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Supplementary Information

Hydrophobic hydration affects growth of clathrate hydrate: insight from NMR relaxometric and calorimetric study

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9 pages, 2 schemes, 1 table and 3 figures

1. Reagents

All reagents used were in analytical-grade in the experiments. Tetrahydrofuran (THF), tributyl citrate (TBC), ethylene diamine (EDA), isopropyl isocyanate, n-butyl isocyanate, cyclohexyl isocyanate, 4-dimethylaminopyridine (DMAP), poly(N-vinylpyrrolidone) (PVP, K29-32), methanol, perdeuterated THF (d₈-THF), N,N²-dimethylacetamide (DMAc), and N,N-dimethylformamide (DMF) were all available from Aladdin Reagent Co. (Shanghai, China). *N*-Vinyl caprolactam was purchased from Sigma Co. Acetone was available from Hangzhou Chemical Reagent Co., respectively. Poly(*N*-vinylcaprolactam) (PVCap) was prepared by radical polymerization of *N*-vinylcaprolactam according to the previous report.³² 2. Experimental procedures for preparation of polycitramides and their modifications

2.1 Preparation of poly(ethylene citramide)s (PECs)

Condensation polymerization between tributyl citrate and ethylene diamine leads to PEC with a highly branched structure (see Scheme 1S). The process for the preparation of the polycitramides has been described in Reyes et al.²⁵ In short, tributyl citrate (TBC) and ethylene diamine (EDA) were mixed in freshly distilled N,N'-dimethyl acetamide (DMAc) in a 100 mL round-bottom flask and refluxed at 70 °C for 6 hr. A yellowish precipitate was gradually formed, and the reactants were transferred to a beaker, and precipitated with large amount of acetone. The precipitate was filtered and washed with acetone three times. The solid powder was grounded, vacuum dried at 35 °C for 15 hr, yielding the poly(ethylene citramide) (see Scheme 1S).



Scheme 1S. Poly(ethylene citramide) prepared by condensation polymerization of tributyl citrate and ethylene diamine.

2.2 Preparation of hydrophobically modified poly(ethylene citramide)s

The poly(ethylene citramide)s contain NH₂ terminal groups, which can be modified with different alkyl isocyanate compounds through an addition reaction (see Schemes 2S) and form substituted urea structures

 $R-NH_2 + O=C=N-R' \rightarrow R-NH-C(=O)-NH-R'$



Scheme 2S. The terminal NH₂ groups in poly(ethylene citramide) are modified by different alkyl isocyanate, R-NCO, where R=isopropyl, n-butyl, or cyclohexyl group.

It is possible that the alkyl isocyanate R'-N=C=O may further add to the resulting urea structures, giving rise to biuret.²⁵

 $R-NH-C(=O)-NH-R' + O=C=N-R' \rightarrow R-NH-C(=O)-NR'-C(=O)-NH-R'$

Thus, 1 g of the poly(ethylene citramide) was mixed with 15 mL of DMAc in a 100 mL round-bottom flask. A mixture of 4-dimethylamino pyridine (DMAP, 1 mg) and isopropyl isocyanate were added to the polymer solution and the reactants were heated at 85 °C for 6 hr. The product was poured into 200 mL of acetone, precipitated, washed with acetone for three times, filtered, and dried in vacuum oven at 35°C for 15 hr. The polymer modified by isopropyl isocyanate, n-butyl isocyanate, or cyclohexyl isocyanate were prepared with a molar ratio of the polymer repeating unit to the corresponding isocyanate in 1:1, 1:1, and 1:0.8, respectively.

The modified poly(ethylene citramide) with isopropyl urea, n-butyl urea, and cyclohexyl urea groups are hereinafter abbreviated as PEC isopropyl, PEC n-butyl, and PEC cyclohexyl, respectively (see chemical structures in Scheme 2).

Gel permeation chromatographic analysis has been performed to obtain the molecular weights of the poly(ethylene citramide)s before and after modification. The number-averaged and weight-averaged molecular weight M_n of the polycitramide increases moderately from approximately 2890 to around 9230 before and after modification, while the weight-averaged molecular weight M_w of the polycitramide increases moderately from approximately 3670 to 13600 before and after modification.

3. Measurements

The characterization procedures are analogous to those reported in Wang et al.³¹ THF forms structure II hydrates, which are the most common form encountered in oil and gas operations (Sloan, E. D., Koh, C. A. (2008) Clathrate Hydrates of Natural Gases. Third Edition, CRC Press, p.80; Ginley, D.S., Cahen, D. (2011) Fundamentals of Materials for

Energy and Environmental Sustainability. Cambridge University Press, p.140; Kelland, M.A. (2014) Production Chemicals for the Oil and Gas Industry. Second Edition, CRC Press, p.219). Viscosity increases by several orders of magnitude and is indicative of rapid hydrate growth and agglomeration. The rheological data are collected by using a rotational rheometer (Discovery Hybrid Rheometer, DHR-1, TA Instruments, New Castle, DE, USA) equipped with a concentric cylinder. The sample temperatures are controlled by a Peltier jacket attached to the rheometer and chilled with a coolant provided from an external bath. A 24 mL portion of THF solution (THF/water at a 1:15 molar ratio) was gently transferred into the measuring concentric cylinder of the rotational rheometer where the shear rate was set at 21 rad s⁻¹. The temperature of the sample was set to 8° C, equilibrated for 10 min, and cooled to -5° C with a temperature ramp of 1 °C/min. The time of reaching the THF hydrate phase equilibrium temperature 4.9 °C is defined as t_{eq} . The critical time of rapid growth of the hydrate is defined as t_c , and the hold time of inhibition is $t_i = t_c - t_{eq}$. Since hydrate formation is an exothermic process, the hold time can be measured by monitoring the dramatic changes of temperature and viscosity (Figure 1S). The rotational rheometric tests of the THF hydrate formation were carried out by adding 0.5 wt % of different inhibitors, averaging six tests per sample.



Figure 1S. Typical traces of changes of viscosity and temperature of THF hydrate formation from THF- H_2O at -5°C in the absence (top) and in the presence (bottom) of polymer inhibitors.

NMR relaxometry measurements of the water in the hydrate and in the polymers were performed by using a Niumag Pulsed NMR Analyzer PQ001 (Niumag Electric Corporation, Shanghai, China) at a proton resonance frequency of 11.05 MHz (0.26 Tesla), similar to the previous report.³¹ Perdeuterated THF (d_8 -THF) was used to prepare aqueous solutions with and without the polymers in order to monitor the pure proton signals from H₂O. The transverse relaxation time (T₂) was obtained using the Carr-Purcell-Meiboom-Gill sequence with a 90° pulse of 3.2 µs and 180° pulse of 6.4 µs. d_8 -THF and de-ionized water solution were mixed in the 1:17 molar ratio with or without a polymer. The water-to-polymer mass ratio was 2:1. The sample temperature was at 15 °C or -15°C. The relaxation curves were converted to T₂ distribution curves through inverse Laplace transformation. Details of the

principle and protocol of the NMR relaxometry for this type of work have been described in recent publications (Chi, Y.; Xu, S.; Xu, X.; Cao, Y. Dong, J. Studies of relationship between polymer structure and hydration environment in amphiphilic polytartaramides. *J. Polym. Sci., Part B: Polym. Phys.* **2017**, *55*, 138–145; Li, Y.; Li, X.; Chen, C.; Zhao, D.; Su, Z.; Ma, G.; Yu, R. A rapid, non-invasive and non-destructive method for studying swelling behavior and microstructure variations of hydrogel. *Carbohydr. Polym.* **2016**, *151*, 1251–1260) The polymers do not show significant T₂ signals above 0.2 ms, therefore, the NMR relaxometry analysis provides water proton signals from the liquid phase of the THF solution or from the aqueous solvent.

Differential scanning calorimetric (DSC) analysis of the nonfreezable bound water (NFBW) was conducted on a Diamond DSC instrument (Perkin Elmer Instruments Co.), following our previous report.²⁶ Samples (3-6 mg) of polymer/water mixtures with variable water contents were prepared by adding certain amounts of water with a micro-syringe into polymers with known weights, tightly sealed in the aluminum pans and allowed to disperse the water at room temperature for 24 hrs. The sample temperatures were held at 15 °C for 5 min, cooled to -65 °C at a rate of 5 °C/min, held at -65 °C for 25 min, and heated to 60°C at 5 °C/min. Experiments in the measurements of nonfreezable bound water have been repeated for three times. The uncertainties of the heat of melting data in Figure 3 are approximately ± 5.0 J/g.



Figure 2S. DSC curves of polycitramides with various water contents R (water-to-polymer mass ratio). The values (n) in the brackets after the R values denote moles of water molecules normalized by the polymer repeating unit.

Sample	NMR peak areas of NFBW	Intercept in mass ratio	NFBW in mol/mol
poly(ethylene citramide)	765	0.155	2.82
poly(ethylene citramide) isopropyl	867	0.153	3.43
poly(ethylene citramide) n-butyl	1161	0.288	6.68
poly(ethylene citramide) cyclohexyl	1413	0.643	15.8

Table 1S. NFBW values of the polycitramides



Figure 3S. Relationship between total heat of melting of water in PVCap and PVP samples and water content in the polymer (R is water-to-polymer mass ratio). (top) PVCap-H₂O mixture; (bottom) PVP-H₂O mixture. PVP and PVCap have NFBW of 5.07 and 6.04 mol, respectively.