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Isothermal crystallization study on aqueous solution of poly(vinyl methyl ether) by DSC method

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ABSTRACT

A study on the isothermal crystallization of water in aqueous solutions of poly(vinyl methyl ether) (PVME) was carried out by the differential scanning calorimetry (DSC). The influence of PVME concentration (49.5, 44.5 and 39.5 v%) and the crystallization temperature (T_c) on crystallization rate G, crystallization enthalpy (ΔH_c) and melting enthalpy (ΔH_m) was investigated. Avrami equation cannot be used to describe the crystallization process of water in aqueous PVME solution. Within the measured temperature range, the crystallization rate G increases with the crystallization temperature T_c and with the decreasing PVME content. The crystallization enthalpy ΔH_c linearly increases with the degree of supercooling. The influence of T_c on the ΔH_c becomes more marked with increasing PVME concentration. For 49.5 and 44.5 v% PVME solutions, the amount of water arrested in solution during the isothermal crystallization and the final concentration of PVME-rich phase increase linearly with the T_c, whereas for 39.5 v% PVME solution, these two values almost do not change with T_c. The amount of frozen water in the subsequent cold crystallization is approximately proportional to the initial T_c. The approximately constant ΔH_m for a given concentration at the different initial isothermal crystallization temperatures suggests that the total amount of ice from the first isothermal crystallization and the second cold crystallization is same. The quantitative relation of the amount of frozen water in the cold crystallization and the initial T_c demonstrates that PVME/water complexes are thermodynamically unstable.

1. Introduction

As a water-soluble polymer [1–3], poly(vinyl methyl ether) (PVME) has the potential to be applied in a wide range of area [4], such as bio-hydrogel [5–7], thermo-responsive materials [8,9], membranes [10,11], viscosity enhancement [12], emulsification agent and so on [13,14]. The special properties of PVME mainly result from its two kinds of functional groups: hydrophilic ether oxygens, which can stabilize the aqueous solution by forming hydrogen bonds with water molecules, and hydrophobic parts (such as methyl groups), which can destabilize the solution by altering normal water structure and decreasing the entropy of water. A small change in the balance between the hydrogen bonding and the hydrophobic interaction can induce the phase transition of aqueous PVME solution, and therefore the interactions of water molecules and PVME chains play a key role in the phase behavior [15–19].

Aqueous PVME solution has a bimodal lower critical solution temperature (LCST) (type III) partial miscibility behavior at the physiological temperature (around 35 °C), showing two stable liquid–liquid critical points [20,21]. It is generally believed that there are complexes between water molecules and PVME [22]. H. Maeda [24] and Y. Maeda [23] investigated respectively the interaction of water with PVME by using near-infrared (NIR), differential scanning calorimetry (DSC), and viscometric method. A different kind of coordination water was suggested, in which a maximum of five water molecules were coordinated to ether group and methyl group below the LCST, whereas above the LCST, most of methyl groups of PVME were dehydrated and only partial dehydration of the ether groups occurred.

Berghmans et al. [22] suggested that each repeating unit of PVME chain was coordinated with two water molecules, and consequently a critical concentration of 61 wt% was found. Above

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this critical concentration, no free water exists. The glass transition temperature T_g was therefore plotted in two different regions as a function of concentration. A constant T_g at −30 °C was observed for $0\ \text{wt\%} < c < 61\ \text{wt\%}$. For the concentrations ($c > 61$ wt%), the crystallization of water will not occur anymore and the solution vitrifies upon cooling, giving a glass transition temperature that decreases with the increasing water content as expected for homogeneous solutions or mixtures. However, further investigation of highly concentrated PVME/water ($c = 70$ wt%) demonstrated that the crystallization of water could be realized once ice nuclei are added, which indicated that the arrested crystallization of water in highly concentrated mixtures is not only related to ice nucleation problems but also to the stability of molecular complexes [25].

Using Wertheim lattice thermodynamic perturbation theory (Wertheim-LTPT), Nies et al. [26–28] not only predicted the melting line with a step but also a LCST and two narrow adjacent upper critical solution temperature (UCST) miscibility gaps in aqueous PVME solution, which currently is in qualitative agreement with the experimental LCST, melting line and UCST in the higher concentration area, which were obtained respectively from Fourier transform infrared (FTIR) or modulated temperature DSC (MTDSC) or small-angle neutron scattering (SANS) measurements. Especially, the double melting endotherm observed in conventional DSC or MTDSC measurements can be effectively interpreted using the melting line with a step of aqueous PVME solution obtained by using FTIR method. However, in the past, the overlapped double melting peaks in PVME/water system was attributed to the existence of bond waters and free waters which melt at the different temperature once heated [29,30].

Another predicted UCST in the lower concentration area is not still experimentally observed because of the fast crystallization of water in aqueous PVME solution.

Like many other aqueous solutions of polymers [31–33], say, the aqueous solution of poly(vinylpyrrolidone) (PVP), gelatin and polyethylene glycol, the crystallization behavior of aqueous PVME solution at the temperature below the normal freezing point of water is also rather complicated. Although the thermodynamics behavior of aqueous PVME solution has been researched extensively, the crystallization kinetics of this system is relatively little known. Through using FTIR technique and optical microscopy method, the isothermal crystallization kinetics was recently investigated [34]. Measurements of IR spectra indicate that the red shift of ν_s (CH_3) absorption band occurred only after the transparent phase changed to the opaque crystallization phase at the different crystallization temperature T_c. The final concentration of PVME in crystallization phase is 94 wt%. There is no remarkable shift of ν_s (CH_3) absorption band in the non-crystallization area compared with that in the crystallization area. The growth rate G and morphologies of ice at the different crystallization temperature T_c or the concentration of PVME were observed. However, in order to deeply understand the isothermal crystallization of the aqueous PVME solution, only the observations of crystallization rate and morphologies of ice is not enough, the further measurements of crystallization enthalpy, crystallization model and other crystallization characteristics will be rather necessary.

In the present study, we investigated the crystallization of water in aqueous PVME solution through using DSC, and then analyzed the influence of crystallization temperature T_c and the concentration of PVME on the crystallization enthalpy ΔH_c, melting enthalpy ΔH_m and the amount of frozen water, and therefore disclosed the thermodynamical crystallization characteristics of PVME solutions. Furthermore, an important comparison of present DSC observations and previously reported FTIR results of PVME solution was made.

2. Experimental section

2.1. Materials

Poly(vinyl methyl ether) (PVME) dissolved in water (mass percentage PVME, $c = 50$ wt%) was purchased from Aldrich Chemical Company. This PVME solution was first rotary evaporated and then dried at 50 °C under vacuum for several days until the water mass fraction was less than 0.5 wt% as determined by thermogravimetric analysis (TA Instruments TGA 2950). The glass transition temperature of dried PVME sample is ca. −25 °C. Mass average $M_w = 20\ \text{kg mol}^{-1}$, determined from SANS; polydispersity, $M_w/M_n = 2.5$, derived from gel permeation chromatography (GPC) in THF using polystyrene as the calibration standard. PVME solutions were homogenized at around 10 °C for a period up to one month for the higher polymer concentrations. The concentrations are expressed in volume percentage of PVME (c) in solution according to the density of PVME sample used in our experiment ($1.02\ \text{g mL}^{-1}$ at 25 °C) and the density of water ($1.00\ \text{g mL}^{-1}$ at 25 °C). The excess volume of the mixture of PVME/water is omitted [26,35].

2.2. Calorimetric measurements

A Perkin–Elmer DSC7 was used for the calorimetric observations. The temperature calibration was done with indium and water (melting temperature T_m of In is 156.6 °C, T_m of water is 0 °C). The calibration of enthalpy change was done with indium (melting enthalpy ΔH_m of In is $28.45\ \text{J g}^{-1}$). The weight of the samples sealed in aluminum pans was approximately 10–15 mg, and cooling rate and heating rate is $40\ ^\circ\text{C min}^{-1}$ and $1\ ^\circ\text{C min}^{-1}$, respectively.

2.3. Rheological measurements

Rheological data were obtained with a strain-controlled rheometer (Advanced Rheometrics Expansion System of Rheometrics Scientific, equipped with a 200FRTN1 transducer) with parallel plate (25 mm diameter) geometry. Dynamic frequency sweep measurements were performed $0.1–100\ \text{rad s}^{-1}$ (log increase) and at a strain of 10% (include pure PVME, 1%). A liquid bath connected with an external thermostatic bath was used to regulate the temperature.

3. Results and discussion

With a cooling rate of $40\ ^\circ\text{C min}^{-1}$, four samples with $c = 34.6$ v%, 39.5 v%, 44.5 v% and 49.5 v% were quickly cooled to the setting temperature and held to observe the isothermal crystallization behaviors respectively. Some thermograms of 49.5 v%, 44.5 v%, 39.5 v% and 34.6 v% PVME samples are shown in Fig. 1.

3.1. The influence of the crystallization temperature T_c on the crystallization rate G of water

The crystallization half-time ($t_{1/2}$) is the difference of the time $t_{50\%}$ (at which the crystallization degree is 50% of the maximum achievable crystallinity) and the time t_{onset} (at which the crystallization starts) (see Fig. 1d), namely $t_{1/2} = t_{50\%} - t_{\text{onset}}$. The crystallization rate G is defined as the reciprocal of $t_{1/2}$, e.g., $G = (t_{1/2})^{-1}$. The degree of supercooling ΔT ($= T_m - T_c$) will remarkably influence the rate of crystallization. T_m of 49.5, 44.5, and 39.5 v% PVME solution is − 7, − 4, and − 2 °C, respectively [30]. Take 49.5 v% PVME solution as an example. Its melting temperature T_m is − 7 °C, when $\Delta T = 21$ °C, that is to say, when the isothermal crystallization occur at − 28 °C, the crystallization half-time ($t_{1/2}$) is 12.07 min. With the higher

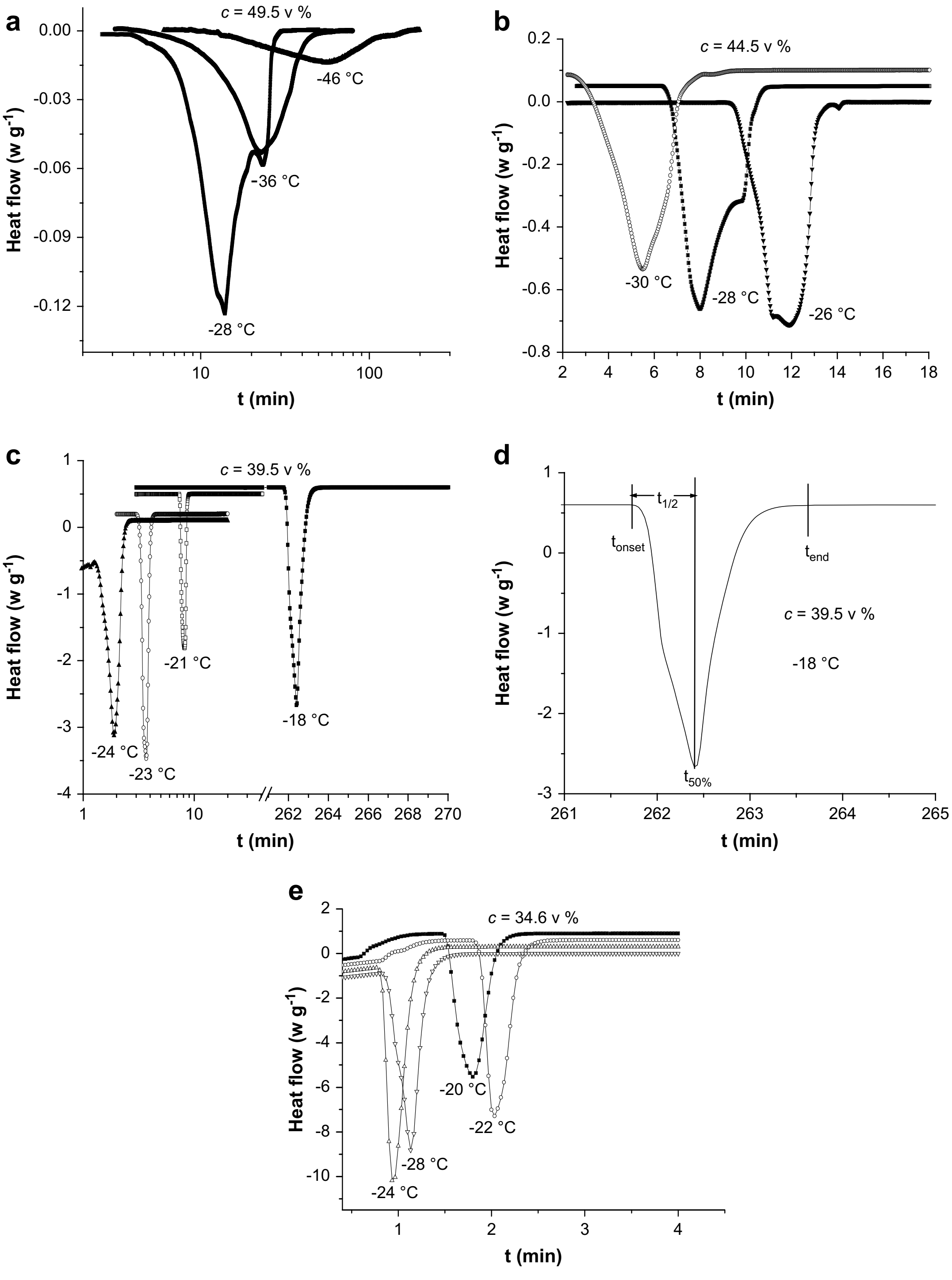

Fig. 1. DSC thermograms of isothermal crystallization for 49.5, 44.5, 39.5 and 34.6 v% PVME solutions: (a) 49.50 v%; (b) 44.5 v%; (c and d) 39.5 v%; (e) 34.6 v%. Curves were shifted vertically for clarity.

degree of supercooling, say, $\Delta T = 41$ °C, $T_c = -48$ °C, $t_{1/2}$ is much longer up to 74.87 min. The crystallization rate at -28 °C and -48 °C is 0.083 and 0.013 min^{-1} respectively. The crystallization rate G at different crystallization temperatures T_c for 49.5 v% PVME solution is listed in Table 1. Within the measured temperature range, the G increases with the crystallization temperature T_c. The fastest crystallization rate ($G = 0.083$ min^{-1}) occurred at around -28 °C. When T_c is higher than -28 °C for 49.5 v% PVME solution, no crystallization was found by DSC. For example, although 49.5 v% PVME sample was held at -20 °C overnight, the thermogram curve (Heat flow vs. Time) is still flat. It possibly needs a much longer time than a day to finish crystallization at -20 °C. For 44.5 and 39.5 v% PVME solutions, the crystallization rate also approximately increases with the crystallization temperature. The crystallization rate G at the different temperatures for 39.5, 44.5 and 49.5 v% PVME samples is illustrated in Fig. 2. For 34.6 v% PVME sample, the crystallization rates G at the different crystallization temperature were not calculated because only two thermograms (at -20 °C and -22 °C) can be used for the rate calculation. Other two thermograms (at -24 °C and -28 °C) in Fig. 1e were only used to illustrate that the

Table 1
Kinetics crystallization data for 49.5 v% PVME solution as determined from the analytical DSC curves.

T_c (°C)	G	ΔH_c	ΔH (T_c)	W^f_{ice}	ΔH_m	Final c
−28	0.083	−79.57	−276.60	0.2877	92.86	69.8(68.8)
−30	0.050	−74.90	−272.50	0.2749	93.27	68.5(68.9)
−32	0.034	−70.02	−268.40	0.2609	91.61	67.2(68.5)
−34	0.054	−67.36	−264.30	0.2549	99.98	66.7(71.0)
−36	0.050	−61.86	−260.20	0.2377	84.85	65.1(66.6)
−38	0.033	−64.23	−256.10	0.2508	88.21	66.3(67.5)
−40	0.029	−58.81	−252.00	0.2334	94.37	64.8(69.3)
−42	0.028	−50.79	−247.90	0.2049	86.16	62.4(66.9)
−44	0.030	−51.35	−243.80	0.2106	94.46	62.9(69.3)
−46	0.019	−59.63	−239.70	0.2488	90.38	66.1(68.1)
−48	0.013	−35.65	−235.60	0.1513	88.31	58.4(67.5)

Unit: G, min^{-1}; ΔH_c, ΔH (T_c), ΔH_m, J g^{-1} solution; W^f_{ice}, frozen water, g g^{-1} solution; final c, v%. The values in brackets are obtained based on ΔH_m.

crystallization has started before the DSC machine reaches its equilibrium, where the exothermal peaks cannot be integrated accurately to obtain the crystallization enthalpy of water.

Within the measured temperature range, with the decreasing temperature, the viscosity of solution (characterized here by the loss modulus G'') will increase. Fig. 3 shows that G'' increases when the temperature decreases from 20 °C to − 20 °C. So, when the T_c decreases, the diffusion rate of water will decrease, accordingly the crystallization rate will slow down. The diffusion of water mainly controls the crystallization rate within the measured temperature range.

3.2. The influence of the concentration of PVME on the crystallization rate G of water

Based on the observations of three samples (c = 39.5 v%, 44.5 v% and 49.5 v%), we can find that the crystallization rate G increases with the decreasing concentration (Fig. 2). For example, when T_c is − 28 °C, 49.5 v% PVME sample has a crystallization rate of 0.083 min^{-1} while that of 44.5 v% PVME solution is 0.427 min^{-1}. The decrease of only 5 v% in the concentration from 49.5 v% to 44.5 v% leads to an increase of crystallization rate by 5 times. When c = 34.6 v%, it is impossible anymore to calculate the crystallization rate because of the mentioned reason in Section 3.1 (Fig. 1e). For the other samples (c < 34.6 v%), the fast crystallization of water makes the conventional DSC measurement too difficult to be carried out.

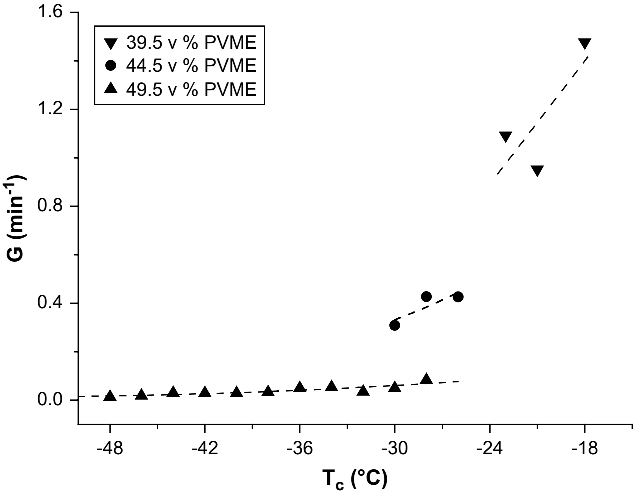

Fig. 2. The influence of crystallization temperature T_c on the crystallization rate G for 49.5, 44.5 and 39.5 v% PVME solutions.

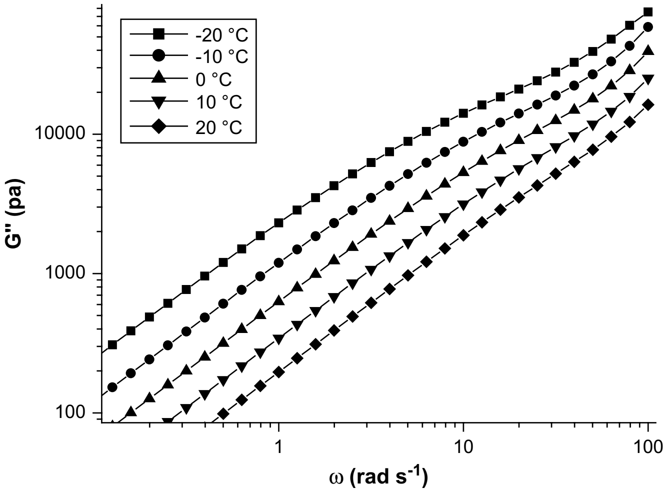

Fig. 3. The loss modulus G'' increases with the decreasing temperature for 49.5 v% PVME solution.

It is very clear that the viscosity of aqueous PVME solution increases with the PVME concentration [24]. The diffusion rate of water will accordingly decrease with the increasing viscosity of solution. Therefore, the crystallization rate of water will decrease with the increasing PVME concentration at the same crystallization temperature.

3.3. The influence of the crystallization temperature T_c on the crystallization enthalpy ΔH_c and melting enthalpy ΔH_m

The crystallization enthalpy ΔH_c of water was obtained by integrating from the onset time t_{onset} to the end time t_{end} of the exothermic peak from the crystallization. The melting enthalpy ΔH_m of ice was determined by integrating from the onset temperature to the end temperature of the endothermic peak from ice melting according to the method described by O'Neill et al. [36–39] The enthalpy changes for ΔH_c and ΔH_m are expressed as J per gram solution (J g^{-1}). The temperature dependence of the enthalpy of water crystallization was taken into consideration when determining the ice content. The following approximation is used to calculate the crystallization enthalpy of pure water at T_c.

$$\Delta H(T_c) = \left[\Delta H_0 - \int_{T_c}^{273} \Delta C_p \, dT\right] \approx [-334 - 2.05(T_c - 273)]\left(\mathrm{J\,g^{-1}}\right) \quad (1)$$

where the T_c is the crystallization temperature in K, and the ΔH_0 is the crystallization enthalpy at 273 K corresponding to 334 J g^{-1} and the ΔC_p is the difference in heat capacity between liquid water and ice at the T_c. The ratio of the crystallization enthalpy ΔH_c measured by DSC and the crystallization enthalpy ΔH (T_c) of pure water is a measure of the amount of ice separated per gram solution at the T_c.

$$W^f_{ice} = \Delta H_c / \Delta H(T_c) \quad (2)$$

Eq. (1) doesn't involve the interaction of water and PVEM chains. According to [21], the demixing enthalpy is about 22.5 J g^{-1} for 39.5, 44.5 and 49.5 v% PVME solutions, which is the main source of the excess free energy in the present PVME solution. The omission

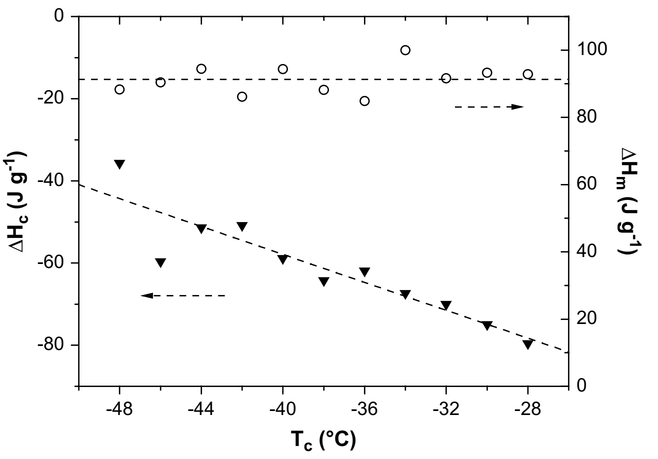

Fig. 4. The crystallization enthalpy ΔH_c and the melting enthalpy ΔH_m change with the crystallization temperature T_c for 49.5 v% PVME solution.

of the demixing enthalpy only can result in a maximum error of the final concentration of PVME-rich phase, 2.6, 3.4 and 3.9 v%, for 39.5, 44.5 and 49.5 v% PVME solution, respectively. So the omission of the demixing enthalpy is rational, and therefore Eq. (1) is valid to calculate the crystallization enthalpy of water in the present PVEM solution.

For the determination of ice content from the ΔH_m, the melting enthalpy of pure water at 273 K was used, namely, $\Delta H_{273} = 334\ \mathrm{J\,g^{-1}}$. The amount of melted ice per gram solution was calculated approximately as:

$$W_{\mathrm{ice}}^{\mathrm{m}} = \Delta H_{\mathrm{m}}/\Delta H_{273} \tag{3}$$

For 49.5 v% PVME solution, the crystallization enthalpy increases linearly with the decreasing crystallization temperature, whereas the melting enthalpy is nearly a constant that did not change with the initial crystallization temperature (Table 1 and Fig. 4).

Following Eqs. (1) and (2), the amount of frozen water in the isothermal crystallization was calculated. The result indicates that the amount of frozen water linearly increases with the crystallization temperature (Fig. 5). The final concentration c of PVME-rich phase follows a same trend.

For example, at -48 °C, there is only 0.1513 g frozen water for 1 g solution, while at -28 °C, this value is 0.2877 g. Accordingly, the final concentration c of PVME-rich phase at -48 °C and -28 °C is 58.4 v% and 69.8 v% respectively. In other words, this means that the amount of unfrozen water is different at the different crystallization temperatures. However, once slowly heated with a rate of 1 °C min^{-1}, those water arrested in the solution can crystallize out

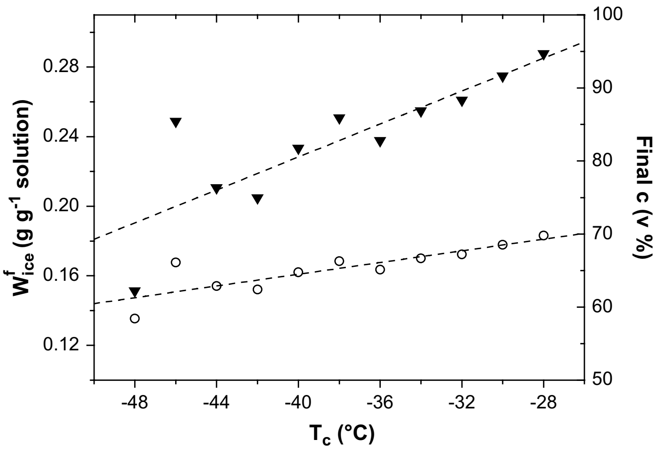

Fig. 5. The amount of frozen water and the final concentration c (v%) of PVME-rich phase change with the crystallization temperature T_c for 49.5 v% PVME solution (frozen water: solid points; final c: hollow points).

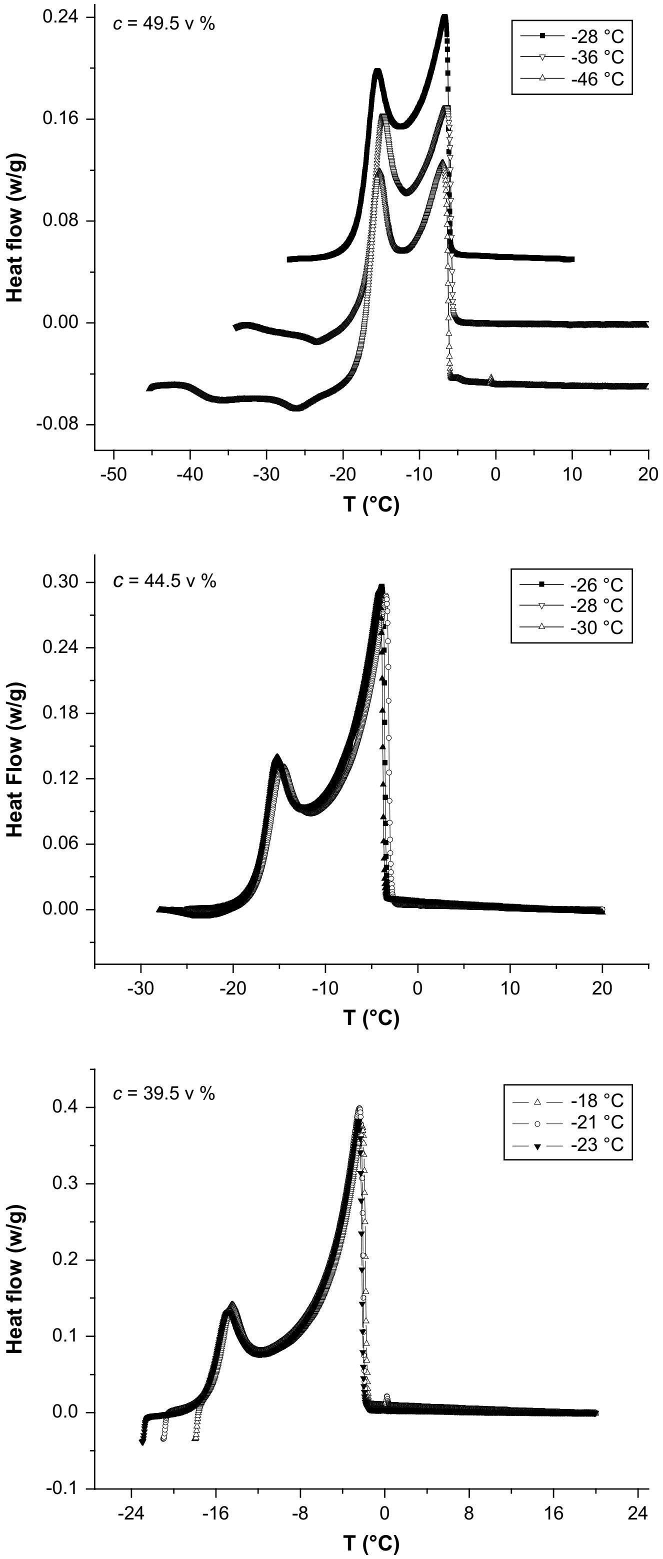

Fig. 6. The melting curves with double peaks of 49.5, 44.5 and 39.5 v% PVME solutions (curves were shifted vertically for clarity for 49.5 v% PVME solution).

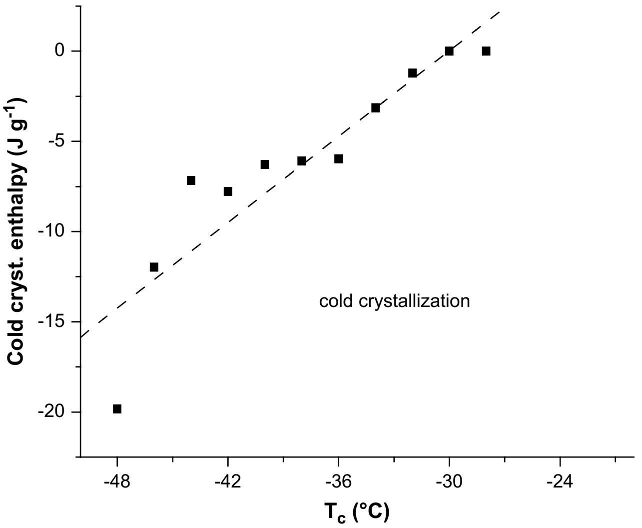

Fig. 7. The enthalpy of cold crystallization during warming changes with the initial crystallization temperature T_c for 49.5 v% PVME solution.

(Fig. 6), which is called as the cold crystallization. This cold crystallization demonstrates that the PVME/water complex is thermodynamically unstable. This kind of PVME/water complex is the polymer's hydration sheath [24]. During the heating, with the decrease of the solution viscosity, some water in PVME-rich phase start to further crystallize with the ice from the first isothermal crystallization as the nucleation sites. A similar experiment, crystallization of water from an aqueous PVME solution (70 wt%) induced by ice nuclei formed at its surface at – 35 °C, was reported by Berghmans and Shen et al. [25]. This kind of cold crystallization of water also has been confirmed by Shen et al. through infrared spectroscopic study [40,41]. The intensity of the H_2O bending vibration decreases rapidly at the temperatures ranging from – 38 °C to – 24 °C during heating, which means that the transition of water molecules from amorphous liquid to cubic ice increases H bond strength, and then the oscillation strength of the H_2O bending vibration consequently decreases. The amount of frozen water from this cold crystallization is approximately proportional to the initial degree of supercooling (Fig. 7).

Although the initial crystallization temperature is different, which ranges from – 48 °C to – 28 °C, the melting enthalpy is almost a constant, around 91.3 kJ g^{-1}.

Figs. 8 and 9 illustrate the crystallization enthalpy, melting enthalpy, the amount of frozen water and the final concentrations of PVME-rich phase for 44.5 and 39.5 v% PVME solutions.

The similar phenomena were found for 44.5 v% PVME solution, too. The melting enthalpy is 118.3 for 44.5 v% PVME solution (Figs. 6 and 8). Therefore, during twice crystallization process for 49.5 and 44.5 v% PVME solutions, where the first one is the isothermal crystallization and the second one is the so-called cold crystallization during slowly heating, the total amount of frozen water is approximately a constant for a given solution although the initial crystallization temperatures are different.

The crystallization enthalpy ΔH_c involves the different change of heat capacity of water and ice from room temperature to the different crystallization temperatures. By contrast, the melting enthalpy ΔH_m only involves the nearly same change of the heat capacity of water and ice. For example, for 49.5 v% PVME sample, the melting range is always from – 22 °C to – 6 °C although the initial T_c is different, so ΔH_c shows a higher dependence of crystallization temperature than ΔH_m. After twice crystallizations, the nearly same thermodynamic state (final PVME concentration) was obtained, and then the initial state (PVME concentration is 49.5 v%)

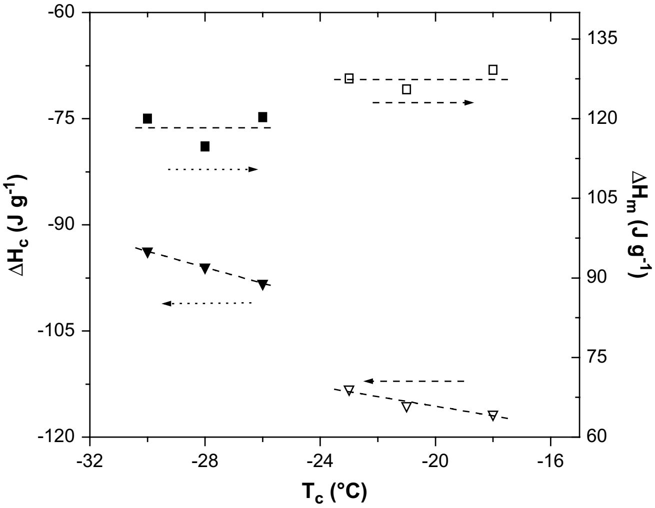

Fig. 8. The crystallization enthalpy ΔH_c and the melting enthalpy ΔH_m change with the crystallization temperature T_c for 44.5 and 39.5 v% PVME solutions (44.5 v%: solid points; 39.5 v%: hollow points).

was recovered after the melting of water, so ΔH_m is almost same and less dependent on the crystallization temperature.

The temperature dependence of ΔH_c also leads to a bigger difference between the absolute values of ΔH_c and ΔH_m. The greater the degree of supercooling, the greater the contribution of the second item in Eq. (1) to ΔH_c, the greater the cold crystallization enthalpy, and finally the greater the difference between the absolute values of ΔH_c and ΔH_m. For example, at – 28 °C, the final concentration c of PVME-rich phase for 49.5 v% PVME solution is 69.8 v% (calculated from ΔH_c) and 68.8 v% (calculated from ΔH_m) respectively, the difference between them is only 1.0 v%; at – 48 °C, the final concentration c of PVME-rich phase is 58.4 v% (calculated from ΔH_c) and 67.5 v% (calculated from ΔH_m), the difference is 9.1 v%. However, when the enthalpy of cold crystallization is considered, the final concentration is approximately 64.9 v% (calculated from ΔH_c + cold crystallization enthalpy), and the difference is only 2.4 v%. The average difference between two final concentrations of PVME-rich phase, which are calculated from ΔH_c + cold crystallization enthalpy and ΔH_m respectively, is only 0.9 v% throughout the crystallization temperature range from – 28 °C to – 48 °C. Although this calculation is only approximate because the cold crystallization is not the isothermal

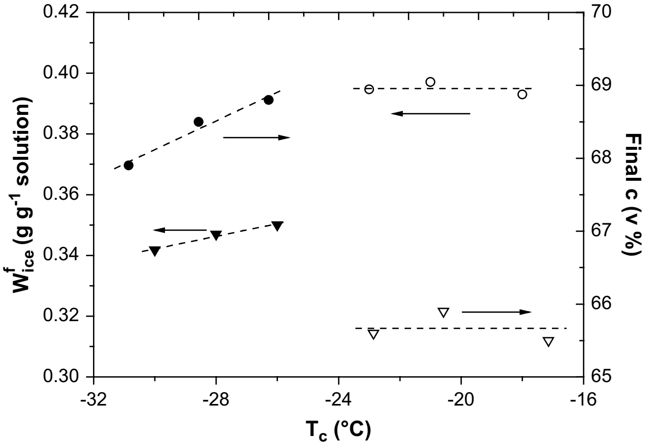

Fig. 9. The amount of frozen water and the final concentration c (v%) of PVME-rich phase change with the crystallization temperature T_c for 44.5 and 39.5 v% PVME solutions (44.5 v%: solid points; 39.5 v%: hollow points).

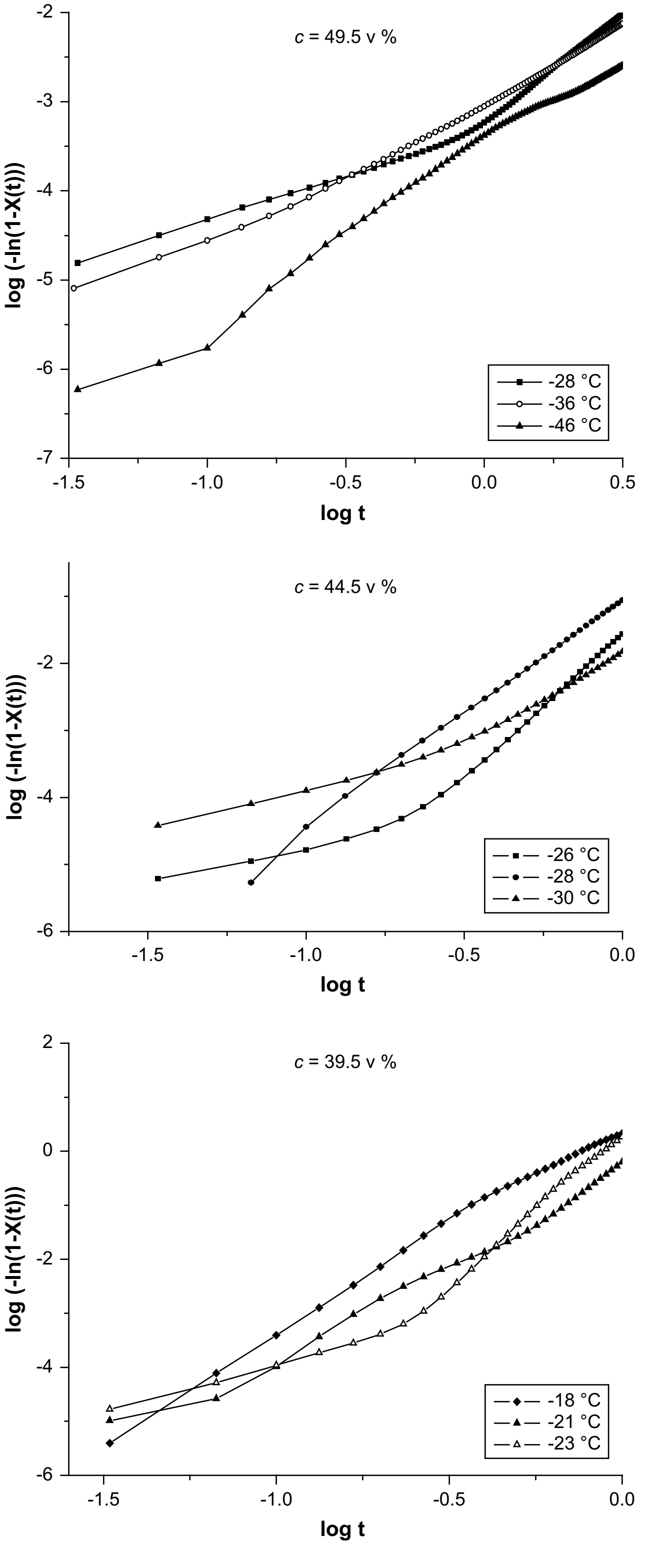

Fig. 10. The crystallization model at the different crystallization temperature T_c for 49.5, 44.5 and 39.5 v% PVME solutions.

crystallization and therefore its enthalpy cannot be added directly to ΔH_c, it can help us effectively to understand this difference between the absolute values of ΔH_c and ΔH_m.

Further comparisons of the crystallization enthalpy at the different crystallization temperature disclose that the crystallization temperature will more remarkably influence the crystallization enthalpy ΔH_c of the higher concentration solution than that of the lower concentration solution. The increase rate of ΔH_c with the T_c for 39.5 v%, 44.5 v% and 49.5 v% PVME solution is respectively 0.68, 1.13 and 1.69 $\mathrm{J\,g^{-1}\,K^{-1}}$, which is also proportional to the concentration of PVME. This is largely due to a fact that the total interaction energy between water and PVME chains increases with the PVME concentration [26]. In fact, the crystallization enthalpy ΔH_c comprises the crystallization enthalpy of pure water and the demixing enthalpy, so under the isothermal crystallization conditions, the higher PVME concentration (below 61 wt%) will more strongly influence the ΔH_c.

The previously reported results suggested that each repeating unit of PVME chain interact with 2.7–5.0 water molecules through hydrogen bonds [24].

However, for 39.5 v% PVME solution, the case is different. Although the crystallization enthalpy ΔH_c also increases with the degree of supercooling with a rate of 0.68 $\mathrm{J\,g^{-1}\,K^{-1}}$ and the melting enthalpy is a constant of 127.4 $\mathrm{J\,g^{-1}}$ (Figs. 6 and 9), the amount of frozen water and the final *c* of PVME-rich phase for 39.5 v% PVME solution almost do not change with the crystallization temperature contrary to the case of 49.5 and 44.5 v% solutions. This is an important concentration bending point, which is in agreement with the measurements made by Yang and Maeda et al. through checking infrared band shift of ν(C–O) and ν_s (CH_3) with PVME concentration [23,42].

It is well worth noting that the final PVME concentration in PVME-rich phase obtained from DSC measurements here is different from the previous IR results [34]. For example, for 44.5 v% PVME solution, according to DSC measurements, the final PVME concentration in PVME-rich phase changed from 68.8 v% to 68.2 v% when the crystallization temperature ranged from −26 °C to −30 °C. However, according to IR observations, the final PVME concentration in PVME-rich phase is always 94 wt% (or 94 v%) after the isothermal crystallization finished although the crystallization temperatures or the concentrations of PVME solution are different. There is an around 25 v% concentration difference between DSC and IR measurements.

Because the final concentration obtained from DSC measurement is the calculated average value, while IR results only indicates the local or highest concentration in a round area of 2 mm (because the aperture used is 2 mm in IR measurement), so DSC and IR results are not in conflict with each other. However, the further investigation has to be done.

3.4. *Isothermal crystallization process of water*

The Avrami equation was tried to analyze the isothermal crystallization process [43].

$$\log\{-\ln[1-X(t)]\} = n\log t + \log K \tag{4}$$

where $X(t)$ is the degree of crystallinity at time *t*, *n* is the Avrami exponent and *K* is the isothermal crystallization rate parameter. The plots of $\log\{-\ln[1-X(t)]\}$ vs. log *t* are presented in Fig. 10. The values of *n* and *K* for the isothermal crystallization of 49.5 v%, 44.5 v% and 39.5 v% PVME solutions are listed in Tables 2 and 3, respectively.

Table 2
Values of *n* and *K* for isothermal crystallization of 49.5 v% PVME solution.

T (°C)	−48	−46	−44	−42	−40	−38	−36	−34	−32	−30	−28
n	2.24	2.11	1.70	1.24	1.44	1.12	1.19	1.16	1.00	1.07	1.00
K	1.22	3.87	4.06	0.01	7.72	3.90	4.47	2.94	0.83	1.38	4.65

Unit: *K*, 10^{-4} $\mathrm{min^{-1}}$.

Table 3
Values of n and K for isothermal crystallization of 44.5 v% and 39.5 v% PVME solutions.

	44.5 v% PVME			39.5 v% PVME		
T (°C)	−30	−28	−26	−23	−21	−18
n	1.15	3.87	1.13	1.83	3.18	4.16
K	1.8×10^{-3}	0.224	2.52×10^{-4}	7.9×10^{-3}	0.27	5.77

Unit: K, min^{-1}.

In most of the cases, the exponent n is not integer; therefore the Avrami equation cannot be used effectively to describe this isothermal crystallization process. Nevertheless, some useful information still can be obtained. In our previous research [34], it was found that the diameter of spherulites increases linearly with the isothermal crystallization time and the density of PVME-rich phase did not change with the isothermal crystallization time (the characteristic absorption of ν_s (CH_3) didn't change any more after the complete crystallization with the time). So, this promotes us to further analyze the mechanism of nucleation and crystal growth forms. For 49.5 v% PVME solution, n value is between 1.00 and 2.24 (Table 1), which means the crystal growth is one or two-dimensional. Whereas for 44.5 v% PVME solution, one-dimensional ($n = 1.13$ at −26 °C) or three ($n = 3.87$ at −28 °C) dimensional crystal growth can be found. The case of 39.5 v% PVME solution is similar (Tables 2 and 3). The non-integer n value also means that different mechanism of nucleation and various crystal growth forms can exist simultaneously at the given crystallization temperature.

4. Conclusions

To summarize, the isothermal crystallization kinetics of aqueous PVME solutions has been systematically investigated here. At the same crystallization temperature, the crystallization rate G increases with the decreasing PVME concentration c. The crystallization rate G also increases with the crystallization temperature within the measured temperature range. This variation of crystallization rate with PVME concentration or crystallization temperature mainly depends on the viscosity of solution. The decrease of crystallization temperature T_c or the increase of PVME concentration will lead to the consequent increase of viscosity of solution and therefore the decrease of the crystallization rate G. Avrami equation cannot be used to describe the crystallization process of water in aqueous PVME solution.

During the isothermal crystallization, the crystallization enthalpy ΔH_c increases linearly with the decreasing crystallization temperature T_c. The effect of crystallization temperature T_c on the crystallization enthalpy ΔH_c becomes more marked with the PVME concentration. Water in the solution cannot completely crystallize out, the amount of frozen water changes with the degree of supercooling. Through analyzing the relation of the amount of frozen water and the crystallization temperature, it was found for 39.5 v% was observed that the amount of frozen water and the final c of PVME-rich almost do not change with crystallization temperature. However, for 49.5 and 44.5 v% PVME solutions, the amount of frozen water and the final c of PVME-rich phase increased with the crystallization temperature.

The quantitative relation of the amount of frozen water in the cold crystallization and the initial isothermal crystallization temperature demonstrates that PVME/water complexes are thermodynamically unstable. The constant melting enthalpy ΔH_m of the samples further confirms that the total amount of frozen water from the isothermal crystallization and cold crystallization is same. The final c of PVME-rich phase obtained from DSC results is lower than that previously reported by IR measurements; the detailed reasons are still under investigation in our lab.

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