# Structure and Properties of Aqueous Methylcellulose Gels by Small-Angle Neutron Scattering

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## Supporting Information

### Size exclusion chromatography (SEC)

The methyl cellulose materials were characterized by size-exclusion chromatography to obtain the molecular weight distribution and differential solution viscosity data. The method was primarily that of Keary.[1] A key update to this method was the use of a multi-angle laser light scattering (MALLS) detector; this detector enabled extrapolation of the scattering data to zero angle, and enables characterizations of MC materials with a wider range of molecular weights. The MALLS detector also enables measurement of the radius of gyration of the chains in dilute solution. The detector update is especially valuable for extending the weight-average molecular weight $M_w$ limit to values exceeding about 300 kg/mol.

SEC was performed using a Waters 2695 HPLC Module coupled with a Wyatt 18-angle light scattering (LS) and Optilab rEX DRI/aRI detectors. The Wyatt MALS was equipped with a red laser at a wavelength of 658 nm and operated at room temperature. The light scattering was calibrated with HPLC-grade toluene filtered by 0.05 μm filters. The 18-angle light scattering channels were normalized to the 90° channel, based on the analysis of mono disperse bovine serum albumin. Wyatt Optilab rEX, the DRI/aRI detector, was operated at 28 °C. The inter-detector delay volume was determined by aligning the

90° LS peak with DRI peak of bovine serum albumin monomer. The separation was performed on two TSKgel GMPW mixed-bed 17μm column (7.5mm×300mm) operated at 28 °C. 100 μL of polymer solution was injected for each SEC analysis. The analysis was conducted at a flow rate of 0.5 ml/min with 0.05% $NaN_3$ filtered de-ionized aqueous mobile phase. The differential solution viscosity data (28 °C, 0.02-0.2 wt.% MC) relative to that for pure solvent were converted into intrinsic viscosity data [$\eta$], and ultimately used to determine the chain overlap concentration $c^* = 1/[\eta]$.

***Data processing and analysis***: Wyatt's ASTRA V software was used to generate slice molecular weight (*MW*) and radius of gyration ($R_g$) with the Debye Plot by fitting the angular dependence of the light scattering data and extrapolating to zero angle according to the 1st-order fit of the Zimm formalism. A *dn*/*dc* of 0.140 was used. Conformation plot of the slice *MW* and $R_g$ was used for persistence length estimation using non-linear least square fitting algorithm $[\log R_g - \log R_g \text{ (calc.)}]^2$.

***Persistence length estimation***: The *Kratky–Porod (KP) chain model*[2] is used to model cellulose ether macromolecules, where the macromolecule chain is between random coil and rod-like behavior. A measure of chain stiffness can be expressed in terms of persistence length, $L_p$, the average distance that the direction of the polymer segment persists. This persistence length can be predicted by the Kratky–Porod (KP) chain model[2-3] as expressed in Equation S1.

$$R_g^2 = \frac{L_p(MW)}{3M_L} - L_p^2 + \frac{2L_p^3 M_L}{(MW)} - \frac{2L_p^4 M_L^2}{(MW)^2}\left(1 - e^{-\frac{(M_w)}{L_p M_L}}\right) \quad \text{(S1)}$$

$R_g^2$ is the *z*-average mean-square radius-of-gyration $\langle R_g^2 \rangle_z$; $M_w$ is the molecular weight; and $M_L$ is the molar mass per unit contour length with a unit of g/mol/nm. Knowing the structure of the repeat unit of macromolecules, $M_L$ can be estimated. $R_g$ and $M_w$ can be measured from Size Exclusion Chromatography coupled with multi-angle light scattering detector (SEC-MALS) experiments. Using these parameters the persistence length, $L_p$, can be calculated from Equation S1.

## Rheology

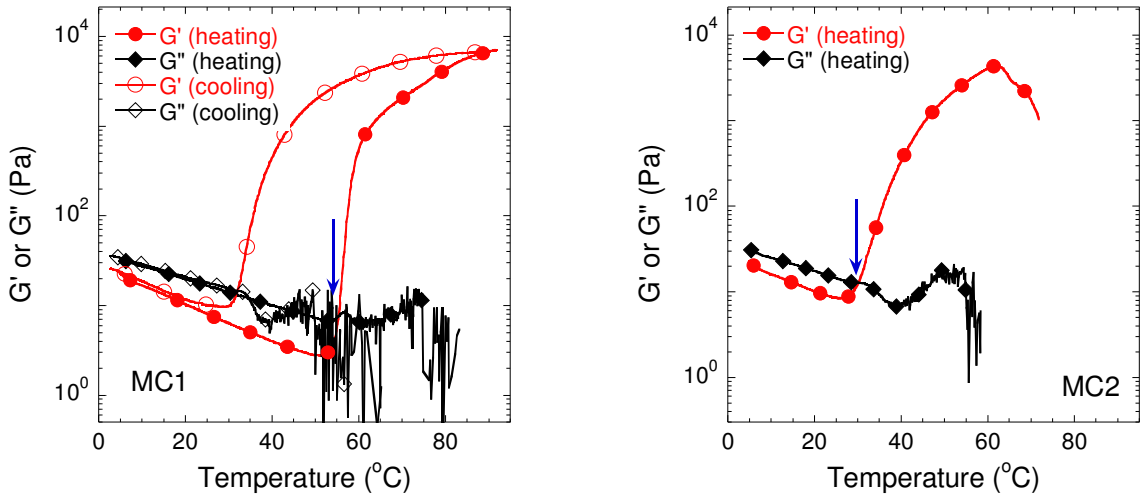


**Figure S1**: Dependency of the shear storage modulus (*G'*) and shear loss modulus (*G"*) on temperature for a 1.5 wt% (left) MC1 and (right) MC2 solution in $D_2O$ warmed (closed symbols) and cooled (open symbols) at thermal ramp rate ±1.0 °C/min and at a frequency 0.5 Hz. The cross-over points are denoted by the arrow. Cooling cycle data for MC2 sample has not been reported since the collected data were erroneous (for details please see the main text)

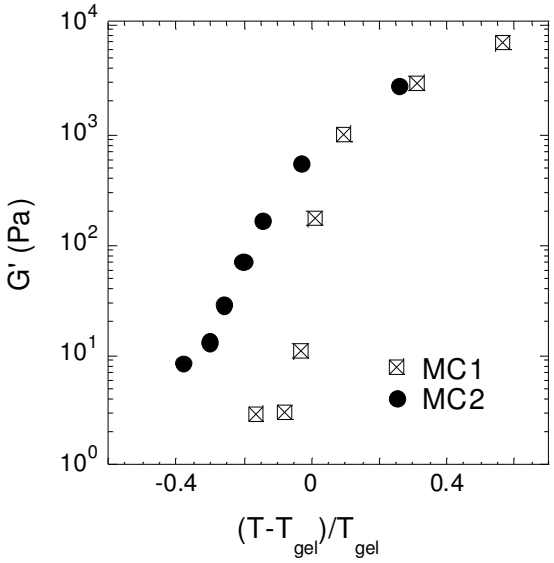


**Figure S2**: Comparison of shear storage modulus (*G'*) for a 1.5 wt% MC1 and MC2 solution in $D_2O$ on renormalized temperature scale. *G'* data at the SANS measurement temperatures are extracted from the heating cycle rheology measurements (at thermal ramp rate ±1.0 °C/min and at a frequency 0.5 Hz, shown in Figure S1). For MC2 sample *G'* data above $T > 60$ °C are not used to prepare this plot. This representation shows that at same thermal history with respect to the $T_{gel}$, MC2 gel exhibits higher modulus than MC1 gel.

## Reversibility in SANS measurements

As described in the Experimental section, to check the reversibility of the gelation process, after the highest temperature measurement the lowest temperature measurement was repeated. In Figure S3 we compare the initial (or the first) low-temperature measurement with the repeat experiment. The cooling process at the NCNR, NIST was executed by switching the sample chamber connection from the highest temperature bath to another circulating water bath which was preset with the previously measured lowest temperature. While, a reasonable waiting period was allowed to attain a steady state at low temperature, this equilibration differs significantly from the rheological and NMR thermo-reversibility experiments. We observed (Figure S3, left) that for MC1, the scattering profile of the repeat measurement almost matches the initial measurements except at very low $q$. This is expected since the cooling process, at SANS beamline, probably fails to reach thermodynamic equilibrium, especially at very large spatial correlations. Hence, a mis-match in scattering at low $q$ is manifested. For MC2 (Figure S3, right) the repeat experiment $I(q)$ not only differs from the initial low temperature measurement, a clear difference between the scattering profiles (or line shapes) are observed. The repeat experiment data show a hint of gel like intermediate-$q$ shoulder which arises from the presence of residual gel structure even after cooling down well below the gel temperature ($\Delta T$ ~ 38 $^{o}$C). This observation corroborates rheological and ART-NMR findings that the gel formation and dissolution from MC solutions appears to be reversible but the dynamics are quite slow so that preparation of a kinetically equilibrated structure at any temperature requires extremely long time.

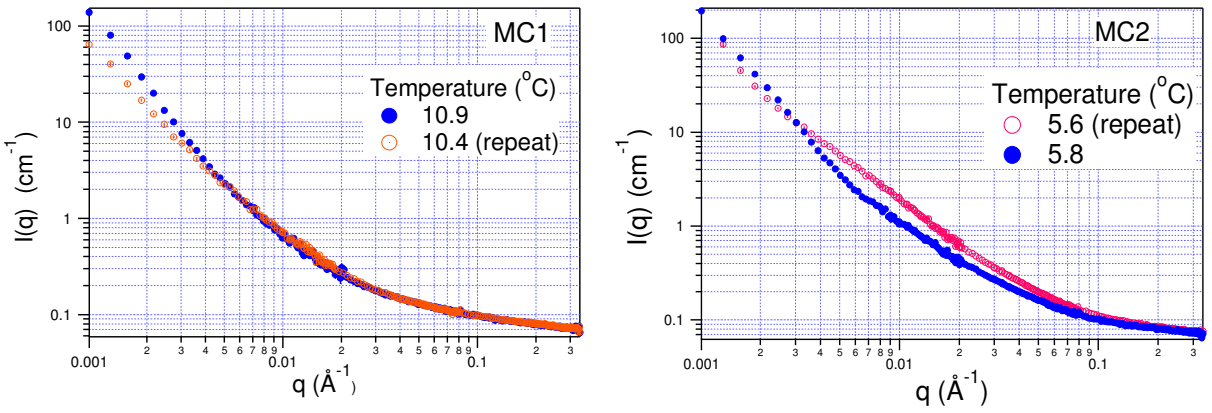


**Figure S3:** Reproducibility of the scattering data at low temperature. The closed symbols are the initial low-temperature measurements, and the open symbols are the repeat measurement after cooling down from a high temperature measurement (~ 90 °C). (a) MC1 scattering data show good agreement between the original and repeat measurements indicating structural reversibility. (b) MC2 data show a difference in scattering profile indicating the residual gel structure remains after cooling below $T_{gel}$.

**SANS Model fit to data *($T>T_{gel}$)***

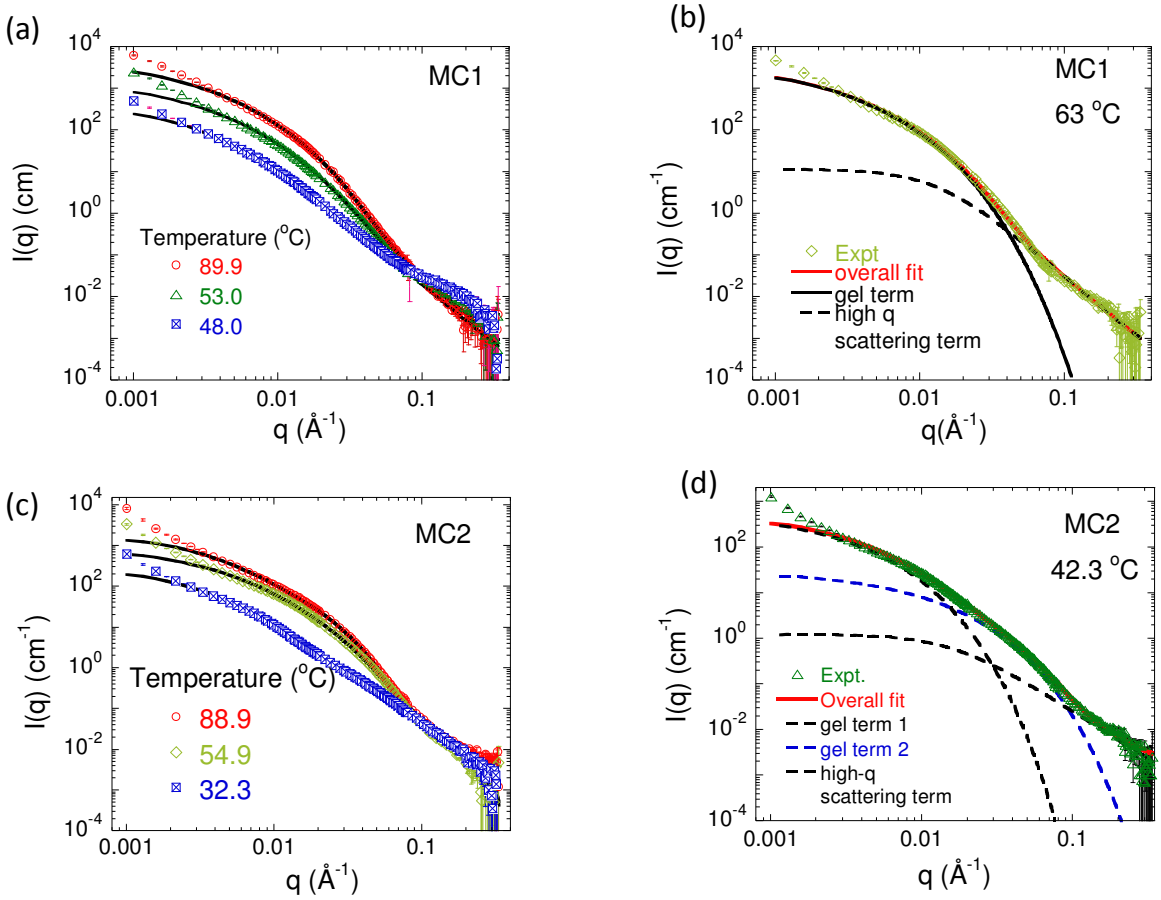


**Figure S4:** (left) Fits of MC1 and MC2 gel scattering data to Model 2 at selected post-gel temperatures. (right) The fits for each term in the model are shown for a selected post-gel temperature. The temperature was selected such that each aqueous methylcellulose material is at a comparable $T$-$T_{gel}$ condition. MC1 data are modeled with a single gel term (Equation 8). Two gel terms (Equation 9) are used to model MC2 SANS data. Extracted characteristic gel length scales are reported in Table 3, main text.

## References:


1. Keary, C. M., Characterization of METHOCEL cellulose ethers by aqueous SEC with multiple detectors. *Carbohyd Polym* **2001,** *45* (3), 293-303.
2. Rubinstein, M.; Colby, M. H., *Polymer Physics*. Oxford University Press, USA: 2003.
3. Mourey, T.; Le, K.; Bryan, T.; Zheng, S. Y.; Bennett, G., Determining persistence length by size-exclusion chromatography. *Polymer* **2005,** *46* (21), 9033-9042.