

# Crystallization Behavior of PVDF in PVDF-DMP System via Thermally Induced Phase Separation

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**ABSTRACT:** The crystallization behavior of PVDF (poly(vinylidene) fluoride) in PVDF-dimethylphthalate(DMP) system was investigated in the liquid–liquid (L–L) phase separation region, solid–liquid (S–L) phase separation region and different quenching conditions via thermally induced phase separation (TIPS). Differential scanning calorimetry (DSC) indicated the crystallinity of PVDF in PVDF-DMP system increased in the early stage of phase separation and polymer-rich phase crystallized completely in the late stage of phase separation. The scanning electron microscopy (SEM) showed the different quenching temperatures had effects on the spherulite size of polymer rich phase and the ultimate membrane structure

in the different phase separation regions. The wide angle X-ray diffraction (WAXD) was used to quantify the crystal structure of PVDF in PVDF-DMP system. The  $\alpha$ -phase PVDF was obtained when the system quenched to different temperatures above 40°C, and the area of diffraction peaks changed when quenching temperatures changed. While the  $\beta$ -phase PVDF was formed when PVDF-DMP system was quenched from liquid nitrogen and crystallized for 24 h in 25°C water bath. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3714–3719, 2006

**Key words:** crystallization behavior; thermally induced phase separation; PVDF; DMP; spherulite; crystal structure

## INTRODUCTION

Thermally induced phase separation (TIPS) is a method to make microporous membrane.<sup>1</sup> In TIPS process, a polymer is dissolved in a diluent at a high temperature, and a homogenous polymer-diluent solution is obtained. When the solution is cooled from one-phase region to the temperature below cloud points curve, L–L phase separation occurs, and droplets of one phase form within a continuous matrix of a second phase. The droplet phase is diluent rich and the matrix phase is polymer rich.<sup>2</sup> When the solution is cooled from one-phase region to the temperature below crystal points curve, S–L phase separation occurs, and the polymer crystallizes prior to L–L phase separation, the membrane structure is determined by the polymer crystal structure.

A lot of researches have focused on the behavior of the polymer-lean phase (droplets) in late stage of L–L phase separation. The scaling exponent of droplets growths were frequently studied and calculated in the different polymer-diluent systems.<sup>3,4</sup> It is found that the droplets growths scaling exponent increased as the temperature decreased which resulted in the difference of pore size of membrane.<sup>5</sup> However, little works have focused on the behavior of polymer-rich phase. As TIPS is the process with the quench step which results in the crystallization and the membrane structure is fixed and

supported by the polymer-rich phase.<sup>6</sup> As PVDF is a typical semicrystal polymer which is proper material for membrane with its chemical and aging resistance, in different quenching depths and conditions, PVDF in the polymer-diluent system is probable to crystallize in different extent or form different crystal structure.

PVDF crystallizes in three main polymorphs,  $\alpha$ ,  $\beta$ ,  $\gamma$  forms.<sup>7</sup> The unit cell of the lattice of  $\alpha$ -phase PVDF consists of two chains in tg + tg-conformations, and the  $\alpha$ -phase PVDF exhibits nonpolar behavior. The  $\beta$ -phase PVDF consist of all trans (TTT) planar zigzag conformations;  $\beta$ -phase contains the largest spontaneous polarization per unit cell.<sup>8</sup> The  $\gamma$ -phase resulted from solid–solid transition from the  $\alpha$ -phase is usually designated as  $\gamma'$ -phase. It exhibits nonpolar behavior as  $\alpha$ -phase.<sup>9</sup>

Therefore, this research is focused on the polymer-rich behavior in the preparation of PVDF-DMP membrane process. WAXD was used to quantify the crystal structure of PVDF in PVDF-DMP system in different quenching temperature conditions, the DSC was used to quantify the kinetics of PVDF crystallinity in different quenching times and temperatures, and the morphology of membrane was showed by scanning electron microscopy.

## EXPERIMENTAL

### Material

Membranes were prepared by the systems of PVDF-DMP. The polymer was poly(vinylidene fluoride),

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FR904, purchased in Shanghai 3F New Materials Co., China. DMP was used as the diluent without further purification, purchased from Shanghai Reagents Co., China. Ethanol was used as the extractant, purchased from Shanghai Reagents Co., China.

### Membrane preparation

The 60 g of polymer-diluent was mixed for 20 min by Brabender Rheometer (W50EHT-3Zones, German) at 180°C, and the mixtures were separated for 0.5 g per share in the tubes, which were quenched in different conditions, then solidified in ice-water bath. Finally, the diluent was extracted from the membrane with ethanol. The extractant was evaporated and the membranes were dried further in a vacuum oven in a slight elevated temperature.

### Phase diagram

Differential scanning calorimetry (CD-34, Shanghai, China) was used to determine the crystallization temperature for the dynamic phase diagram. The solid polymer-diluent samples were sealed in an aluminum DSC pan, melted at 180°C for 10 min, and then cooled at 10°C/min. The onset of the exothermic peak during the cooling was taken as the dynamic crystallization temperature. The cloud points by noting the appearance of turbidity are obtained under a microscope (X-4, Beijing, China).

### Scanning electron microscopy observation

The microporous membrane was fractured in liquid nitrogen and mounted vertically on a sample holder. The sample of the membrane was sputtered with Au/Pd in vacuo. A scanning electron microscope (SX-40, AKASHI, Japan) with an accelerating voltage of 10 kV was used to examine the membrane cross sections.

### Measurement of PVDF crystallinity

Polymer-diluent samples weighting about 10 mg closed in aluminum pans were heated from room temperature up to 180°C at 10°C/min, the PVDF crystallinity  $X_C$  was evaluated by:

$$X_C = \frac{\Delta H_f / 0.2}{\Delta H_f^*}$$

where  $\Delta H_f^* = 104.5 \text{ J/g}^{10}$  is the melting enthalpy for a 100% crystalline sample of PVDF, 0.2 was the weight fraction of PVDF in polymer-diluent system.

### Wide angle X-ray diffraction as a polymer structure method

Wide angle X-ray diffraction (WAXD) (XD-3A, Shimadzu, Japan) was used to analyze the PVDF crystal structure

at room temperature, the scanning angle ranged from 60° ~ 5°, and the scanning velocity was 4°/min.

## RESULTS AND DISCUSSION

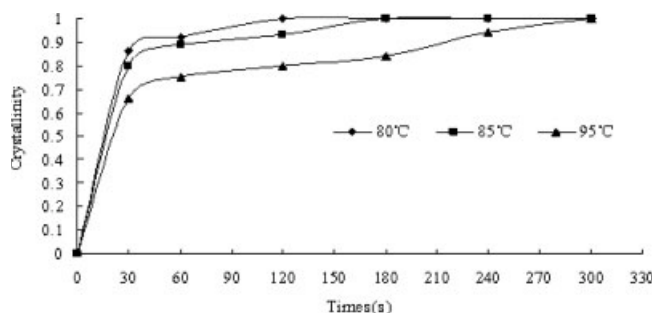
### Phase diagram

The typical semicrystal PVDF-DMP system dynamic phase diagram is showed in our previous work.<sup>11</sup> It is showed that as the weight fraction of PVDF increases, the cloud points decrease and crystallization temperatures increase. The monotectic point<sup>2,12,13</sup> ( $\varnothing_m$ ) is the intersection of liquid-liquid phase separation curve and a crystallization line, and the  $\varnothing_m$  of PVDF/DMP system is between 25 and 30% of PVDF weight fraction. When PVDF weight fraction is less than  $\varnothing_m$  and the quenching temperature is below the cloud points and above the crystal line, the solution undergoes L-L separation. While the quenching temperature is below the crystal line, the solution undergoes S-L separation. So three temperatures are chosen: 95°C (L-L phase separation region), 85°C (crystal line) and 80°C (below crystal line) with the PVDF weight fraction of 20%, to study the crystallization behavior of PVDF during different phase separation regions.

### Times dependence of crystallization fraction for 20% PVDF/DMP system quenched to three temperatures

The effects of quenching time and temperature on the crystallinity of PVDF-DMP solution are shown in Figure 1. The crystallinity of PVDF increases with increasing quench depth in the early stage of phase separation. Since quenching depth increases to the certain times, the trend of crystallinity approaches to the fixed value, which indicated that the crystallization of PVDF was nearly complete in the late stage of phase separation.<sup>14</sup>

Figure 1 also shows that as the same quench depth, the crystallinities are in the order of 80°C, 85°C, and 95°C in the early stage of phase separation. As 95°C is in the L-L phase separation region, the rich-polymer phase experiences L-L phase separation prior to poly-



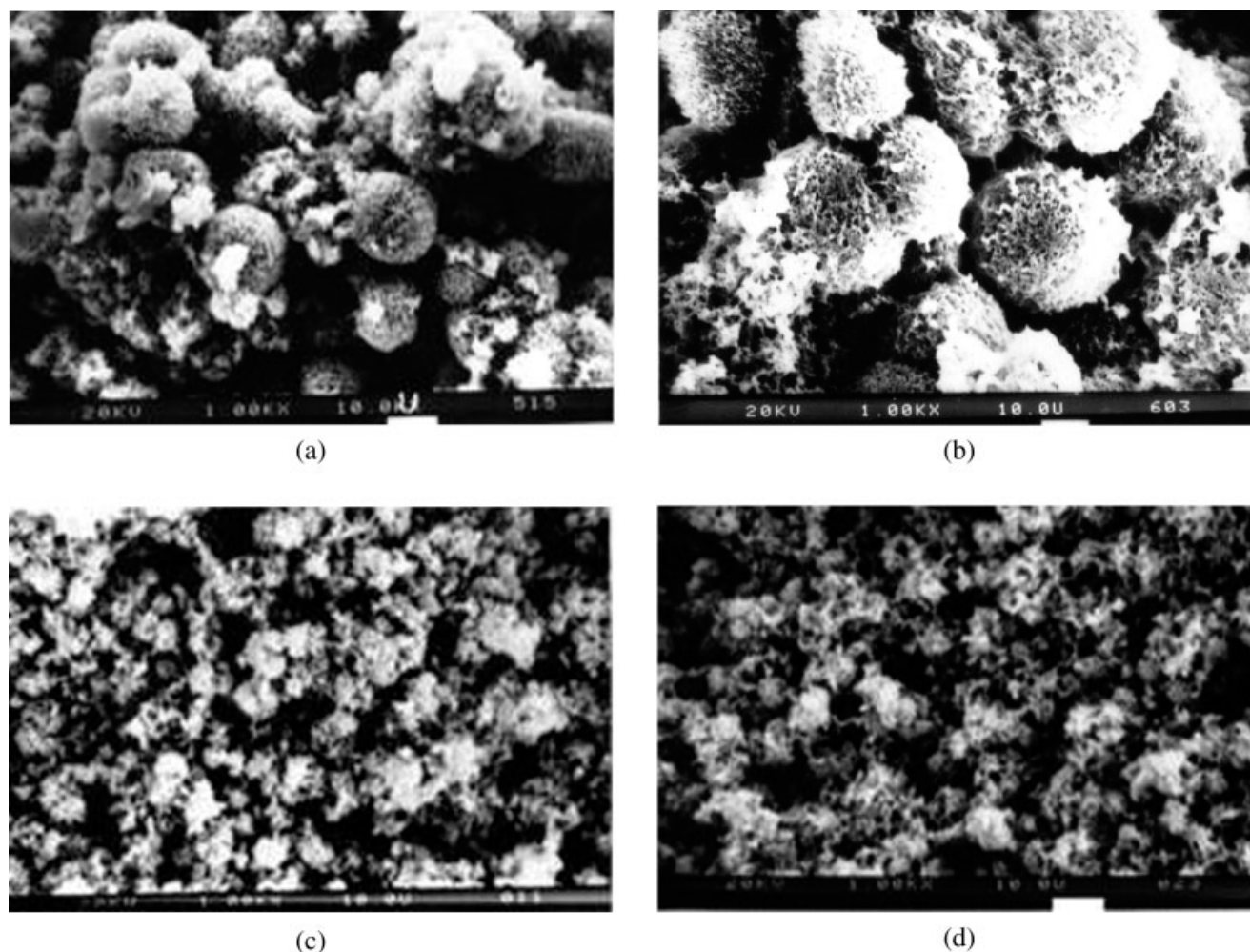
**Figure 1** Time dependence of the fractional crystallization for 20 wt % PVDF-DMP solution quenched to three temperatures.

mer crystallization. As a result, in the early quenching stage at 95°C, the lowest crystallinity was obtained compared to quenching at 80°C and 85°C. As quench depth increased to the late stage of phase separation, the crystallinity of PVDF-DMP solution quenching to three temperatures nearly increased to the same value, while the complete crystallinity was fastest obtained when quenching at 80°C, next are 85°C and 95°C, which indicates that the fastest crystallization rate is obtained at 80°C as the greatest supercooling when melting from 180°C.

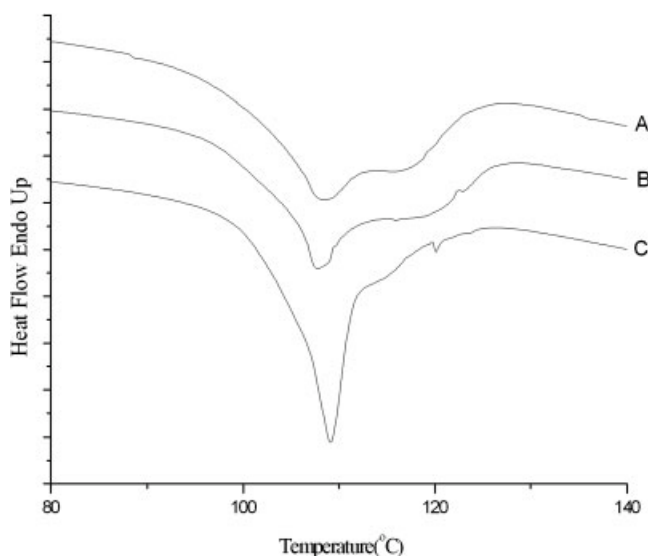
### Morphology of PVDF in the membrane through different phase separation region

As for the polymer-diluent system, the ultimate membrane morphology is determined by the two factors: L-L phase separation and polymer crystallization, while these two factors are infected by polymer concentration and temperatures of phase separation. When phase separation temperatures undergo L-L phase separation region, L-L phase separation occurs prior

to polymer crystallization. As the effect of coarsening, the cellular membrane morphology with the polymer crystallization limited. When phase separation occurs in S-L phase separation region, polymer-diluent solution undergoes L-L phase separation with great rate; therefore, the polymer crystallizes without coarsening and the spherulite membrane structure is formed.<sup>15</sup> Figure 2 shows the PVDF-DMP membrane quenched at four temperatures for 180 s. The largest spherulite were obtained at 80°C; as 80°C was below the onset crystal line, the spherulites grew with the fastest crystallization rate and cooling depth and the spherulites have enough energy to congregate and impinge. While the less spherulite size showed at 30°C, though it showed the largest cooling depth, the lowest quenching temperature limited the molecular movement. The lowest spherulite size was obtained at 85°C. As 85°C was the onset crystal temperature, the spherulites grew with the slowest crystallization rate with brief quenching time. The congregated rich polymer was obtained in 95°C as the effect of L-L phase separation prior to S-L phase separation with less effect of polymer crys-



**Figure 2** Cross section of 20 wt % PVDF/DMP membrane quenched at four temperatures for 180 s ( $\times 1$  K). (a): 30°C; (b): 80°C; (c): 85°C; (d): 95°C.



**Figure 3** Heating thermograms of PVDF-DMP system cooled from different quenching conditions. A: ice water; B: 30°C water bath; C: air bath at room temperature (30°C).

tallization. Therefore, the nondiscernable spherulites were formed.

#### Effect of different quenching conditions on the crystallization behavior of PVDF in PVDF-DMP system

The melting curves and melting data of PVDF-DMP system cooled from different conditions are showed in Figure 3 and Table I. In Table I, it is showed the crystallinity of PVDF is nearly the same in air bath at room temperature and 30°C water bath, as the close cooling depth was obtained in the above two quenching conditions when melting from 180°C. While with the slower cooling rate in air bath than in 30°C water bath, the spherulites have enough times to grow complete before the polymer molecular chains are fixed. Meanwhile, in Figure 3 it is showed that the melting curve peak is narrower in air bath than in 30°C water bath.  $\Delta T_m$  of air bath was lower nearly 3.4°C than that of 30°C water bath, and  $T_m^{on}$ ,  $T_m^p$  are higher than that of 30°C water bath, which indicate that PVDF crystallizes completely with slower cooling rate. However according to the theory of NG (Nucleat-Growth),<sup>16</sup> as the cooling depth

increases, the more nuclei are created, and the amount of spherulites increase, therefore the greatest crystallinity is obtained when quenched in ice water. As shown in Figure 3, the melting curve peak is widest in ice water than above two quenching conditions.  $T_m^{on}$ ,  $T_m^p$  are the lowest and  $\Delta T_m$  is the highest in the ice water condition, which indicate that with the fastest crystallization rate, the spherulites grow incomplete.

The morphology of PVDF-DMP system quenching in three conditions was showed in our previous work.<sup>11</sup> It was showed that the bulk of the membranes are dominated by spherulites with a typical diameter ( $D$ ) of about 5–15  $\mu\text{m}$ . The spherulites have a rugged surface, and they do not form an ordered arrangement. Some variation in the size of them is encountered when membrane samples originating from PVDF solidified under different conditions. Size differences of spherulites are attributable to the different densities of crystallization nuclei. The greatest size of them is obtained in air bath with the slowest cooling rate compared to other two conditions, and they arrange the most compact, which indicates they grow the most complete, while the mature and immature spherulites with irregular size were formed in 30°C water bath with the fast cooling rate. With the fasted cooling speed, the more nuclei are created, the more amount of spherulites increase, and the size of them decrease, which indicates they have not enough time to grow with such highest supercooling,<sup>16</sup> therefore the least sperulities size were formed in ice water. However, DMP, as the diluent, must have the interactions with PVDF, which should affect the crystallization behavior of PVDF. Figure 4 shows that the spherulites of PVDF grew freely and DMP is squeezed and attracted in the surface of them.

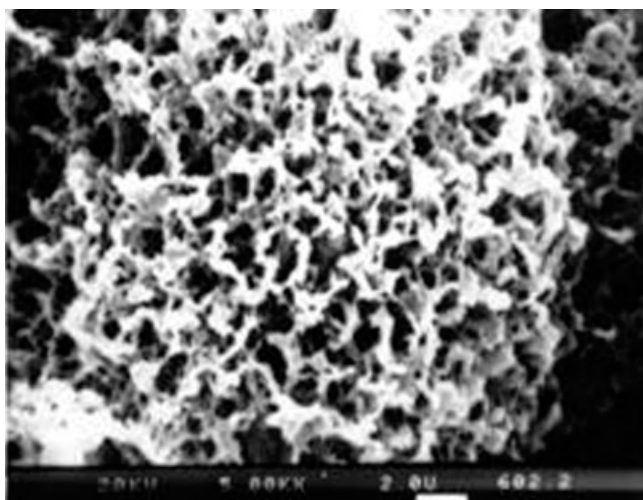
#### Wide angle X-ray diffraction studies on the PVDF crystallization behavior in PVDF-DMP system

Figure 5 shows the crystallization behavior of PVDF in PVDF-DMP system quenching in different temperatures for 1 min measured by WAXD. Three discernable diffraction peaks appear at 17.55°–17.74°(1<sup>#</sup>), 18.17°–18.47°(2<sup>#</sup>) and 19.75°–20.05°(3<sup>#</sup>). According to Lovinger,<sup>17</sup> the diffraction peaks of (1 0 0), (0 2 0), and (1 1 0) of  $\alpha$  forms appear at 17.3°, 18.5°, 19.4°, while the

**TABLE I**  
The Melting Temperatures and Melting Enthalpy and Crystallinities of PVDF/DMP System in Different Quenching Conditions

Quenching environment	$T_m^{on}$ (°C)	$T_m^p$ (°C)	$\Delta T_m$ (°C)	$\Delta H_m$ (J · g <sup>-1</sup> )	$X_C$
Ice water	101.6	108.1	24.6	12.3	0.59
Air bath at room temperature (30°C)	104.2	109.1	20.8	12.0	0.57
30°C water bath	103.8	107.7	24.2	11.9	0.57

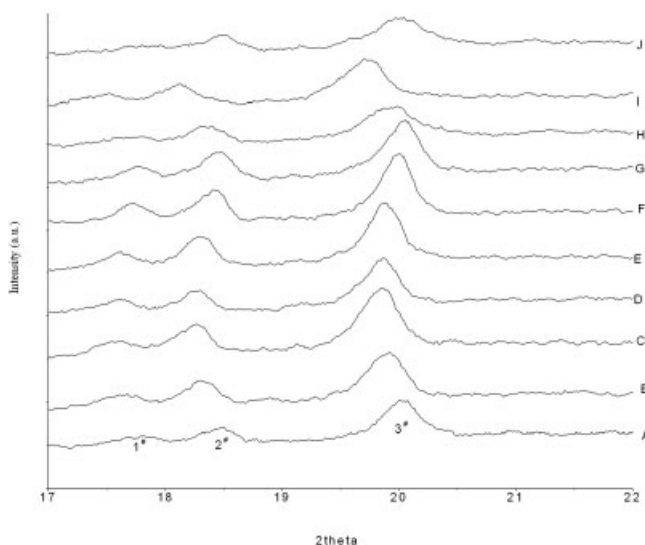
$T_m^{on}$ : onset melting temperature;  $T_m^p$ : melting peak temperature;  $T_m^f$ : final melting temperature;  $\Delta T_m = T_m^f - T_m^{on}$ ;  $\Delta H_m$ : melting enthalpy;  $X_C$ : crystallinity.



**Figure 4** Cross section of spherulite surface of 20% PVDF-DMP membrane ( $\times 5$  K).

diffraction peak of  $\beta$ -forms appears at  $18.6^\circ$ , and the diffraction peak of  $\gamma$ -forms appears at  $14^\circ$ ,<sup>18</sup> and the diffraction peaks have tendency to draft with the width factor<sup>19</sup> when the diluent was added in the polymer.<sup>20</sup> Therefore, it is likely that PVDF-DMP system contains  $\alpha$ -phase.

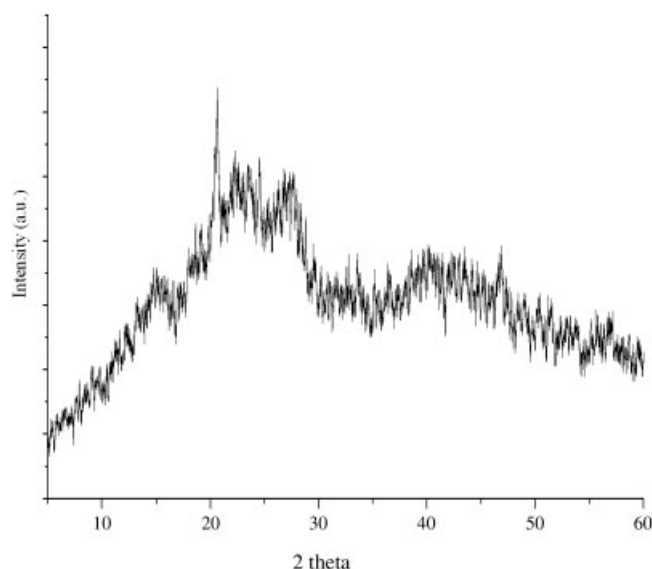
Figure 5 also shows that as the quenching temperatures increase from  $40^\circ\text{C}$  to  $90^\circ\text{C}$ , the areas of 1<sup>#</sup> peak, 2<sup>#</sup> peak, and 3<sup>#</sup> peak increase. Because these quenching temperatures locate in the S-L phase separation region, PVDF crystallizes prior to L-L phase separation, and the crystallinity of PVDF increases, which results in the increasing of the diffraction intensity when the quenching temperatures increase. As the quenching



**Figure 5** Wide-angle X-ray diffraction (WAXD) measured between  $2\theta = 17^\circ$  and  $22^\circ$  of PVDF-DMP system quenching in different temperatures for 1 min. A- $40^\circ\text{C}$ ; B- $50^\circ\text{C}$ ; C- $60^\circ\text{C}$ ; D- $70^\circ\text{C}$ ; E- $80^\circ\text{C}$ ; F- $85^\circ\text{C}$ ; G- $90^\circ\text{C}$ ; H- $95^\circ\text{C}$ ; I- $100^\circ\text{C}$ ; J- $110^\circ\text{C}$ .

temperatures increased from  $95^\circ\text{C}$  to  $100^\circ\text{C}$ , the areas of three diffraction peaks decreased, as these temperatures are in the L-L phase separation region, PVDF undergoes L-L phase separation prior to PVDF crystallization. When quenching temperatures increased to  $110^\circ\text{C}$ , the 1<sup>#</sup> peak begins to disappear as PVDF-DMP system begins to melt.

The crystal form of PVDF in PVDF-DMP system measured by WAXD quenching from liquid nitrogen and crystallized for 24 h in  $25^\circ\text{C}$  water bath is shown in Figure 6. Compared to Figure 5, only one discernable diffraction peak appears at  $20.6^\circ$ . According to Lovinger<sup>17</sup>, the diffraction peaks of (1 0 0) and (2 0 0) of  $\beta$ -phase overlap at  $20.6^\circ$ , so it can be concluded that the PVDF-DMP only contains  $\beta$ -phase PVDF. As for pure PVDF crystallizes from glass state,  $\beta$ -phase often appears when crystallizes under  $30^\circ\text{C}$ , while  $\alpha$ -phase is formed quenching between  $80^\circ\text{C}$  to  $140^\circ\text{C}$ , and  $\gamma$ -phase is formed in higher temperature of  $165^\circ\text{C}$ .<sup>21</sup> Therefore, when PVDF crystallized for 24 h in  $25^\circ\text{C}$  water bath with high-rate heating quenching from liquid nitrogen to keep glass state, the molecular chains moved in the limited area (chain segment movement region),  $\beta$ -phase microcrystal was formed. Moreover, from the Figure 5 it is shown that the  $\alpha$ -phase PVDF in PVDF-DMP system occurred in the common conditions with the obvious congregated spherulite membrane structure, which limited the membrane permeation quality and enhanced membrane strength. While the  $\beta$ -phase of PVDF in this system occurred in the rigorous condition with the less influence of DMP, it is also possible to change the crystal structure of PVDF to change the membrane structure to obtain the proper membrane in both strength and properties.



**Figure 6** Wide-angle X-ray diffraction measured between  $2\theta = 5^\circ$  and  $60^\circ$  of PVDF-DMP system quenching from liquid nitrogen and crystallized for 24 h in water bath ( $25^\circ\text{C}$ ).

## CONCLUSIONS

The crystallization rate and crystallinity were in the order of 80°C, 85°C, and 95°C in the early stage of phase separation. The crystallinity of PVDF in PVDF-DMP system increased in the early stage of phase separation, and PVDF crystallized completely in the late stage of phase separation. Different quenching temperatures had effects on the spherulite size in L-L and S-L phase separation region. The largest spherulites were obtained in 80°C, while the less spherulite size was showed in 30°C. The lowest spherulite size existed in 85°C, and the congregated rich polymer was obtained in 95°C. In different quenching conditions, the greatest size and the mature of spherulites were obtained in air bath with the slowest cooling rate, the great amount of spherulites were obtained in ice water, and the irregular size of spherulites were formed in 30°C water bath. In particular, when PVDF-DMP system quenching to different temperatures above 40°C from melting to 180°C, the  $\alpha$ -phase PVDF was obtained in PVDF-DMP system, and as quenching temperatures changed, the area of diffraction peak changed. The  $\beta$ -phase PVDF was formed when PVDF-DMP system was quenching from liquid nitrogen and crystallized 24 h in 25°C water bath.

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