

THE GOLD NANO-PARTICLE ALIGNMENT USING SUPERCRITICAL CO₂ ON SELF-ORGANIZED NANO-STRUCTURE OF AMPHIPHILIC DI-BLOCK COPOLYMER

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ABSTRACT

Alignment of gold nano-particles (AuNPs) was successfully achieved in hexagonally packed hydrophilic cylinders of amphiphilic liquid crystalline di-block copolymer, PEO-*b*-PMA(Az), by supercritical carbon dioxide (SCCO₂) treatment. PEO-*b*-PMA(Az) forms highly ordered hexagonally packed PEO cylinders in nano-scale. Structural changes of PEO-*b*-PMA(Az) and AuNPs alignment on PEO-*b*-PMA(Az) were investigated by AFM, TEM, SAXS and DSC. SCCO₂ treatment induced the expansion of PEO cylinders without destroying the nano-scale organization and the retardation of PEO crystallization. SCCO₂ absorbed in hydrophilic PEO cylinders selectively, and swollen PEO cylinders interacted with hydrophilic AuNPs. The interaction between PEO and AuNPs, which was induced by SCCO₂ treatment, realized two-dimensional alignment of AuNPs.

Keywords: gold nano-particles, amphiphilic di-block copolymers, supercritical carbon dioxide, self-organization

INTRODUCTION

Nano-composite materials based on noble metal gold nano-particles (AuNPs) and dispersed in polymer matrix are expected to exhibit unique and versatile properties, i.e. physical, optical and chemical. The gold hybrid materials are of high nano- and bio-technological relevance due to their numerous applications including use as catalyst, bio-markers, bio-sensors etc. [1-7]. In order to tailor the new generation of “smart” materials, new ways to organize the nano-particles into controlled and well-defined architectures must be exploited. The polymer templatings can have different purposes such as self-assembling block copolymers [8-10].

Recently, Iyoda *et al.* reported the high ordered nano-scale structure of liquid crystal amphiphilic di-block copolymers, based on poly(ethylene oxide)-*b*-poly(methacrylate) derivative containing mesogene azobenzene units, PEO_m-*b*-PMA(Az)_n [11-13]. The highly ordered PEO cylinder structure is expected to be used as templates for nano-networks, like electronic circuit [14] and for addressing nano-particles [15]. The application of supercritical carbon dioxide (SCCO₂) as a selective solvent of hydrophilic PEO domain in nano-scale ordered structure is expected to several inclusions of AuNPs into PEO nano-cylinders array. A full thermodynamic investigation of the isotropic phase transition temperature (T_{iso}) at elevated pressures for PEO_m-*b*-PMA(Az)_n and homopolymers PMA(Az)_n was conducted by scanning transitiometry (ST) [16]. The effect of hydrostatic pressure transmitted by

nitrogen and carbon dioxide on T_{iso} of $\text{PEO}_m\text{-}b\text{-PMA}(\text{Az})_n$ supported the idea that PEO cylinders acted as CO_2 pathway to approach the equilibrium state rapidly [17, 18].

In this work, the CO_2 pressure effect was investigated from a nano-scale point of view. The structural organization of amphiphilic $\text{PEO}_m\text{-}b\text{-PMA}(\text{Az})_n$ and the thermal behaviour of PEO domain after CO_2 treatment were studied. The selective interactions between $\text{PEO}_m\text{-}b\text{-PMA}(\text{Az})_n$ and AuNPs under supercritical conditions of CO_2 permitted to control the two-dimensional alignment of AuNPs deposition.

EXPERIMENTAL

Amphiphilic di-block copolymer

Amphiphilic di-block copolymer $\text{PEO}_m\text{-}b\text{-PMA}(\text{Az})_n$ consisted of hydrophilic semicrystalline poly(ethylene oxide), PEO, and hydrophobic 11-[4-(4'-butylphenyl-azo)phenoxy]-undecyl methacrylate, PMA(Az). It was synthesized with atom transfer radical polymerization [11]. The degree of polymerization of PEO and PMA(Az) parts was indicated with 'm' and 'n', respectively. In this study, $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Az})_{46}$ was used.

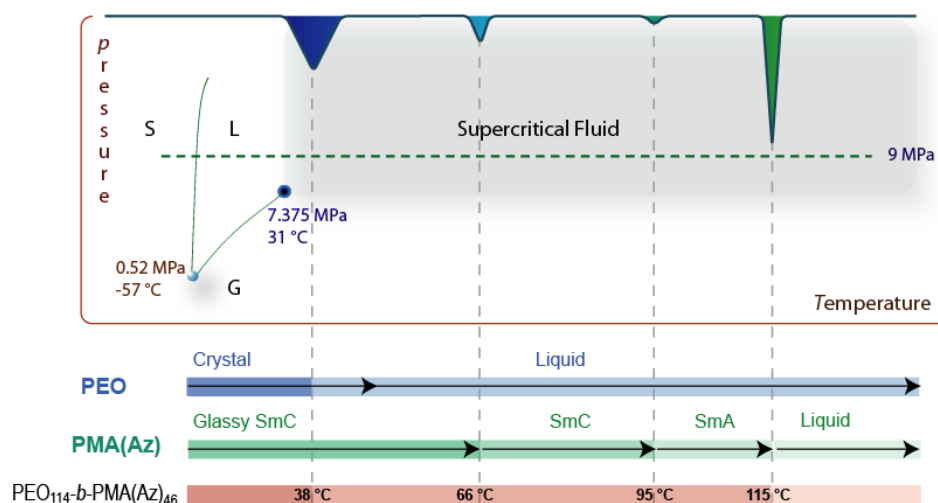


Figure 1 Phase transitions profile of amphiphilic di-block copolymer $\text{PEO}_{114}\text{-}b\text{-PMA}(\text{Az})_{46}$ with phase diagram of carbon dioxide.

With increasing temperature, $\text{PEO}_m\text{-}b\text{-PMA}(\text{Az})_n$ showed four phase transitions assigned successively to the melting of PEO crystal, glass transition of azobenzene moieties PMA(Az), liquid crystal transition from the smectic C (SmC) phase to the smectic A (SmA) phase and isotropic transition as shown in **Figure 1** [19]. $\text{PEO}_m\text{-}b\text{-PMA}(\text{Az})_n$ formed highly ordered hexagonal packed PEO cylinders structures over a wide range of volume fraction by simple annealing at the isotropic state as a result of microphase separation due to amphiphilicity.

Gold nano-particles synthesis

Hydrophilic AuNPs were prepared by reducing aqueous solution of tetrachlorauric acid by sodium borohydride with oligoethylene glycol [20]. The scheme of the synthesis is summarized in **Figure 2 a)**. Transmission electron microscopic (TEM, JEOL FX2000) profile analysis of the size distributions of AuNPs is given in **Figure 2 b) and c)**. Spherical-shaped single nano-particles were distributed randomly. AuNPs were nearly uniform in their size distribution. The synthesized AuNPs, calculated with 180 nano-particles, were 5.13 ± 1.19 nm in diameter. UV-visible spectrum of AuNPs in water showed a typical plasmon absorbance peak at 522 nm closed to the well-know absorption band around 520 nm [21].

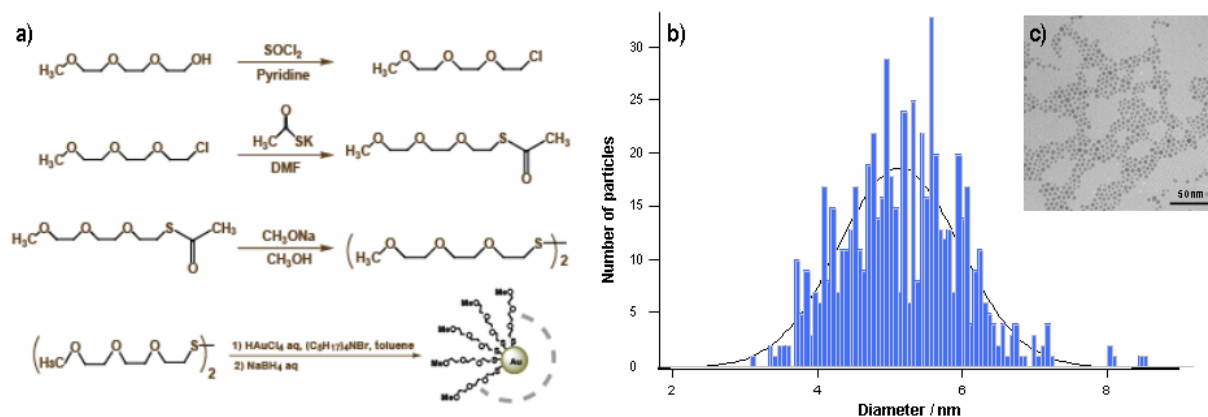


Figure 2 a) Synthesis of gold nano-particles stabilized by thiol functionality, b) TEM image of gold nano-particles. TEM was done after drop coating the gold nano-particles on carbon coated copper grid, c) Size distribution histogram of gold nano-particles.

Carbon dioxide

Carbon dioxide CO₂ was supplied by Taiyo Toyo Sanso Co. Ltd Japan and used without further purification. The critical pressure (7.38 MPa) and temperature (31 °C) are shown in **Figure 1**.

RESULTS AND DISCUSSION

Morphological changes

Selective expansion of PEO cylinders was controlled by CO₂ treatment at 5 MPa and 9 MPa at room temperature (r.t.) and various temperatures for 2 hrs. After CO₂ treatment temperature was decreased to room temperature under 9 MPa, then pressure was suddenly decreased to atmospheric conditions and CO₂ evaporated. The morphological changes with CO₂ treatment were observed by atomic force microscopy (AFM, Shimazu SPM) on PEO₁₁₄-*b*-PMA(Az)₄₆ as illustrated in **Figure 3 a-d**) in left hand side. The schematic morphology can be described as shown in **Figure 3** in right hand side.

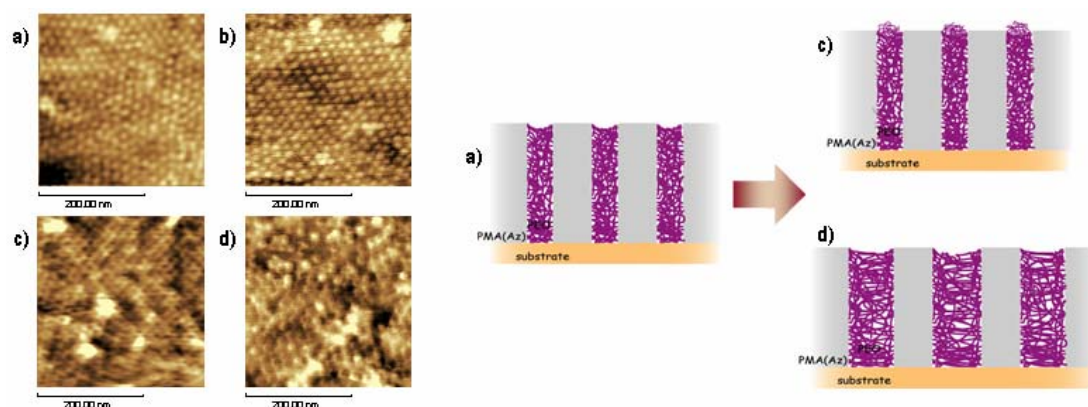


Figure 3 AFM phase images on silicon substrate of PEO₁₁₄-*b*-PMA(Az)₄₆, a) before CO₂ treatment, b) after CO₂ treatment at 5 MPa and r.t., c) after CO₂ treatment at 9 MPa and r.t., and d) after CO₂ treatment at 9 MPa and 80 °C. Polymer film was laid on a polyethylene terephthalate (PET) support. Modified structures were observed for 2 hrs exposure CO₂ treatment. In right hand side, the schematic picture illustrates the expansion changes of PEO cylinders.

PEO domain kept the dense periodic hexagonally arranged cylinder array before and after CO₂ treatment. Before CO₂ treatment, PEO cylinders were 'softer' than PMA(Az) domain and appeared as the white area (**Figure 3 a**)). Under gaseous CO₂ treatment, at 5 MPa and r.t. (**Figure 3 b**)), no

significant expansion change of PEO cylinders was observed. Under liquid CO₂ treatment, at 9 MPa and r.t., a drastic change occurred. PMA(Az) domain surrounding PEO cylinders became ‘softer’ (**Figure 3 c**). PMA(Az) was in the glassy smectic C (SmC) phase and still couldn’t expand. Then, PEO cylinders dissolved with CO₂, expanded preferentially perpendicularly to the surface substrate and appeared as the darkest area. With increasing temperature at 80 °C (**Figure 3 d**), liquid CO₂ changed to supercritical CO₂. PMA(Az) domain was in the SmC phase and got potential mobility. The easiness of SCCO₂ to dissolve within liquid PEO cylinders increased the diameter of the nano-tubes and PEO cylinders were again identify as the white area. In the example of PEO₁₁₄-*b*-PMA(Az)₄₆ the values in diameter changed from 11.8 nm at r.t. to 18.4 nm at 80 °C. In addition, plane distance between PEO cylinders slightly increased after treatment from 19.8 nm at r.t. to 24.9 nm at 80 °C. After two weeks at r.t. and atmospheric conditions, PEO cylinders shrunk to the initial values [16]. These results confirmed the ability of SCCO₂ to modify and control the copolymer interfacial self-organization in nano-scale through more efficient hydrophilic SCCO₂/PEO interactions when PMA(AZ) domain was in the SmC phase.

Distribution of AuNPs

SCCO₂ was used to control both the dispersion and location of AuNPs with the organization of di-block copolymer in nano-scale. Hydrophilic AuNPs were dispersed by solvent casting on the hexagonally packed PEO array of PEO₁₁₄-*b*-PMA(Az)₄₆. **Figure 4** in left hand side shows TEM images of AuNPs on PEO₁₁₄-*b*-PMA(Az)₄₆ after isothermal SCCO₂ treatment aging at 80 °C for 2 hrs, and quenching to room temperature. TEM images were obtained without staining. The black spots corresponded to AuNPs, which aligned hexagonally as same as the hexagonally packed PEO array of PEO₁₁₄-*b*-PMA(Az)₄₆. Favorable interactions between SCCO₂ and PEO cylinders enabled hydrophilic AuNPs to be driven, selectively and homogeneously, to be assembled in the site of ordered PEO hexagonal array. The size and arrangement of nano-particles were consistent with the values of AFM observation. The structural characteristics of the hexagonal organization was supported by small X-ray scattering analysis (SAXS, BL10C, PF, High Energy Accelerator Research Organization - Japan).

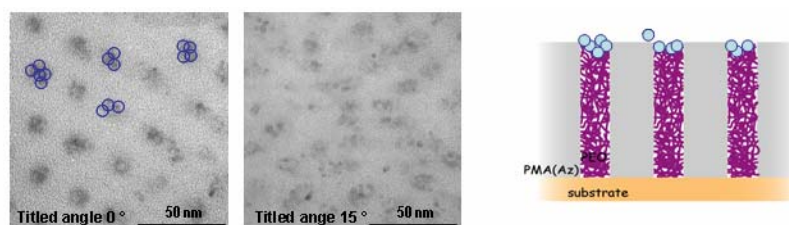


Figure 4 TEM images of PEO₁₁₄-*b*-PMA(Az)₄₆/AuNPs/SCCO₂ after treatment at 9 MPa and 80 °C for 2 hrs. The black spots (some accentuated with circles) were AuNPs located on PEO cylinders selectively. In right hand side, the schematic picture illustrates the repartition of AuNPs (circles) on PEO cylinders array.

The locational analysis of AuNPs was done by TEM images with a titled angle of 15 °, as **Figure 4** in left hand side illustrates. AuNPs located on the head of PEO cylinders not inside of PEO cylinders as represented in the schematic picture in **Figure 4** in right hand side. AuNPs dots were about 10 nm in thickness, PEO cylinders were about 50 nm in length. The local concentration disturbed shrinkage of PEO cylinders since it was observed the same size structure after two months. The nano-dots made the CO₂ modified structure stable.

Effect of thermal annealing on the crystallization studied by DSC

Differential scanning calorimetry (DSC, DSC6200 Seiko) clarified the structural evolution. The experiments were carried out by cooling (crystallization) at 5 K/min after CO₂ treatment at a constant pressure of 9 MPa. Interactions between polymer and CO₂ depended on time and temperature of saturation. The first approach investigated the time-depending effect at room temperature (r.t.). Results are shown in **Figure 5 a**). PEO part dissolved in liquid CO₂. After the decrease of pressure, PEO had

free volume much larger than in the native polymer. The surplus of free volume may alter physical interactions of the polymer. Then it became difficult for PEO to crystallize after 1 h and 6 hrs treatment. After 24 hrs treatment, time of equilibrium enabled an rearrangement of PEO polymer chains, and PEO part could crystallize. The exothermic heat of crystallization, after annealing at 9 MPa and r.t. for 24 hrs, was lowering by 20 % compared to polymer before CO₂ treatment. Many vacancies in PEO part were created because of the plasticization of CO₂, and the polymer changed to a lower density state.

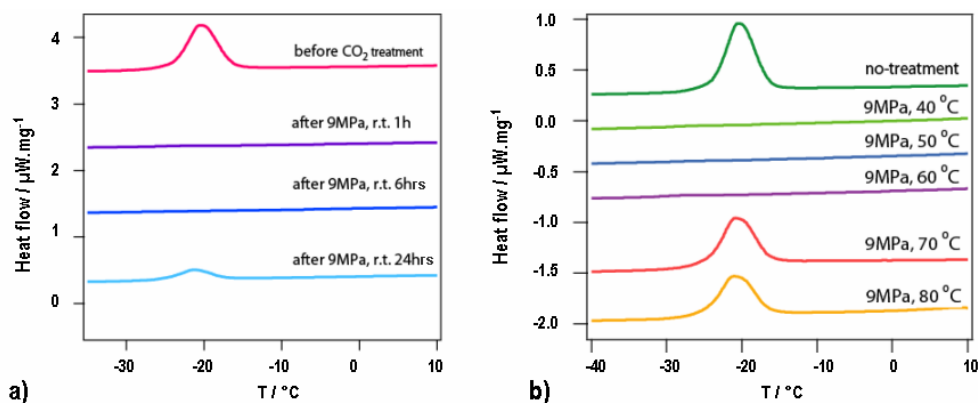


Figure 5 DSC cooling of PEO₁₁₄-*b*-PMA(Az)₄₆ before and after CO₂ treatment at 9 MPa, **a**) at room temperature (r.t.) and for 1, 6 and 24 hrs, **b**) at 40, 50, 60, 70 and 80 °C for 2 hrs.

The second study dealt with the temperature-depending effect, namely 40, 50, 60, 70 and 80 °C for 2 hrs CO₂ treatment. Results are shown in **Figure 5 b**). Crystallization temperature shifted to lower values during first cooling. The minimal crystallization entropy was found for treatments between 40 °C and 60 °C. In that range, PEO part was in the liquid state and PMA(Az) part was in the glassy SmC state. CO₂ was in the supercritical state. The interactions between polymer and SCCO₂ favoured the expansion PEO cylinders but the expansion was constraint by the presence of glassy SmC phase. At 70 °C and 80 °C, PMA(Az) was in the SmC phase. Density of CO₂ at 9 MPa and 40 °C being larger than the one at 80 °C, the solubility of CO₂ in PEO at 40 °C was much larger than at 80 °C. The stress induced by the presence of PMA(Az) decreased, and it became easily for PEO cylinders to expand explaining the crystallization of PEO.

Mecanism, AuNPs coagulation on the head of PEO cylinders

AFM and TEM analysis revealed that hexagonally packed PEO cylinders were used as templates to direct the deposition of AuNPs with treatment of SCCO₂. It was a well-illustration of the formation of Au-nano-dots. PEO molecular mobility increased and could catch AuNPs because of the hydrophilic ligands. Linear relationship between the number of AuNPs located on the head of PEO cylinders depended on the size of PEO cylinders diameter due to the sorption of CO₂. The presence of 4, 5 and 8 AuNPs were found, respectively, for 'm' = 114, 272 and 454. Thermogravimetric analysis (TGA, TGDTA6200 Seiko) gave us more informations about hydrophilic gold nano-ligands available.

CONCLUSION

In a new way, the SCCO₂ treatment in the nano-scale was presented to arrange gold particles into well-organized LC amphiphilic di-block copolymers. The driving force of the assembly process was attributed to the selective interactions of SCCO₂ with hydrophilic semicrystalline PEO and to the good compatibility of AuNPs with PEO part. The inclusion of AuNPs stabilized the SCCO₂ modified organization of di-block copolymer while keeping the nano-scale regular organization. Successfully, the control of the supercritical conditions enabled the control of the creation of Au-nano-dots based on PEO_m-*b*-PMA(Az)_n.

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REFERENCES

- [1] EUSTIS, S., EL-SAYED, M., Chem. Soc. Rev., Vol. 35, **2006**, p. 209
- [2] CORTI, C.W., HOLLIDAY, R.J., THOMPSON, D.T., Gold Bull., Vol. 35, **2002**, p. 111
- [3] AHMADI, T.S., WANG, Z.L., GREEN, T.C., HENGLEIN, A., EL-SAYED, M.A., Science, Vol. 272, **1996**, p. 1924
- [4] ALIVISATOS, A.P., Science, Vol. 271, **1996**, p. 933
- [5] HARUTA, M., Chem. Rec., Vol. 3, **2003**, p. 75
- [6] JAIN, P.K., EL-SAYED, I.H., EL-SAYED, M.A., Nanotoday, Vol. 2, **2007**, p. 18
- [7] BARBILLON, G., BIJEON, J.-L., PLAIN, J., LAMY DE LA CHAPELLE, M., ADAM, P.-M., ROYER, P., Gold Bull., Vol. 40, **2007**, p. 240
- [8] WEINBERGER, M.R., RENTENBERGER, S., KERN, W., Monatsh. Chem., Vol. 138, **2007**, p. 309
- [9] LI, B., LI, C.Y., J. Am. Chem. Soc., Vol. 129, **2007**, p. 12
- [10] PEREIRA, G.G., Current Appl. Phys., Vol. 4, **2004**, p. 255
- [11] TIAN, Y., WATANABE, K., KONG, X., ABE, J., IYODA, T., Macromolecules, Vol. 35, **2002**, p. 3739
- [12] YOSHIDA, H., WATANABE, K., WATANABE, R., IYODA, T., Trans. Mater. Res. Soc. Jpn., Vol. 29, **2004**, p. 861
- [13] KOMURA, M., IYODA, T., Macromolecules, Vol. 40, **2007**, p. 4106
- [14] LI, J., KAMATA, K., KOMURA, M., YAMADA, T., YOSHIDA, H., IYODA, T., Macromolecules, Vol. 40, **2007**, p. 8125
- [15] WATANABE, S., FUJIWARA, R., HADA, M., OKAZAKI, Y., IYODA, T., Angew. Chem. Int. Ed., Vol. 46, **2007**, p. 1120
- [16] BOYER, S.A.E., GROLIER, J.-P.E., PISON, L., IWAMOTO, C., YOSHIDA, H., IYODA, T., J. Therm. Anal. Cal., Vol. 85, **2006**, p. 699
- [17] YAMADA, T., BOYER, S.A.E., IYODA, T., YOSHIDA, H., GROLIER, J.-P.E., J. Therm. Anal. Cal., Vol. 89, **2007**, p. 9
- [18] YAMADA, T., BOYER, S.A.E., IYODA, T., YOSHIDA, H., GROLIER, J.-P.E., J. Therm. Anal. Cal., Vol. 89, **2007**, p. 717
- [19] WATANABE, R., IYODA, T., YAMADA, T., YOSHIDA, H., J. Therm. Anal. Cal., Vol. 85, **2006**, p. 713
- [20] BOAL, A.K., ROTELLO, V.M., Langmuir, Vol. 16, **2000**, 16, p. 9527
- [21] JEWRAJKA, S.K., CHATTERJEE, U., J. Polym. Sci.: Part A: Polym. Chem., Vol. 44, **2006**, p. 1841