Entanglement Effect on Film Retention of Poly(methyl methacrylate) in Methanol

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Morphology for films of poly(methyl methacrylate) with various molecular weights was observed before and after methanol immersion by using atomic force microscopy so that the effect of chain entanglement on film retention of a polymer in a liquid can be discussed.

Thin polymer films have been widely used in technological applications such as biomaterials, electronic devices, and sensors[1–3] as well as traditional usage including coatings, lubricants, and so on.[4] However, when a polymer film becomes thinner, its physical properties deviate from the corresponding bulk ones.[5–7] This can be mainly explained in terms of surface effect. Thus, understanding physical properties at the surface in polymers is of pivotal importance for the design of thin polymer films. Thus far, we have systematically studied aggregation states and molecular motion at the surface in polymer films and accumulated experimental evidence dealing with how the surface differs from the internal bulk phase.[8] However, if we really think about the aforementioned applications of thin polymer films, the outermost surface of polymers with a different phase such as a solid or a liquid, namely, the interface, should be studied as the next step after understanding polymer surfaces.

We have hitherto studied density profiles of a perdeuterated PMMA (dPMMA) film in various nonsolvents along the direction normal to the interface by specular neutron reflectivity (NR).[9] The general definition of "nonsolvents" is that the liquids can not macroscopically dissolve a polymer. However, careful analysis of the interface for dPMMA with the nonsolvents revealed that the dPMMA/nonsolvent interfaces were much more diffused than the pristine interface with the air. Such a diffuse interface with the nonsolvents would be realized by interfacial roughening and partial dissolution of segments at the outermost region of the film.[9]

Methanol is one typical nonsolvent for dPMMA. Nevertheless, the dPMMA film was strikingly swollen in methanol in addition to the formation of a diffuse interface. The overall content of methanol in the film was surprising and the value was claimed to be 37 vol %.[9b] A typical soft material which can be swollen in liquids is a class of polymer gel. In this case, chemical or physical cross-linking prevents polymer chains from being dissolved into the liquids. However, the dPMMA film used was spin-coated from a solution onto a substrate, and thus, dPMMA chains did not have any cross-linking points. Then, a question that should be addressed is why the film retains its shape although the film was swollen. A possible answer to this question is the presence of chain entanglement. This is because the number-average molecular weight (M_n) of the dPMMA used was 296 k being much larger than the entanglement molecular weight (M_e).[10] The objective of this study is to examine how chain entanglement is important for film retention of a polymer in a liquid, which possesses a good affinity for the polymer.

As a material, monodisperse PMMA with various M_n's such as 9, 18.2, 41.5, 145, and 222 k, which were purchased from Polymer Source Inc., was used without further purification. In the case of our previous NR study,[9] dPMMA was used to confer a contrast to solvents. However, in this study, the morphology of the films was observed as mentioned below. Thus, it was not necessary to use deuterated species. Films of the PMMA were prepared from a toluene solution, spin-coated onto silicon wafers with a native oxide layer. The films were dried under ambient atmosphere at room temperature for more than 24 h and then annealed under vacuum at 423 K for at least 24 h. The film thicknesses evaluated by ellipsometry (M-150, JASCO Co., Ltd.), was approximately 150 nm, which was sufficient to avoid any ultrathinning effects on physical properties of the films. As a liquid, spectroscopic grade methanol was used. To examine the entanglement effect on the film retention, the films were soaked in methanol for 24 h at room temperature without stirring. Thickness and morphology of the PMMA films before and after soaking them in methanol were measured by atomic force microscopy (AFM, SPA300HV, SII NanoTechnology Inc., fitted with an SPI3800 controller).

Figure 1 shows typical topographic images of PMMA films with M_n of 9 and 222 k, in which a part of the film was cut by a blade, before and after methanol immersion. After immersion, they were well dried and annealed under vacuum for 24 h at 423 K. The brighter and darker regions correspond to PMMA phase and the Si substrate, respectively. In the case of PMMA with M_n of 222 k, the area observed was the same before and after the methanol immersion. Comparing panels (a) and (b), it seems that the film was retained during the methanol immersion. The root-mean-square roughness after the immersion was 0.27 ± 0.04 nm and was almost the same as the original one of 0.26 ± 0.05 nm. Hence, it can be claimed that the initial state for the film of PMMA with M_n of 222 k was recovered even after

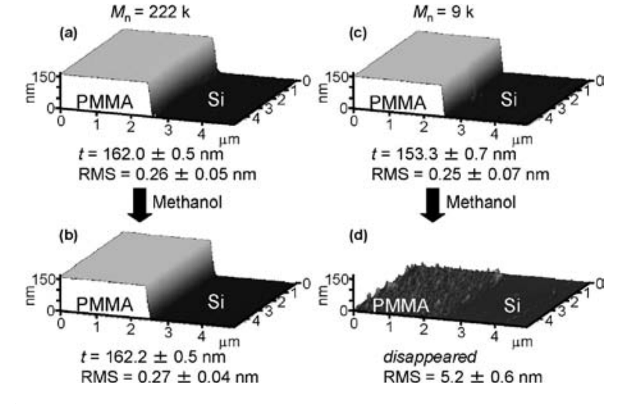

Figure 1. Topographic images of PMMA films in part scratched by a blade; before and after methanol immersion (a) and (b) for $M_n = 222$ k, (c) and (d) for $M_n = 9$ k.

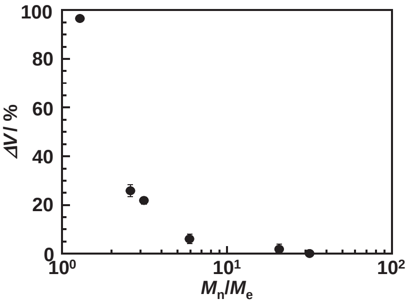

Figure 2. Volume decrement of the film (ΔV) of PMMA as a function of M_n/M_e.

the swelling by methanol molecules. On the other hand, in the case of PMMA with M_n of 9 k, the film surprisingly disappeared after the methanol immersion, as shown in panel (d). The M_e of PMMA is 7 k[11] and is comparable to the M_n of 9 k.

To study how the entanglement effect is crucial for film retention, the film morphology of PMMA with various molecular weights was observed after methanol immersion for a given time at room temperature and the successive drying. Figure 2 shows the relation between volume decrement of the film (ΔV) after methanol immersion and M_n/M_e. The abscissa is an index of the number density of the chain entanglement in the film. The ΔV should correspond to what extent the PMMA chains transfer into the methanol phase. When the chain entanglement was not good enough to retain the film geometry, ΔV increased with decreasing M_n/M_e. According to many rheological data, this would be the case at $M_n/M_e < 10$.[10] Actually, PMMA chains seem to be transferred into the methanol phase at $M_n/M_e <$ 3–4. Interestingly, at $M_n/M_e < 2$, most chains disappeared from the substrate. This is in good accordance with a well-established concept of chain entanglement. That is, if $M_n/M_e > 2$, it seems reasonable to imply that an apparent network structure is developed in the system because a chain is supposed to possess two entanglements, like cross-linking points. Besides, the film collapse in methanol agrees with our experience that the M_n/M_e value must be larger than 2 to prepare a polymer film with mechanical properties which are good enough for handling.

As an alternative explanation, one should also consider the fact that the solubility of a polymer into a liquid generally becomes better with decreasing molecular weight and is controlled by the product of the Flory–Huggins interaction parameter (χ) and the degree of polymerization (N). Thus, the χ parameter for PMMA with methanol is discussed here. According to van Laar–Hildebrand, the χ parameter can be given as follows,[12]

$$\chi = 0.35 + (V_S/RT) \cdot (\delta_S - \delta_P)^2 \qquad (1)$$

where V_S is solvent molar volume, and δ_S and δ_P are solubility parameters for the solvent and polymer, respectively. The solubility parameters for methanol and PMMA are 29.6 and 22.7 $\mathrm{MPa}^{1/2}$, respectively, and the solvent molar volume is 41 $\mathrm{cm}^3/\mathrm{mol}$.[12] From the equation, the χ parameter for PMMA–methanol at 298 K is estimated to be 1.14 which is an unrealistic number for a miscible system. Thus, the results at $M_n/M_e <$ 3–4 in Figure 2 can be hardly explained in terms of the dissolution of whole chains into methanol. Taking into account chemical structures of PMMA and methanol, it is likely that the chemical interaction between them is relatively good because of the presence of hydrogen bonding. Thus, methanol molecules can penetrate into the PMMA film. Then, the osmotic pressure of methanol in the film increases to gain mixing entropy. That is, stress is induced in the film due to methanol penetration. If the film does not possess mechanical strength owing to a lack of chain entanglement, it should be broken under such a condition. This would be what was observed at $M_n/M_e <$ 3–4 in Figure 2.

In conclusion, the effect of chain entanglement on the film retention of PMMA in methanol was discussed on the basis of AFM. Although methanol is a typical nonsolvent for PMMA, chains with M_n lower than $10M_e$ were removed from on the substrate after methanol immersion for 24 h. However, it seems that the phenomenon should be a dynamic process and thus should be dependent on immersion time and temperature. A more conclusive study including these effects will be reported in the near future.

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