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PVDF Membrane Formation via Thermally Induced Phase Separation

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PVDF microporous membranes were prepared via thermally induced phase separation (TIPS) method. γ -Butyrolactone (γ -BA), Propylene carbonate (PC), Dibutyl phthalate (DBP) and Dibutyl sebacate (KD) were used as diluents, and ethanol as extractant. The melting temperatures and crystallization temperatures of different PVDF/diluent systems were determined using difference scanning calorimeter (DSC). Membrane cross-section morphologies from different systems were observed using scanning electron microscope (SEM). The effects of diluent, cooling rate, and polymer concentration on the polymer crystallization and membrane cross-section morphology were investigated in detail.

Keywords: thermally induced phase separation; poly(vinylidene fluoride) membrane; membrane morphology; polymer crystallization

1 Introduction

The thermally induced phase separation process is one of the most useful techniques to prepare porous membranes. In the membrane preparation via TIPS, a polymer is dissolved in a diluent at high temperature and then the homogenous polymer solution is cooled to induce the phase separation. After the polymer is solidified by crystallization or glass transition, the diluent is removed by extract or drying. The TIPS method has several well-documented advantages including (1) greater flexibility and ease of control than conventional casting process; (2) a very low tendency for defect formation; and (3) very high overall porosity and effective control of the final pore size.

Many studies have been carried out on the porous membrane formation by the TIPS process. Most of these studies concentrated on polypropylene (PP) and polyethylene (PE) microporous membranes. Lloyd et al. have published a series of literature on PP membrane formation via TIPS process. They (1–7) investigated the effects of cooling rate, polymer concentration, diluent and nuclear agent on the membrane cross-section morphology and the phase separation. Matsuyama et al. prepared the polyethylene hollow fiber membranes by introducing the diluent in the inner orifice and clarified the effects of polymer molecular

weight, diluent, water bath temperature, air gap distance and take-up speed on the pore size and the water permeability (8). Apart from that, poly(ethylene-co-vinyl alcohol) (EVAL) with a hydrophilic segment was also selected as membrane material for TIPS process due to its superior prevention of membrane fouling in the water treatment application. Matsuyama et al. investigated the phase diagrams and the structure growth mechanism of EVAL/glycerol systems (9, 10). And they further studied the effects of various preparation conditions on the morphologies of the EVAL hollow fiber membranes and water permeability and solute rejection (11). In addition, other polymers were also ever prepared into microporous membranes via TIPS method, such as PMMA, PS, nylon and so on (12–15).

PVDF is an acknowledged and perfect membrane material due to its excellent solvent-resistance, acid and alkali resistance, oxide-resistance and climate-resistance. Hellman et al. ever prepared PVDF membrane via thermally assisted evaporation phase separation method. They utilized the evaporation of solvent and non-solvent to induce the L-L phase separation and obtain PVDF membrane with microstructure (16). We adopted TIPS method to prepare PVDF membrane and expected it to possess the advantages of both PVDF material and TIPS method. Until now, the literature on the PVDF membrane via TIPS method was rare (1, 17–20). And this literature only made some brief description rather than the detailed and systemic study on the PVDF membrane formation.

The purpose of this paper is to study the effect factors of PVDF membrane formation in the solid-liquid phase

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separation process. We used four diluents to investigate detailedly the effects of cooling rate, polymer concentration and diluent on the membrane cross-section morphology and the crystallization of PVDF.

2 Experimental

2.1 Materials

PVDF (weight-averaged molecular weight of 170000) was purchased from SOLEF International Ltd. of Belgium. γ -Butyrolactone (γ -BA), propylene carbonate (PC), Dibutyl phthalate (DBP) and Dibutyl sebacate (KD) were used as diluents. They possess different polarity, viscosity and boiling points, and these properties are listed in Table 1. Ethanol was used as extractant. All chemicals were commercial and analytical grade; and were used without further purification.

2.2 Membrane Preparation

PVDF and diluent were added into a glass vessel with a stirrer, and then the mixed system was heated and kept at a certain high temperature until the polymer was dissolved completely in the diluent. The obtained homogenous solution was rapidly poured into the membrane-preparation module that was fabricated by us, and then the module was sealed. Thereafter, the module with the polymer solution was cooled by putting it into ice water, an icebox, or ambient air. As the polymer crystallized, the membrane formed gradually. The obtained membrane was immersed into ethanol to remove the diluent. The final membrane was dried in air.

2.3 DSC Measurement

A DSC(Seiko, DSC6200) was used to determine the polymer dynamic crystallization temperature and melting temperature. Samples were prepared by weighing the polymer and the diluent into a sample pan. The weight of each component was known to an accuracy of 0.1 mg. The pan was sealed and heated at the desired heating rate to at least 40°C above the melting point of PVDF-diluent mixtures. After waiting 3 ~ 5 min to ensure complete melting and equilibration, the sample was cooled at the desired cooling rate. The polymer

crystallization temperature (T_c) (that is, the solid-liquid phase separation temperature) was taken as the peak temperature on the resulting exotherm. Similarly, the polymer melting temperature (T_m) (that is, the temperature when the polymer dissolved in diluent) was taken as the peak temperature on the endothermic curve.

Crystallization enthalpy(ΔH_c , mJ/mg) ~ time curve can be obtained by integrating the exotherm (DSC-time curve). Then, the ΔH_c was further transformed into absolute crystallinity (X_c) to obtain X_c ~ time curve using the following formulation:

$$X_c = \Delta H_c / 105$$

The crystallization enthalpy of PVDF with 100% crystallinity was considered to be 105 mJ/mg (21). (Note: Since a different PVDF/diluent system had a different melting temperature, the different system had a different initial temperature in the cooling process of DSC measurement. As a result, in Figures 4, 6 and 8, the position of the curve cannot denote the crystallization order of the different system).

2.4 Observation of Membrane Cross-Section Morphology

The membrane sample was fractured in liquid nitrogen and mounted vertically on a sample holder. The cross-section of sample was coated with gold-palladium. A scanning electron microscope (SEM) (JEOL JSM-6301F, Japan) with an accelerating voltage of 5KV was used to examine the membrane cross-section morphology.

3 Results and Discussions

3.1 The Effects of Different Factors on the Thermodynamics of PVDF/diluent Systems

3.1.1 The Effect of Diluents

Figure 1 showed the solid-liquid phase separation curves of four PVDF/diluent systems. With the increase of polymer concentration, the crystallization temperature of PVDF increased. However, the increase degree was different in a different diluent. The crystallization temperature of PVDF in γ -BA and PC rose more quickly than in KD and DBP. In addition, at the same polymer concentration, the crystallization temperature of PVDF in four diluents ranked: $T_c(\gamma\text{-BA}) < T_c(\text{PC}) < T_c(\text{DBP}) < T_c(\text{KD})$. In Figure 2, the melting temperature curves of PVDF/diluent systems showed a similar tendency. These results indicated that PVDF had better affinity with γ -BA and PC than with KD and DBP. That is to say, the molecule interaction between PVDF and γ -BA (or PC) was stronger.

PVDF is a polar polymer, and it has better solubility in the polar solvent. Thus, the polarity factor was considered as an important reason for the above results. As shown in Table 1, compared with DBP and KD, the dipole moments of γ -BA and PC were higher, which indicated they had the

Table 1. The properties of diluents (22)

Diluents	Dipole moment (10^{-30}C m)	Viscosity (mPa · s)	Boiling point of diluent ($^{\circ}\text{C}$)
γ -BA	13.74	1.7	204
PC	14.3 ^a	1.38	242
DBP	8.0	9.72	339
KD	8.27	7.96	345

^aDipole moment was replaced by the δ_p of solubility parameter because we didn't find out the Dipole moment of PC.

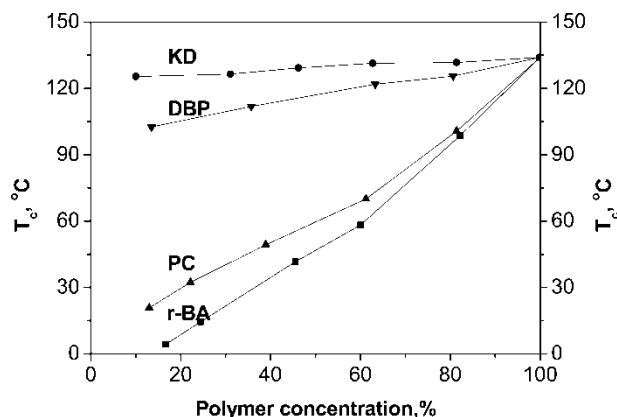


Fig. 1. The solid-liquid phase separation curves of PVDF/diluent systems.

stronger polarity. Therefore, they exhibited the stronger interaction with PVDF molecules. The strong interaction prevented the accumulation and crystallization of PVDF molecules and promoted the dissolution of PVDF. Accordingly, when γ -BA and PC were used as diluents, the crystallization temperature and melting temperature of system were lower.

4 The Effect of Cooling Rate

Figure 3 showed the solid-liquid phase separation curve of the PVDF/ γ -BA system at a different cooling rate. With the increase of cooling rate, the crystallization temperature of PVDF decreased gradually, and this phenomenon also occurred when PC, DBP and KD were used as diluents. The similar phenomenon was ever reported in the literature that focused on polypropylene membrane preparation via the TIPS method (1, 2). Lloyd et al. thought that increasing the cooling rate permitted supercooling; that is, the polymer solution might cool to temperature below its corresponding

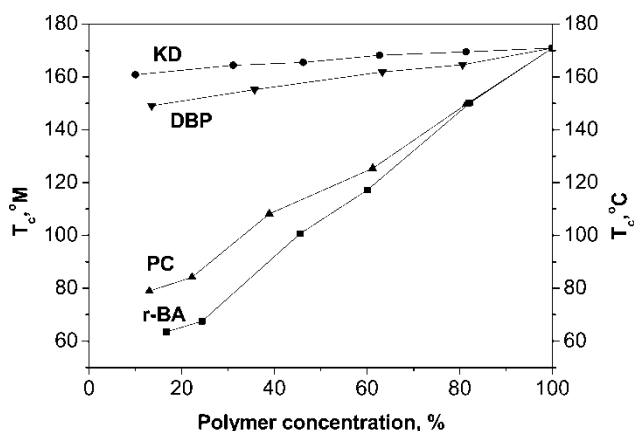


Fig. 2. The melting temperature curves of PVDF/diluent systems.

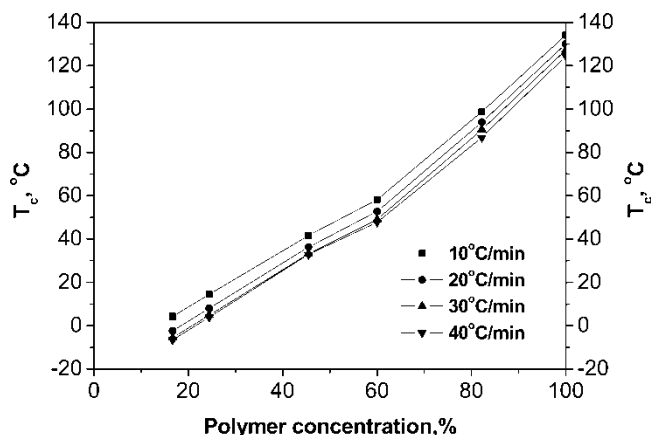


Fig. 3. The solid-liquid phase separation curves of PVDF/ γ -BA system at a different cooling rate.

equilibrium crystallization temperature prior to the actual crystallization of the polymer from solution.

4.1 Crystallization of PVDF and Membrane Cross-Section Morphology

4.1.1 The Effect of Diluents

Figure 4 showed the absolute crystallinity (X_c) vs. time curves of different PVDF/diluent systems. The slope of the curves reflected the crystallization rate of polymer (R_c). Thus, it can be seen that the crystallization rate of PVDF in different diluent ranked: $R_c(\gamma\text{-BA}) < R_c(\text{PC}) < R_c(\text{DBP}) \approx R_c(\text{KD})$, and the final absolute crystallinity (X_c) ranked: $X_c(\gamma\text{-BA}) < X_c(\text{PC}) < X_c(\text{DBP}) < X_c(\text{KD})$. PVDF had the higher crystallization temperatures in DBP and KD than in γ -BA and PC. When the crystallization occurred at the high temperature, PVDF molecules had the higher activity, which helped for the regular folding of polymer molecules. Thus, the crystallinity in DBP and KD was higher.

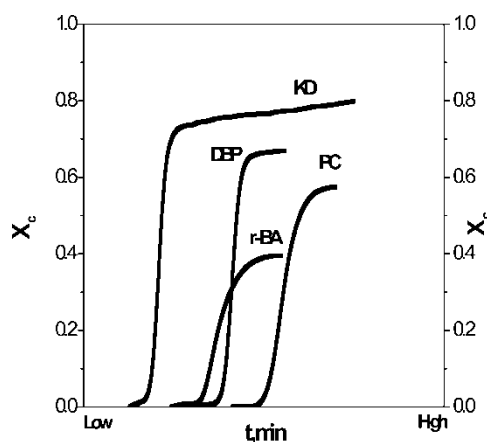


Fig. 4. The crystallinity vs. time curves of PVDF/diluent systems.

As shown in Figure 5, all the membrane cross-section exhibited the granule-like structure. The formation of this type of structure was ascribed to the solid-liquid phase separation. When γ -BA and PC were used as diluents, the membrane cross-section showed the spheric granules, and the size of spheric granules was large and the number was less. However, when DBP and KD were used as diluents, the membrane cross-section showed the granules with an irregular shape, and the granules were small and loose, as well as the number of granules was greater. The polymer crystallization temperatures in DBP and KD were by far higher, and thereby the polymer solution would reach quickly to the higher supercooling. The higher supercooling made more primary nuclei to form at the beginning of crystallization. Since the quantity of polymer molecules was limited, every nucleus could only grow up into the granule of a small size. As a result, when DBP and KD were used as diluents, the granules were more numerous and small.

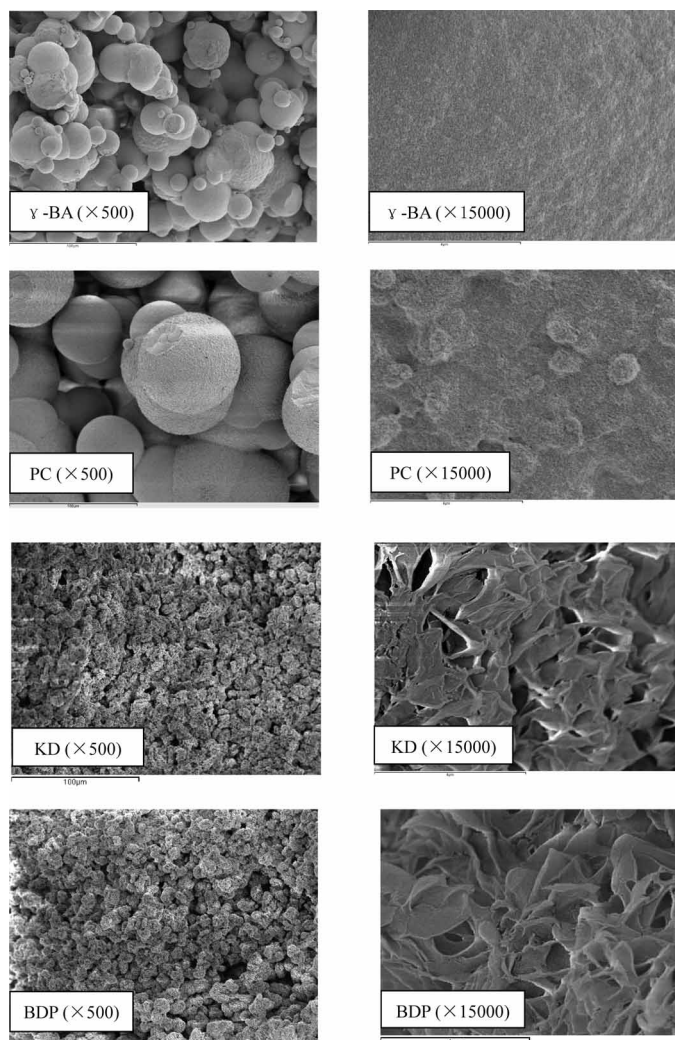


Fig. 5. The effect of diluent on the membrane cross-section morphology (polymer concentration: 25 wt%; Cooling environment: icebox).

In addition, as the polymer crystallized into lamellae and then granules, the low molecular weight diluent was rejected to the inter-lamellae and inter-granule regions, and it was continuously pushed ahead by the growing granule. Finally, some of the rejected diluent accumulated in the inter-granule regions, with the other diluent remaining between the lamellae. Consequently, the accumulated diluent caused disruption of the lamellae formed at the latter stages of the crystallization process and the outer regions of the granule structure. Thus, the diluent fluidity would affect the membrane formation, which was studied by Lloyd et al. (4–7, 22). PVDF molecules crystallized more rapidly in DBP and KD, as well as DBP and KD, and by far had higher viscosity (as shown in Table 1) than γ -BA and PC. Thus, when DBP and KD were used as diluents, they were difficult to flow out from the inter-lamellae in time. Therefore, the granules were loose. Furthermore, the DBP(or KD) accumulated in the inter-granule regions prevented the nuclei from growing equally toward the radiation direction. Therefore, the granules from DBP and KD showed the irregular shape.

On the contrary, in γ -BA and PC, the crystallization occurred at the low temperature. Thus, the two systems were difficult to reach the high supercooling, and thereby they only made limited primary nuclei at the beginning of crystallization. As the temperature of polymer solution decreased further, new primary nuclei would form continuously. These primary nuclei forming at a different moment would grow into spheric granules with a different size. Thus, in the membrane cross-section from γ -BA (or PC), the size of spheric granules was different. However, as a whole, the granules were larger and less than those from DBP and KD. In addition, γ -BA and PC had low viscosity and good fluidity. They gave less resistance for the growth of nuclei. Thus, the granules showed the perfect spheric shape and the surface of granules was tight.

4.2 The Effect of Cooling Rate

In this series of experiments, we selected γ -BA and KD as diluents to investigate the effect of cooling rate on the PVDF crystallization and membrane cross-section morphology. As shown in Figure 6, when γ -BA was used as a diluent, the crystallization rate of PVDF increased and the crystallinity decreased with the increase of cooling rate. However, when KD was used as a diluent, the crystallization rate of PVDF only showed a slight increase and the crystallinity had no obvious change.

Figure 7 gave the membrane cross-section morphology from a different cooling rate. In the membrane preparation process, the module with the polymer solution was put into ice water, icebox and ambient air of room temperature, respectively. And the average cooling rates of module in different environment was about 20°C/min, 5°C/min and 2°C/min, respectively. At the fast cooling rate, the polymer solution quickly reached the higher supercooling degree,

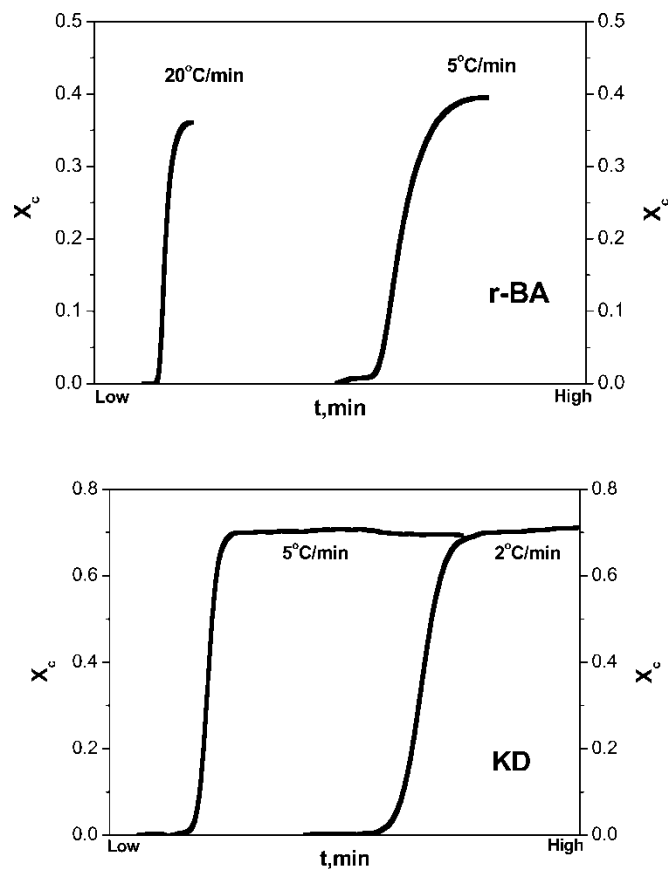


Fig. 6. The crystallinity vs. time curves of PVDF/diluent system at a different cooling rate.

which promoted the formation of more primary nuclei. Thus, as shown in Figure 7, with the increase of cooling rate, the membrane cross-section showed the smaller and more granules.

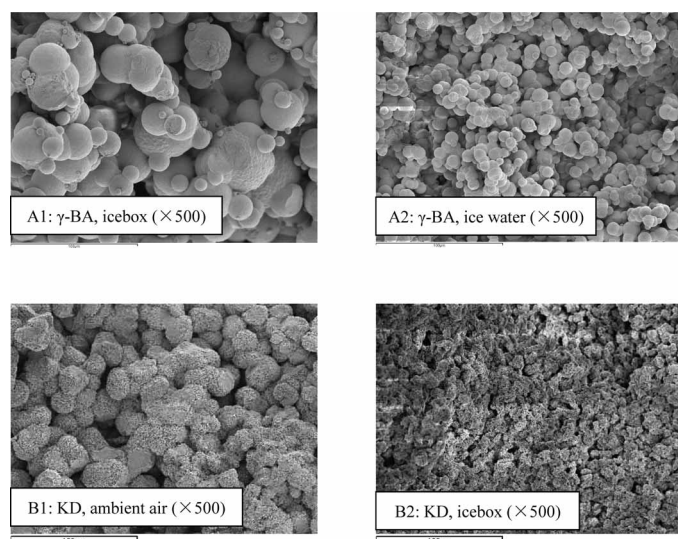


Fig. 7. The effect of cooling rate on the membrane cross-section morphology. (Polymer concentration: 25 wt%).

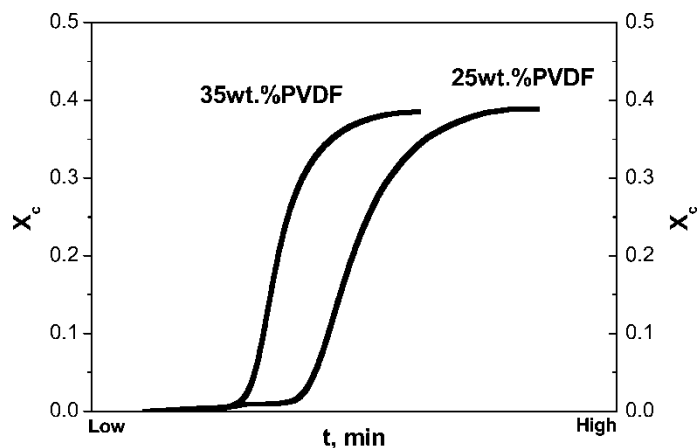


Fig. 8. The crystallinity vs. time curves of PVDF/ γ -BA system with different polymer concentration.

In addition, comparing Figure 7(A1) and Figure 7(A2), the size of spherulites in Figure 7(A1) was quite different, whereas the size of spherulites in Figure 7(A2) was nearly similar. This phenomenon suggested that most of the primary nuclei in Figure 7(A₂) formed nearly at the same moment. The average cooling rate of Figure 7(A₂) was about 20°C/min, and thereby the polymer solution would quickly reach a high supercooling degree. Thus, an abundance of primary nuclei formed and then grew up within a very short time. The remaining polymer was difficult to form new primary nuclei after ample crystal granules from primary nuclei formed because the critical free energy of secondary nucleation was lower than the primary nuclei (23). Thus, the membrane cross-section in Figure 7(A₂) had the spherulites of similar size.

5 The Effect of Polymer Concentration

In this experiment, γ -BA was used as a diluent to investigate the effect of polymer concentration. It can be seen from Figure 8 that the crystallization rate and the crystallinity had no obvious changes as the polymer concentration increased. Figure 9 exhibited the membrane cross-section

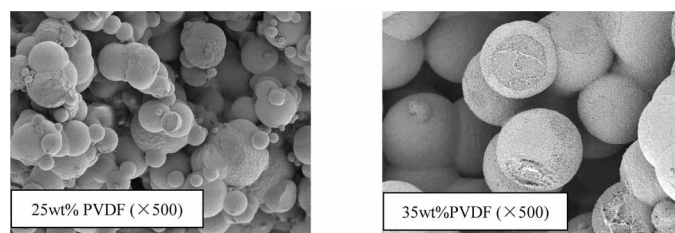


Fig. 9. The effect of polymer concentration on the membrane cross-section morphology. (Diluent: γ -BA; Cooling environment: icebox).

morphology from a different polymer concentration system. With the increase of polymer concentration, the size of granules increased and the number of granules diminished. This result was similar to the literature reported by Ye (23). However, we did not find a reasonable explanation for this phenomenon.

6 Conclusions

PVDF membranes were prepared via the TIPS method using γ -BA, PC, DBP and KD as diluents. The solid-liquid phase separation occurred in the membrane formation process, and induced the granule-like structure in the resultant membrane cross-section. Furthermore, no obvious liquid-liquid phase separation was observed before the solid-liquid phase separation. PVDF showed a different crystallization temperature in four diluents and the order was: $T_c(\gamma\text{-BA}) < T_c(\text{PC}) < T_c(\text{DBP}) < T_c(\text{KD})$. The membrane cross-sections from γ -BA and PC had larger and less spheric granules, and the surface of granules was tight. Contrarily, the membrane cross-sections from DBP and KD showed smaller and more granules, and the shape of the granules was irregular and the granules were loose. Moreover, the increase of cooling rate decreased the crystallization temperature of PVDF and promoted the crystallization rate, as well as led to the smaller and more granules in the membrane cross-section. The increase of polymer concentration enhanced the crystallization temperature of PVDF and resulted in the larger granules in the membrane cross-section.

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