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Molecular Weight Dependence of Shear Viscosity of a Polymer Monolayer: Evidence for the Lack of Chain Entanglement in the Two-Dimensional Plane

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Introduction

Monolayers at the air/water interface have been widely studied as a system providing a feasible quasi two-dimensional space.[1−4] In particular, polymer monolayers are of interest because of the prominent effect of the space dimensionality owing to the restricted conformation of the polymer chain at the interface.

Mechanical properties of polymeric materials are related to the polymer chain morphology. As known for the bulk polymers, the viscosity depends on the molecular weight, and the degree of dependence is altered at a certain critical molecular weight M_c.[5] The strong dependence in the high molecular weight region is explained as the effect of the chain entanglement of the polymers. By the analogy with the three-dimensional case, investigation on the molecular weight dependence of the monolayer viscosity will provide information on the polymer chain morphology in a two-dimensional plane: whether the polymer chains can entangle each other at the air/water interface.

Molecular weight effects on the mechanical properties of polymer monolayers have been investigated by several researchers.[6−9] It is generally accepted that the higher molecular weight of the polymers gives rise to higher elasticity and higher viscosity. However, there are few studies on the mechanical properties in terms of the polymer chain morphology. In this study, we investigated the molecular weight dependence of the viscosity of polymer monolayers using the canal surface viscometry. This study will clarify the chain morphology in the two-dimensional plane.

Experimental Section

Materials. As a sample polymer, we employed poly(vinyl octanal acetal) (PVO) fractionated by GPC. PVO was obtained through the acetalization of poly(vinyl alcohol) (PVA; Wako Pure Chemical and Aldrich) with 1-octanal (Nacalai Tesque). The detailed synthetic procedure was described elsewhere.[10] Each polymer was fractionated by GPC with THF as the eluting solvent, and then all the polymers were purified again by the reprecipitation. GPC was also used for determining the molecular weights of the fractionated polymers. The characteristics of the obtained polymers are listed in Table 1.

Table 1. Molecular Weights of PVO Fractionated by GPC

$10^{-4}M_n$[a]	$10^{-4}M_w$[a]	M_w/M_n
73.8[b]	85.0	1.15
63.1[b]	71.4	1.13
59.3[b]	114	1.93
38.3[b]	51.2	1.34
12.2[b]	21.7	1.77
12.2[c]	14.9	1.23
10.1[c]	11.2	1.12
6.25[c]	7.09	1.14
3.13[c]	3.64	1.17

[a] M_n and M_w were calculated from GPC data and calibrated with light scattering measurement. [b] Source PVA was purchased from Wako Pure Chemical [c] Source PVA was purchased from Aldrich.

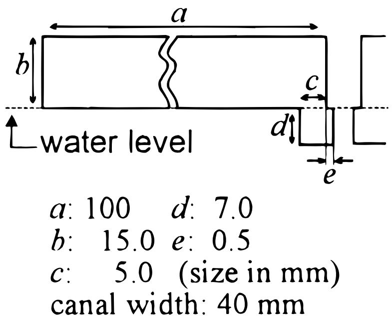
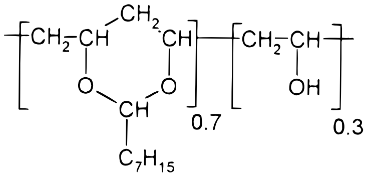


Figure 1. Side-view illustration and dimension of the canal.



Monolayer Preparation. A benzene solution (ca. 0.1 g/L) of the sample polymer was dropped on a clean surface of pure water, which was ion-exchanged, distilled, and then treated with a water purification system (Barnstead NANO Pure II). The subphase temperature was regulated to 20.0 ± 0.1 °C by circulating water under the trough, while the ambient temperature was roughly controlled at 20 °C. All measurements were carried out 20 min after the monolayer preparation to allow the equilibrium of the monolayer and the complete evaporation of the spreading solvent. The equipment was enclosed in a chamber to avoid dust. A homemade Brewster angle microscope[12] was employed for the in situ observation of monolayer morphology at the air/water interface.

Surface Viscosity Measurement. The canal viscometer used was similar to that described in the report by Sacchetti et al.[11] Schematic representations of the canal design and the surface viscosity measurement are depicted in Figures 1 and 2, respectively. The slit width, *w*, was arranged in the range 0.8−2.0 mm with a precision of 0.05 mm. To make a monolayer flow through the canal, a constant surface pressure difference, $\Delta\Pi$, was applied between the two sides of the canal. In this study, the surface pressure was applied and measured only on one side of the canal; that on the

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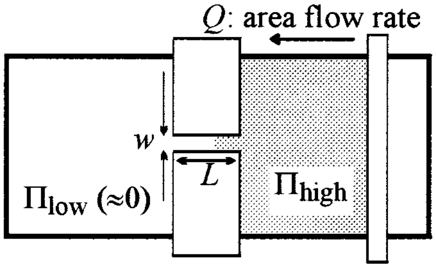

Figure 2. Schematic representation of the surface viscosity measurement. The surface pressure was measured only on the Π_{high} side. The surface pressure difference, $\Delta\Pi$, was obtained by $\Pi_{high} - \Pi_{low}$.

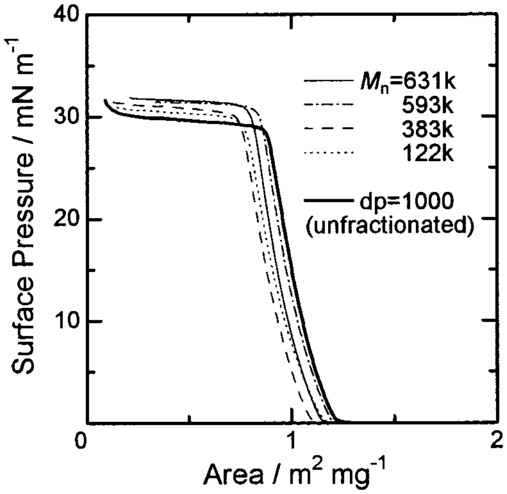

Figure 3. Surface pressure–area isotherms of several samples. The thin lines are isotherms for GPC-fractionated polymers which were synthesized from PVA of dp = 2000. The bold line is that for the unfractionated polymer synthesized from PVA of dp = 1000.

other side was regarded as approximately 0 mN/m because the area on this side was sufficiently large. The higher surface pressure, which was equal to $\Delta\Pi$, was set to be 2.0 mN/m. The area flow rate, Q, was in the range from 0.006 to 0.2 cm^2/s. The surface viscosity, η_s, was calculated by the following equation:[11]

$$\eta_s = \frac{\Delta\Pi w^3}{12LQ} - \frac{w\eta_0}{\pi}$$

where L is the canal length and η_0 is viscosity of water. In the whole range of Q studied here, η_s was constant for a given sample within experimental errors, proving that the use of this equation was valid. The viscosity was measured three times for each sample, and the average value was adopted.

Results and Discussion

Figure 3 shows the surface pressure–area isotherms for several samples of the PVO monolayers studied. The isotherms showed similar profiles with only slight difference. The difference in area was attributed to experimental errors because the area shift showed no specific tendency with the molecular weight change. On the other hand, the plateau pressure where the collapse of the monolayer occurred exhibited a certain tendency: it reached a higher value with the increase in molecular weight. There are two possible explanations for this result. One is that the monolayer of higher molecular weight becomes more rigid and more stable under a higher surface pressure. The other is as follows. Strictly speaking, the compression of the monolayer is a kinetic process, so that the surface pressure depends on the compression rate and the relaxation of the film-forming molecules. The surface pressure is higher for a higher molecular weight polymer under a constant compression rate owing to the longer relaxation time of the polymer chain.

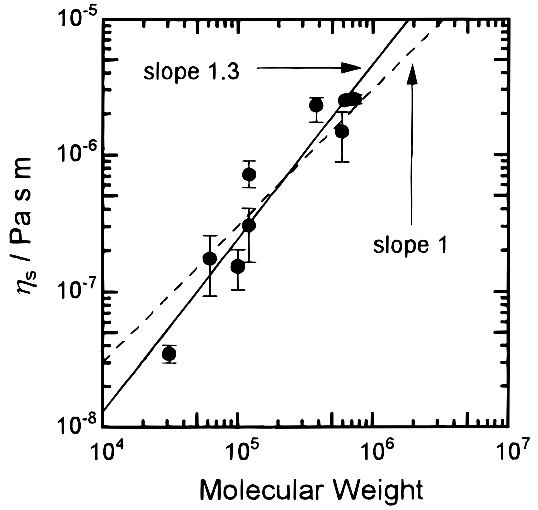

Figure 4. The log–log plot of the monolayer viscosity vs number-average molecular weight. The error bars correspond to the maximum and minimum values observed, and the symbols show the mean value. From the slope of the solid line obtained by the least-squares method, η_s is proportional to the 1.3 power of M. The broken line shows slope 1.0 for reference.

It is generally said that the molecular weight effect on the surface pressure–area isotherms appears in the very low surface pressure region (<0.1 mN/m).[1,3,4] However, our experimental apparatus did not have sufficient sensitivity for the precise discussion on such a low surface pressure under 0.1 mN/m.

Figure 4 shows the molecular weight (M) dependence of the monolayer viscosity (η_s). In this logarithmic plot, the data points are on a line with a slope of 1.3, meaning $\eta_s \propto M^{1.3}$. It is well-known that the shear viscosity, η, of polymer liquids in the bulk state such as polymer melts and concentrated solutions of polymers, is dependent on the polymer's molecular weight, M.[5] While η is proportional to M below a certain critical molecular weight, M_c, the viscosity becomes proportional to $M^{3.4}$ in the high molecular weight region beyond M_c. Such a strong dependence of η is attributed to the chain entanglement of polymers. In our study, η was nearly proportional to M in the whole range and no distinct M_c could be found up to the molecular weight of 10^6, suggesting that there exists little entanglement of the polymer chains in the monolayer at the air/water interface. This fact can readily be understood in consideration of the process of monolayer formation. The monolayer was prepared by spreading a dilute solution of the polymer in which each chain was isolated. Although the chains came close together as the solvent evaporated, they could not overlap since the chains were confined at the interface.

Figure 5 shows an image of the Brewster angle microscopy observation. The PVO monolayer had a flexible and liquid-like character; that is, this monolayer was a two-dimensional melt. de Gennes pictured from the following consideration that each chain is segregated in such two-dimensional polymer melts.[13] In the three-

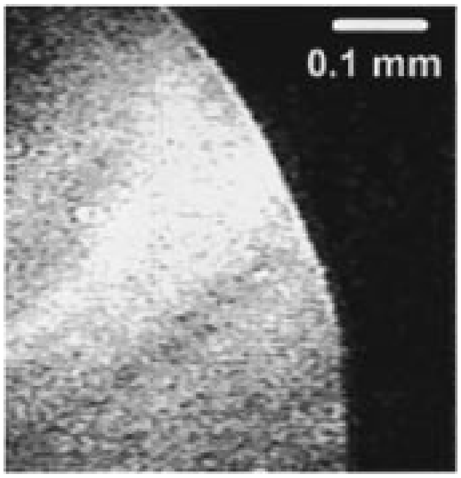

Figure 5. Image of the PVO monolayer viewed by Brewster angle microscopy. Condensed domains (bright part) with smoothly curved boundaries were readily deformed with a surface flow of water, indicating that this monolayer had a flexible and liquidlike character.

dimensional polymer melt with degree of polymerization (dp) of N and bond length of a, the volume occupied by a single polymer chain is $\sim(N^{1/2}a)^3$ and the local concentration of the segments is $\sim N/(N^{1/2}a)^3 = N^{-1/2}a^{-3}$. This means that the chains overlap to make the local segment concentration coincide with the total concentration in the melt. On the other hand, in two-dimensional melts, the local concentration is $\sim N/(N^{1/2}a)^2 = a^{-2}$, indicating each chain is segregated because the local concentration is the same as the total concentration. His theoretical insight into the polymer chain morphology in the two-dimensional plane is valid for our results obtained here.

The monolayer viscosity was not exactly proportional to M: the exponent of M was slightly larger than unity. Although the variation in the slope of the straight line may cause the deviation of the exponent from unity, it can also be explained in terms of the chain end effect, as known for the bulk polymers.[5] When the molecular weight becomes lower, there exist more chain ends in the system which offer additional free areas. The monolayer viscosity in the lower molecular weight region, as a result, becomes lower than the prediction by the proportional relation, resulting in the larger exponent than unity.

Conclusion

We demonstrated that the shear viscosity of a polymer monolayer at the air/water interface is proportional to the 1.3 power of the molecular weight in the range of 10^4-10^6, and no distinct M_c could be found. This indicates that the polymer chains in the monolayer have little entanglement. Although more direct clarification of the polymer chain morphology is required, this result offers evidence that the chains are segregated at the two-dimensional plane.

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