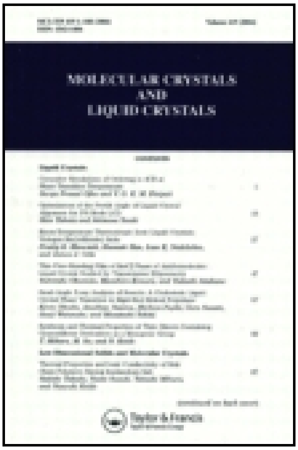

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Behavior of Poly(σ-aklyl α, L-glutamate)-Polyethylene Oxide Copolymer at the Air/Interface

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To cite this article: Chul Kim, Kunwoo Kim, Youngil Lee & Daewon Sohn (2001): Behavior of Poly(σ-aklyl α, L-glutamate)-Polyethylene Oxide Copolymer at the Air/Interface, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 370:1, 211-214

To link to this article: http://dx.doi.org/10.1080/10587250108030072

Mol. Cryst. and Liq. Cryst., 2001, Vol. 370, pp. 211-214

Behavior of Poly(γ-aklyl α, L-glutamate)-Polyethylene Oxide Copolymer at the Air/Interface

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Side chain polyglutamate-poly(ethylene oxide) (PALG-PEO) diblock copolymers were synthesized by side chain glutamete NCA (N-carboxy anhydride). These molecules form monolayer at the air/water interface due to the amphiphilic character of the hydrophobic side chains of the rod and hydrophilic poly(ethylene oxide). Conformational change of the poly(ethylene oxide) and topology of the rodlike polymer have been studied by surface area-surface pressure isotherm. At low density PEO block contributes surface pressure and generates pancake to blush-like transition. PALG block is laid down at the air/water interface and contributes the high surface pressure. We have observed two different phase transitions that depend on the size of the rod and the area of the absorbed PEO block at the air/water interface.

Keywords PEO; polyglutamate; amphiphilic copolymer

INTRODUCTION

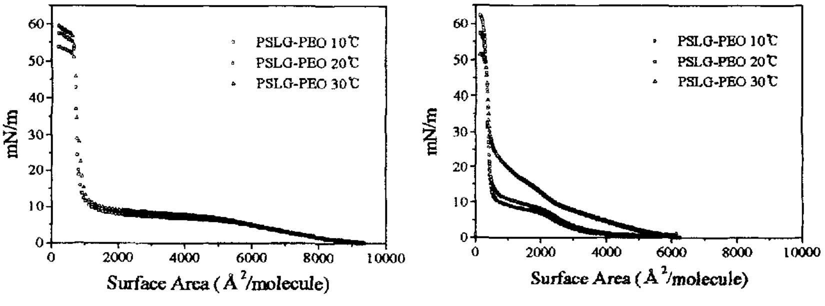
Amphiphilic diblock copolymers have been widely studied for their ability to form micelle structure in solution and monolayer at the air/water interface.[1] PALG-PEO copolymers in here are constituted of a hydrophobic rodlike block anchoring with the hydrophilic random coil segments. The side chain rodlike polypeptides (PALGs) are thermally stable, and their α-helical backbones give the chain stiffness. PEO is a unique material since it is soluble in both water and aromatic solvents. Previous experimental data show that PEO is highly surface active and its conformation change from pancake to brush by increasing the surface pressure.[1] Several block copolymers containing PEO such as polystyrene (PS)-PEO, poly(methyl methacrylate) (PMMA)-PEO, and phospholipid-PEO were introduced due to many industrial applications. Self-consistent-filed (SCF) theories and scaling theories predict the pancake to blush transition with increasing values of surface coverage.[2] Here we prepare the rod and random coil block at the air-water interface and study the conformational transition depending on the size of the rod and the absorbed PEO layer. PEO and PALG chain lengths were varied over a finite range to verify the conformational change of the copolymer.

EXPERIMENTAL

Alkyl-L-glutamates(ALG)-PEOs were synthesized by ring-opening polymerization of N-carboxyanhydride (NCA) monomer. ALG was prepared from alkyl alcohol (stearyl or methyl) and L-glutamic acid. And γ-alkyl α, L-glutamate-NCA monomers (ALG-NCAs) were prepared by phosgenation of ALG in THF at 45℃. Polymerization was performed by initiation of ALG-NCA with polymeric amine initiator in methylene chloride at 30℃. Polymeric amine initiators were purchased from Shearwater Polymers and their molecular weights and purity were 5,000, 10,000 and 99%, respectively. All polymerization flasks were flame dried prior to use, and moisture was excluded during polymerization with calcium chloride. ^{1}H NMR, ^{13}C NMR, FT-IR, and GPC were used to characterize the PALG-PEO. To confirm the molecular weight, GPC and NMR by the peak integration of the signal of methyl protons of the glutamate and the signal of the ethylene protons (3.6 ppm) of the PEO backbone, were used. LAUDA FW-2 (LAUDA instruments, Germany) was used to get the π-A isotherms and LB films. The compression speed of the barrier was 20 cm^2/min. The copolymer films were deposited vertically with dipping speed of 5 mm/min on hydrophilic substituted silicon wafers for the ellipsometry. The Rudolph automatic-nulling ellipsometer, Auto EL2, was used to measure the thickness of the LB film with operating wavelength, 632.8nm, and angle of incidence, 70°±0.02. The experimental errors in the values of the phase difference (Δ) and azimuth (ψ) were less than 0.03 and 0.02.

RESULTS AND DISCUSSION

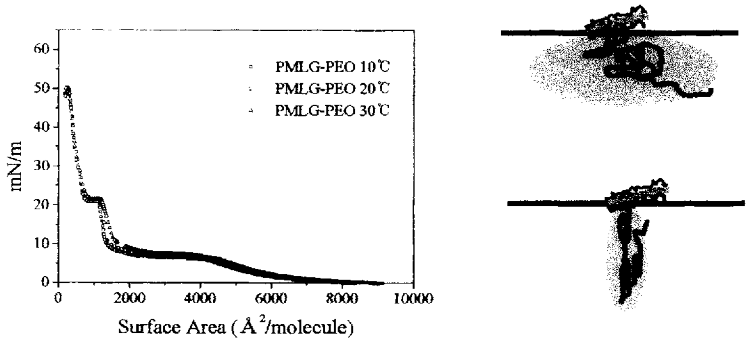
The PALG homopolymer has stiff transition in the π-A isotherm and the surface area increase with temperature for a range 20 to 50°C. It indicates a gradual lessening of interdigitation of side chains with temperature.[3] The PEO homopolymer is known to adsorb weakly to the air/water interface and has long plateau due to the mushroom to brush transition in the decreased surface area. There is no significant temperature dependence in the π-A isotherms of the PEO homopolymer. Figure 1 (a) show the π-A isotherm at various temperatures, 10, 20, and 30°C, for PSLG-PEO copolymer (Mw 15,000, PEO Mw: 10000). At low surface pressure a liquid expanded monolayer is observed, and PEO block makes a gradual increase of the surface pressure in contact with the water subphase. The plateau at 10mN/m in the isotherms coincides with the PEO homopolymer, which indicates the conformational transition of the PEO block. Pancake to brush transition in this region was predicted by the scaling theories and verified by several authors. At high surface coverage there is a steep increase due to the rodlike polymers that laid down on the air/water interface. Figure 1(b) shows the π-A isotherm PSLG-PEO copolymer, Mw 9,000, PEO Mw: 5,000, which has less number of PEO segments. The area on the air/water interface of PEO block in Figure 1(b) is smaller than that of the Figure 1(a). So, the PALG block contributes the shift of the isotherm to the large surface area.



(a) (b)

FIGURE 1. π-A isotherms at various temperatures, 10, 20, and 30°C, for (a) PSLG-PEO copolymer: Mw 15,000, PEO Mw: 10,000, and (b) PSLG-PEO copolymer: Mw 9,000, PEO Mw: 5,000

PMLG is more easily prepared and has relatively high aspect ratio than that of PSLG, so the contribution of rod would be more significant. Figure 2(a) shows the π-A isotherm of PMLG-PEO copolymer (Mw 15,000, PEO Mw: 5000) which has two transitions at 10 and 20 mN/m. The second transition at 20 mN/m is due to the retardation of the tail-to-tail to side-by-side attachment of the rod block wherein the length of the rod is longer than the diameter of the PEO segment (Figure 2(b)). Figure 2(a) also shows that the chain of PMLG does not influence by the side chain intercrossing due to the temperature increment. The contribution of the rod and the coil at the air/water interface was clear in the π-A isotherm and the PALG-PEO copolymer is a good model to verify the size contribution of each segment at the air/water interface.



(a) (b)

FIGURE 2. (a) π-A isotherm of PMLG-PEO copolymer, Mw 15,000, PEO Mw: 5000, (b) The schematic illustration for the conformational change of PALG-PEO copolymer.

Acknowledgments
This work was supported by fund from the Hanyang University in 2000.

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