

Ice nucleation and supercooling behavior of polymer aqueous solutions[☆]

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Abstract

We determined the homogeneous nucleation temperature depression, $\Delta T_{f,\text{hom}}$, the equilibrium melting point depression, ΔT_m , and the value λ , which can be obtained from the linear relationship $\Delta T_{f,\text{hom}} = \lambda \Delta T_m$, for aqueous solutions of PEG (200–20,000 g mol⁻¹), PVP (10,000, 35,000, 40,000 g mol⁻¹), and dextran (10,000 g mol⁻¹) in the concentration range 0–40 wt% using the emulsion method. The molecular weight dependence of $T_{f,\text{hom}}$, T_m , and λ in PEG aqueous solutions was found to change in the vicinity of Mw 600–1540 at all concentrations. In addition, it was confirmed that for all of the polymers studied, there was a good linear relationship between λ and the logarithmic value of the self-diffusion coefficient D_0 of the solute molecule. These results indicate that the parameters that describe non-equilibrium freezing, such as $T_{f,\text{hom}}$ and λ , are dependent on solution properties such as viscosity and self-diffusion of solute molecules.

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The prediction and control of supercooling and the crystallization temperature of aqueous solutions are important in the areas of meteorology, physical chemistry, and cryobiology, and numerous studies have been conducted on this subject. For example, it has been reported that aqueous solutions of polymers such as PEG, PVP, and hydroxyethyl starch have different characteristics to aqueous solutions of small molecules. They show low crystallization temperatures and low equilibrium melting points, considering their concentration, and they can easily be supercooled [15,3,10]. In recent years, there have been numerous reports describing special-function polymers such as antifreeze protein (AFP) [22,16]. Thus, the low-temperature properties of polymer aqueous solutions are attracting attention in various areas.

Mackenzie et al. [15,11] have shown, based on the emulsion method, that there is a first-order linear relationship between the equilibrium melting point and the homogeneous nucleation temperature of various aqueous solutions. They also showed that the value of λ is large in polymer aqueous solutions compared with aqueous solutions of small molecules; in other words, they can easily be supercooled.

$$\Delta T_{f,\text{hom}} = \lambda \Delta T_m \quad (1)$$

Here, $\Delta T_{f,\text{hom}} = T_f^0 - T_f$ and $\Delta T_m = T_m^0 - T_m$; T_f^0 and T_m^0 are the homogeneous nucleation temperature and the equilibrium melting point of pure water, respectively, and T_f and T_m are the homogeneous nucleation temperature and the equilibrium melting point of the solution, respectively. In this study, $\Delta T_{f,\text{hom}}$ and ΔT_m were calculated using a value of -37.6 °C for T_f^0 and 0 °C for T_m^0 , which are the results measured for distilled water. Based on this equation, λ can be regarded as the solute-specific supercooling capacity. Zobrist et al. [23] also determined, using the emulsion

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method, the homogeneous nucleation temperatures and equilibrium melting points for aqueous solutions of PEG with Mw 300, 1000, and 6000, and showed that these temperatures are dependent on water activity. They have also shown that λ roughly increases with increasing molecular weight. Furthermore, Kanno et al. [6] investigated the homogeneous nucleation temperature of PEG solution (Mw 200–2000) by the emulsion method, and showed that additivity rule holds for molecular weight and homogeneous nucleation temperature. Antonsen et al. [1] measured the equilibrium melting points and latent heats of fusion for 30 wt% PEG aqueous solutions of Mw 200–200,000, although they were not in an emulsion state, and showed that these values change in the vicinity of Mw 1000. These results indicate that polymer behavior in solution has a direct influence on the low-temperature properties of the solution. Another study investigated the relationship between low-temperature properties and solution properties, although only aqueous solutions of small molecules were used. In this study, Miyata et al. [12] found that the homogeneous nucleation temperatures of aqueous solutions of alcohols, sugars, and alkali salts depended on the functional groups and structural units present in the molecules,

such as the number of hydroxyl groups in the solute and the radii of alkali ions. In addition, Kimizuka et al. [9] recently determined the value of λ for the aqueous solutions of small molecules (salts, alcohols, and sugars) by the emulsion method, and showed that there was a linear relationship between λ and the logarithmic value of the solute self-diffusion coefficient. If the effect on supercooling behavior of solution properties such as the self-diffusion coefficient can be elucidated for polymer aqueous solutions as well as for the aqueous solutions of small molecules, this will contribute to the prediction and control of supercooling of aqueous solutions.

In this study, the homogeneous nucleation temperature depression, $\Delta T_{f,\text{hom}}$, the equilibrium melting point depression, ΔT_m , and the value of λ for PEG, PVP, and dextran aqueous solutions were determined in the concentration range 0–40 wt%, and the molecular weight dependence of these values was investigated for PEG aqueous solutions. In addition, the supercooling behavior of the aqueous solutions was discussed based on the relationship between the solute self-diffusion coefficient and the value of λ for PEG, PVP, and dextran solutions of various molecular weights.

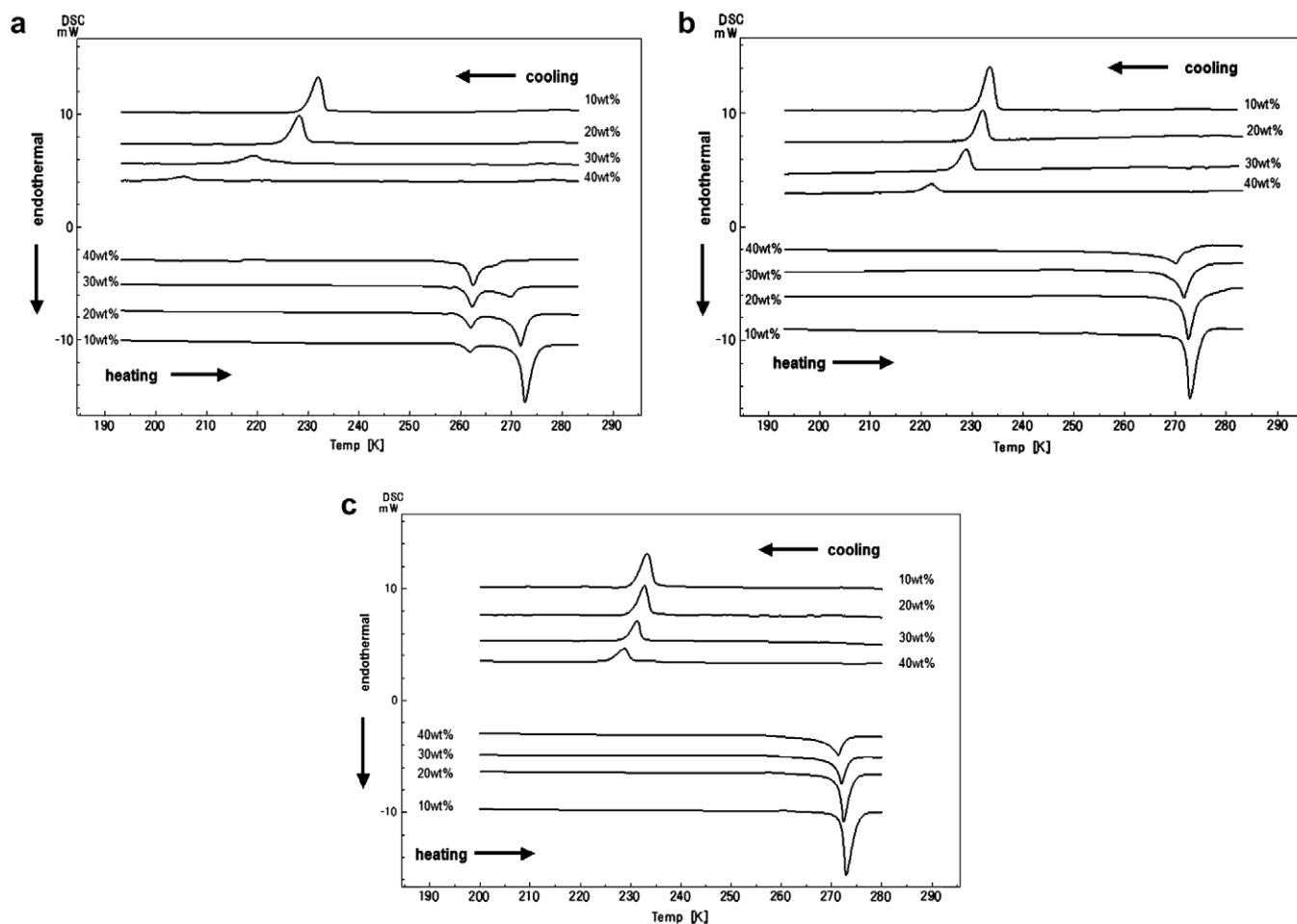


Fig. 1. DSC curves for aqueous polymer solutions with concentrations of 10–40 wt%. The upper curve shows cooling; the lower curve shows warming. (a) PEG 20000; (b) PVP K-30 (40,000 g mol⁻¹) and (c) Dextran 10000 (10,000 g mol⁻¹).

Materials and methods

Preparation of aqueous solutions

The solutes PEG 200, 300, 600, 1540, 2000, 4000, 6000, 10,000, and 20,000 (Wako Pure Chemical Industries, Ltd.), PVP-10 (10,000 g mol⁻¹, Sigma Chemical Co.), PVP K-25 (35,000 g mol⁻¹), PVP K-30 (40,000 g mol⁻¹, Wako Pure Chemical Industries, Ltd.), and dextran 10000 (10,000 g mol⁻¹, Wako Pure Chemical Industries, Ltd.) were used without further purification. Distilled water (Wako Pure Chemical Industries, Ltd.) was used for preparing aqueous solutions with concentrations of 10, 20, 30, and 40 wt%. In this study, the molecular weights of the various polymers provided by the companies mentioned were considered as average molecular weights.

Preparation of emulsions

Emulsions were prepared using silicone oil (TSF451-10, GE Toshiba Silicone Co., Ltd.), and sorbitan tristearate (SPAN 65, Sigma Chemical Corporation) as the interfacial active agent. An identical quantity of each of the aqueous solutions described above was added dropwise to 5 ml of silicone oil containing 10 wt% SPAN 65, while the mixture was agitated for 10 min with a glass homogenizer (1500 rpm).

DSC measurement of homogeneous nucleation temperatures and equilibrium melting points

A Shimadzu DSC-50 calorimeter was used to measure homogeneous nucleation temperatures and equilibrium melting points. A sample of each of the emulsions prepared as described above (2.0 ± 0.1 mg) was encapsulated in an aluminum cell. The nucleation temperature of each of the samples was measured by scanning at a cooling rate of -3.0 °C/min to -80 °C (193 K); next, the equilibrium melting point was measured by scanning at a heating rate of $+3.0$ °C/min to $+10$ °C (283 K). For correction of the measured temperatures, we used distilled water and set the temperature at the highest point of the peak for melting ice at 273 K. For this reason, we used the highest peak values for homogeneous nucleation temperatures, equilibrium melting points, and other temperature results.

Results and discussion

Fig. 1(a) shows DSC curves for PEG 20000 (10–40 wt%) aqueous solutions in the emulsion state. It was previously reported that for $M_w > 500$ –1000, two endothermic peaks (melting and eutectic) were generated during heating of PEG aqueous solutions [23,13,21]. In this study, two endothermic peaks were clearly identified for all aqueous solutions of $M_w > 600$. The peaks were interpreted based on the results of Zobrist et al. [23] the peak on the lower-tem-

perature side was assigned to the eutectic, and the peak located on the higher-temperature side, which varies depending on the concentration of the solution, was assigned to melting of ice. In contrast, one exothermic peak was observed during the cooling process, with a Gaussian peak shape. Because this shape is normally observed during measurement of the homogeneous nucleation temperature, we considered that this peak was due to homogeneous nucleation. Fig. 1(b) and (c) show DSC curves of K-30 (40,000 g mol⁻¹) and dextran 10000 (10,000 g mol⁻¹) aqueous solutions in an emulsion state. For all concentrations, one peak was observed during the cooling process and one during the heating process (One peak was also observed for PVP aqueous solutions of other molecular weights during the cooling and heating processes.). Therefore, we considered that these represented homogeneous nucleation and ice melting, respectively. Although this is not shown in

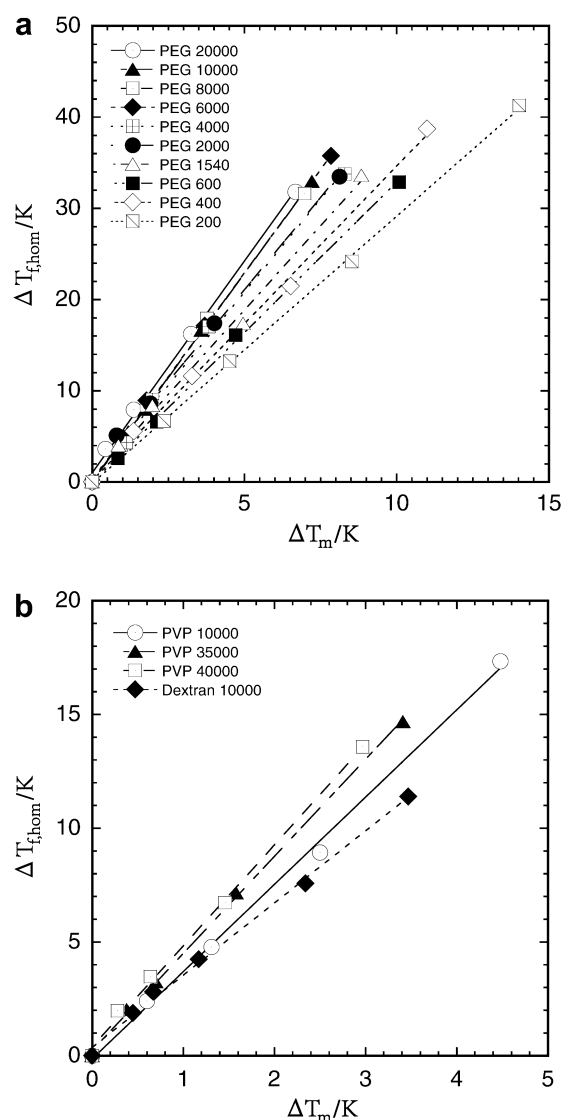


Fig. 2. Homogenous nucleation temperature depression ($\Delta T_{f, \text{hom}}$) as a function of equilibrium melting point depression (ΔT_m) in aqueous polymer solutions. (a) polyethylene glycol solutions and (b) polyvinyl pyrrolidone and dextran.

the figure, the homogeneous nucleation temperature of distilled water was $-37.6\text{ }^{\circ}\text{C}$. This temperature is approximately the same as those reported by Mackenzie et al. [15,11] and Kanno et al. [6]. Accordingly, crystallization due to non-homogeneous nucleation may be negligible in all measurements of homogeneous nucleation temperature in this study.

The relationships between $\Delta T_{f,hom}$ and ΔT_m for the polymers, obtained by DSC measurement as described above, are shown in Fig. 2(a) and (b). Khvorostyanov et al. [8] described a case in which λ is not strictly fixed by concentration. However, in the present experiment, a good first-order linear relationship holds for all solutes (correlation coefficient $R = 0.998\text{--}0.999$), and it is possible to regard λ as the solute-specific supercooling capacity. The values obtained for $\Delta T_{f,hom}$, ΔT_m , and λ are summarized in Tables 1 and 2 along with the self-diffusion coefficients [20,14,2] and the average molecular weights in order to facilitate the discussion below.

Molecular weight dependence of T_m , $T_{f,hom}$, and λ in PEG aqueous solution

The relationships between T_m and molecular weight and between $T_{f,hom}$ and molecular weight for PEG aqueous solutions of various concentrations are shown in Fig. 3(a) and (b), respectively. The results show that for all concentrations, there are different trends for both T_m and $T_{f,hom}$ in the Mw ranges of 200–600 and 1540–20,000. Therefore, the molecular weight range 600–1540 is critical not only for T_m but also for $T_{f,hom}$. Detailed examination at each concentration showed that the critical molecular weight is located around Mw 600 for high concentrations (40 wt%) and around Mw 1000 for the low concentrations (10 wt%). Thus, the critical molecular weight has a tendency to shift to the lower molecular weight side as the concentration increases. Because the

critical molecular weight varies with changing concentration, both T_m and $T_{f,hom}$ may be affected by the overlap of polymers in the solution. In order to clarify the molecular weight dependence of λ , the relationship between λ and the inverse of molecular weight was examined; the results are shown in Fig. 4. When the value of λ was plotted against the inverse of molecular weight, a linear relationship did not apply throughout. Similarly to the trends observed for the relationships between $T_{f,hom}$ and molecular weight and between T_m and the molecular weight, a large change was observed on the higher molecular weight side of 1000. Thus, the value of λ also shows a dependence on molecular weight.

Based on the above results, the molecular weight dependences of $T_{f,hom}$, T_m , and λ can be discussed as follows: examples of polymer solution parameters that show a strong dependence on molecular weight include the intrinsic viscosity, the square radius of gyration, and the self-diffusion coefficient. Kawaguchi et al. [7] investigated the molecular weight dependence of the intrinsic viscosity $[\eta]$ for PEG aqueous solutions, and found that the exponential term of the equation that relates the above parameters and the weight-average molecular weight became large above Mw 600 for all solutions. Generally, for a polymer solute, the value of $[\eta]$ is obtained from the Mark–Houwink–Sakurada equation.

$$[\eta] = KM_w^a \tag{2}$$

Here, K and a are constants representing the interaction between the polymer and the solvent. The exponential term is a parameter that reflects the shape of the polymer in the solution: when the value is small, the degree of molecular bending is high; as it becomes larger, the shape of the molecule approaches a chain [4]. Accordingly, in PEG aqueous solution, the molecules are considered to assume an expanded random coil conformation in water if the molecular weight is higher than 600 [7]. Thus, the molecular weight

Table 1
Homogeneous nucleation temperature depression ($\Delta T_{f,hom}$) and equilibrium melting point depression (ΔT_m) of PEG, PVP, and dextran solutions

	ΔT_m	$\Delta T_{f,hom}$	ΔT_m	$\Delta T_{f,hom}$	ΔT_m	$\Delta T_{f,hom}$	ΔT_m	$\Delta T_{f,hom}$	ΔT_m	$\Delta T_{f,hom}$
	PEG200		PEG300		PEG400		PEG600		PEG1540	
10 wt%	2.36	6.67	1.23	3.40	1.37	5.55	0.85	2.62	0.86	3.98
20 wt%	4.52	13.24	2.74	9.01	3.28	11.60	2.12	6.60	1.98	8.37
30 wt%	8.53	24.17	5.63	18.50	6.52	21.47	4.71	16.13	4.96	17.36
40 wt%	14.03	41.27	10.80	33.70	11.00	38.70	10.08	32.90	8.85	33.60
	PEG2000		PEG4000		PEG6000		PEG8000		PEG10000	
10 wt%	0.80	5.09	1.13	4.33	1.05	4.72	0.96	4.06	1.19	5.48
20 wt%	1.91	8.63	1.98	9.05	1.78	8.94	1.78	8.41	1.75	7.97
30 wt%	4.01	17.42	3.83	17.02	3.70	17.13	3.77	17.94	3.59	16.61
40 wt%	8.13	33.47	8.30	33.76	7.85	35.72	6.98	31.60	7.22	32.96
	PEG20000		PVP10000		PVP35000		PVP40000		Dextran10000	
10 wt%	0.44	3.63	0.60	2.40	0.38	2.03	0.28	1.97	0.45	1.88
20 wt%	1.37	7.94	1.31	4.78	0.70	3.25	0.64	3.47	0.67	2.81
30 wt%	3.25	16.20	2.50	8.93	1.58	7.15	1.46	6.73	1.17	4.24
40 wt%	6.68	31.82	4.48	17.34	3.41	14.69	2.97	13.57	2.34	7.58

Table 2
Supercooling capacities ($\lambda = \Delta T_{f,hom}/\Delta T_m$) and self-diffusion coefficients of PEG, PVP and dextran solutions

EG	PEG200	PEG400	PEG600	PEG1540	PEG2000	PEG4000	PEG6000	PEG8000	PEG10000	PEG20000	PVP10000	PVP35000	PVP40000	Dextran 10000
Supercooling capacity	1.70 ^b	2.93	3.44	3.69	4.03	4.08	4.53	4.56	4.57	4.64	3.83	4.26	4.43	3.17
$\lambda = \Delta T_{f,hom}/\Delta T_m$	11.4 ^a	4.86 ^a	3.15 ^a	1.35 ^a	0.74 ^a	0.58 ^a	0.48 ^a	0.27 ^a	0.19 ^a	0.19 ^a	1.07 ^c	0.56 ^c	0.52 ^c	1.50 ^d
Self-diffusion coefficient														
$D_0 \times 10^{-10}/m^2 s^{-1}$														

^a Ref. [20].

^b Ref. [9].

^c Ref. [14].

^d Ref. [2].

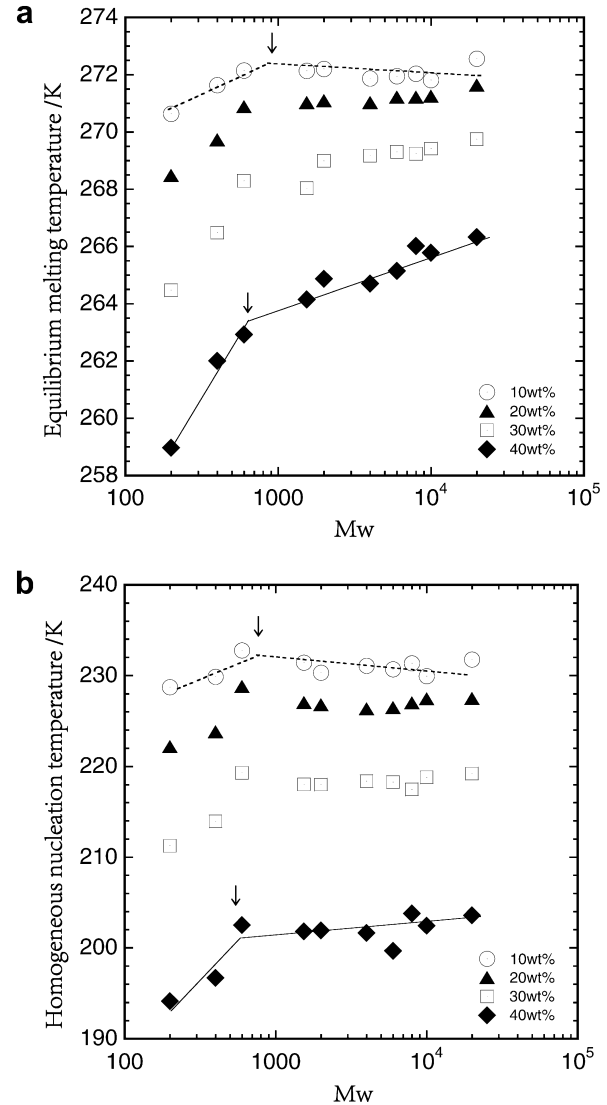


Fig. 3. Transition temperature for polyethylene glycol solutions as functions of molecular weight (Mw). (a) Equilibrium melting temperature and (b) homogeneous nucleation temperature.

dependencies of $[\eta]$ and those of $T_{f,hom}$, T_m , and λ show changes in the same molecular-weight region. Therefore, it can be implicitly considered that the state of the molecular chain in water affects the values of $T_{f,hom}$, T_m , and λ . That is, up to Mw 600, $T_{f,hom}$ and T_m increase mainly due to the colligative properties of the solution, but for higher values of Mw, $T_{f,hom}$ and T_m increase due to the change in molecular shape. The molecular weight dependence of $T_{f,hom}$ and λ in this study can be interpreted as indicating the possibility that the parameter that reflects non-equilibrium freezing is dependent on the solution properties.

Solute dependence of λ in various polymer aqueous solutions

It is known that the λ value of aqueous polymer solutions is around 4–5 [15,11,23]. However, there have been few studies which were specifically focused on the depen-

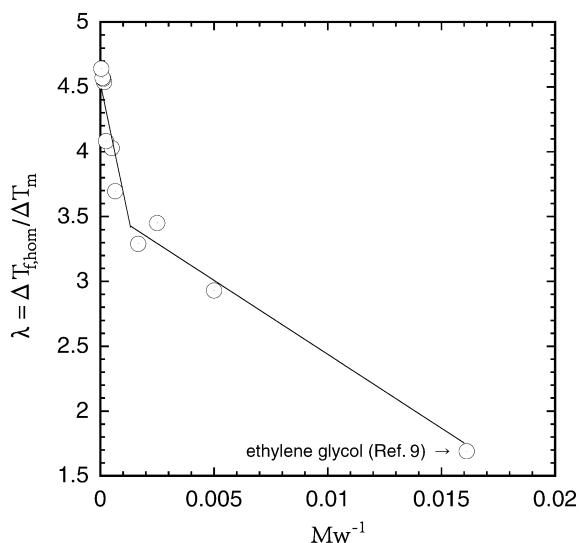


Fig. 4. Relationship between supercooling capacity (λ) and the inverse of molecular weight (Mw^{-1}) for polyethylene glycol solutions. The λ data of ethylene glycol solutions (Ref. [9]) were included in the graph.

dence of λ on polymer solutes. Fig. 5 shows the relationship between λ and the logarithm of the molecular weight for each of the polymers studied. For all polymers, the value of λ increases with increasing molecular weight, similarly to the relationship shown in Fig. 4; thus, it is clear that λ is a function of molecular weight. However, the relationship between λ and molecular weight varies for different polymers. For example, when the values of λ for three polymers of Mw 10,000 are compared, the order is PEG > PVP > dextran. The fact that the values of λ are different for polymer solutions of the same molecular weight, depending upon the solute, may be explained in the following way. When the viscosities of PEG, PVP, and dextran aqueous solutions are compared for polymers of the same molecular weight and at the same concentration, the

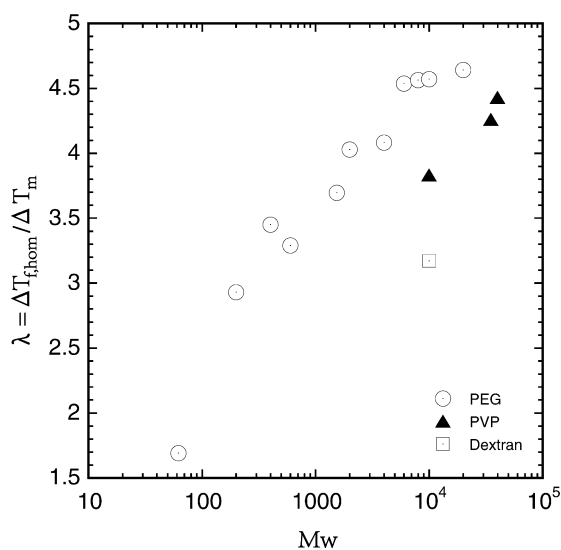


Fig. 5. Relationship between supercooling capacity (λ) and the logarithm of the molecular weight (Mw) for each polymer.

Table 3
Scaling behavior and intrinsic viscosities of PEG, PVP and dextran solutions^a

Compounds	Temperature (K)	$K \times 10^{-4}$ (dl g ⁻¹)	a	$[\eta]$ (dl g ⁻¹)
PEG	298	4.33 ^b	0.67 ^b	0.21
PVP	298	5.0 ^c	0.56 ^c	0.087
Dextran	298	2.23 ^d	0.43 ^d	0.012

^a The table shows the intrinsic viscosity of each polymer at a molecular weight of 10,000. K and a are the constants from Eq. (2) (see text).

^b Ref. [7].

^c Ref. [14].

^d Ref. [5].

PEG aqueous solution shows the highest value [14,7,5]. Although the reported values vary depending upon the measurement method, both the parameters in the exponential term of the Mark–Houwink–Sakurada equation and the intrinsic viscosities obtained from the equation at Mw 10,000 are shown as references in Table 3.

When the exponential terms for the polymers are compared, it can be seen that the degree of molecular bending in solution is higher for dextran and PVP than for PEG. In addition, the intrinsic viscosity is in the order PEG > PVP > dextran, which is the same as the trend in the order of λ obtained in this study. This suggests that the viscosity of the solution may be a factor in the solute dependence of λ , as is the case for molecular weight dependence, as described above.

Kimizuka et al. recently showed that for aqueous solutions of small molecules, there is a linear relationship between λ and the logarithmic value of the self-diffusion coefficient, D_0 , of the solute molecule [9]. Here, D_0 is the self-diffusion coefficient of the solute in an aqueous solution at 25 °C. When the solute is an ionic species, D_0 may be calculated based on the molar conductivity at infinite dilution; for other solutes, it is mainly measured by NMR. D_0 depends on the steric conformation of a solute molecule, as well as other factors. The parameter is correlated with molecular size (the hydrodynamic size and shape of the solute molecule) and with the effect of electrostatic interactions [19]. As shown above, if the value of λ for an aqueous polymer solution is correlated with the molecular state of the solute (as indicated by the viscosity of the solution), the value of λ for any polymer should be correlated with the self-diffusion coefficient, in a similar manner to the behavior of aqueous solutions of small molecules. Fig. 6 shows the relationship between λ and the logarithmic value of D_0 for PEG, PVP, and dextran at each molecular weight. A linear relationship is observed for all materials.

$$\lambda = 3.90 - 1.91 \log D_0 \quad (R = 0.986) \quad (3)$$

The λ values for small molecules [9] are also plotted in this figure; these can be seen to follow approximately the same straight line that was obtained in this study (the above-described correlation equation is based on the small molecules NaI, NaCl, NaBr, MgCl₂, CaCl₂, ethylene glycol, glycerol, urea, glucose, fructose, xylose, maltose, sucrose,

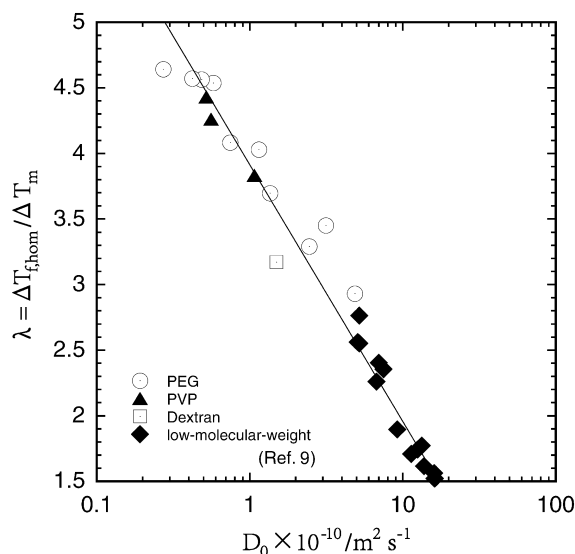


Fig. 6. Relationship between supercooling capacity (λ) and the logarithmic value of the self-diffusion coefficient (D_0). The following substances were used as low molecular weight solutes (Ref. [9]): NaI, NaCl, NaBr, $MgCl_2$, $CaCl_2$, ethylene glycol, glycerol, urea, glucose, fructose, xylose, maltose, sucrose, trehalose.

and trehalose). Accordingly, it was confirmed that the correlation between λ and D_0 holds widely, from aqueous solutions of small molecules to polymer solutions. All the self-diffusion coefficients used in this study are the values at 298 K, which are different from the values in the vicinity of 230 K, the nucleation temperature. However, the temperature dependence of the solute self-diffusion coefficient for various aqueous solutions shows approximately the same trend in the temperature range below 273 K as in the vicinity of 298 K. In addition, it has been shown that the solute self-diffusion coefficient does not change to a significant extent compared to that at 298 K [17]. Accordingly, the correlation between λ and the self-diffusion coefficient is considered to apply even at 298 K.

The relationship between λ and D_0 may be explained based on known nucleation theory as follows: for example, if we assume that the Stokes–Einstein equation, which relates the diffusion coefficient and the viscosity coefficient, can be applied to a supercooled liquid, the equation for nucleation rate can be expressed as follows: using the viscosity η of the supercooled liquid [18]:

$$J = \frac{k\Gamma_z}{\eta(T)} \exp\left(\frac{-\Delta G^*}{kT}\right) \quad (4)$$

Here, ΔG^* is the activation energy for nucleation, and Γ_z is the Zeldovich constant. From Eq. (4), we see that the homogeneous nucleation temperature can be calculated as the temperature at which the number of nuclei per unit volume becomes 1, using the following equation with cooling velocity V_t

$$\int_{T_m}^{T_{f,hom}} \frac{J}{V_t} dT = 1 \quad (5)$$

Based on these relationships, D_0 is considered to influence the nucleation rate, and thereby the possibility of supercooling, through $\eta(T)$.

Based on the above results, the possibility of supercooling in aqueous polymer solutions may be explained by the low self-diffusion coefficients of the solute molecules. The nucleation rate, or nucleus growth rate, is lowered due to the viscosity of the solution, thus promoting supercooling.

Conclusions

Although the values of $T_{f,hom}$, T_m , and λ for PEG aqueous solutions are dependent on molecular weight, it became apparent that all of these values vary in the Mw range 600–1540. These results show a similar trend to the molecular weight dependence of intrinsic viscosity $[\eta]$. This indicates that $T_{f,hom}$ and λ may depend on the molecular state of the solute in the solution, as represented by solution properties such as viscosity.

The values of λ for PEG, PVP, or dextran aqueous solutions were confirmed to show good correlation with the logarithmic values of the self-diffusion coefficients D_0 of the solute molecules. This correlation also applies for aqueous solutions of small molecules, which could be plotted on the same straight line. Thus, the value of λ , as obtained by the emulsion method, for all solutes from small molecules to polymers may be explained based on the self-diffusion coefficient D_0 , which reflects the structure of the solute molecule. We expect that the results of this study will contribute to efforts to predict and control supercooling in aqueous solutions.

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