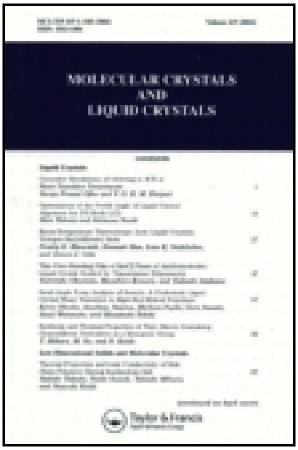


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Scaling Property of Polymer Liquid Crystal Langmuir Monolayers

Y.-M. Zhu [a], Z.-H. Lu [a] & Y. Wei [a]
[a] Laboratory of Molecular and Bimolecular Electronics, Southeast University, Nanjing, 210096, China

Version of record first published: 23 Sep 2006.

To cite this article: Y.-M. Zhu, Z.-H. Lu & Y. Wei (1994): Scaling Property of Polymer Liquid Crystal Langmuir Monolayers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 257:1, 49-52

To link to this article: http://dx.doi.org/10.1080/10587259408033762

Mol. Cryst. Liq. Cryst., 1994, Vol. 257, pp. 49–52
Reprints available directly from the publisher
Photocopying permitted by license only

Scaling Property of Polymer Liquid Crystal Langmuir Monolayers

Y.-M. ZHU, Z.-H. LU and Y. WEI

Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing 210096 China

(Received October 15, 1993; in final form December 16, 1993)

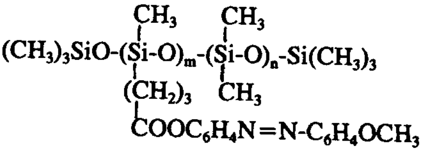
Different kinds of polymers may show different scaling properties at the air-water interface. In this paper the scaling behavior of Langmuir monolayers of a polymer liquid crystal with side chains has been checked by the measurement of surface pressure-molecular area isotherm. The scaling power relating surface pressure and surface area is 6.7, which gives the exponent $v = 0.59$. The latter reflects the polymerization index dependence of the radius of gyration of two-dimensional polymer chains. The overlap degree of polymer coils in a dense state has also been discussed.

Keywords: Polymer liquid crystal, Langmuir monolayer, scaling property

The surface pressure has been extensively studied to understand the polymer behavior at an interface such as the air-water interface. Recently the scaling concept [1] has been successfully applied to describe the isotherms of polymer films [2–4]. In terms of scaling theory, for instance, the radius of gyration for an isolated chain (R_f) can be written as $R_f \sim aN^v$ where N is the polymerization index, a the monomer size and v a critical exponent. For good solvents, $v = 3/(d+2)$, which is known as Flory's formula, where d is the spatial dimensionality. For poor solvents, v stays close to 0.5, independent of d. For the case of polymers in an interface, furthermore, the osmotic compressibility (surface pressure) can also be expressed in terms of scaling theory as a function of polymer concentration c: $\pi \sim c^y$, where y is directly related to v by $y = 2v/(2v-1)$ [2], or equivalently $\pi \sim A^{-y}$, where A is the area occupied by one molecule at the interface. Thus, by measuring surface pressure-molecular area isotherms, the exponent v can be determined. Furthermore, based on the above results, the overlap degree of polymer coils in a semidilute solvent and/or in a dense state can be evaluated.

In this paper we will study the scaling property of a polymer liquid crystal (PLC) Langmuir monolayer at the air–water interface. The overlap degree of polymer coils at the air-water interface will also be discussed.

The molecular structure of PLC is shown in Figure 1. Its average molecular weight $M = 3680$, and $m/n = 3.380$. The PLC monolayer was spread with the use of a solvent of the polymer dissolved in chloroform (0.5 mg/ml) and delivered onto the water surface by a syringe. The subphase temperature was kept at $25(\pm 0.5)$°C. Evaporation of the organic solvent left the PLC molecules uniformly distributed on the water surface. The surface pressure, the reduction of surface tension due to the presence of the monolayer,



$$(CH_3)_3SiO\text{-}(\underset{\underset{COOC_6H_4N=N\text{-}C_6H_4OCH_3}{(CH_2)_3}}{\overset{CH_3}{Si}}\text{-}O)_m\text{-}(\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_n\text{-}Si(CH_3)_3$$

FIGURE 1 Molecular structure of polymer liquid crystal.

was measured throughout the experiment by a Wilhelmy balance (Face, Japan product) with an accuracy of better than 0.1 dyne/cm. The area per molecule was decreased by squeezing of the water surface area with a movable barrier. The compression ratio was kept at a relatively low value of 0.4 Å^2/sec.

Figure 2 shows the measured surface pressure (π) as a function of the molecular area (A) for the PLC on the water surface. There are two evident kinks in the isotherm, implying that the monolayer undergoes phase transitions, which are accompanied by a change of molecular conformations. The kink at a higher surface pressure does not appear when the temperature of the subphase is lower than 20°C. Through the analysis of molecular conformations and the ratio of limiting areas in different phases, we have found that these transitions can be reasonably ascribed to the change of molecular conformations. We will discuss these transitions in detail elsewhere [6].

To understand the isotherm of PLC monolayer in terms of scaling theory, Figure 2 was replotted in a log–log fashion of surface pressure versus molecular area, as shown in Figure 3. The slope of the isotherm gives the scaling exponent y which is 6.7, implying that the polymer at the air–water interface behaves nearly as in a θ solvent [1, 2, 4]. The scaling isotherm reasonably fits the experimental data up to the area per molecule of 300 Å^2. This indicates that the isotherm is mainly dominated by the backbone of the polymer, particularly in the low surface pressure region. The siloxane backbone in the polymer studied here is in contact with the water surface.

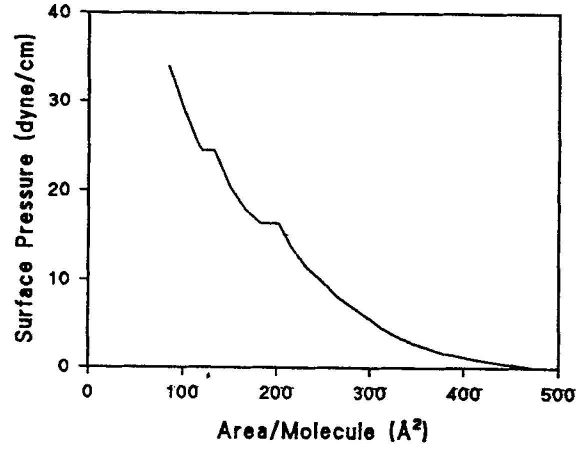


FIGURE 2 Surface pressure vs. molecular area of polymer liquid crystal monolayer on the air–water interface at 25°C.

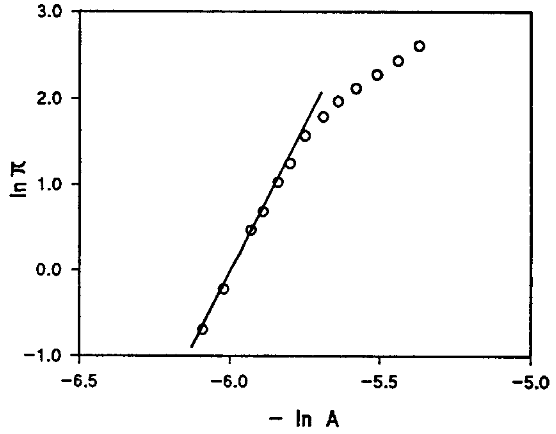


FIGURE 3 Log–log plot of surface pressure (π) vs. molecular area (A) of polymer liquid crystal monolayer. The slope of the solid line fitting the scaling isotherm at low surface pressure gives a value of 6.7. π is in units of dynes per centimeter, and A is in units of square angstroms per molecule.

We note that the scaling isotherm is valid only at relatively low surface pressures. The deviation between the scaling isotherm and the real one in a high surface pressure region signals that, in this region, the role of the mesogens cannot be neglected. Other possibilities such as polydispersity may also contribute to this deviation. However, understanding all these factors is a difficult problem.

We have also estimated the value of v according to $y = 2v/(2v - 1)$ which is equal to 0.59. Based on the exponent, the area of polymer coil can be roughly estimated as $A_0 \approx \pi R_f^2 \approx \pi a^2 N^{2v} \approx 475\,\text{Å}^2$, at which the ideal gas isotherm changes to the scaling isotherm [2]. (We have taken $N \approx 15$ according to the molecular weight and the m/n ratio, $a = 2.42$ Å. The choice of a value is referred to [5].) Thus, it is possible to evaluate the overlap degree when the monolayer is compressed tightly. The difference of the molecular area and the coil area can be ascribed to the overlap of polymer coils. For example, the molecular area at surface pressure of 14 dyne/cm is 215 Å^2. Compared to 475 Å^2, one should say that in this case the polymer coils interpenetrate each other remarkably. Generally, the larger the difference is, the more strongly the polymer coils interpenetrate each other.

In comparison, the measured v for the PLC monolayer is 0.59, rather than 0.75 as for good solvents or 0.5 as for poor solvents. This can be addressed by investigation of the chemical structure of the polymer in terms of the hydrophilic and hydrophobic balance as Kim *et al.* suggested [3]. This question could also be elucidated by using different kinds of polymer materials such as polymers with the same main chains but quite different side chains.

To conclude, we have checked the scaling property of polymer liquid crystal Langmuir monolayers by measuring the surface pressure-molecular area isotherm. We have found that the overlap degree of polymer coils in a dense state can be roughly evaluated based on the difference of the coil area and the molecular area.

Acknowledgement

The author would like to thank Dr. Z. H. Luo of Wuhan University, China for kindly supplying the sample of polymer liquid crystal.

References

1. P. G. de Gennes, Scaling Concepts in Polymer Physics (Cornell University Press, Ithaca, New York, 1979).
2. R. Vilanove and F. Rondelez, *Phys. Rev. Lett.*, **45**, 1502 (1980).
3. M. W. Kim, S. N. Liu and T. C. Chung, *Phys. Rev. Lett.*, **60**, 2745 (1988).
4. J. Adams, A. Buske and R. S. Duran, *Macromolecules*, **26**, 2871 (1993).
5. R. C. Weast, (ed.) *Handbook of Chemistry and Physics*, 67th (ed.), (CRC Press, Florida, 1986).
6. Y. M. Zhu, Z. H. Lu and Y. Wei, *Phys. Rev. E* (1994). In press.