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Application of mean-field theory to the spin casting of polystyrene and poly(methyl methacrylate) blend films from toluene

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Highlights:

- In situ light scattering can be used to monitor film thermodynamics
- Flory-Huggins theory describes the spin-coating of immiscible polymer blends
- Polymers retain their random walk configuration during spin-coating
- Spin-coating thermodynamics independent of initial solvent concentration

Keywords: spin-coating, phase separation, Flory-Huggins theory

Abstract. The Flory-Huggins free energy of mixing is shown to be appropriate for the analysis of the temporal evolution of a ternary blend of polystyrene and poly(methyl methacrylate) during spin-coating from toluene using an in-situ light scattering technique. For the range of concentrations studied, both the onset of film instability and the observation of a scattering ring occur at the same toluene volume fraction. The success of Flory-Huggins theory indicates that polymer chains retain random walk characteristics during spin-coating. It is also concluded that the thermodynamics of phase separation during film formation is independent of the initial solvent concentration.

More often than not polymers are immiscible due to the low gain in entropy upon mixing. Spin coating can be used to make films of immiscible polymers, for example for optoelectronic devices, in which case the phase separation length scale, the uniformity and the thickness of films affects the quality of the devices. Despite the longstanding utility of the technique, the spin-coating mechanism is still not fully understood.

In situ light scattering techniques enable significant progress in the understanding of the phase separation in spin-coated films [1-3]. Scattering data reveal two distinct features: the first is the onset of off-specular scattering and corresponds to the first observation of an instability in the film, and the second is the observation of a well-defined scattering peak. It is believed that initial phase separation in spin-coated films is due to a stratified layer as a consequence of the different surface energy of the polymers [4]. In fact, it has been shown experimentally and theoretically that the presence of a surface breaks the symmetry of bulk phase separation and can even lead to the formation of layers [3, 5, 6]. It has been postulated that a gradient in the surface tension due to a gradient in the evaporation rate in the film creates Marangoni convection cells which break the self-stratified structure [3, 7-9].

Films deposited from solution give rise to distinct morphologies but very little is known about the thermodynamic path followed or the kinetics of the phase separation [10]. The thermodynamics of polymer blend films is usually described by Flory–Huggins mean field theory, which describes the free energy of mixing of bulk polymer solution; at a given pressure and temperature it depends on the volume fraction of all the components, the interaction between the components and the length of the polymers.

Recently a semi-empirical model was presented, which enabled a modelling of the solvent and the polymer volume fraction [11]. Here, this model is used alongside Flory-Huggins theory to calculate the free energy of polystyrene (PS) and poly(methyl methacrylate) (PMMA) films coated from solution with equal ratio of polymer and different concentration of toluene. The expression of the Flory–Huggins free energy for a ternary system with equal amount of polymer can be expressed as

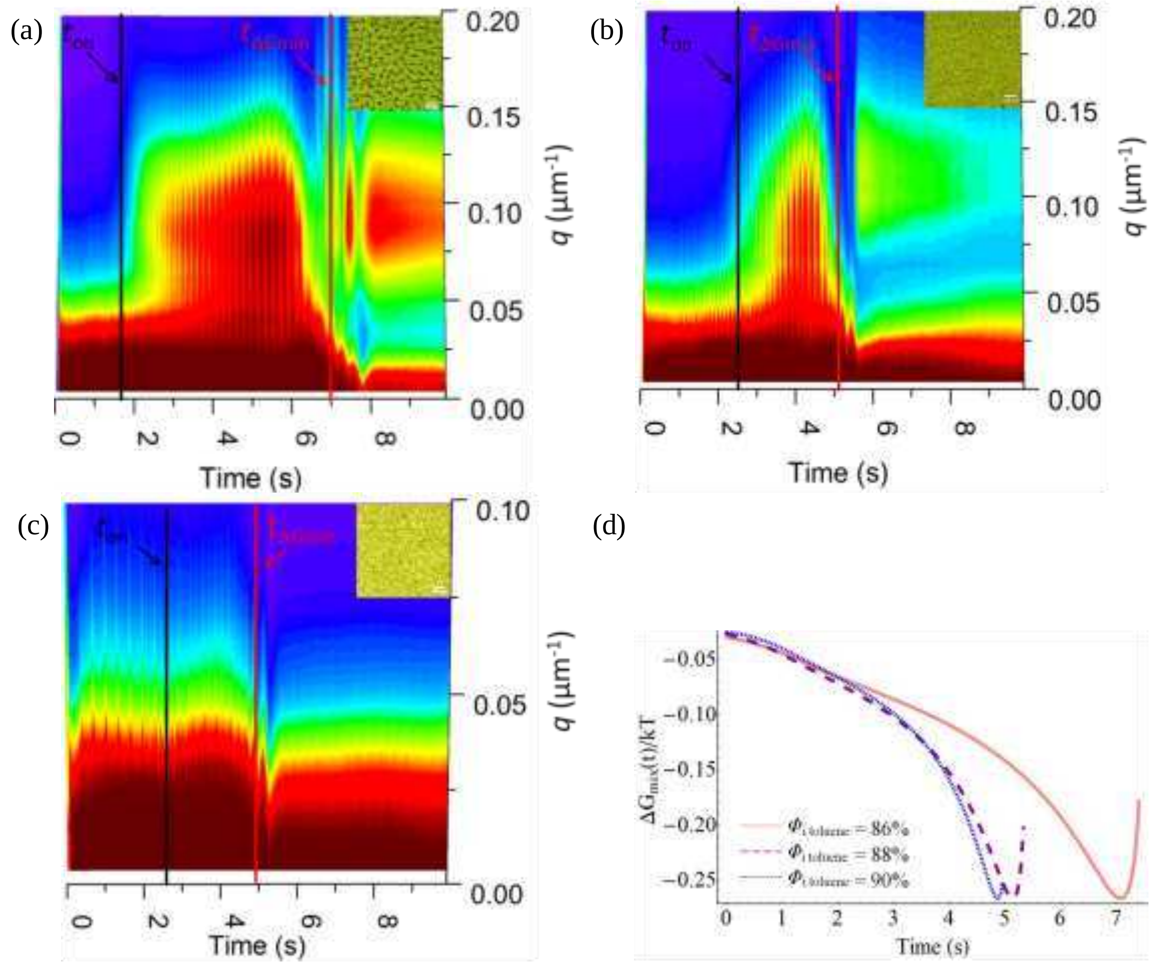

Figure 1. Off-specular scattering (q) for the film cast from a solution of (a) 7% PMMA, 7% PS, and 86% of toluene; (b) 6% PMMA, 6% PS, and 88% toluene; and (c) 5% PMMA, 5% PS, and 90% toluene. The insets in (a), (b), and (c) show optical images of the films (scale bars 100 µm). (d) Free energy of mixing as a function of time for the film cast from solution containing 90% of toluene (dotted line), 88% of toluene (dashed line), and 86% of toluene (solid line)

$$\frac{\Delta G_{\mathrm{mix}}}{k_B T} = \phi_p\left(\frac{1}{N_1}+\frac{1}{N_2}\right)\ln\phi_p + \left(1-2\phi_p\right)\ln\left(1-2\phi_p\right) + \phi_p\left(1-2\phi_p\right)\left(\chi_1+\chi_2\right)+\phi_p^2\chi_3. \qquad (1)$$

In this equation N_1 is number of monomers in the PS chain, N_2 is the number of monomers in the PMMA chains, χ_1 is the interaction parameter between PS and toluene, χ_2 is the interaction parameter of PMMA and toluene, χ_3 is the interaction between PS and PMMA, $\Phi_p(t)$ is the time-dependent polymer volume fraction of each component, so that the total polymer volume fraction is $2\Phi_p(t)$, and $1 - 2\Phi_p(t) = \Phi_{\mathrm{toluene}}(t)$ is the time-dependent toluene volume fraction. In thin films $\Phi_p(t)$ can be approximated by $\Phi_p(t) = h_f/2h(t)$ in which h_f is the final thickness and h(t) is the thickness at a given time. This thickness calculation does not depend on the solution conformation of polymer chains, but it does assume that the film is uniform. A more sophisticated calculation of film thickness has been applied, and it was found to agree with the simple method used here [12].

In order to follow the thermodynamics during spin coating, films were cast from toluene solution on silicon wafers with an approximate surface area of 1 cm^2. Uniform PS and PMMA with molar masses of 96 and 106 kg mol^{-1} respectively were purchased from Polymer Laboratories. The polymer solutions had a solvent concentration of 90%, 88%, and 86% by weight. The densities of toluene, PS, and PMMA were taken to be equal to 0.886 g cm^{-3}, 1.49 g cm^{-3}, and 1.05 g cm^{-3} respectively. Solutions with less toluene content could not be investigated due to the poor resolution of the reflectivity data. Each experiment was performed three times and the results were routinely reproducible.

The film formation was followed in situ by collecting scattering and reflectivity data from a He-Ne laser with a wavelength of 633 nm, which was mounted at 45° to the spin coater. The intensities of the incoming and reflected beams were measured with two photodiodes and both specular and off-specular reflectivity were recorded. The scattered light was used to monitor the development of lateral structure in the film. The apparatus has been described elsewhere [1, 2]. The temperature during the coating was kept constant at 21°C by using a custom-made cell fitted with a copper coil. Two pipes connected the coil to a water circulator. The pump of the circulator allowed a constant motion of the water in the coil. The temperature in the cell, which is referred to as the coating temperature, was controlled by setting the temperature of the circulator and was monitored with a digital thermometer. The temperatures of the solutions were controlled by immersing them in a beaker which in turn was immersed in a water bath. The temperature of the water bath was set to be equal to the coating temperature. Prior to coating, the silicon wafer was also allowed to reach the coating temperature by enclosing it in the cell. The data presented were obtained when the coating temperature was set to 21°C. The light scattering images are unwrapped from the centre of the scattering ring and radially averaged. The radial average intensities were plotted as function of time, this graph having units of pixels versus time. A TEM grid of 10 nm was used to correlate the number of pixels to the scattering vector **q**. The films were spun at ω = 2000 rpm and their thicknesses were measured using an ellipsometer.

The semi-empirical model which enables h(t) to be modelled is described elsewhere [11]. The interaction parameters of the system are equal to $\chi_1 = 0.44$, $\chi_2 = 0.409$, and $\chi_3 = 0.041$, where the lattice parameter is taken to be 4.8 Å [13, 14]. Here the solvent and polymer concentrations are expressed in percentage by weight, although these have been converted into volume fractions in the subsequent analysis. **Figure 1** (**a** and **b**) shows the radial average off-specular scattering profiles for the film deposited from solutions with 86% and 88% toluene. Here, three stages can be observed. At first there is no light scattering which implies that the films are homogeneous. The beginning of the second stage is marked by a black line which represents the onset of instabilities and is denoted t_{on}. This phase ends with the appearance of dominant length scales of 71 µm and 52 µm for films cast from a toluene solution of 86% and 88%, respectively. For the film cast from solution with 90% of toluene there is no scattering ring.

Figure 1d shows a plot of the free energy as a function of time. The time at which the minimum in the free energy is reached is defined as $t_{\Delta Gmin}$. In the off-specular scattering profile $t_{\Delta Gmin}$ is marked by a red line and corresponds to the time at which the dominant length scale appears for the film deposited from the solution with 88% and 86% toluene. Before $t_{\Delta Gmin}$ there is enough toluene in the film to shield the interaction between the PS and PMMA. At $t_{\Delta Gmin}$ the free energy increases because the increase in enthalpic contacts between PS and PMMA overcomes the compatibilizing effect of toluene. After this point a ring is observed in the off-specular data, which is indicated by the enhanced scattering at $q = 0.10\ \mu m^{-1}$. This is not visible in **Figure 1c**, although there is some low intensity scattering for $q > 0.08\ \mu m^{-1}$, which is barely visible in the plot. It is therefore likely that the limitations of the instrument prevent quantitative measurements at this toluene concentration.

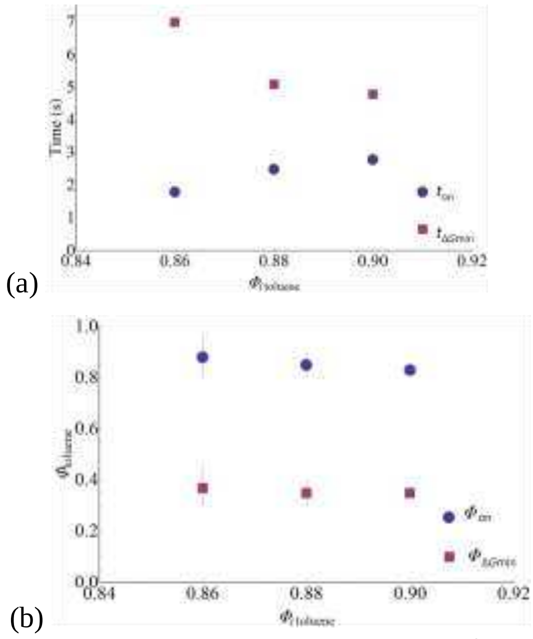

Figure 2. (a) $t_{\Delta Gmin}$ (squares) and t_{on} (circles) as a function of the initial toluene volume fraction $\Phi_{i\ toluene}$. (b) $\phi_{\Delta Gmin}$ (squares) and Φ_{on} (circles) as a function of the initial toluene volume fraction $\Phi_{i\ toluene}$.

In order to compare the kinetics of the phase separation in the three films t_{on} and $t_{\Delta Gmin}$ were compared. **Figure 2a** is a plot of t_{on} and $t_{\Delta Gmin}$ as a function of the initial toluene content in the coated solution. An increase in the initial toluene concentration changes both t_{on} and $t_{\Delta Gmin}$. A larger initial polymer concentration means that the evaporation rate is slower. That the time scales are different is due to the different evaporation rates and so t_{on} and $t_{\Delta Gmin}$ as presented in **Figure 2a** cannot be compared. However, it is possible to calculate $\Phi_{toluene}(t_{on})$ and $\Phi_{toluene}(t_{\Delta Gmin})$, and these are included in **Figure 2b**. Here, $\Phi_{toluene}(t_{on})$ and $\Phi_{toluene}(t_{\Delta Gmin})$ are independent of $\Phi_{i\ toluene}$, which again indicates that standard mean-field theory is suitable for analysing the thermodynamics of polymer films during spin coating.

The entropic component in Flory-Huggins theory assumes that chains follow a random walk conformation. It can therefore be concluded that, because the Flory-Huggins model is successful at explaining solution behaviour during spin coating, the polymer chains retain this random walk. For this to happen, it means that the polymer relaxation time scales are less than those of the spin coating, i.e. inverse shear rate, which is related to ω^{-1}, and inverse strain rate, $h(t)/(\partial h/\partial t)$.

Here, the free energy of mixing during the spin coating of polymer blends of PS, PMMA and toluene was calculated and correlated to in situ off-specular scattering data. As the solvent evaporates the number of configurations increases which results in the lowering of the free energy, reaching a minimum when the interaction between the polymer chains increases and phase separation takes place. Although the kinetics and the morphology of films coated from solution with different concentration are very distinct, the minimum in the free energy takes place at the same toluene concentration. In conclusion, despite spin coating being a non-equilibrium process, Flory–Huggins theory can be used to explain the film formation thermodynamics.

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