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Analysis of solidification rate of polymer solutions during PVDF membrane fabrication via TIPS method

Keisuke Nakatsuka, Yoshikage Ohmukai, Tatsuo Maruyama, Hideto Matsuyama*

Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada-ku, Kobe 657-8501, Japan
Tel. +81788036180; Fax +81788036180; email:matuyama@kobe-u.ac.jp

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ABSTRACT

It is necessary to know the solidification rate of the polymer solution when designing the membrane fabrication process. The effect of the composition of poly(vinylidene difluoride) (PVDF) solution on its solidification rate during membrane preparation via the thermally induced phase separation (TIPS) method was studied. Using time-dissolved light scattering, we observed that PVDF crystallized upon quenching in a water bath. With an increase in the concentration of PVDF in the solution, the solidification time decreased. Addition of glycerol to the solution was more effective in accelerating the solidification process during the TIPS process. Increase in the crystallization temperature of the PVDF solution was considered to be the reason for the above-mentioned observations. Since the difference between the crystallization temperature and water bath temperature is a driving force for crystallization, solutions with higher PVDF concentrations showed higher crystallization temperature, thereby showing faster solidification rates. The addition of glycerol also increased the crystallization temperature, owing to the transformation of the solid–liquid phase separation to the liquid–liquid phase separation, and the polymer-rich phase in which the polymer concentration was higher than that of the bulk solution appeared during the latter phase separation. The crystallization temperatures of the polymer solutions were observed to correlate well with the solidification time. Correlation curves of PVDF solutions with other diluents were also examined.

Keywords: Thermally induced phase separation; Solidification rate; Crystallization temperature; PVDF

1. Introduction

Membrane separation technology, which is widely applied for water treatment, is attracting considerable attention owing to its efficiency in removing particles, turbidity, and microorganisms in natural and wastewater. Further, since it does not involve a phase change, it also has the advantage of low energy consumption when compared with conventional processes. A number of studies on this technology have focused on the antifouling property, rejection, and morphology, which affect membrane performance [1–3]. These studies are important for improving the performance of polymer membranes and membrane modules products.

Although the solidification rate of a polymer solution is a crucial parameter in membrane fabrication, few studies have focused on this parameter. In crystalline polymers, membrane solidification occurs due to polymer crystallization. Thus, in order to determine the solidification rate, detailed investigation of the crystallization behavior must be carried out. In previous studies, crystallization behavior during

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*Corresponding author.

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thermally induced phase separation (TIPS) was studied for moderate cooling rates. Song et al. investigated the effect of the addition of polyethylene with a very high molecular weight to a high-density polyethylene solution on the crystallization behavior of polyethylene at a cooling rate of 10°C min^{-1} [4]. Li et al. constructed a mathematical model to describe the solid–liquid TIPS process from the initiation of casting to the development of the final membrane structure [5]. Although the model considered fast-cooling TIPS process, the result was mainly focused on the spherulite diameter of isotactic polypropylene.

Knowledge of the solidification rates during TIPS involving extremely rapid cooling is necessary to determine the conditions for the fabrication of industrial membranes. During the hollow fiber membrane fabrication process, polymer solution extruded from the spinneret must be immersed in a coagulation bath until the membrane strength is sufficient for spinning. If the fabrication process, especially the residence time in the coagulation bath, is optimized, the membrane spinning rate will increase, thereby decreasing the cost of fabrication.

In this study, flat membranes were prepared by employing the TIPS process; the process involved the immersion of a small heated sample of poly(vinylidene difluoride) (PVDF) solution in a water bath. The preparation process simulates the actual membrane fabrication process. The solidification rates of the samples were investigated by using time-resolved light scattering to observe the in situ crystallization growth. We also tried to elucidate the key factors affecting the solidification rate during the TIPS process.

2. Experimental

2.1. Preparation of polymer solution

For membrane preparation, PVDF (Mw = 136,000) was used as the polymer; glycerol triacetate, as the diluent; and glycerol, as the non-solvent. 25–35 wt% homogeneous polymer solutions were prepared by stirring in an oil bath at 200°C for 3 h.

2.2. Phase diagram

A sample of the prepared homogeneous solution was placed between cover glasses separated by a 100-μm-thick Teflon® sheet spacer. The sample was heated at 200°C for 2 min on a hot stage (HFS91, LINKAM) and then cooled at a rate of 10°C min^{-1}. The cloud point temperatures during cooling were observed using a microscope (BX50, Olympus), and the measurements were repeated at least four times.

The crystallization temperatures of the polymer solutions were measured by differential scanning calorimetry (DSC; DSC-7, PerkinElmer). The temperature profile of the measurement was the same as that observed using the microscope; the homogeneous PVDF solution was heated at 200°C for 2 min and then cooled at a rate of 10°C min^{-1}.

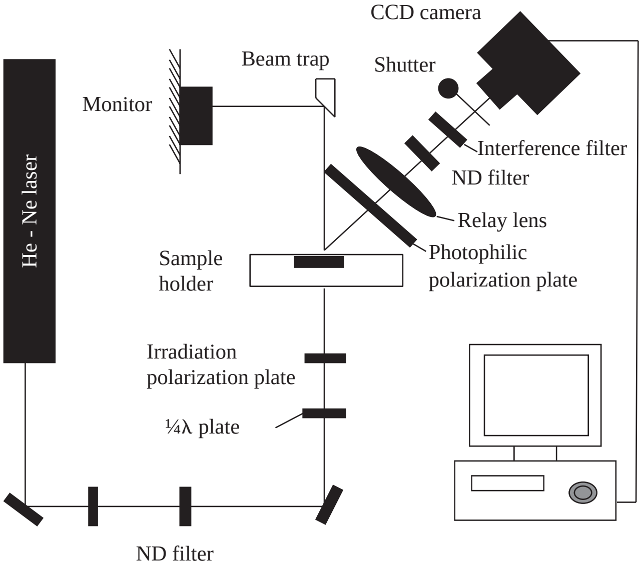

Fig. 1. Schematic diagram of time-dissolved light scattering apparatus.

2.3. Measurement of solidification rate of membrane

Time-resolved light scattering was used for the measurement of crystallization growth in the membrane during the TIPS process. A schematic diagram of the apparatus used (DYNA 3000, Ohtsuka Electric Co.) is shown in Fig. 1. The sample was prepared using a method identical to that employed for observing the phase separation using cover glasses and a Teflon® sheet of thickness 200 μm. The solution in the sample melted at 200°C on the hot stage. The sample was then quickly cooled by immersing in water at ambient temperature. The induced phase separation led to a change in the scattering intensity, and the measurement was carried out until the intensity became constant. The light scattering intensity at 8° was plotted against time in order to determine the crystallization time. The point corresponding to 90% of the final constant intensity was defined as the solidification point, and the time required to reach this point was defined as the solidification time.

3. Results and discussion

3.1. Phase diagram

The crystallization and cloud point temperatures of the solutions with 25–35 wt% PVDF and 0–20 wt%

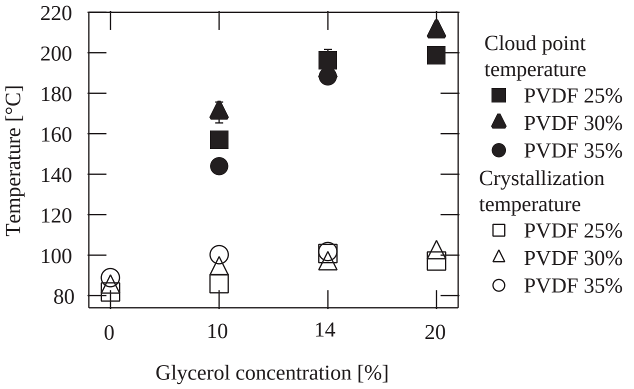

Fig. 2. Effect of PVDF and glycerol concentrations on cloud point and crystallization temperature.

glycerol were measured. As shown in Fig. 2, in the case where no glycerol was added, only crystallization occurred. The crystallization temperature increased with an increase in the PVDF concentration. This is because a highly concentrated polymer is easily crystallized. Since the cloud point appeared upon the addition of more than 10 wt% of glycerol, the phase diagram changed from solid–liquid phase separation to liquid–liquid phase separation by the addition of glycerol. Moreover, the cloud point increased when the amount of glycerol added in the polymer solution was greater than 10 wt%. Upon the addition of glycerol, a non-solvent, the compatibility of the polymer and the solution decreased. This led to an increase in the cloud point temperature.

Fig. 3 is a schematic diagram showing the mechanism of the change in the phase diagram. The cloud point line is above the crystallization temperature for the liquid–liquid phase separation, whereas in the case of the solid–liquid phase separation, the cloud point line is lower than the crystallization temperature, owing to the high compatibility between the polymer and the solvent [6,7]. Since the compatibility between PVDF and glycerol triacetate is high, no cloud point was observed without the addition of glycerol, as shown in Fig. 2. On the other hand, upon the addition of glycerol, the compatibility between PVDF and glycerol triacetate decreased, thereby resulting in liquid–liquid phase separation. Therefore, in Fig. 2, cloud points are observed for the solutions containing glycerol.

The crystallization temperature also depends on the phase separation mechanism. In the case of solid–liquid phase separation, when a solution with concentration C_1 is cooled, the crystallization starts at temperature T_1 at point A. For liquid–liquid phase separation, on the other hand, the solution is separated into two phases—polymer-rich phase and polymer-lean phase—at point B. The composition of the polymer-rich phase changes along the cloud point line, and the cloud point line intersects the crystallization line at point C. This point represents crystallization temperature T_2 and the corresponding polymer concentration C_2. Thus, the polymer solution showing liquid–liquid phase separation has higher crystallization temperatures than that of a solution showing solid–liquid phase separation.

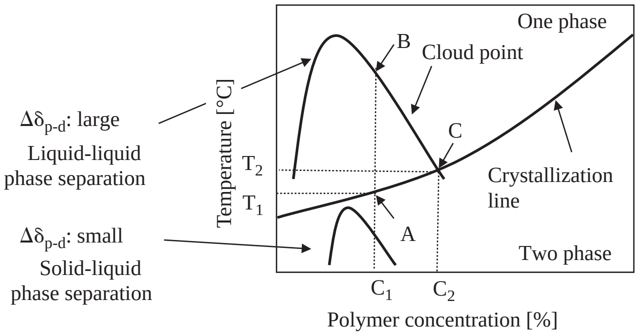

Fig. 3. Effect of adding non-solvent to polymer solution on phase diagram. $\Delta\delta_{p\text{-}d}$ is the difference in the solubility parameters between the polymer and diluent.

3.2. Validity of the light-scattering measurement

The in situ solidification behavior of the membrane during the TIPS process was examined by using time-resolved light scattering. The result of the solid–liquid phase separation is shown in Fig. 4a. When the sample was immersed in a water bath, the scattering intensity increased with time and became constant after the completion of crystallization growth. This was observed for a wide range of scattering angles. For the data shown in Fig. 4a, the scattering intensity at 8°C was re-plotted against time in Fig. 4b. The ordinate represents the relative intensity normalized by the final intensity. An approximated curve was drawn by joining these points, as shown by the solid line. The point corresponding to 90% of the final constant intensity was defined as the solidification point, and the time required to reach this point was defined as the solidification time.

The liquid–liquid phase separation example is shown in Fig. 4c. Liquid–liquid phase separation occurred before crystallization. Thus, the light scattering intensity initially increased due to this phase separation. However, the increase in the intensity was much smaller than that resulting from the crystallization. Therefore, the intensity curve obtained in the case of liquid–liquid phase separation was similar to that obtained in the case of solid–liquid phase separation.

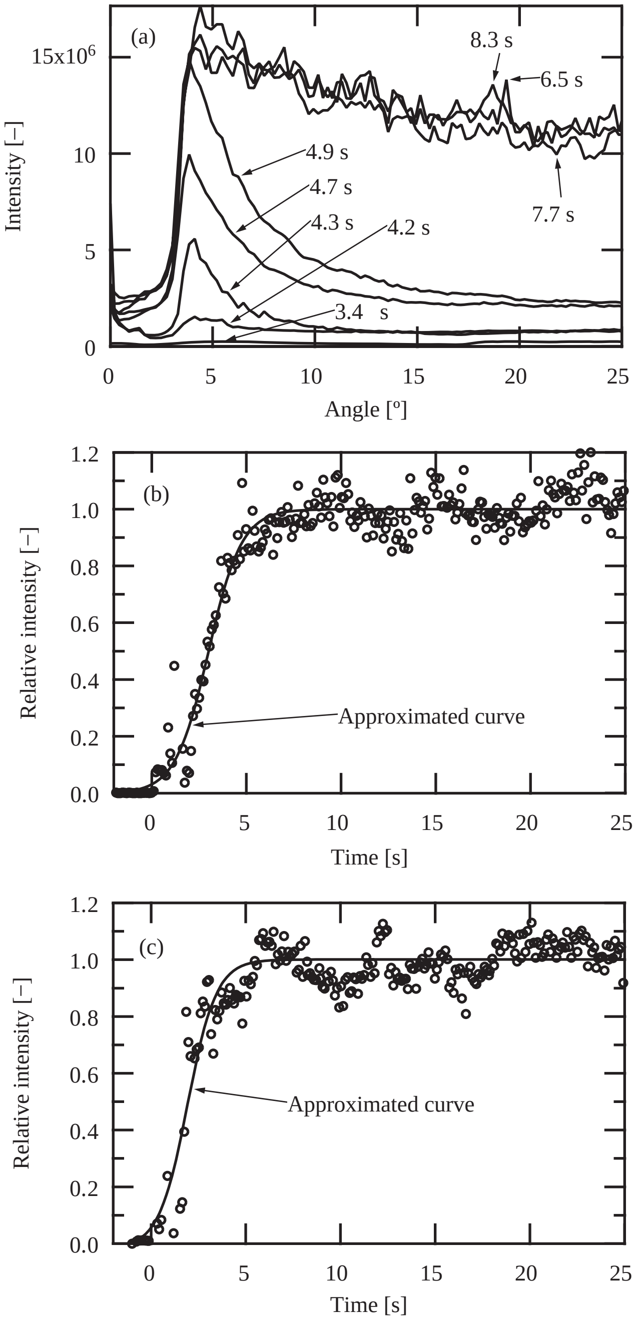

Fig. 4. Example of light scattering measurement. (a) Observed light scattering intensity of PVDF (30 wt%) cooled in a water bath and (b) time course of relative intensity for solid–liquid phase separation (30 wt% PVDF is cooled in a water bath). (c) Time course of the relative intensity during liquid–liquid phase separation (30 wt% PVDF and 10 wt% glycerol are cooled in a water bath).

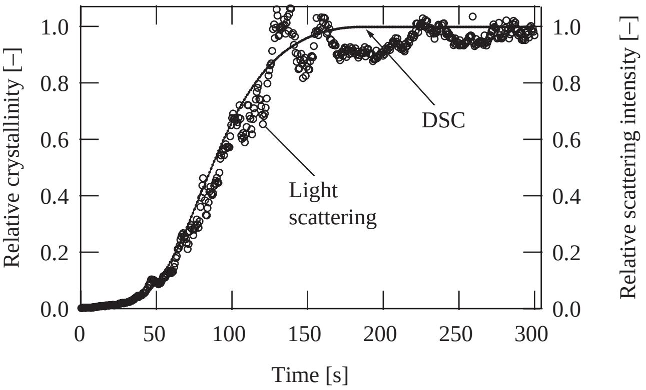

Fig. 5. Comparison of the crystallinity measured by DSC with the relative scattering intensity (polymer concentration: PVDF 30 wt%; cooling rate: 10°C min^{-1}).

To examine the validity of the light scattering measurement, the result from this measurement was compared with the result from DSC. In both the measurements, the same polymer solution and the same cooling rate were employed. The time course of the scattering intensity and the crystallinity measured by DSC are plotted in Fig. 5. The scattering intensity was constant and no peak was observed by DSC 150 s after the crystallization started. The light scattering measurement showed the same scattering intensity 1 h after the cooling. Therefore, we can conclude that the crystallization was completed in 150 s. The crystallinity was calculated by the following equation:

$$X_C = \frac{\Delta H}{\Delta H_0} \times 100, \qquad (1)$$

where X_C is the degree of crystallinity, ΔH is the melting enthalpy, and ΔH_0 is the melting enthalpy for a 100% crystalline sample. ΔH_0 is 104.7 J g^{-1} for PVDF [8]. The relative scattering intensity curve agreed well with the relative crystallinity curve normalized by the final crystallinity. This implies that the crystallization behavior can be examined by carrying out light scattering measurement. At a high cooling rate, the crystallization behavior in the actual membrane fabrication process cannot be determined using the DSC apparatus. However, light scattering measurement is highly reliable under such conditions.

3.3. *Effect of composition*

The effects of PVDF and glycerol concentrations on solidification time were examined by carrying out light scattering measurements. Fig. 6 shows the solidification time for polymer solutions with PVDF concentrations of 25–35 wt% and glycerol concentrations of 0–20 wt%. In all cases, the solidification times were of the order of several seconds. Higher polymer concentrations led to faster solidification rates. Since solutions with higher polymer concentrations have higher

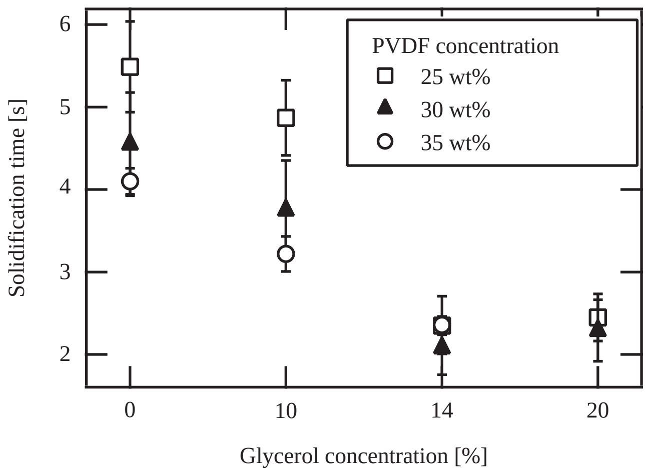

Fig. 6. Effects of PVDF and glycerol concentrations on solidification time.

crystallization temperatures, as shown in Fig. 3, the difference between the crystallization temperature and the water bath temperature increases. Since the difference between the two temperatures is a driving force for crystal formation upon immersing the sample into the water bath, a larger difference would promote faster crystallization, which corresponds to a shorter solidification time.

The glycerol concentration in the solution also affects the solidification rate, and its effect is more significant than that of the PVDF concentration. Solid–liquid phase separation changes to liquid–liquid phase separation upon adding glycerol to the solution, as shown in Fig. 2. As described above, the higher polymer concentrations arise from the polymer-rich phase that appears during the liquid–liquid phase separation, rather than the polymer-rich phase that appears during the solid–liquid phase separation. This higher concentration results in a reduction in the solidification time during liquid–liquid phase separation. The solidification time significantly decreased upon the addition of 0–14 wt% glycerol since the effect of glycerol concentration on the crystallization temperature was significant in this range, as shown in Fig. 2. However, the solidification time slightly increased at 20 wt%. The change in the crystallization temperature was negligible at 14–20 wt%, as shown in Fig. 2. The increase in the viscosity upon the addition of glycerol may have contributed to a slight increase in the solidification time.

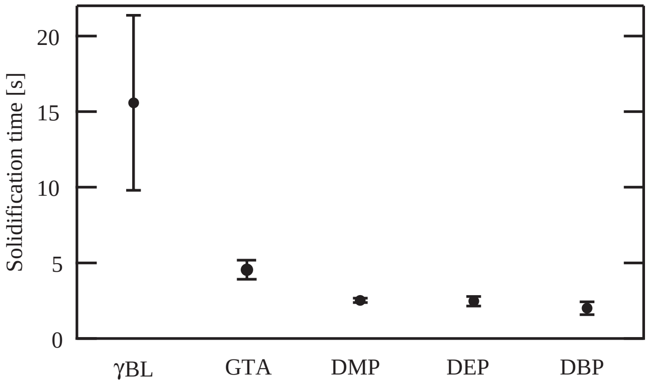

Fig. 7. Effect of diluents on the solidification time of the 30 wt% PVDF solution.

Table 1
Effect of diluents on crystallization temperature and crystallinity

Diluent	Crystallinity [%]	Crystallization temperature [°C]
Γ-Butyrolactone	32.8	37.9
GTA	46.2	82.9
DMP	64.9	95.1
DEP	62.1	99.3
DBP	72.0	122.6

3.4. *Effect of diluent*

In addition to the various factors discussed in the previous sections, the effect of diluents on the solidification rate was also investigated. Fig. 7 shows the solidification time of 30 wt% PVDF solutions mixed with various diluents. On the basis of the solidification rate, the solutions can be ordered as follows: γ-butyrolactone (γBL) < glycerol triacetate (GTA) < dimethyl phthalate (DMP) < diethyl phthalate (DEP) < dibutyl phthalate (DBP). The crystallization temperatures are listed in Table 1. The solution comprising γ-butyrolactone as the diluent, which showed the longest solidification time, had a crystallization temperature of 37.9°C. Since the temperature of the coagulation bath is 25°C, the difference between the two temperatures is quite small, thereby resulting in a longer solidification time. When other diluents were used, the solidification time decreased with an increase in the crystallization temperature. Polymer solutions with higher crystallization temperatures resulted in higher crystallinity. This is because the driving force for crystallization increased, which led to the increase in the crystallinity of the prepared membranes.

3.5. *Correlation of solidification times with crystallization temperatures*

As discussed above, the solidification times of the membranes are correlated with the corresponding crystallization temperatures. For all the data obtained

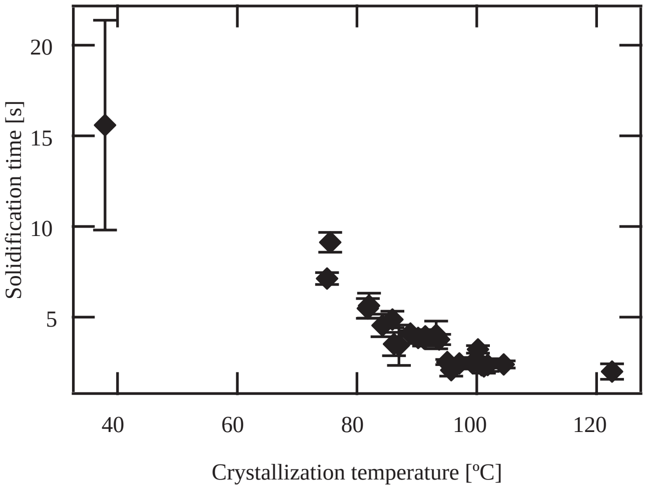

Fig. 8. Relation between crystallization temperature and the solidification time of the PVDF solution.

in this study, the relation between the solidification time and crystallization temperature is shown in Fig. 8. It is clear that the solidification time is strongly dependent on the crystallization temperature. A single master curve is obtained. This implies that as the crystallization temperatures increase, the solidification times decrease. Although the viscosity of the solution may also affect the solidification time, this effect is not so pronounced.

4. Conclusions

In this study, the solidification rates of PVDF membranes during the TIPS process were investigated in order to analyze the kinetic behavior of the polymer solutions during membrane fabrication. The solidification rate is one of the key factors determining manufacturing cost. The crystallization behavior was observed by time-resolved light scattering and DSC. The results obtained from both the methods were compared and it was confirmed that the former is more efficient for studying the crystallization behavior.

PVDF solutions with higher polymer concentrations showed faster solidification rates. This result was due to an increase in the crystallization temperature of the solution. The difference between the crystallization temperature and the coagulation bath temperature was a driving force for crystal growth, and hence, the solidification rate increased with an increase in the crystallization temperature. Moreover, the concentration of glycerol, used as the non-solvent in the PVDF solution, showed a similar effect on the solidification rate. However, the effect of the concentration of glycerol on the solidification rate was more significant than that of the concentration of PVDF. Since the solid–liquid phase separation for the PVDF/glycerol triacetate solution changes to liquid–liquid phase separation upon the addition of glycerol, a polymer-rich phase appears during the phase separation. Further, since the polymer-rich phase is the part having a high polymer concentration, the crystallization temperature increased, thereby resulting in fast solidification.

The effect of crystallization temperature on the solidification rate was similar in solutions comprising other diluents. Under various experimental conditions, the solidification rates observed showed a good correlation with the crystallization temperatures.

Thus, in this study, the key factor influencing the fabrication rate of the polymer membrane during the TIPS process was determined.

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Symbols

C_i	polymer concentration at the designated point (%)
T_i	temperature of the polymer solution at the designated point (°C)
X_C	degree of crystallinity (%)
ΔH	melting enthalpy (J g^{-1})
ΔH_0	melting enthalpy of a 100% crystalline sample (J g^{-1})
$\Delta\delta_{p\text{-}d}$	difference in the solubility parameter between the polymer and the diluent ($MPa^{1/2}$)

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