# Effect of Molecular Weight on Polymer Monolayer Formation

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Monolayer behavior of poly(*N*-dodecylacrylamide) (PDDA) with various molecular weights on water surface was investigated. The surface - area isotherms changed drastically with the molecular weight. The monolayer becomes more stable and more condensed form with increasing molecular weight. We discuss various factors influencing the monolayer formation of polymeric compounds.

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Recently, polymer Langmuir-Blodgett (LB) films have received much attention from the viewpoint of stable mechanical and thermal properties and high resistance to dissolution by organic solvents.[1-2] Previously, we have succeeded in the preparation of fairly uniform polymer LB films using poly(*N*-alkylacrylamides), especially poly(*N*-dodecylacrylamide) (PDDA). Furthermore using the excellent property of PDDA to form stable monolayer and LB films, we can incorporate various functional groups such as vinylaromatics, trisbipyridine ruthenium complex, and chiral binaphthtol into polymer LB films by the copolymerization method with DDA monomer. We consider that the excellent ability to form stable monolayer of PDDA is attributable to the self-assemble property due to hydrogen bonding based on the amide group.

In the present work, we investigated the surface pressure ($\pi$) - area (A) isotherms of the PDDA monolayer as a function of molecular weight to clarify factors causing to stable monolayer formation of polymeric compounds. It was found that the PDDA monolayer property changed drastically with the molecular weight. The monolayer becomes more stable and more condensed form with increasing molecular weight.

PDDA with various molecular weights (Table1) were prepared by free-radical polymerization in toluene at 60℃ with 2,2'-azobis(isobutyronitrile) as a thermal initiator and 1-dodecanethiol as a chain transfer agent to control molecular weight. All polymers were purified by reprecipitation from a filtered chloroform solution into a large excess of acetonitrile. Molecular weights were determined by a Toyo Soda gel permeation chromatography (GPC) using a polystyrene standard.

The polymers with various molecular weights were spread onto the water surface from chloroform solutions of $10^{-3}$ M to measure $\pi$-A isotherms (Figure 1). It is of great interest that the isotherms varied drastically with the molecular weight. The DDA monomer monolayer forms an expanded form and collapses under only 25mN/m surface pressure. The isotherms for PDDA polymers shows steeper rise in surface pressure and higher collapse pressure than those of DDA monomer. The steep rising in surface pressure of the polymer monolayers becomes more distinct with molecular weight. Eventually, over a molecular weight of 7,000, the PDDA monolayer forms a condensed form and the surface area per monomer unit is close to a constant value of 0.28 nm$^2$/repeat unit which is reported in the previous studies as a limiting surface area of PDDA.

**Table 1.** Polymerization conditions and molecular weight of PDDA

| AIBN (DDA mol%) | $C_{12}H_{25}SH$ (DDA mol%) | Mn | Mw/Mn | DP |
|---|---|---|---|---|
| 0.5 | 0 | 20000 | 1.78 | 84 |
| 10 | 0 | 12000 | 1.57 | 50 |
| 10 | 1 | 9500 | 1.47 | 40 |
| 10 | 2 | 7400 | 1.47 | 31 |
| 10 | 10 | 3200 | 1.24 | 14 |
| 10 | 60 | 1300 | 1.15 | 5.4 |

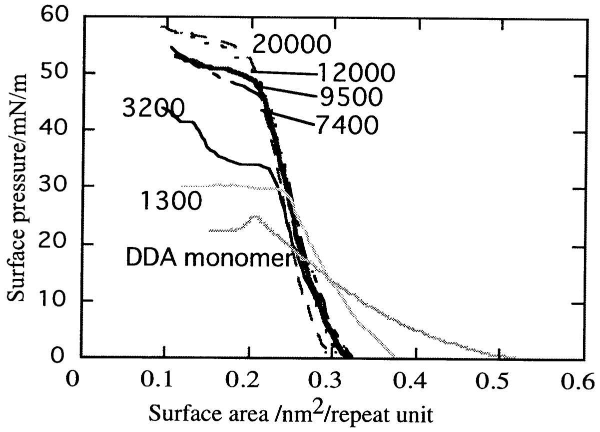

**Figure 1.** Surface pressure-area isotherms of PDDA with various molecular weight.

In a classic concept for stable monolayer formation, both a polar substituent and a hydrophobic tail are considered to be necessary for a hydrophobic - hydrophilic balance. From a standpoint of the balance, polymer monolayer is expected to become less stable with molecular weight, because the polymer becomes too hydrophobic and form a coiled form. However, the effect of molecular weight on PDDA monolayer behavior in the present study shows a reverse tendency.

In previous study,[3] we investigated the effect of pendant alkyl chain length from 8 to 18 carbon numbers in poly (*N*-alkylacrylamides) with molecular weights around 10000 on monolayer formation and the most stable condensed monolayer was obtained from dodecyl substituent. Moreover, it is also concluded that in a series of *N*-alkylacrylamide monomers, the most stable monolayer was formed from *N*-octadecylacrylamide monomer, where a factor of hydrophobic – hydrophilic balance plays an important role as discussed in conventional long alkyl fatty acid monolayers.[4] Different factors are working for the monolayer formation in polymeric materials. The formation of stable polymer monolayer is effected not only by hydrophilic-hydrophobic balance but also by the behavior of polymer main chains and the pendant chains. Although the PDDA behaves as a fexible polymer when it is

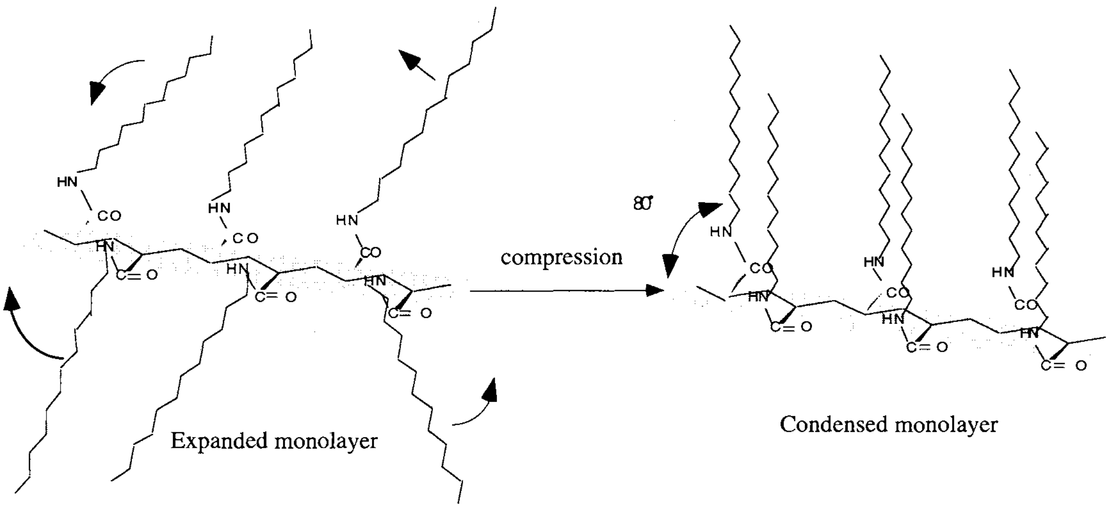

**Figure 2.** Molecular orientation in PDDA monolayer.

**Table 2.** Transfer ratio of PDDA at 20℃

| Mn | 20000 | 12000 | 9400 | 7400 | 4000 | 3400 | 1200 |
|---|---|---|---|---|---|---|---|
| Surface pressure(mN/m) | 30 | 30 | 30 | 30 | 25 | 20 | 20 |
| Transfer ratio down | 0.91 | 0.96 | 0.89 | 0.55 | — | — | — |
| Transfer ratio up | 1.01 | 0.96 | 0.94 | 0.91 | — | — | 0.95 |

spreadon the water surface, the pendant side chains of PDDA gradually stand up from the water surface under compression by a teflon barrier (Figure 2). So polymer main chains change into a rigid form and are closely packed with the orientation shown in Figure 2. In the condensed monolayer (right view in Figure 2), a stress energy is produced around the main chains. A certain main chain length (over 30 repeat units) is necessary to release the stress energy. Thus, the polymers not having sufficient chain length cannot form a condensed form and the pendant alkyl chains are not closely packed (an expanded form) due to an excess strain. This discussion is supported by the following examples; the monolayer of poly(*N*-dodecylmethacrylamide) (PDDMA) gives only an expanded form and low collapse pressure because large stress around the main chain is produced by methyl group attached to the main chain (Figure 3). Moreover, poly(*N*-octadecylacrylamide) (PODA) does not show surface pressure (Figure 3). The cohesive force of the pendant octadecyl chains is too strong, therefore, the polymers aggregate and form a coiled form on the water surface and no monolayer is formed.

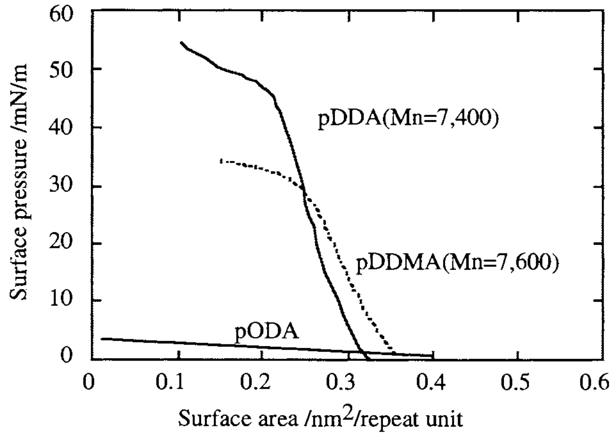

**Figure 3.** Surface pressure-area isotherms of PDDA , pODA and pDDMA.

The condensed monolayer of PDDA is transferred onto a solid support, giving the polymer LB films. Table 2 shows a transfer ratio of the PDDAs with various molecular weights. The transfer ratios also depend on the molecular weight of the PDDAs. The condensed monolayer of the PDDA above 9500 molecular weight is transferred onto a solid support with both up and down strokes with a transfer ratio of $1.0 \pm 0.1$. PDDA with a molecular weight of 7400 can be transferred onto a solid support even with a lower transfer ratio. On the other hand, the monolayer of the PDDA withlower molecular weight is not transferred at any surface pressure, dipping velocity of a solid support and temperatures. Conclusively, the PDDA with higher molecular weights form more condensed monolayer and are transferred regularly on solid supports yielding high quality LB films.

### References and Notes

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