Influences of chain heterogeneity on instability of polymeric thin films: Dewetting of polystyrenes, polychloromethylstyrenes and its copolymers

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Abstract

This study compares the stability of various polymeric thin films supported on SiO_x/Si substrate. Dewetting behaviors of polystyrenes (PS), polychloromethylstyrenes, and random poly(styrene-*co*-chloromethylstyrene)s are investigated by utilizing atomic force microscopy. A systematic addition of the chloromethylstyrene (ClMS) unit into PS chain causes the increase of segment polarity, affecting interfacial and interchain interactions in thin films. It is found that stability of the polymeric films depends on two major parameters, ratio of the ClMS unit and film thickness. For ∼5 nm thick film, the addition of only 5 mol% ClMS unit causes a drastic increase of its stability, attributed to the enhanced interfacial interactions between ClMS group and SiO_x layer. Further increasing the ClMS mole ratio to 20, 45, and 100% is accompanied by a systematic increase of the film stability. Thicker films (thicknesses ∼22 and ∼45 nm) of the copolymer with 5 mol% ClMS unit exhibit rather different behavior. They are found to be less stable compared to the PS films. However, the films of copolymers with ClMS unit of 20, 45, and 100% are still much more stable than the PS films. These dewetting behaviors of the copolymers are correlated to the interfacial interactions, interchain interactions and segmental segregation in thin films.
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1. Introduction

Polymeric thin films are very important for wide range of technological applications. Tremendous scientific efforts, therefore, have been dedicated for exploring parameters that dictate their behaviors [1,2]. When polymeric chains are fabricated into thin film, their physical properties tend to deviate from the bulk counterparts, caused by various factors such as interfacial interactions and chain confinement [1,2]. The dominance of interfacial interactions in thin film results in many interesting phenomena such as the increase/decrease of glass transition temperature (T_g) [3–5], surface ordering and surface segregation [1,2,6–8]. The decrease of film thickness may also cause an instability, which eventually leads to the dewetting on substrate [1,2,9–13]. These molecular behaviors are crucial for the development of various applications including surface coating

and modification, adhesives, and insulating layer for microelectronics, where polymeric films progressively become thinner. In addition, knowledge about the dewetting of thin film can be utilized to fabricate various types of nano/microstructures of desired materials on solid substrates [14–19].

The dewetting behaviors of polystyrene (PS) thin films cast on SiO_x/Si have been extensively investigated by experimental and theoretical studies [1,2,9,13]. A general dewetting process can be summarized as follows. Upon annealing above T_g, the unfavorable interactions between PS and SiO_x/Si substrate and the increase of thermal interfacial fluctuation cause the formation of holes in thin film. The holes expand upon increasing the annealing time and eventually coalesce into interconnected polygon. In final stage of dewetting process, the connected domains disintegrate into hemispherical droplets [9]. Kinetics of the whole process can be controlled by varying annealing temperature and molecular weight of the polymer [9–13]. The dewetting can take place via spinodal and/or heterogeneous nucleation mechanisms [1,2]. For the spinodal one, an increase

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Table 1
Number averaged molecular weight (M_n), polydispersity (M_w/M_n) as determined by GPC and glass transition temperatures (T_g) of polymers used

Polymers	Abbreviation	M_n (g/mol)	M_w/M_n	T_g (°C)
Polystyrene	PS11K	11,000	1.05	93
Polystyrene	PS33K	33,000	1.04	103
Polystyrene	PS942K	942,000	1.08	110
Polychloromethylstyrene	PClMS8K	8000	1.42	77
Polychloromethylstyrene	PClMS29K	28,800	1.40	76
Random copolymer	P(S$_{0.95}$-co-ClMS$_{0.05}$)[a]	29,200	1.12	101
Random copolymer	P(S$_{0.80}$-co-ClMS$_{0.20}$)[a]	27,900	1.18	101
Random copolymer	P(S$_{0.55}$-co-ClMS$_{0.45}$)[a]	31,100	1.48	105

[a] Mole ratios of styrene and chloromethylstyrene units in the random copolymers.

of interfacial fluctuation induced by thermal energy leads to the formation of correlated holes, which are characterized by a specific wavelength [12]. The heterogeneous nucleation, on the other hand, is mainly caused by the heterogeneity of surface energy of substrate and the presence of dust particles [10]. The dimension and position of the holes formed via this mechanism are random.

Since many applications require continuous films, scientific community has explored the procedures to suppress the dewetting of polymeric thin films [20–36]. There are various factors that affect the stability of thin film, including polymer–substrate and interchain interactions [20,28,29,34], surface morphology of substrate [14] and the presence of nanoparticles [21,22,24, 25]. One could increase the film stability by controlling these parameters. It has been demonstrated that the difference between surface energy of substrate and polymers can be tuned by modifying the surface layer, achieved by utilizing polymer brushes [26,36] and other approaches [20,23,32,37]. Adding trace amount of diblock copolymers [27,33], dendrimer [30], hyperbranched [31] and long chain polymers [35] into system has also been shown to be an effective method to retard the dewetting.

The tuning of polymer–substrate interfacial interactions, which in turn leads to the suppression of dewetting kinetics, can also be achieved via the modification of polymeric chain itself. It was demonstrated that the sulfonation of polystyrene resulted in a great improvement of the stability of thin films [28,29]. This was attributed to the increase of ionic–ionic interchain interaction and ionic–dipole interfacial interaction in the system. However, study involving this approach still receives slight attention. In this study, the influences of incorporated heterogeneous group on the stability of thin film are further addressed. The dewetting behaviors of various polymers with systematic modification of chemical structures, which causes a gradual change of chain polarity, are investigated. Understanding these parameters in detail could be used for designing the materials that are appropriate for desired applications. Series of PS, polychloromethylstyrenes (PClMS) and its random copolymers P(S$_x$-co-ClMS$_y$) (see chemical structure in Fig. 1) are used as a model system. The existence of chloromethyl group in PS hardly affects the glass transition temperature (see Table 1). Mole ratios of the ClMS unit in the copolymers are 0.05, 0.20, and 0.45. Their molecular weights are approximately the same. The addition of chloromethyl group into PS chain is found to play crucial roles on the dewetting behaviors of thin film
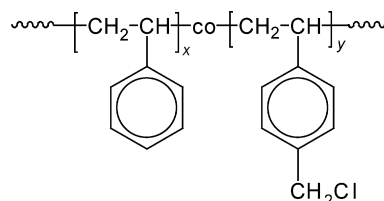

Fig. 1. Chemical structures of random copolymers poly(styrene-*co*-chloro-methylstyrene) P(S$_x$-*co*-ClMS$_y$). Mole ratios of the two repeat units (x:y) are (1:0), (0.95:0.05), (0.80:0.20), (0.55:0.45), and (0:1).

due to the variation of interfacial and interchain interactions. The dipole–dipole interaction in this system is weaker than the ionic–dipole interaction of sulfonated polystyrene system investigated in previous studies [28,29]. Some discrepancy of the results is expected. In fact, effects of the ClMS group on film stability are found to depend on film thickness. Therefore, the first section of this report presents the studies of films with thickness of ∼5 nm. It is followed by the dewetting behaviors of the thicker films with thickness of ∼22 and ∼45 nm.

2. Experimental

The polymers used in this study were purchased from Polymersource Inc. (Canada). The molecular weight, polydispersity (M_w/M_n), determined by gel permeation chromatography, and ratio of the ClMS group are listed in Table 1. The content of ClMS group in each polymer was confirmed by ^{1}H NMR spectroscopy, which compared the integrated peak area of NMR signal of chloromethyl protons (4.5 ppm) to that of the aromatic protons (6.4–7.1 ppm). The copolymers were synthesized by using controlled radical polymerization process. Therefore, random distribution of the two repeat units along the polymeric backbone was anticipated. Since polarity of the two monomers is different, one may also expect the existence of some blocks of each repeat unit, particularly in the copolymer with 45 mol% of ClMS group. This molecular parameter is not known in these samples. However, the detection of only one glass transition region by differential scanning calorimetry (DSC) suggests that the quantity of blocked segments is minimal. In addition, their existence should not affect the results of this study because they still exhibit the same type of dipolar interchain and interfacial interactions.

Thermal properties of all polymers were measured by differential scanning calorimetry (Perkin–Elmer DSC7) using scan-