



Critical residence time in metastable region – a time scale determining the demixing mechanism of nonsolvent induced phase separation



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ABSTRACT

The present work focuses on studying the relationship between the time period of a polymer solution staying in the metastable region and the resulting porous structure after phase separation of the solution. We employed the technique of FTIR microscopy to determine the composition change in the PMMA/NMP (*n*-methylpyrrolidone) solution after its contact with water. By plotting the composition change on the ternary phase diagram of PMMA, NMP and water, and identifying the times that the composition path intersected with the binodal and the spinodal, we then determined the residence time of the solution in the metastable region (t_m). For each polymer solution, we identified a critical residence time (t_{mc}) that played a dominant role in determining the phase separation mechanism and the resulting porous structure: with t_m less than t_{mc} , the corresponding structure was bi-continuous (typical structure resulted from spinodal decomposition); with t_m greater than t_{mc} , the corresponding structure was cellular (typical structure from the mechanism of nucleation and growth). The results show that t_{mc} depended on the polymer molecular weight and the polymer concentration in casting solution. And the dependences can be superimposed into one curve as the polymer concentration was normalized by the polymer chain entanglement concentration. With the relationship between t_{mc} and the normalized polymer concentration and a simple model for the effective diffusivity of water in the polymer solution, we developed a model equation to estimate the positions in PMMA membranes where structure transition occurred from bi-continuous to cellular. Good agreement was obtained between the calculated transition positions and the experimentally determined ones.

1. Introduction

Nonsolvent-induced phase separation (NIPS) is the most widely used process to prepare commercial polymeric membranes [1–3]. In the process, polymer nonsolvent is introduced to a homogenous polymer solution to induce phase separation, resulting in a polymer-rich phase that later turns into the membrane matrix after polymer precipitation, and a polymer-lean phase of which the occupied spaces become the membrane pores after the lean phase is removed from the demixed solution. The polymer solution can phase separate via the mechanism of nucleation and growth (NG) or spinodal decomposition (SD) [4]. Phase separation via NG with the polymer-lean phase as the nuclei results in cellular pores embedded in polymer matrix, while SD gives bi-continuous (lacy) structure with inter-connected pores [4]. Though most of the research works related to NIPS presumed the demixing mechanism was NG, it has been identified that the demixing mechanism can be SD by using light scattering to investigate the domain growth during NIPS [5,6].

Via which mechanism a polymer solution demixes is strongly dependent on where the solution composition is located in the phase diagram when phase separation occurs [4]. For a binary polymer solution (polymer and solvent) with an upper critical solution temperature, the typical temperature-composition phase diagram is shown in Fig. 1(a). The binodal and the spinodal divide the diagram into three regions: homogeneous, metastable, and unstable. Thermodynamically, a solution would demix via NG if its composition is located in the metastable region (in between the binodal and the spinodal) and would demix via SD if the solution composition is located in the unstable region (below the spinodal). However, not only thermodynamics but also kinetics plays important roles in determining the demixing mechanism. For example, if one quenches a polymer solution from A to B as shown in Fig. 1(a), the demixing mechanism depends on the cooling rate: the solution demixes via NG with a slow cooling rate and via SD with a fast cooling rate [7]. The kinetics is important because it takes time for the nuclei to form in the metastable region. Only when the cooling rate is low enough for the nuclei to form in the metastable

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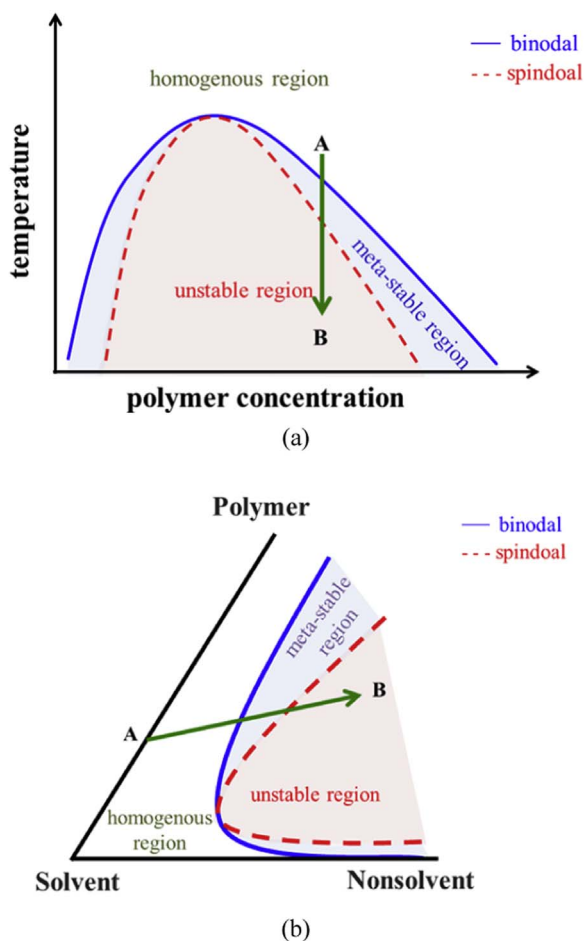


Fig. 1. Schematic phase diagrams of polymer solutions: (a) temperature-composition phase diagram for a binary polymer solution; (b) ternary phase diagram for a solution of polymer/solvent/nonsolvent.

region, the solution demixes via NG; otherwise, the solution still demixes via SD even its composition reaches the metastable region first. The important role of cooling rate in determining the phase separation mechanism has long been identified for researches on thermally induced phase separation (TIPS).

For NIPS, phase separation of a casting solution is not induced by cooling but by introducing polymer nonsolvent into the solution. A typical ternary phase diagram is schematically plotted in Fig. 1(b). Similar to Fig. 1(a), there are homogeneous, metastable, and unstable regions divided by the binodal and the spinodal. Like TIPS, the phase separation mechanism of NIPS is affected by not only thermodynamics but also kinetics. Though the solution composition path during membrane formation (e.g., from A to B in Fig. 1b) enters the metastable region first and then the unstable region, how the solution phase separates depends on how long the solution stays in the metastable region. The solution demixes via NG only when the mass transfer is slow enough to allow the solution to stay in the metastable region long enough for nuclei to form; otherwise, the solution demixes via SD. From the analogy between TIPS and NIPS, it is not difficult to infer that mass transfer rate plays an important role in determining the solution demixing mechanism during NIPS. However, it is more difficult to get insight into the interplay between phase separation mechanism and mass transport for NIPS than to understand the role of quench rate in TIPS, because solution composition is harder to measure than temperature. To get more understanding on the interplay between mass transport, solution property, and membrane structure for the NIPS process, the present work employed the technique of FTIR microscope to measure the composition change in casting solution and

to determine the time period that the solution stayed in the metastable region (t_m), with focus on the relationship between t_m , phase separation mechanism and membrane structure.

The technique of FTIR microscopy has been used to quantify the mass transport for polymer-film dissolution [8,9], drug controlled-release [10], and vapor-induced phase separation [11,12]. We here used the technique to determine the composition change in polymer solution in a liquid cell while the solution was in contact with nonsolvent, then constructing the composition path on the corresponding ternary phase diagram of polymer, solvent, and nonsolvent. By identifying the times that the solution composition path intersected with the binodal and the spinodal, we could thus determine t_m . With t_m and the corresponding porous structures at different positions in the polymer solution, we were able to analyze the relationship between t_m and the resulted porous structure. We found a critical t_m , represented by t_{mc} , for each solution we studied: with t_m less than t_{mc} , the corresponding structure was bi-continuous (typical structure for phase separation via SD); with t_m greater than t_{mc} , the corresponding structure was cellular (typical structure for phase separation via NG).

On the basis of the two time scales (t_m and t_{mc}), we were able to explain why the porous structure inclined to be bi-continuous near the membrane surface and turned to cellular at deeper positions. And simple models for t_m and t_{mc} were developed to predict the positions in membranes where structure transition occurred from bi-continuous to cellular. In addition, we investigated the effect of polymer molecular weight on t_{mc} and on solution viscosity. And the results show that there was a close relationship between t_{mc} and the degree of chain entanglement in polymer solution.

2. Experimental

2.1. Material

Poly(methyl methacrylate) (PMMA) with two molecular weights were used for the study: one with an average molecular weight (MW) of 120,000 (from Aldrich) and the other with MW of 25,000 (from ECHO Chemical). The solvent used to dissolve PMMA was the reagent grade N-methyl-2-pyrrolidone (NMP), purchased from Fluka and used without further purification. And all water used was de-ionized.

2.2. Membrane preparation

PMMA was dissolved in NMP to form homogenous polymer solution, kept in oil bath at 60 °C overnight and then stored at room temperature to degas for 1 day. The degassed polymer solutions were cast on glass plates to form films that were subsequently immersed in water bath at room temperature for 24 h to allow for polymer precipitation and complete exchange of NMP and water. The formed membranes were then removed from the water bath and air-dried at room temperature.

2.3. Construction of the PMMA/NMP/water ternary phase diagram

The binodal and spinodal lines on the ternary phase diagram of PMMA/NMP/water were calculated on the basis of the Flory Huggins theory. One can find the needed equations for the calculations in the book of Mulder [13] and the detailed numerical procedures to solve the equations in the work of Lai et al. [14]. And listed in Table 1 are the molar volumes of PMMA, NMP, water and the interaction parameters between them that are needed for the calculations [14–17]. To validate the calculations, cloud point measurements were conducted following the procedures described in the work of Lai et al. [14].

2.4. Analysis with FTIR microscopy

An FTIR microscope (PerkinElmer LE186-0078) equipped with a

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