

## EFFECTS OF CO<sub>2</sub> PRESSURE ON ISOTROPIC TRANSITION OF AMPHIPHILIC SIDE-CHAIN TYPE LIQUID CRYSTALLINE DI-BLOCK COPOLYMERS

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The effects of high pressure carbon dioxide (CO<sub>2</sub>) on the isotropic transition of three different amphiphilic di-block copolymers, PEO<sub>m</sub>-*b*-PMA(Az)<sub>n</sub>, namely PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub>, PEO<sub>272</sub>-*b*-PMA(Az)<sub>46</sub> and PEO<sub>454</sub>-*b*-PMA(Az)<sub>47</sub>, and on PMA(Az)<sub>30</sub> homopolymer have been investigated by scanning transitiometry. Under CO<sub>2</sub> pressure, the isotropic transition temperature decreased with the increase of pressure up to around 30 MPa due to CO<sub>2</sub> sorption and increased above 40 MPa. Transition entropy of the isotropic transition indicated that the depression of the isotropic transition temperature was caused by the adsorption of CO<sub>2</sub> into the azobenzene moieties and that the increase above 40 MPa was caused by the desorption of CO<sub>2</sub> into the azobenzene moieties. Comparison between PEO<sub>m</sub>-*b*-PMA(Az)<sub>n</sub> copolymers and PMA(Az) homopolymer clarified PEO domain acted CO<sub>2</sub> pathway to approach the equilibrium state rapidly.

**Keywords:** block copolymer, carbon dioxide, liquid crystal, pressure effect, transitiometry

### Introduction

High-pressure technology using gases and organic materials plays an important role for example in materials of nucleation or oil drilling. Particularly interesting are current developments and applications in soft matter science with typical modifications and fundamental understandings of liquid crystals, colloids and polymers including block copolymers, by means of not only hydrostatic medium but also supercritical gases [1–6]. High-pressure experiments require specific experimental techniques. Neutron scattering is one of powerful tools for investigating soft matter through high-pressure experiments involving high material permeability. Effects of carbon dioxide (CO<sub>2</sub>) pressure on the structure of block copolymers using neutron scattering were recently reported [7, 8]. For the investigation of thermal properties under high-pressure, we developed scanning transitiometry for high-pressure experiments [9–11]. A scanning transitiometer is a typical instrument to fully investigate the thermodynamic behavior of materials undergoing phase transition. In a scanning transitiometer the three thermodynamic variables  $p$ ,  $V$  and  $T$ , can be controlled independently in a calorimetric detector. Typically one variable is scanned while maintaining a

second variable constant, and two quantities are simultaneously recorded, the heat flow signal resulting from the thermal effect induced by the scanned variable together with the concomitant change of the third (dependable) variable; from these thermal and mechanical effects and associated partial derivatives, making use of Maxwell relations, several thermo-physical properties are accessed.

Supercritical CO<sub>2</sub> is considered as one of the clean solvents by excellence instead of organic solvents because of its relatively low environmental impact and good recycling. Phase behavior and solubility of substances under supercritical CO<sub>2</sub> are of special interest for the use of such solvent as an efficient medium for engineering processes. Solubility in CO<sub>2</sub> of various substances, like azobenzene, polymethacrylate (PMMA), and PEO has been recently reported [12–18]. The solubility into amorphous polymers increases with the increase of pressure but decreases with the increase of temperature [15, 16, 18] because the molecular motion became more active with increasing temperature. The solubility of the side-chain liquid crystal polyacrylate jumped up at the phase transition and decreased with increasing temperature [19]. All above studies suggest that the amount of gas absorbed is related to the molecular

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motion and the number of interaction sites. CO<sub>2</sub> acts not only as pressure medium but also as plasticizer. The glass transition temperature of amorphous polymers decreased under CO<sub>2</sub> pressure [17, 18]. Krombach and Schneider reported the phase behavior of 4-*n*-hexyloxy- and 4-*n*-decyloxy-4'-cyanobiphenyl (6OCB and 10OCB) under high-pressure of either pure gases or gas mixtures such as helium (He), nitrogen (N<sub>2</sub>), argon (Ar) and Ar/CO<sub>2</sub> mixtures [20]. Under Ar/CO<sub>2</sub> mixture pressure, the isotropic transition temperature ( $T_{\text{iso}}$ ) goes through a minimum around 50 MPa. The difference between  $T_{\text{iso}}$  at 0.1 MPa and the minimum  $T_{\text{iso}}$  is of the order 20~30 K and increases with increasing the CO<sub>2</sub> fraction. The decrease of the isotropic transition temperature under Ar/CO<sub>2</sub> mixture pressure was found much larger than under other neutral gases. Most likely the quadrupole-dipole interaction between CO<sub>2</sub> and the liquid crystal structure plays the major role in the plasticization effect.

Recently, we reported the synthesis of amphiphilic liquid crystal block copolymers consisting of the hydrophilic polyethyleneoxide (PEO) and the polymethacrylate derivative having azobenzene moieties which acted as mesogenic groups in side chain liquid crystals (PMA(Az)), (PEO-*b*-PMA(Az)) [21]. The PEO<sub>*m*</sub>-*b*-PMA(Az)<sub>*n*</sub> copolymers, where 'm' and 'n' are degrees of polymerization of PEO and PMA(Az) sequences respectively, form a highly ordered PEO hexagonal packed cylinder structure over a wide range of volume fraction, and have four kinds of phase transition [21–24]. These four-phase transitions correspond respectively and successively to melting of the PEO crystal, melting of azobenzene moieties, liquid crystal transition from the smectic C phase (SmC) to the smectic A phase (SmA) and the isotropic transition when increasing temperature [22, 25]. The highly ordered PEO cylinder structure is expected to be used as templates for nano networks, like electronic circuit for example. This later application would combine the inclusion of gold nano-particules into the nano-cylinder structure, by using supercritical CO<sub>2</sub> [26]. In order to develop the supercritical processing, it is important to document the effects of the CO<sub>2</sub> pressure on PEO-*b*-PMA(Az) copolymers. We have previously reported the effect of hydrostatic pressure transmitted by mercury as pressurizing fluid on the isotropic transition of PEO<sub>114</sub>-*b*-PMA(Az)<sub>20</sub> [27]. Under mercury pressure, the transition temperature increases with the increase of pressure in agreement with the Clapeyron equation. The transition entropy decreases with the increase of pressure because the molecular motion in the isotropic state is restricted by hydrostatic pressure [27]. In this paper, effects of CO<sub>2</sub> pressure on the

isotropic transition were investigated by scanning transitiometry and results were compared with the results obtained under mercury pressure.

## Experimental

### Samples

PEO<sub>*m*</sub>-*b*-PMA(Az)<sub>*n*</sub> copolymers shown in Fig. 1 and PMA(Az)<sub>*n*</sub> homopolymer were synthesized by the atom transfer radical polymerization as described elsewhere [21]. The molecular dispersion index ( $M_n/M_w$ ) was determined by the gel permeation chromatography. In order to compare the effect of PEO length, PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub> ( $M_n/M_w=1.13$ ), PEO<sub>272</sub>-*b*-PMA(Az)<sub>46</sub> ( $M_n/M_w=1.20$ ), PEO<sub>454</sub>-*b*-PMA(Az)<sub>47</sub> ( $M_n/M_w=1.15$ ) and PMA(Az)<sub>30</sub> homopolymer ( $M_n/M_w=1.19$ ) were studied.

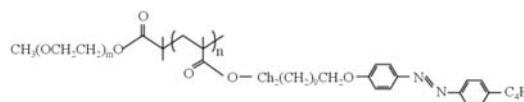


Fig. 1 Chemical structure of PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub>

### Methods

Transitiometric measurements were performed with a scanning transitiometer (BGR-TECH Poland) in which temperature scans were conducted under constant pressure [9–11]. The temperature range was from 330 to 420 K with 0.2 K min<sup>-1</sup> scanning rate. Temperature was calibrated through 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). Enthalpy was calibrated using two 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>). The investigated pressure range was from 0.1 to 150 MPa for PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub> and PMA(Az)<sub>30</sub> homo polymer and from 0.1 to 50 MPa for PEO<sub>272</sub>-*b*-PMA(Az)<sub>46</sub> and PEO<sub>454</sub>-*b*-PMA(Az)<sub>47</sub>. Carbon dioxide (with 99.5% purity) provided from SAGA France was used without further purification. About 350 mg of PEO<sub>*m*</sub>-*b*-PMA(Az)<sub>*n*</sub> copolymers and PMA(Az) homopolymer was placed into a glass ampoule (a tube open on upper part) and annealed at 146°C for 6 h under vacuum. Before filling the CO<sub>2</sub> into the measuring system, the entire pressure line was vacuumed.

## Results and discussion

Calorimetric signals of PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub> under CO<sub>2</sub> pressures are shown in Fig. 2. The single endothermic peak corresponding to the isotropic transition was observed at 395 K at 0.1 MPa. The endothermic peak shifted to lower temperatures with increasing pressure up to 30 MPa and to higher temperatures above 40 MPa (see also Fig. 3). This result indicates that both plasticization effect and hydrostatic effect caused by CO<sub>2</sub> pressure were depending on pressure in competition to each other. The plasticization effect induces first the large temperature depression, ca. 50 K. In that case CO<sub>2</sub> interacts with carbonyl groups and azobenzene moieties in PMA(Az) domain by quadrupole-dipole interactions; since these interactions are chemical ones, a large plasticization effect occurs. Remarkably, in the investigated temperature range, CO<sub>2</sub> was in liquid state at 5 MPa and in supercritical state above 7.3 MPa. However, no clear differ-

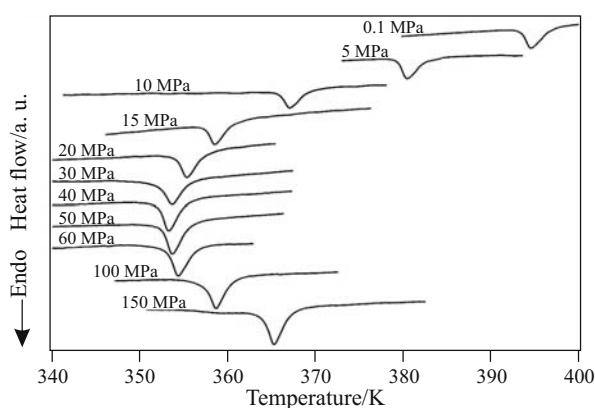


Fig. 2 Calorimetric signals of PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub> under CO<sub>2</sub> pressures

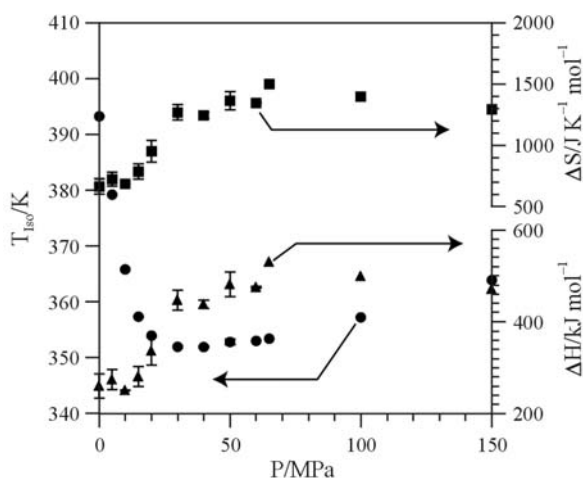
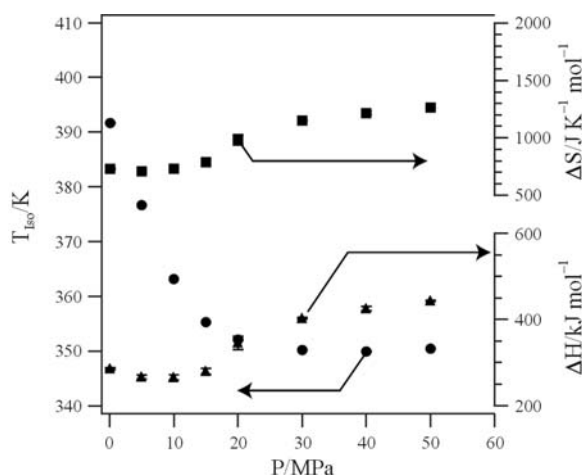


Fig. 3 Plot of transition temperature (filled circles), enthalpy (filled triangles) and entropy of the isotropic transition (filled squares) of PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub> to the pressure under CO<sub>2</sub> pressure

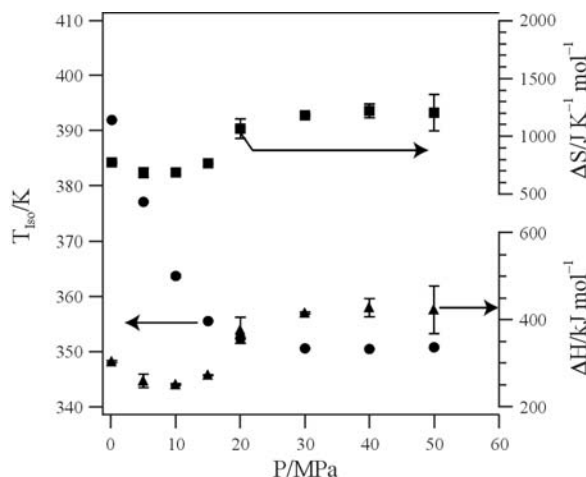
ence between the liquid and supercritical state was observed. It seems that the PEO domain for which CO<sub>2</sub> is good solvent acted as CO<sub>2</sub> pathway and that the PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub> copolymer reaches the equilibrium state rapidly even in the liquid state where CO<sub>2</sub> diffusivity is lower than in the supercritical state.

Figure 3 shows as functions of pressure the onset temperature ( $T_{iso}$ ), the transition enthalpy ( $\Delta H_{iso}$ ) and the transition entropy ( $\Delta S_{iso}$ ) of the isotropic transition. The  $\Delta S_{iso}$  is almost constant up to 15 MPa, and jumps in the pressure range between 15 and 40 MPa to finally  $\Delta S_{iso}$  levels up to a constant value which is 1.5 times larger than the value observed at 0.1 MPa. This jump coincides with the change in behavior of CO<sub>2</sub> from plasticization to hydrostatic vector. The dependency of  $\Delta S_{iso}$  upon CO<sub>2</sub> pressure is quite different from the one observed under mercury pressure. Under mercury pressure,  $\Delta S_{iso}$  linearly decreased with the increase of pressure which induces a loss of molecular motion in the isotropic state [27]. It reveals that not only the isotropic transition but also desorption of CO<sub>2</sub> occurs at the same time because desorption is an endothermic process. The PMA(Az) domain copolymer has two adsorption sites which are the carbonyl groups in PMMA main chain and azobenzene moieties in the side chain liquid crystal part. It has been reported that the dissolved amount of CO<sub>2</sub> into amorphous polymers, like PMMA, polystyrene (PS) and poly(vinylidene fluoride) (PVDF), increases with the increase of pressure and decreases with the increase of temperature due to the enhancement of molecular mobility at higher temperature [8, 16]. Therefore the amount of absorption in amorphous PMMA main chain decreases at the isotropic transition and increases when pressure increases. On the other hand, adsorption of the CO<sub>2</sub> in the azobenzene moieties has a possibility to increase the CO<sub>2</sub> adsorption at the isotropic transition because disappearing of  $\pi$ -stacks increases adsorption site. From experimental results it appears that the plasticization effect is predominating until the adsorption CO<sub>2</sub> in the azobenzene moieties occurs at the isotropic transition and that the hydrostatic effect becomes effective after the CO<sub>2</sub> desorption from azobenzene moieties. Below 20 MPa, where the plasticization effect is dominant, the adsorption of CO<sub>2</sub> on the azobenzene moieties competes with the desorption of CO<sub>2</sub> from the PMMA main chain. Therefore the  $\Delta S_{iso}$  below 20 MPa is smaller than above 40 MPa, where the desorption of CO<sub>2</sub> occurs from both the PMMA main chain and azobenzene moieties.

Figures 4 and 5 show  $T_{iso}$ ,  $\Delta H_{iso}$  and  $\Delta S_{iso}$  for PEO<sub>272</sub>-*b*-PMA(Az)<sub>46</sub> and PEO<sub>454</sub>-*b*-PMA(Az)<sub>47</sub> respectively obtained from transitionometric measurements. Like PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub> both copolymers



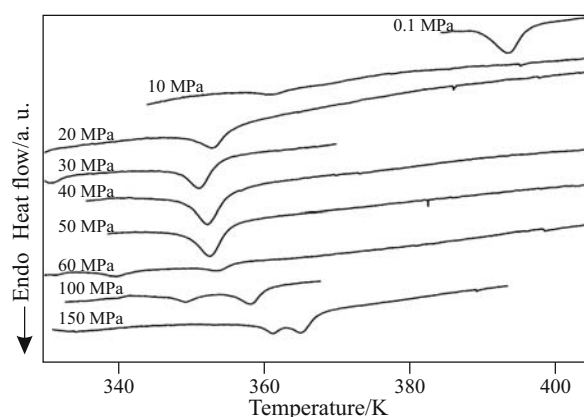
**Fig. 4** Plot of transition temperature (filled circles), enthalpy (filled triangles) and entropy of the isotropic transition (filled squares) of PEO<sub>272</sub>-*b*-PMA(Az)<sub>46</sub> to the pressure under CO<sub>2</sub> pressure



**Fig. 5** Plot of transition temperature (filled circles), enthalpy (filled triangles) and entropy of the isotropic transition (filled squares) of PEO<sub>454</sub>-*b*-PMA(Az)<sub>47</sub> to the pressure under CO<sub>2</sub> pressure

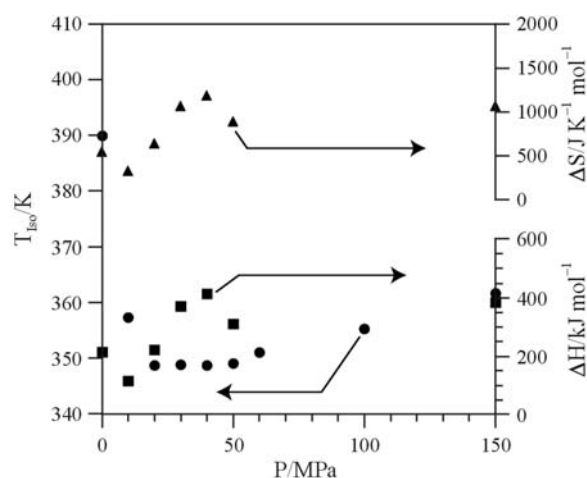
show a single endothermic peak at the isotropic transition. The dependency of  $T_{\text{iso}}$ ,  $\Delta H_{\text{iso}}$  and  $\Delta S_{\text{iso}}$  on pressure is similar to the one observed for PEO<sub>114</sub>-*b*-PMA(Az)<sub>40</sub>. These results clearly indicate that the degree of polymerization of the PEO domain has no influence on the isotropic transition. Under atmospheric pressure, the isotropic transition also does not depend on the degree of polymerization of the PEO domain because the PEO domain is in melted state and cannot limit the molecular motion of PMA(Az) domain [28]. Since CO<sub>2</sub> which has a good solvent capability for PEO keeps the PEO domain in melted state under pressure, the PEO chain length has no influence on the isotropic transition.

Figure 6 shows the transition signals for PMA(Az)<sub>30</sub> homopolymer. The single endothermic



**Fig. 6** Calorimetric signals of PMA(Az)<sub>30</sub> under CO<sub>2</sub> pressures

peak corresponding to the isotropic transition is observed at 390 K under 0.1 MPa. The peak is shifted to lower temperatures with increasing pressure up to 30 MPa whereas it is shifted to higher temperatures above 40 MPa. The behavior under CO<sub>2</sub> pressure is similar to what is observed with the PEO-*b*-PMA(Az) copolymers. However, the endothermic peak under 10 MPa is broader than in the case of PEO-*b*-PMA(Az) copolymer. Above 60 MPa, a broad doublet peak is observed. It appears that PMA(Az)<sub>30</sub> homopolymer needs longer times for reaching the equilibrium state than PEO-*b*-PMA(Az) copolymers under CO<sub>2</sub> pressure because the PMA(Az) domain has less affinity to CO<sub>2</sub> than PEO. Remarkably, between 30 and 50 MPa the single endothermic peak was observed. (It appears that the density of CO<sub>2</sub> would be high enough to approach the equilibrium state within this pressure range.) Figure 7 shows  $T_{\text{iso}}$ ,  $\Delta H_{\text{iso}}$  and  $\Delta S_{\text{iso}}$  of PMA(Az)<sub>30</sub> homopolymer. The temperature decrease below 30 MPa is practically



**Fig. 7** Plot of transition temperature (filled circles), enthalpy (filled triangles) and entropy of the isotropic transition (filled squares) of PMA(Az)<sub>30</sub> to the pressure under CO<sub>2</sub> pressure

similar to what is observed with PEO-*b*-PMA(Az) copolymers. These results support the idea that CO<sub>2</sub> interacts with PMA(Az) domain directly and that the PEO domain acted as CO<sub>2</sub> pathway to approach the equilibrium state rapidly.

## Conclusions

The effects of the CO<sub>2</sub> pressures on the isotropic transition of PEO-*b*-PMA(Az) copolymers and PMA(Az) homopolymer were investigated by scanning transmittometry. Under CO<sub>2</sub> pressure, the isotropic transition temperature decreases with the increase of pressure up to 30 MPa when the plasticization effect is predominant. Above 40 MPa, the isotropic transition temperature increases with the increase of pressure when the hydrostatic effect becomes dominant. The transition entropy remains constant up to 15 MPa and above 40 MPa jumps to a value 1.5 times larger than under 0.1 MPa. This shows that the desorption of CO<sub>2</sub> from PMMA main chain is in competition with the absorption of CO<sub>2</sub> into the azobenzene moieties below 15 MPa, and that desorption of the CO<sub>2</sub> from both PMMA main chain and azobenzene moieties take place at the isotropic transition above 40 MPa. The degree of polymerization of PEO domain has no influence, on the isotropic transition because the PEO is the melted state. Comparing with the result of PMA(Az) homopolymer, the melting PEO acted as CO<sub>2</sub> pathway to approach the equilibrium state more rapidly than the PMA(Az) homopolymer.

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## References

- 1 P. K. Mukherjee and S. J. Rzoska, *Phys. Rev. E*, 65 (2002) 051705.
- 2 Y. Maeda, T. Niori, J. Yamamoto and H. Yokokawa, *Thermochim. Acta*, 428 (2005) 57.
- 3 R. Triolo, A. Triolo, F. Triolo, D. C. Steytler, C. A. Lewis, R. K. Heenan, G. D. Wignall and J. M. DeSimone, *Phys. Rev. E*, 61 (2000) 4640.
- 4 Y. Kawabata, M. Nagao, H. Seto, S. Komura, T. Takeda, D. Schwahn, N. L. Yamada and H. Nobutou, *Phys. Rev. Lett.*, 92 (2004) 056103.
- 5 A. Seeger, D. Freitag, F. Freidel and G. Luft, *Thermochim. Acta*, 424 (2004) 175.
- 6 D. Y. Ryu, J. L. Lee, J. K. Kim, K. A. Lavery, T. P. Russell, Y. S. Han, B. S. Seong, C. H. Lee and P. Thiyagarajan, *Phys. Rev. Lett.*, 90 (2003) 235501.
- 7 J. J. Watkins, G. D. Brown, V. S. Ramachandra Rao, M. A. Pollard and T. P. Russell, *Macromol.*, 32 (1999) 7737.
- 8 B. D. Vogt, V. S. Ramachandra Rao, R. R. Gupta, K. A. Lavery, T. J. Francis, T. P. Russell and J. J. Watkins, *Macromol.*, 36 (2003) 4029.
- 9 S. L. Randzio, J.-P. E. Grolier, J. Zaslona and J. R. Quint, French patent 9109227, Polish patent 295285.
- 10 S. L. Randzio, *Chem. Soc. Rev.*, 25 (1996) 383.
- 11 S. L. Randzio and J.-P. E. Grolier, *Anal. Chem.*, 70 (1998) 2327.
- 12 A. R. E. Brás, T. Casimiro, J. Caldeira and A. Aguiar-Ricardo, *J. Chem. Eng. Data*, 50 (2005) 1857.
- 13 S. Maeda, K. Mishima, K. Matsuyama, M. Baba, T. Hirabaru, H. Ishikawa and K. Hayashi, *J. Chem. Eng. Data*, 46 (2001) 647.
- 14 K. Mishima, K. Matsuyama and M. Nagatani, *Fluid Phase Equilib.*, 161 (1999) 315.
- 15 M. Daneshvar, S. Kim and E. Gulari, *J. Phys. Chem.*, 81 (1977) 1745.
- 16 Y. Kamiya, K. Mizoguchi, K. Terada, Y. Fujiwara and J. Wang, *Macromol.*, 31 (1998) 472.
- 17 S. A. E. Boyer and J.-P. E. Grolier, *Pure Appl. Chem.*, 77 (2005) 593.
- 18 S. A. E. Boyer, M.-H. Klopffer, J. Martin and J.-P. E. Grolier, *J. Appl. Polym. Sci.*, 55 (2006) 1706.
- 19 G. Chen and J. Springer, *Macromol. Chem. Phys.*, 201 (2000) 1552.
- 20 R. Krombach and G. M. Schneider, *Thermochim. Acta*, 231 (1994) 169.
- 21 Y. Tian, K. Watanabe, X. Kong, J. Abe and T. Iyoda, *Macromol.*, 35 (2002) 3739.
- 22 H. Yoshida, K. Watanabe, R. Watanabe and T. Iyoda, *Trans. Mat. Res. Sci. Jpn.*, 29 (2004) 861.
- 23 K. Watanabe, Y. Tian, H. Yoshida, S. Asaoka and T. Iyoda, *Trans. Mat. Res. Sci. Jpn.*, 28 (2003) 553.
- 24 K. Watanabe, H. Yoshida, K. Kamata and T. Iyoda, *Trans. Mat. Res. Sci. Jpn.*, 30 (2005) 377.
- 25 R. Watanabe, T. Iyoda, T. Yamada and H. Yoshida, *J. Therm. Anal. Cal.*, 81 (2006) 713.
- 26 C. Iwamoto, S. A. E. Boyer, H. Yoshida, S. Watanabe and T. Iyoda, *Polym. Preprints Jpn.*, 55 (2006) 3759.
- 27 S. A. E. Boyer, J.-P. E. Grolier, H. Yoshida and T. Iyoda, *J. Pol. Sci. Part B*, in press.
- 28 T. Yamada, R. Watanabe, K. Watanabe, C. Koyanagi, H. Yoshida and T. Iyoda, *Polym. Prepr. Jpn.*, 53 (2004) 1089.

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