECH Poland) [12–14] in which temperature scans were made under constant pressure from 380 to 420 K with 0.2 K min^{-1} scanning range. Temperature was calibrated through the temperature of melting T_m using three 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 response was also calibrated through the enthalpy of melting ΔH_m using two standard materials: *p*-dibromo benzene (ΔH_m= 87.03 J g^{-1}) and benzoic acid (ΔH_m=147.9 J g^{-1}). The investigated pressure range was from 0.1 to 150 MPa. Nitrogen (with 99.5% purity) provided by SAGA France was used without further purification. A sample of about 326 mg of PEO$_{114}$-*b*-PMA(Az)$_{40}$ copolymer was placed into a glass ampoule (a small opened test tube) and annealed at 146°C for 6 h under vacuum. Before filling nitrogen into the measuring system, the entire pressure line was vacuumed.

Results and discussion

Figure 2 shows calorimetric signals under N_2 pressures. The single endothermic peak corresponding to the isotropic transition of the PMA(Az) domain was observed at 395 K on 0.1 MPa. The transition temperature under 10 MPa was almost the same as under 0.1 MPa. Above 20 MPa, the isotropic transition temperature increased with increasing pressure. These results indicate that the plasticization effect and the hydrostatic effect counterbalance each other under 10 MPa and that the hydrostatic effect becomes predominant above 20 MPa. It was previously observed [22] that carbon dioxide interacts with PMA(Az) domain by quadrupole–dipole interactions and induces a large plasticization effect up to 40 MPa. The present results indicate that the plasticization effect under nitrogen pressure is much smaller than under carbon dioxide pressure because nitrogen weakly interacts with PMA(Az) domain by only physical interactions.

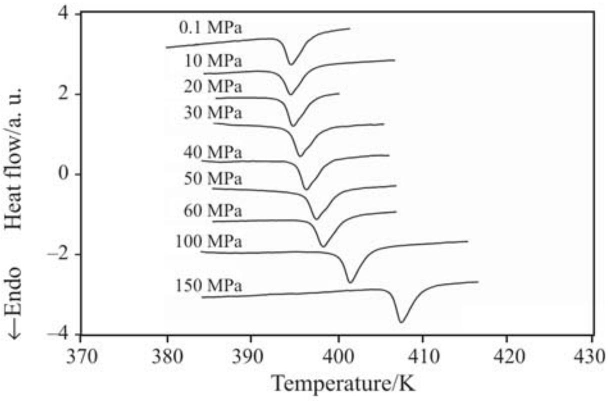

Fig. 2 Calorimetric signals showing the isotropic transition of PEO$_{114}$-*b*-PMA(Az)$_{40}$ copolymer under different nitrogen pressures (in the range from 0.1 and 150 MPa)

In Fig. 3 transition temperature, enthalpy and entropy of the isotropic transition are shown. The transition entropy remains practically constant in the measuring range. Under mercury pressure it was observed that the transition entropy decreased linearly with increasing pressure because of the restricted molecular motion under pressure by inert mercury [20]. However, under nitrogen pressures no decrease of the transition entropy is observed especially above 20 MPa, where the hydrostatic effect becomes predominant. Most likely this indicates that nitrogen desorption of which enthalpy is always positive overlaps with the isotropic transition; as a result of the increase of molecular motion of PMA(Az) domain at the isotropic transition, the amount of adsorbed gas decreases.

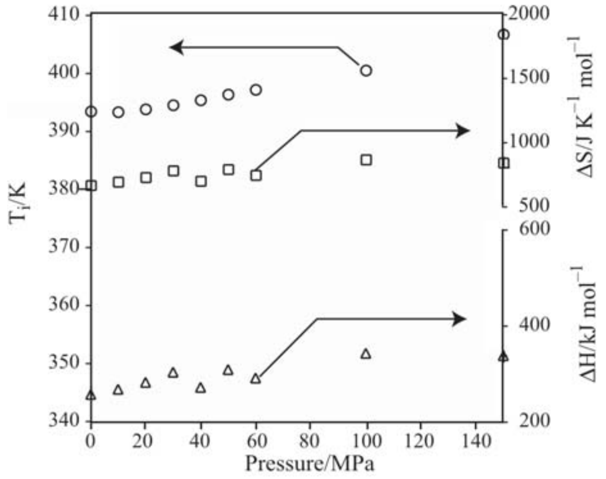

Fig. 3 Plot of the ○ – transition temperature, △ – enthalpy and □ – entropy of the isotropic transition of PEO_{114}-*b*-PMA$(Az)_{40}$ copolymer *vs*. pressure under N_2

Interestingly, for di-block copolymers the hydrostatic effect as described by the Clapeyron equation

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

can be compared depending on the nature of the pressurizing fluid. Figure 4 shows the dependence with pressure of the isotropic transition temperature when the hydrostatic pressure is transmitted by nitrogen, mercury [20] or carbon dioxide [22] respectively. The d*P*/d*T* value for PEO_{114}-*b*-PMA$(Az)_{40}$ under nitrogen pressure above 20 MPa, where the hydrostatic effect is prevailing, is 10.2 MPa K^{-1}. The d*P*/d*T* value for PEO_{114}-*b*-PMA$(Az)_{20}$ under mercury pressure is 2.85 MPa K^{-1} [20]. The larger value under nitrogen pressure suggests that the ΔV_{tr} under nitrogen pressure is smaller than under mercury pressure. The nitrogen sorption takes place on the PEO_{114}-*b*-PMA$(Az)_{40}$ and reduces the free volume. Since the compressibility of nitrogen is much smaller than that of the free volume, the volume change under nitrogen pressure is smaller than the change under mercury pressure. The d*P*/d*T* value for PEO_{114}-*b*-PMA$(Az)_{40}$ under carbon dioxide pressure above 50 MPa is 8.8 MPa K^{-1}. The smaller value than under nitrogen pressure shows that the volume change under carbon dioxide pressure at the isotropic transition is larger than nitrogen pressure. Since the interaction between the PMA(Az) domain and carbon dioxide by dipole–quadrupole interactions is stronger than the physical interaction between the PMA(Az) domain and nitrogen, the space (the molecular distance) between the PMA(Az) domain and carbon dioxide is smaller than under nitrogen. Therefore the free volume under carbon dioxide pressure is larger than under nitrogen pressure with consequently a larger volume change at the isotropic transition.

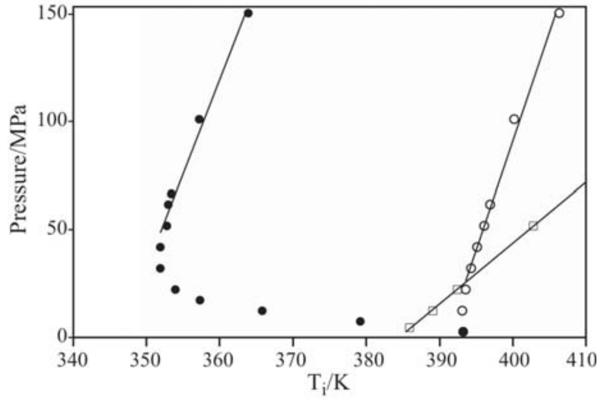

Fig. 4 Plot of pressure *vs*. the isotropic transition temperature for PEO_{114}-*b*-PMA$(Az)_{40}$ copolymer under ○ – nitrogen pressure or ● – carbon dioxide [22] and for PEO_{114}-*b*-PMA$(Az)_{20}$ [20] under □ – mercury pressure

Figure 5 shows the volume change (Δ*V*) and the temperature derivative of the volume change (d*V*/d*T*) for PEO_{114}-*b*-PMA$(Az)_{40}$ under 150 MPa together with corresponding calorimetric and pressure signals. Usually it is possible to precisely detect the volume change making use of a scanning transitiometer however, in the present case no clear signal for the volume change of the PEO_{114}-*b*-PMA$(Az)_{40}$, was detected because the thermal expansion of nitrogen in the measuring system is too large compared to the polymer sample.

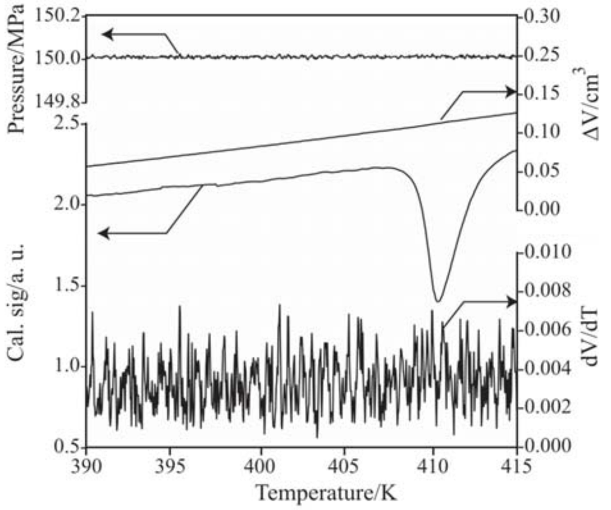

Fig. 5 Plots of volume change Δ*V* and of its temperature derivative d*V*/d*T* *vs*. temperature for PEO_{114}-*b*-PMA$(Az)_{40}$ copolymer under 150 MPa, together with the corresponding calorimetric cal. sig. and pressure signals over the temperature range investigated

Conclusions

The effects of nitrogen pressure on the isotropic transition of the PEO_{114}-*b*-PMA(Az)$_{40}$ were investigated by scanning transitiometry. Under 10 MPa, the isotropic transition temperature is almost the same as under 0.1 MPa. Above 20 MPa, the transition temperature increases with increasing pressure. These results indicate that under nitrogen pressure both plasticization and hydrostatic effects occur simultaneously. The plasticization effect is smaller than under carbon dioxide pressure, because nitrogen interacts with PMA(Az) domain by weak physical interactions rather than by chemical interaction. The transition entropy of the isotropic transition remains almost constant over the investigated pressure range. No decrease of the transition entropy shows that the modifications due to the gas desorption on the PMA(Az) domain simultaneously take place during the isotropic transition. The larger $\mathrm{d}P/\mathrm{d}T$ value above 20 MPa, where the hydrostatic effect prevails, than the $\mathrm{d}P/\mathrm{d}T$ value under mercury pressure indicates that the hydrostatic effect under nitrogen pressure is smaller than under mercury pressure because the compressibility of adsorbed nitrogen is smaller than the compressibility of the free volume of PMA(Az) domain.

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