

Supporting Information

Unraveling Amphiphilic Poly(N-vinylcaprolactam)/Water Interface by Nuclear Magnetic Resonance Relaxometry: Control of Clathrate Hydrate Formation Kinetics

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Table S1. Activation energies (E_A) and correlation times (τ_0) of bound and free water in d_8 -THF-water solutions with and without PVCap measured in the temperature range of 303 K to 263 K.

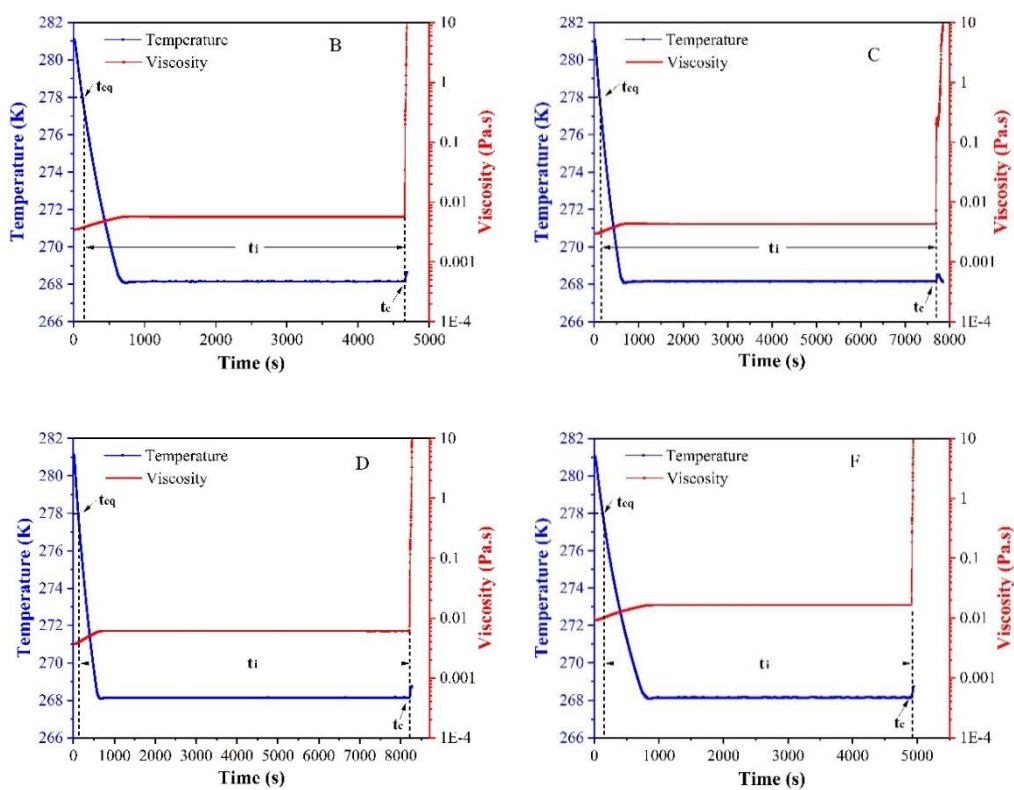


Figure S1. Isothermal hold time measurement of THF-water solutions by rotational rheometer in the presence of PVCap with different MWs. Sample B to F correspond to samples listed in Table 1, respectively. (B) $M_n=13.5$ kD; (C) $M_n=24.9$ kD; (D) $M_n=40.5$ kD; (F) $M_n=106$ kD.

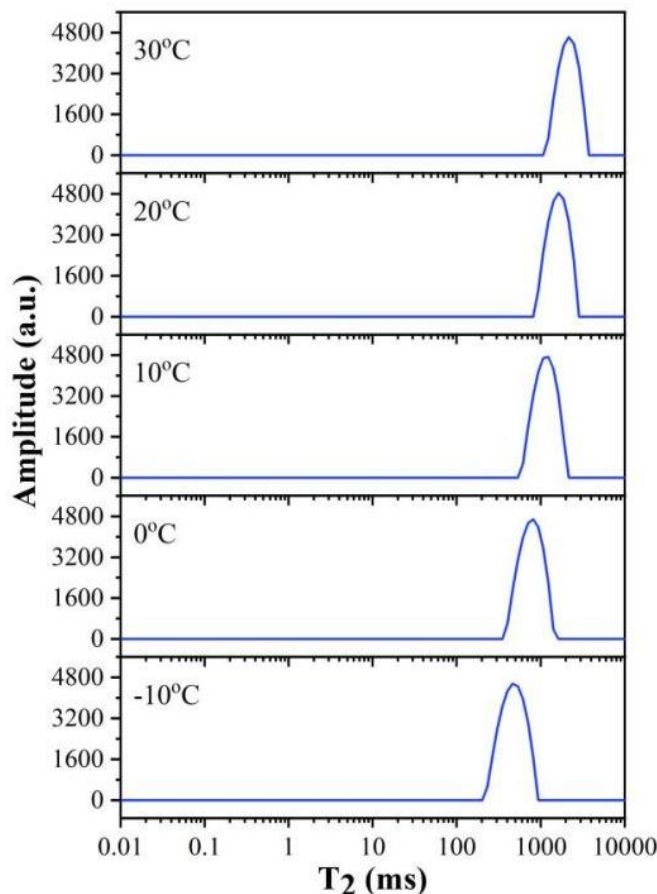


Figure S2. T_2 distribution curves of d_8 -THF aqueous solution (THF/water 1/3 v/v) without the polymer during cooling.

Determination method of free and bound water dynamics based on BPP theory. Dynamics of water motions can be extracted from the variable temperature data of T_2 by using a classical Bloembergen Purcell and Pound (BPP) description for the intrinsic T_2 relaxation rate (Bloembergen, et al. 1948; Solomon, 1955; McConville et al., 2002; McConville and Pope, 2001; Mallamace et al., 2016).⁵⁷⁻⁶¹ The BPP theory assumes rapid molecular motional averaging and describes the dependence of T_2 on the correlation time (τ_c) for the motion of water in the sample:

$$\frac{1}{T_2} = \frac{c}{2} \left[3\tau_c + \frac{5\tau_c}{1 + \omega_0^2\tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2\tau_c^2} \right] \quad (\text{Equation S1})$$

where correlation time τ_c is the time needed for the deflection (rotation) of the molecules to be one radian (60°), ω_0 is the Larmor frequency, C is hydrogen dipole-dipole interaction constant and calculated to be $5.33 \times 10^9 \text{ s}^{-2}$. The interproton distance is 1.58 \AA for evaluation of C constant in Equation S1 (A. Yilmaz, H. Budak, F. S. Ulak, Determination of the effective correlation time modulating ^1H NMR relaxation processes of bound water in protein solutions. *Magnetic Resonance Imaging* **2008**, *26*, 254-260). An Arrhenius activation law can then be used to describe thermal activation of the molecular motion:

$$\tau_c = \tau_0 e^{E_A/kT} \quad (\text{Equation S2})$$

where E_A is the activation energy of molecular rotation and translation, T is temperature, τ_0 is correlation time at infinite temperature, k is the Boltzmann constant.

The instrument works at $\omega_0 = 11.92 \text{ MHz}$, namely, $1/\omega_0 = 8.39 \times 10^{-8} \text{ s} \gg \tau_c$, which satisfies the condition $\omega_0 \tau_c \ll 1$. Thus, the above BPP Equation S1 is simplified into

$$\frac{1}{T_2} \approx \frac{10C\tau_c}{2} = 5C\tau_0 e^{E_A/kT} \quad (\text{Equation S3})$$

$\ln T_2$ is confirmed to have a linear relationship with $1/T$ in the experiments described below. Therefore, the T_2 relaxation process shows an Arrhenius dependence on temperature T , while τ_0 and E_A can be obtained from the intercept and slope by linear fitting $\ln T_2$ versus reciprocal temperature $1/T$,

$$-\ln(T_2) = \ln(5C\tau_0) + \frac{E_A}{kT} \quad (\text{Equation S4})$$

The temperature-variable T_2 distributions of d_8 -THF aqueous solution without the polymers are shown in Figure S2. Analytical results of the temperature-variable T_2 peaks in the presence of the polymers in Fig.3 in the manuscript as well as those of

the d_8 -THF aqueous solution without the polymer in Figure S2 using Equation S4 are shown in Figure S3. The obtained activation energies E_A and correlation times τ_0 are listed in Table S1 which show that the motion of the bound and free water are sensitive to the addition of polymers and the rotation of the bound water is 3-4 orders of magnitude slower than that of the free water.

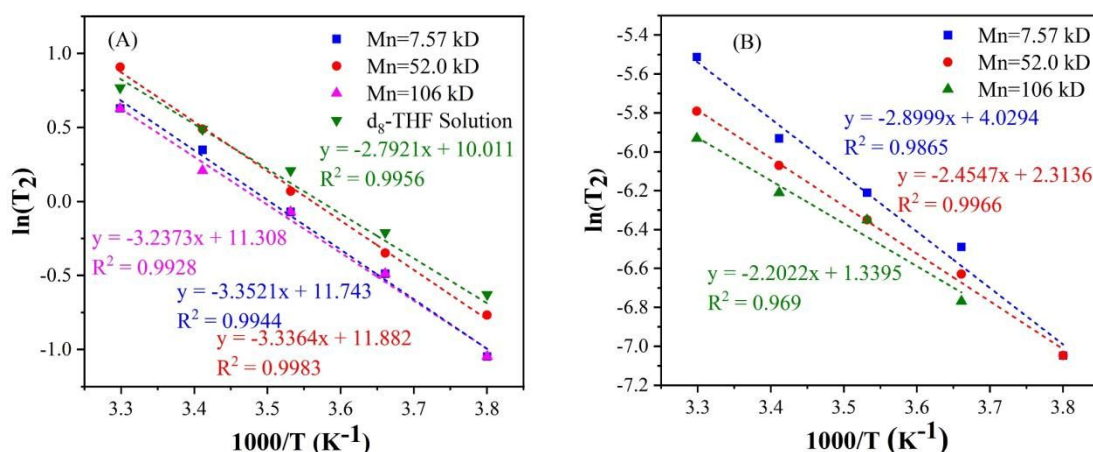


Figure S3. Arrhenius plot of T_2 relaxation peak position in logarithmic values of free water species (panel A) and bound water species (panel B) in d_8 -THF-water with PVCap versus reciprocal temperature during cooling from 303 K to 263 K (30°C to -10°C). The data without PVCap are also shown in the left panel.

Table S1. Activation energies (E_A) and correlation times (τ_0) of bound and free water in d_8 -THF-water solutions with and without PVCap measured in the temperature range of 303 K to 263 K.

d_8 -THF Solution Type	E_A (kJ mol ⁻¹) Free Water	E_A (kJ mol ⁻¹) Bound Water	τ_0 (s) Free Water	τ_0 (s) Bound Water
d_8 -THF without PVCap	23.21±0.89	-	(1.68±0.66)×10 ⁻¹⁵	-
with PVCap $M_n=7.57$ kD	27.87±1.20	24.11±1.63	(2.98±1.60)×10 ⁻¹⁶	(6.67±5.04) ×10 ⁻¹³
with PVCap $M_n=52$ kD	27.74±0.67	20.41±0.69	(2.59±0.75)×10 ⁻¹⁶	(3.71±1.11) ×10 ⁻¹²
with PVCap $M_n=106$ kD	26.91±1.32	18.31±2.32	(4.61±2.74)×10 ⁻¹⁶	(9.83±6.12)×10 ⁻¹²

Equation S1 describes only the random modulation of interproton dipolar interactions by water molecules rotation but water translation can affect T_2 relaxation. Chemical exchange between free and bound water may affect diffusion ability. The

protons in the repeating units of the polymer are connected to the carbon atoms through covalent bonding (C-H). The tertiary amide group, methylene and methine groups of the polymer do not have exchangeable protons with water (labile protons such as -OH, -NH are absent in the repeating units). Only a very minor amount of protons in the end group of the polymer (less than 0.1%) may exchange with water. Therefore, chemical exchange between water and the polymer is negligible. The model based on BPP theory is sufficient to obtain a picture of two types of water with significantly different mobility shown in Fig.3.

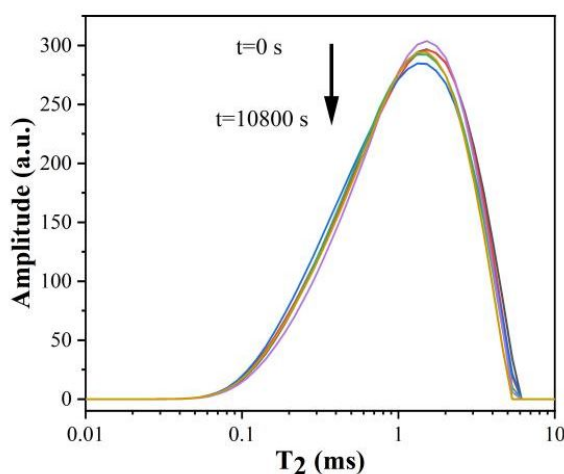


Figure S4. Time-dependent changes of bound water in their T_2 relaxation distributions in the solution with PVCap $M_n = 49.4$ kD during isothermal crystallization at -15°C .

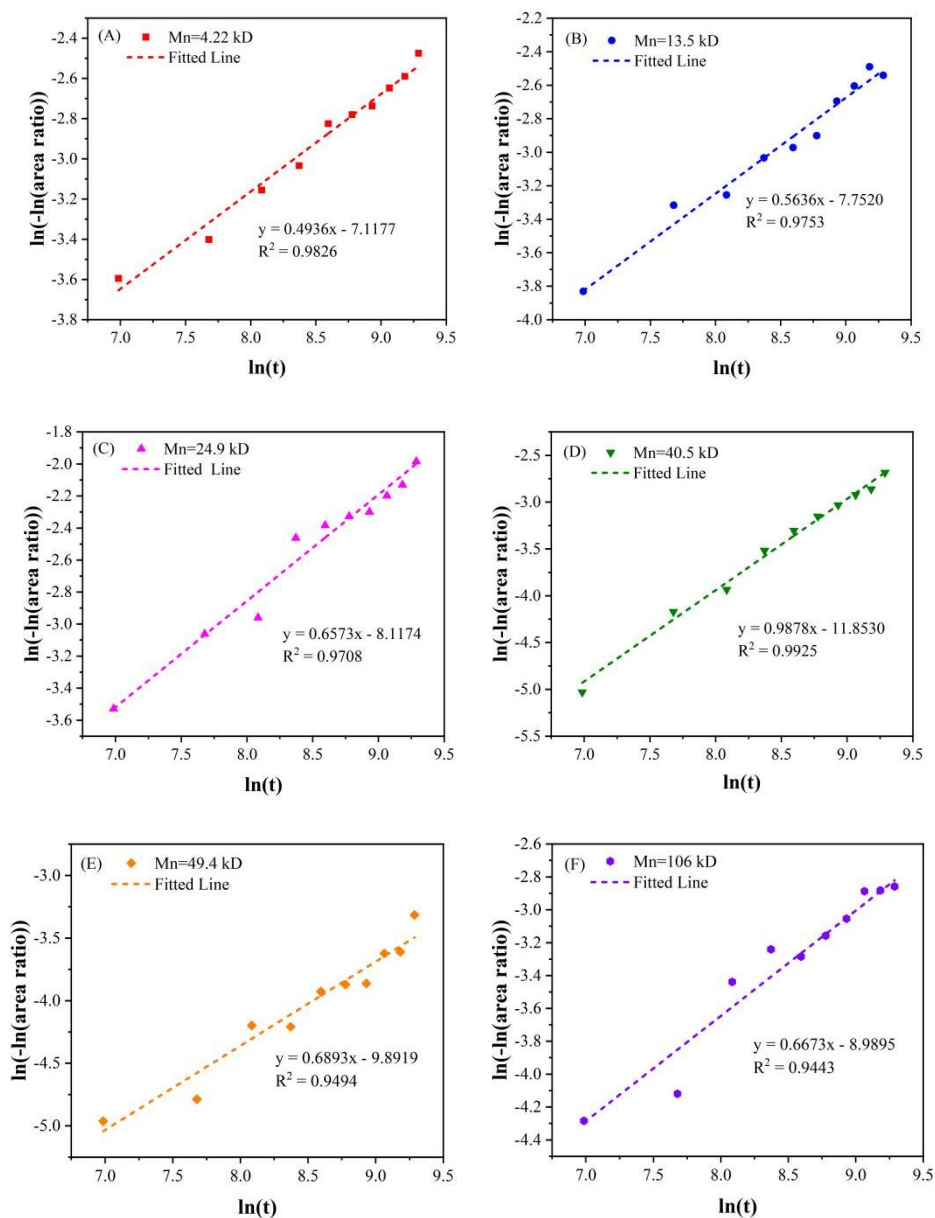


Figure S5. Isothermal changes of the bound water peak areas in the presence of PVCap with time at 258 K (or -15°C). The MW of each polymer A to F in each panel are also listed in Table 1.

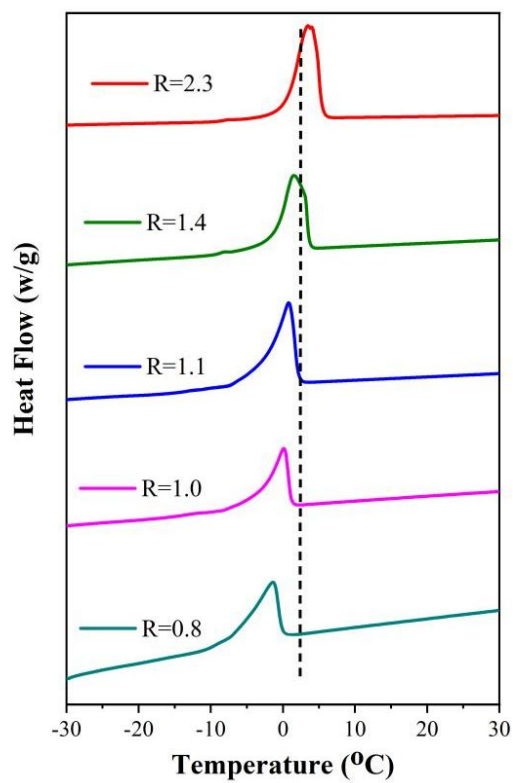


Figure S6. Typical calorimetric traces of water mixed with different amounts of PVCap polymers recorded from -30 to 30°C. The ratio R means the mass ratio of water to polymer. The heat flow unit is watt per gram.