

IN-SITU STUDY OF THE SOLVENT ANNEALING PROCESS OF THIN POLYMER FILM

Huanhuan Zhang ^{ac}, Lin Xu ^b, Yuqing Lai ^a, Tongfei Shi^{*a}

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China; *E-mail tfshi@ciac.ac.cn (T.F.S)

^b Laboratory of Surface Physics and Chemistry, Guizhou Normal College, Guiyang 550018, P. R. China;

^c University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

ABSTRACT

Solvent annealing is an important method to control the surface morphologies, the orientation and order of microdomains in polymer thin films¹. On nonwetting substrate, the solvent annealing process of thin polymer film includes the swelling process and the dewetting process. However, owing to difficulties in in-situ analysis of the swelling process and dewetting process of ultra-thin films at the same time, one used to focus on the single swelling process² or single dewetting process³, which make the correlation between swelling and dewetting is unclear. In the paper, we combine spectroscopic ellipsometry with optical microscopy to in-situ study the solvent annealing process of thin polystyrene (PS) films. We use quantitative experimental results to analyze the swelling process and the influence of swelling film structure on the dewetting kinetics of thin polymer films. In the case of PS with high molecular weight, the curve of swelling degree with time discloses the relaxation of the long polymer chains accompanies the diffusion of acetone molecules. However, in the case of PS with low M_w , the whole swelling process cannot be observed because the dewetting of thin PS film rapidly occurs before the equilibrium of swelling is reached. The results of spectroscopic ellipsometry prove that acetone molecules can form ultrathin enriched layer between the PS film and the solid substrate during the swelling process of PS films with low M_w , and the enriched layer thickness decreases with the increase of the original PS film thickness; but the acetone enriched layer cannot form in the case of PS with high M_w . The acetone enriched layer greatly influences the dewetting kinetics of thin polymer films and is the main reason behind the exponential kinetic behavior in the case of PS film with low M_w .⁴

Acknowledgement: This work is supported by the National Natural Science Foundation of China (51503048, 21234007, 51473168).

References:

¹ Bai, W.; Yager, K. G.; Ross, C. A. *Macromolecules* **2015**, *48*, 8574

² Visser, T.; Wessling, M. *Macromolecules* **2007**, *40*, 4992-5000.

³ Verma, A.; Sekhar, S.; Schan, P.; Reddy, P. D. S.; Sharma, A. *Macromolecules*, **2015**, *48*, 3318.

⁴ Zhang, H. H.; Xu, L.; Lai, Y. Q.; Shi, T. F. *Phys.Chem.Chem.Phys.* **2016**, *18*, 16310