BEHAVIOUR OF MONOLAYERS OF 4-METHYLBENZENETHIOL ENCAPSULATED GOLD NANOPARTICLES AND TWO KINDS OF POLY(ETYLENEOXIDE) DERIVATIVES ON WATER SURFACE

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Abstract

In this study monolayers of poly(ethyleneoxide) derivatives with gold thiol nanoparticles and lithium ions on water surface have been prepared. Surface pressure-area (Π-A) isotherms of these monolayers at the water surface has been studied. The area per molecule on water surface changes in size when gold thiol or lithium ions are added to monolayers of poly(ethyleneoxide) derivatives. Isotherm graphs of mixed monolayer using poly(ethyleneoxide) derivatives show a plateau region and a phase transition.

Keywords: PEO polymers; Surface isotherms; Lithium ions; nanoparticles

Özet

Bu çalışmada altın thiol nanoparçacıkları ve lityum ionları kullanılarak poly(ethyleneoxide) türevlerinin su yüzeyi üzerinde tek katlı tabakaları oluşturulmuştur. Bu tek katlı tabakaları su yüzeyi üzerindeki yüzey basınç – alan (Π-A) izotermleri çalışılmıştır. Poly(ethyleneoxide) türevine ait tek katlı tabakaya altın thiol nanoparçacıklar veya lityum iyonu eklendiğinde molekül başına düşen alan değişmektedir. Poly(ethyleneoxide) türevleri karıştırılarak hazırlanan tek katlı tabakanın izotherm grafiği plato bölgesi ve faz geçişi göstermektedir.

Anahtar kelimeler: PEO polimerleri; Yüzey izotermleri; Lityum iyonları; nanoparçacıklar

1. INTRODUCTION

In recent years there is great interest to nanoparticles because of their potential applications [1-4]. As in nano applications dimensions in nonoscale is needed colloidal gold nanoparticles can find many applications in the area of optoelectronics [5,6], medicine [7], and sensor industry [8-9] because of their radius which is around 2-4 nm.

Solvent-free polymer electrolytes based on poly(ethylene oxide) derivatives are relatively stable polymers and dissolves lithium salts to give semicrystalline or fully amorphous complexed phases [10]. Poly(ethylene oxide) is a good candidate material through the ions are transported [11] and can have many applications in the optoelectronic area. It is important to know the conformation of monolayer at the water surface for a fabrication of Langmuir-Blodgett thin film. For this purpose, in this work poly(ethylene oxide) derivatives are choosed to study their behaviour at the water surface and to form the gold nanoparticles at these monolayer using standard Langmuir-Blodgett thin film trough [12.].

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2. EXPERIMENTAL DETAILS

Two type of poly(ethyleneoxide) derivatives and 4-methylbenzenethiol ($HS-C_6H_4-CH_3$) encapsulated gold nanoparticles were used in this work. The chemical structures of these materials are shown in Figure 1. The synthesis of these molecules are described in previous studies [8, 13-14]. Poly[tetraoxyethyleneoxymethylene (5-hexadecyloxy-1,3-phenylene) methylene] and poly[tetraoxyethyleneoxymethylene (5-hexadecyloxy-1,3-phenylene) methylene]-co-poly[tetraexyethyleneoxymethylene (5-dodecyloxy-1,3-phenylene) methylene] are named C16 and C1216 respectively. Solutions were prepared using chloroform with concentrations of 0.94, 1.06 and 1.816 $mg.ml^{-1}$ for gold thiol, C16 and C1216.

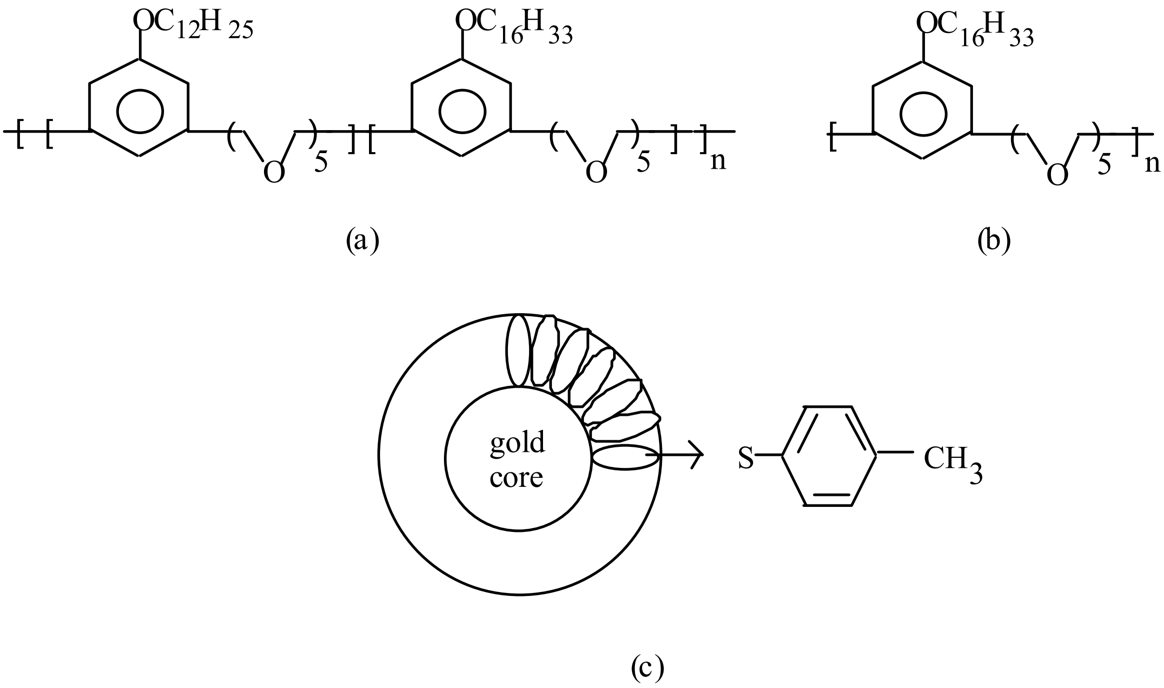

Fig. 1: Chemical structures of the molecules coded C1216 (a) and C16 (b) and gold thiol (c).

A computer-controlled Langmuir-Blodgett film trough was employed to investigate the isotherm behaviour of all materials and gold thiol with incorporated lithium ions. The surface pressure was controlled using a Wilhemly plate consisting of a 1 cm wide strip of filter paper which takes part between water in the trough and microbalance head above the through. The routine cleaning procedure of the trough was made with a special soup solution which was prepared using octanoic acid and potassium hydroxide. 4.5 mg of $LiClO_4$ salt were added to the water in the trough before recording the isotherm graph and solution with a known volume was spread dropwise onto a cleaned water surface using a Hamilton micro syringe. After waiting about 10-15 minutes, the molecules were compressed by a moveable barrier with a predetermined barrier speed until they form a close-packed structure. Surface pressure-area graph is recorded at room temperature during the compression and all the details will be given in the next section.

3. RESULTS AND DISCUSSION

Figure 2 shows a series of isotherm graphs of C1216 of gold thiol. The area per repeating unit (APRU) is decreased when gold thiol is added to the C1216 monolayer. A bigger amount of gold thiol causes a smaller APRU. If lithium ions are added to the monolayer (the amount of gold thiol is increased), the APRU decreases for the C1216 polymer.

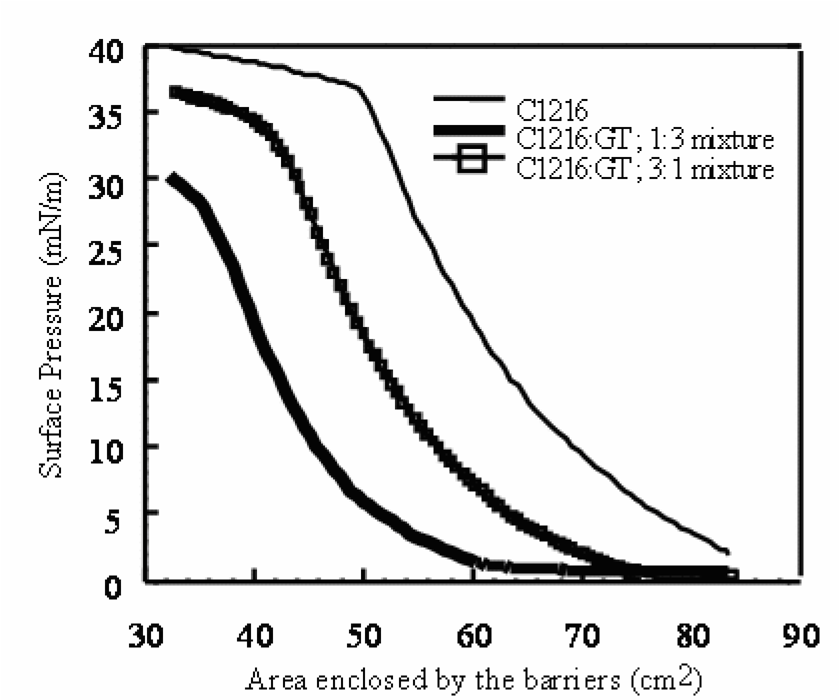

Fig. 2: Isotherm graphs of C1216 polymer and gold thiol (GT) mixed in different ratios 1:0, 1:3 and 3:1.

Isotherm graphs for this situation are given in Figure 3. Two isotherms for C16 polymer without gold thiol in the monolayer are shown in Figure 4. These isotherms indicate that there is a decrease in APRU when lithium ions are incorporated in the C16 polymer showing a plateau region, which means a reorganization of the monolayer on the water surface.

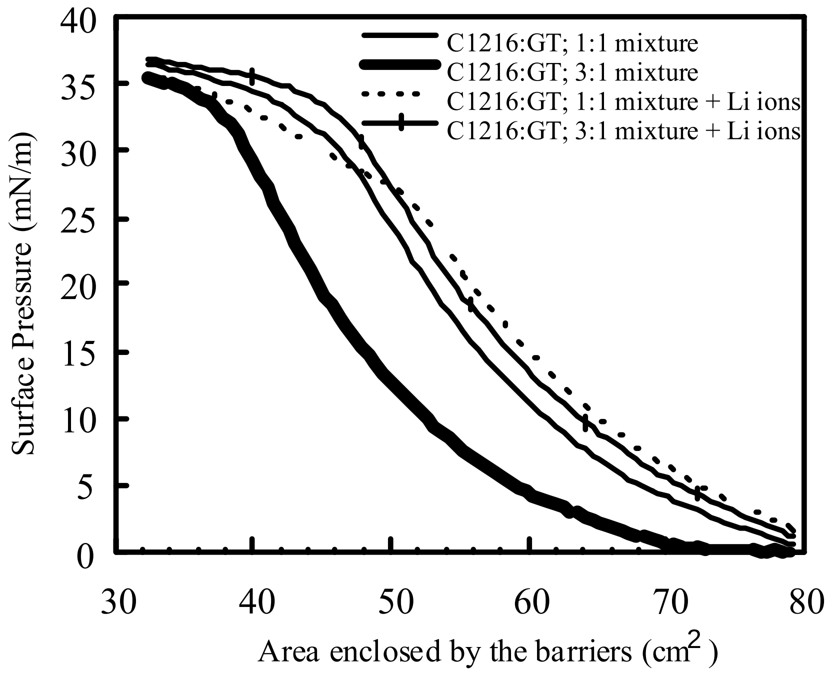

Fig. 3: Isotherm graphs of C1216 polymer and gold thiol (GT) mixed in different ratios 3:1 and 1:1 with incorporated Li ions and without incorporated Li ions.

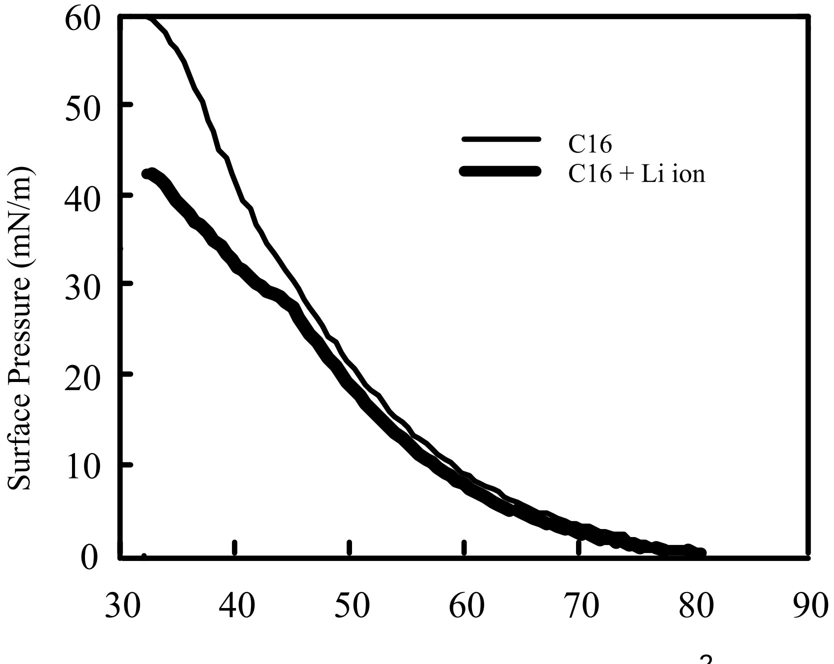

Fig. 4: Isotherm graphs of C16 polymer with and without incorporated Li ions.

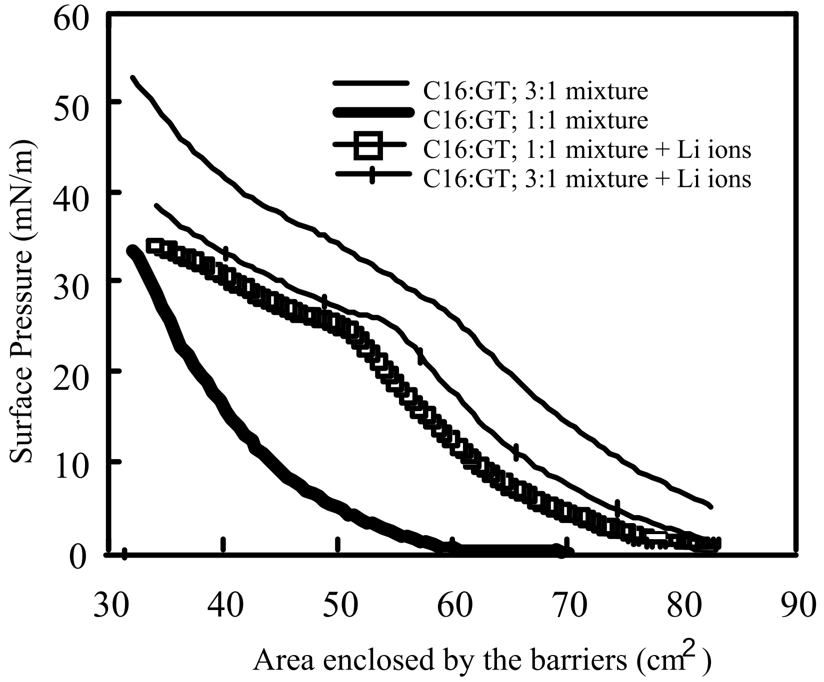

Fig. 5: Isotherm graphs of C16 polymer and gold thiol (GT) mixed in different ratios 3:1 and 1:1 with incorporated Li ions and without incorporated Li ions.

Figure 5 shows isotherms for the C16 polymer which gold thiol with a ratio of 1:1 and 3:1 both with Li ions and without ions. Ion effects in the mixture for 1:1 ratio increases the APRU. Figures 3, 4 and 5 show that the interaction of ions with polymers is different than the interaction with gold thiol and depends on the added ratio.

The isotherms of the C1216 and C16 polymers in the ratio 1:1 with incorporated lithium ion and also two polymers with gold thiol in ratio 1:1:1 with incorporated lithium ion are shown in the Fig. 6. When ions are incorporated to two polymer mixture the APRU is increased while ion is incorporated to three molecules mixture APRU decreases. Fig. 7 shows the isotherms of the mixture of C1216 polymer and C16 polymer with gold thiol in 1:1 ratio and also the mixture of three of the molecules in 1:1:1 ratio. Three molecule mixtures show an isotherm with a phase transition indicating a reorganization of the monolayer.

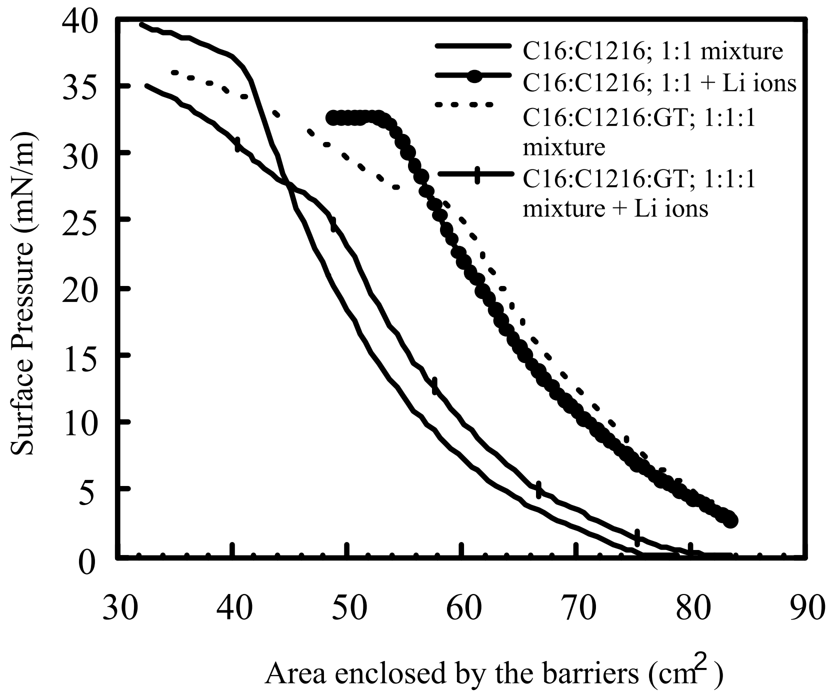

Fig. 6: Isotherm graphs of C16, C1216 and gold thiol (GT) mixed in equimolar ratios with incorporated Li ions and without incorporated Li ions.

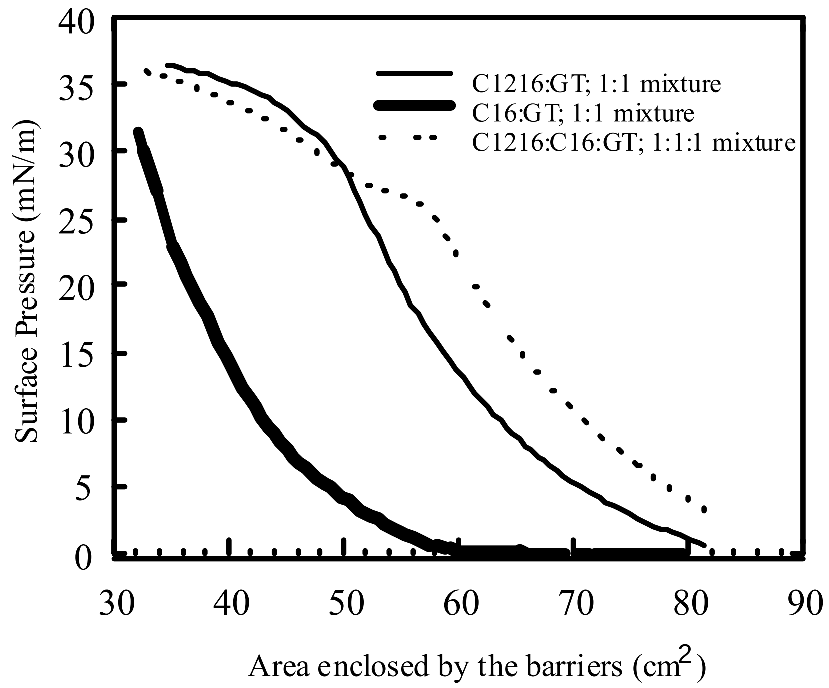

Fig. 7: Isotherm graphs of C16, C1216 and gold thiol (GT) mixed in equimolar ratios without incorporated Li ions.

There are two possible configurations on the water surface. One of them can be described as same molecules come together and form small groups of molecules on water surface and interact with the other groups formed by other molecules (Figure 8a). The other one is every molecule interacts with the other one and the molecules are randomly placed on the water surface (Figure 8b).

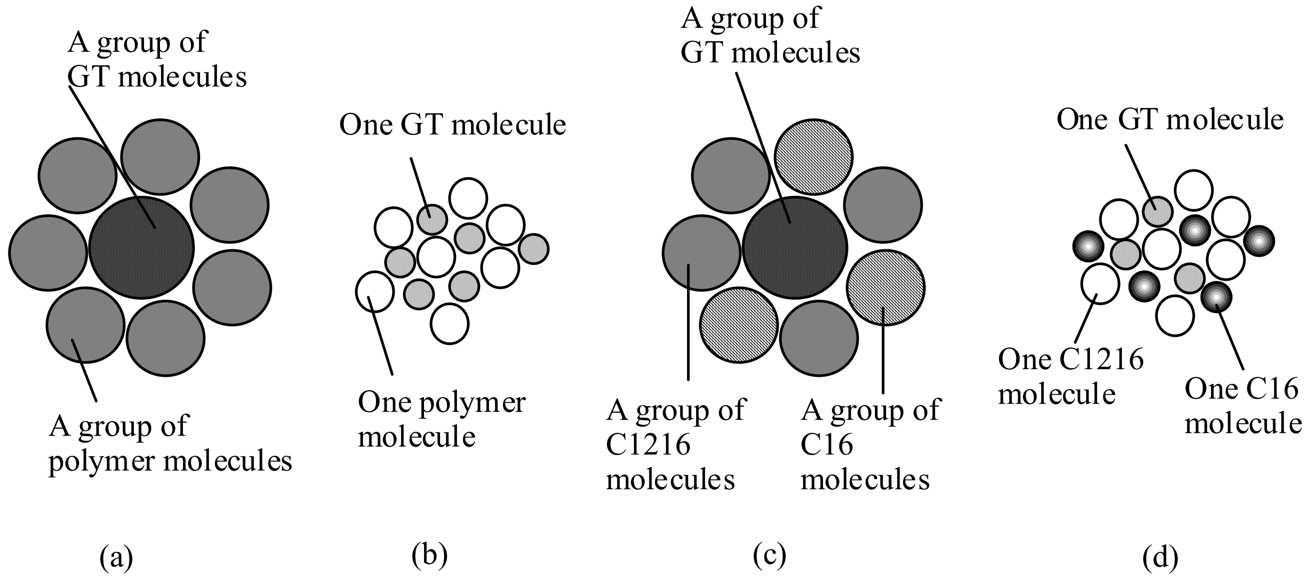

Fig. 8: A proposal for the conformation of molecules on the water surface. (a) and (b) indicate one of any polymers and gold thiol (GT), (c) and (d) indicate a three molecules mixture.

4. CONCLUSION

The aim of this work is to investigate and characterize the surface behaviors of the polymers and nanoparticles and to observe the changes of surface interactions when lithium ions are added to the monolayer. The interaction of lithium ions with two polymer mixtures and three molecule mixtures are different, while the interaction with gold thiol differs according to the added ratio of gold thiol. The monolayer prepared with a mixture of three molecules gives an isotherm with a plateau region which indicates a phase transition.

5. ACKNOWLEDGEMENTS

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