Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary Information

Molecular Origin of the Viscoelastic Transition in Molecular Granular Materials: Insights from Molecular Dynamics Simulations

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Methods of calculating configurational entropy

The method of calculating configurational entropy[1] is using the approximate entropy *S'* as a function of the classical variance,[2]

$$S^{'} = \frac{k}{2}\ln\left(\frac{kT}{\hbar^2}me^2\langle\Delta x^2\rangle_{cl} + 1\right)\#(1)$$

with classical limit of the coordinate variance

$$\langle\Delta x^2\rangle_{cl} = \frac{kT}{m\omega^2}\#(2)$$

where m and ω are the mass and frequency of the one-dimensional quantum-mechanical harmonic oscillator respectively.

Generalizing the formula to multiple dimensions by introducing the covariance matrix of the coordinate fluctuations,[3]

$$\sigma_{ij} = \langle(x_i - \langle x_i\rangle)(x_j - \langle x_j\rangle)\rangle\#(3)$$

yields

$$S^{'} = \frac{k}{2}\ln det\left(\frac{kTe^2}{\hbar^2}M\sigma + 1\right)\#(4)$$

Where $\boldsymbol{M}$ and **1** are the mass matrix and the unity matrix respectively.

So herein, we can get the covariance matrix $\boldsymbol{\sigma}$ by the simulation trajectory and further obtain the approximate configurational entropy *S'*.

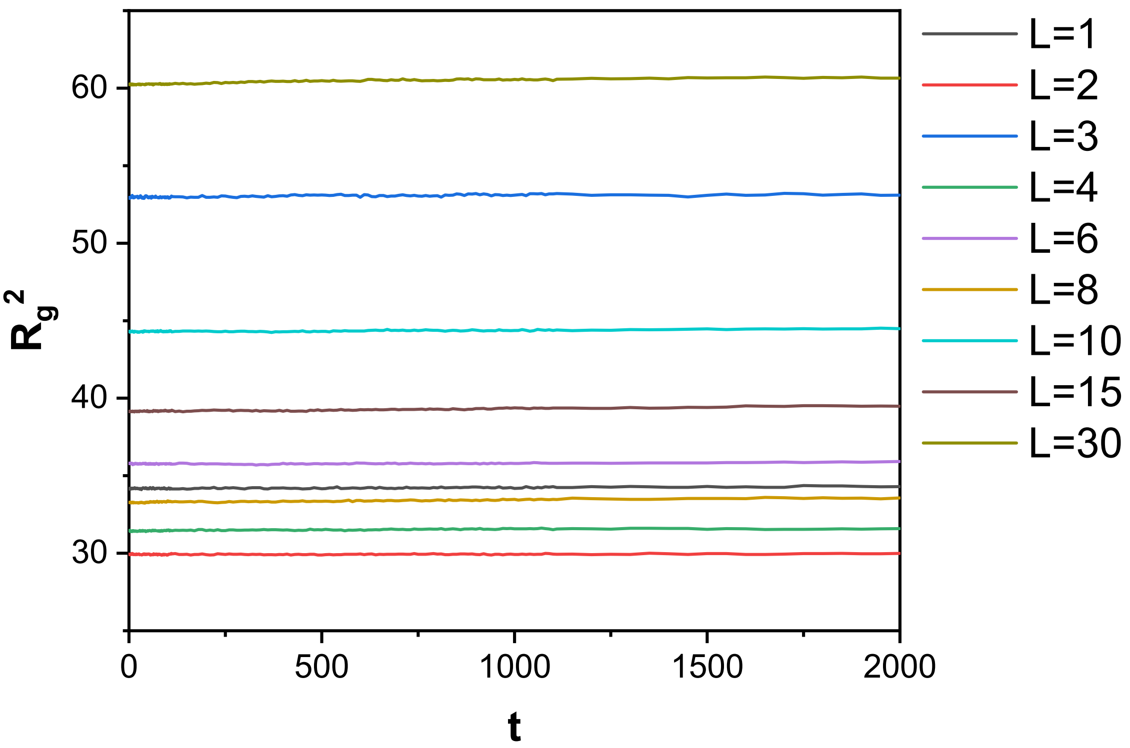

Fig. S1 Squared radius of gyration versus time plot after relaxation process in *NPT* ensemble.

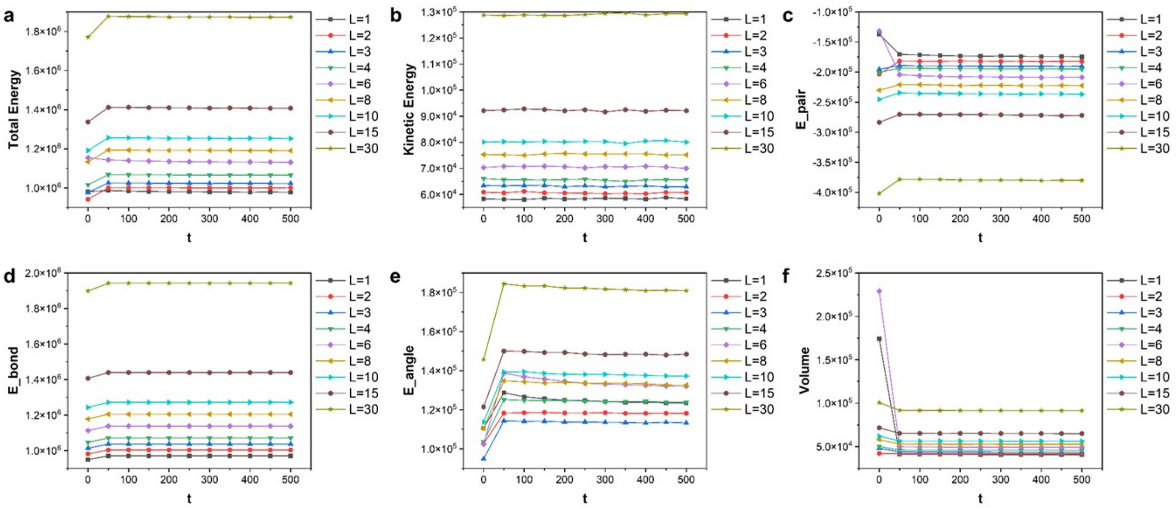

Fig. S2 Energy parameters (a)-(e) and volume (f) during equilibrium process. Specifically, (a) total energy, (b) kinetic energy, (c) E_pair, (d) E_bond, (e) E_angle.

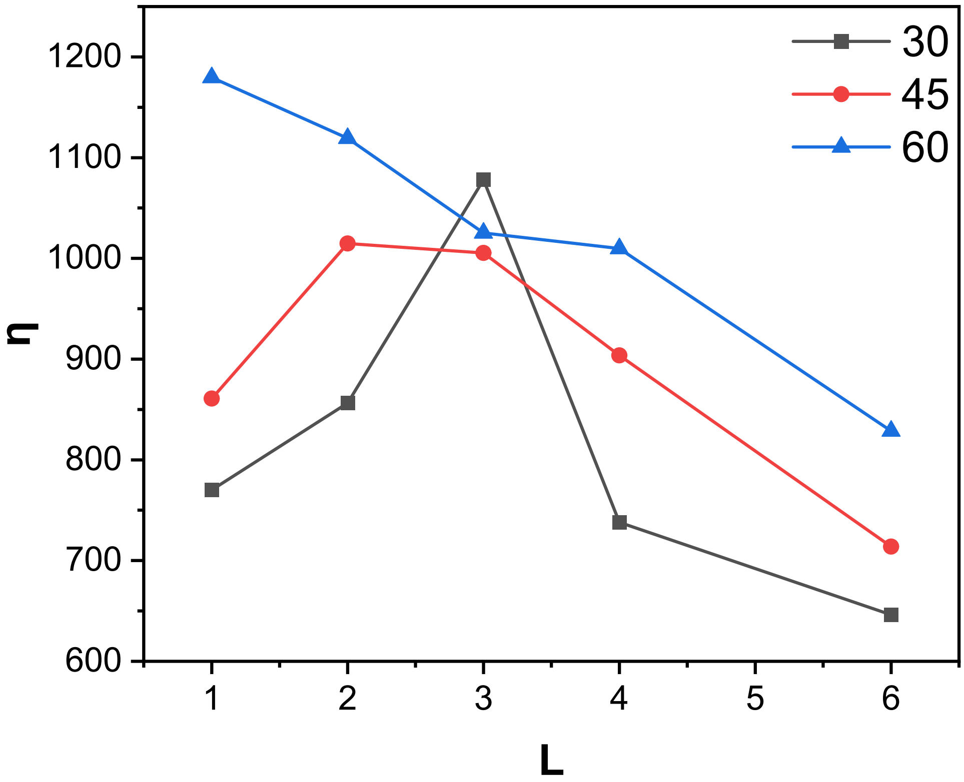

Fig. S3 The linker chain length *L* dependence at temperature *T* = 1.0 and pressure *P* = 1.0 of the shear viscosity *η* with different main chain length.

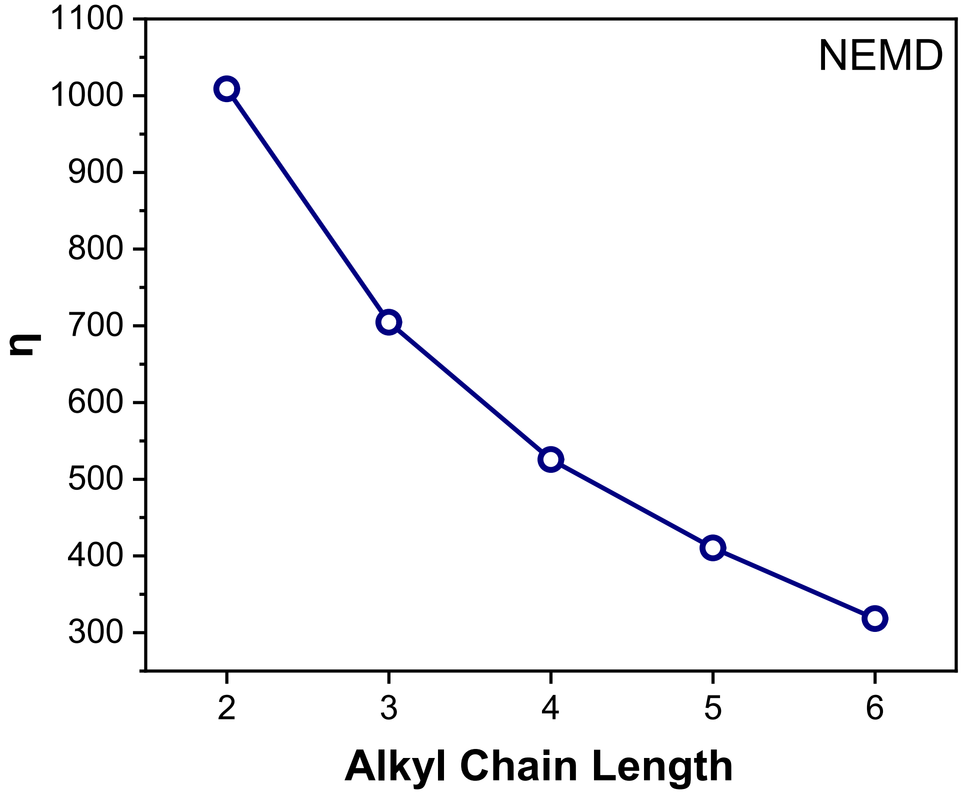

Fig. S4 The alkyl chain length dependence at temperature T = 1.0 and pressure P = 1.0 of the shear viscosity η with linker chain length $L = 3$.

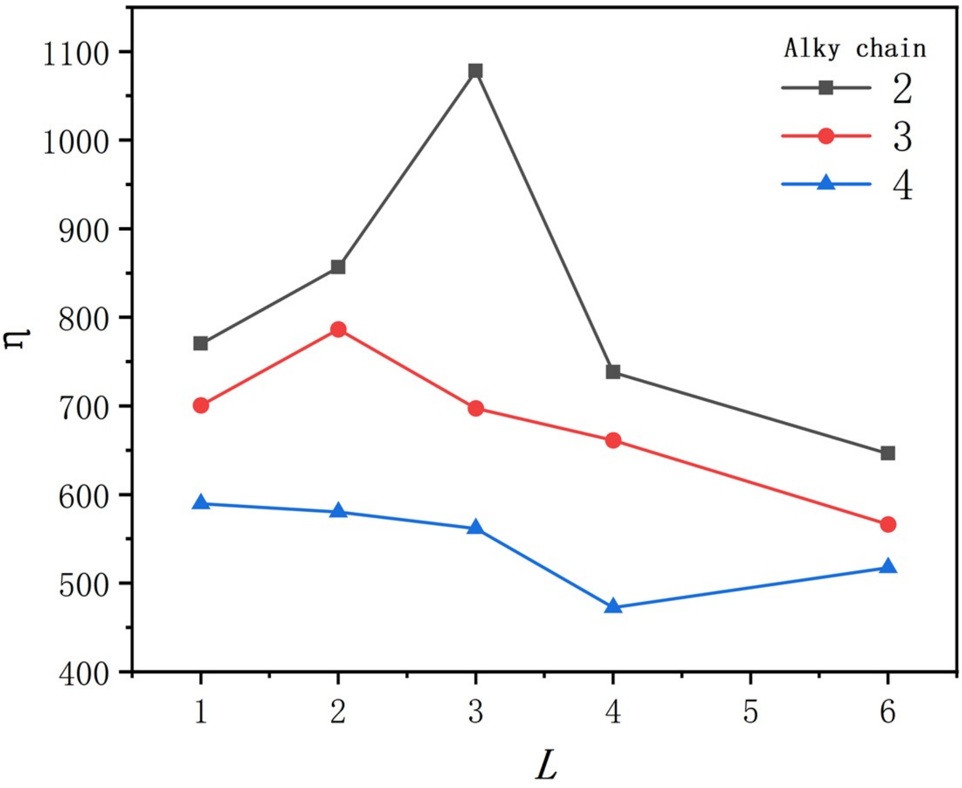

Fig. S5 The linker chain length *L* dependence at temperature *T* = 1.0 and pressure *P* = 1.0 of the shear viscosity *η* with different alkyl chain length.

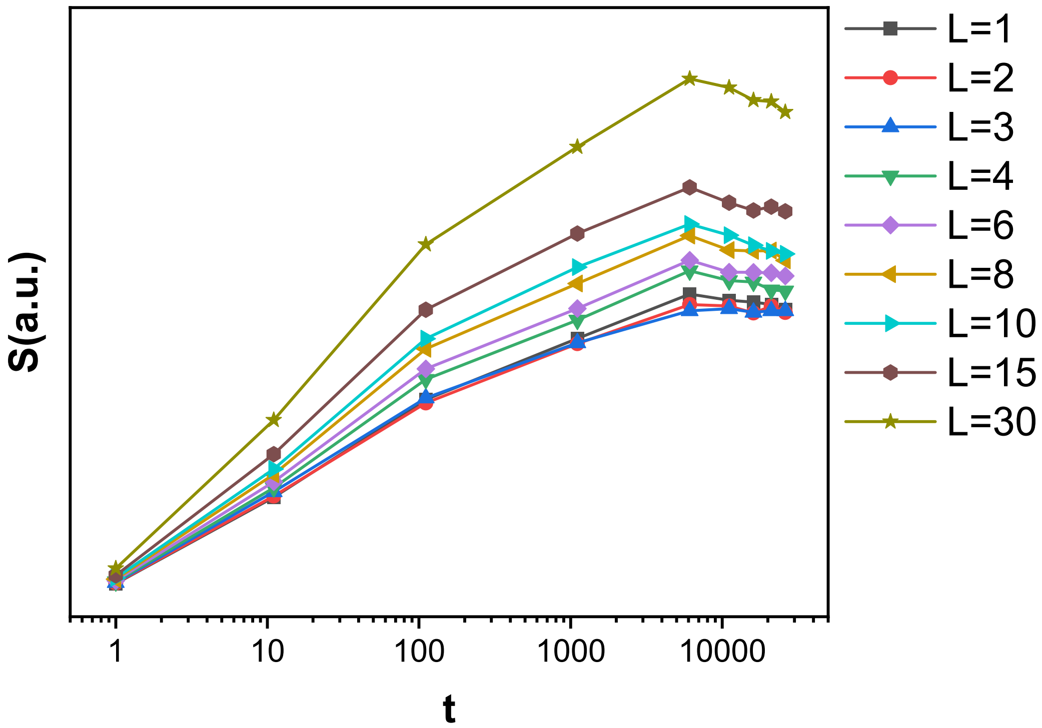

Fig. S6 Time dependence of configurational entropy of different linker length *L*.

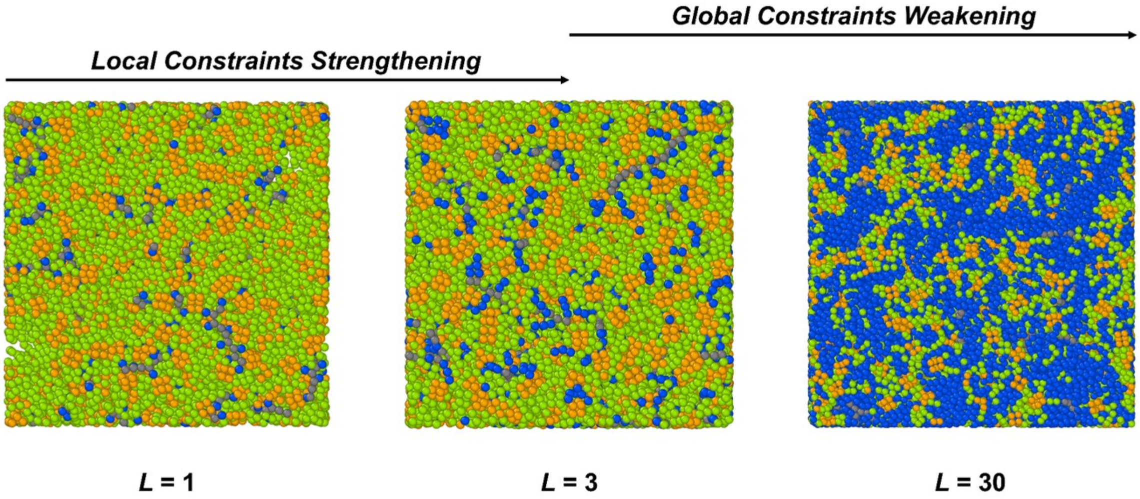

Fig. S7 The MD simulations cross sections snapshots of different linker chain length *L*. Beads are colored using the same coloring scheme as Figure 1.

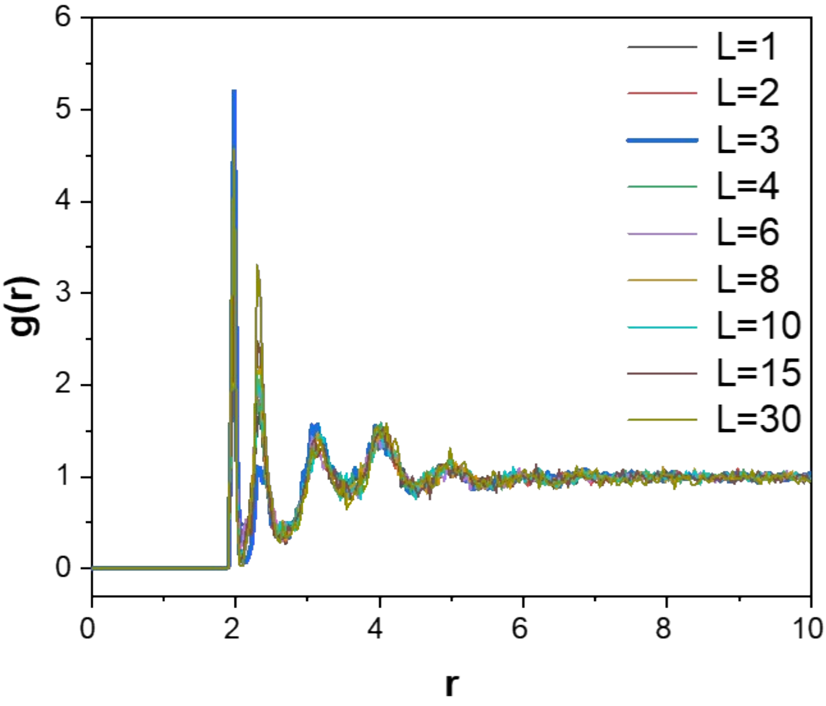

Fig. S8 The radial distribution function of the center of mass of POSS cages (full-data version, $0 < r < 10$).

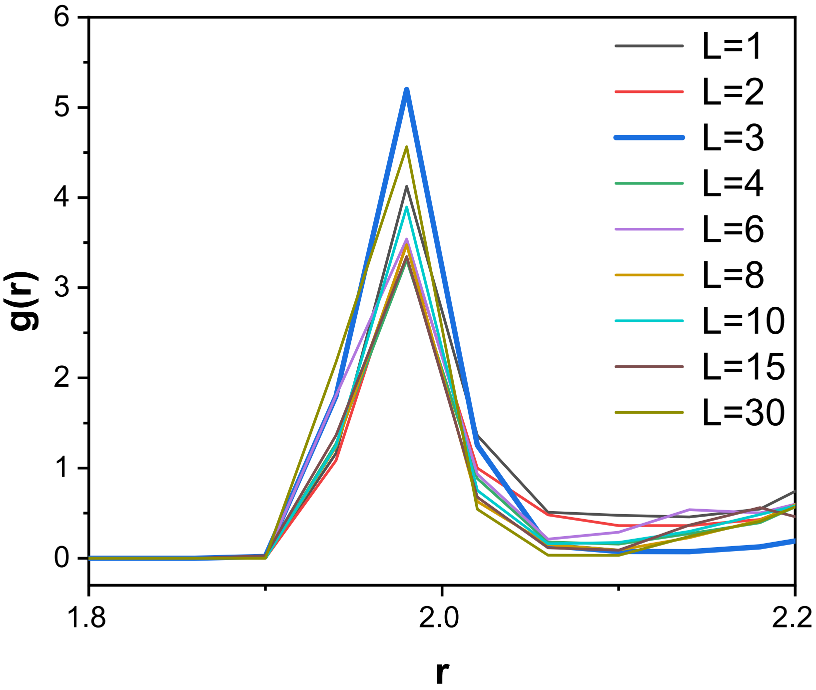

Fig. S9 The radial distribution function of the center of mass of POSS cages (zoomed-in version, $1.8 < r < 2.2$).

Table S1 The peak value of the first peak of the radial distribution function of the center of mass of POSS cages.

L	1	2	3	4	6	8	10	15	30
peak value	4.13	3.50	5.20	3.31	3.54	3.48	3.90	3.35	4.56

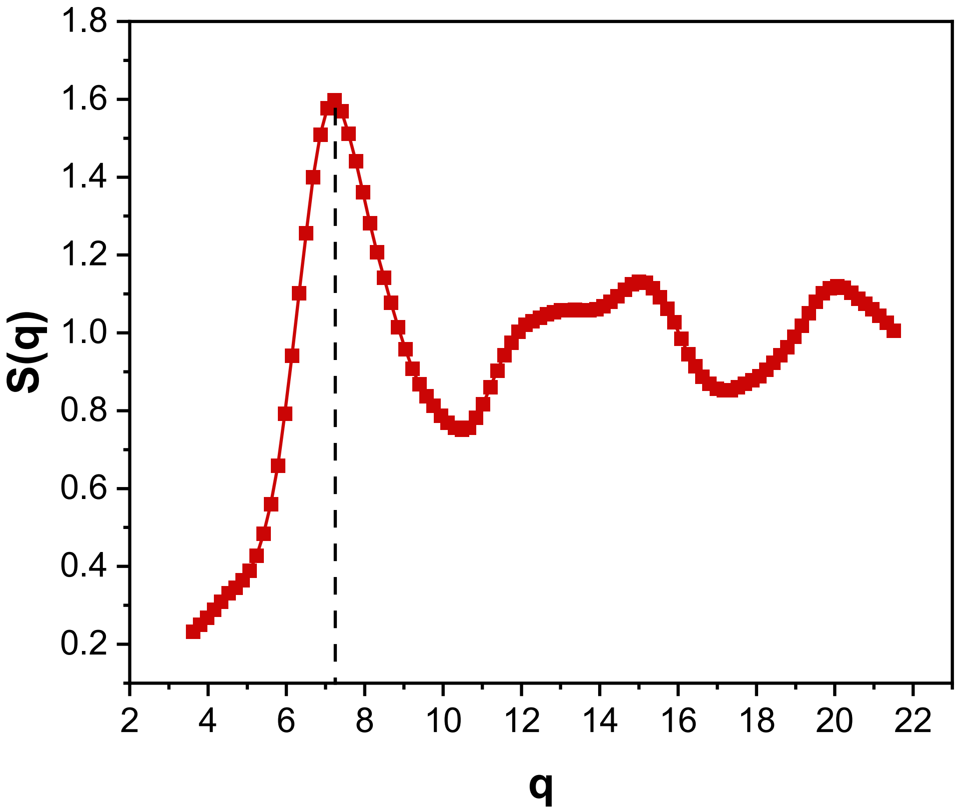

Fig. S10. The structure factor versus *q* plot, where the *q* value corresponding to the first peak represents the q_0 value.

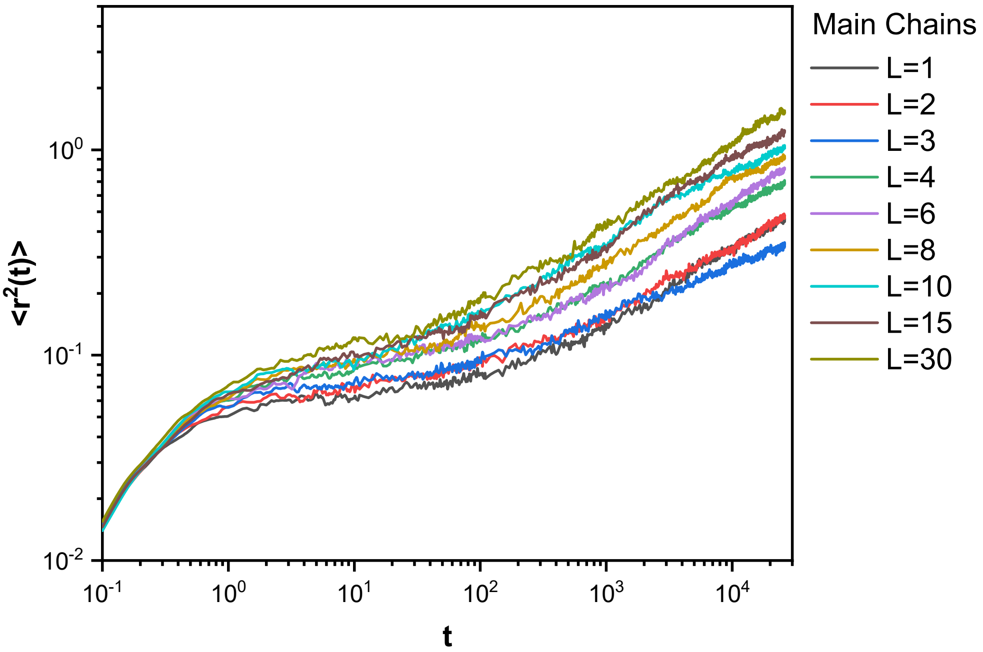

Fig. S11. Mean square displacement of main chain structure of PolyPOSSs with various linker chain length *L*.

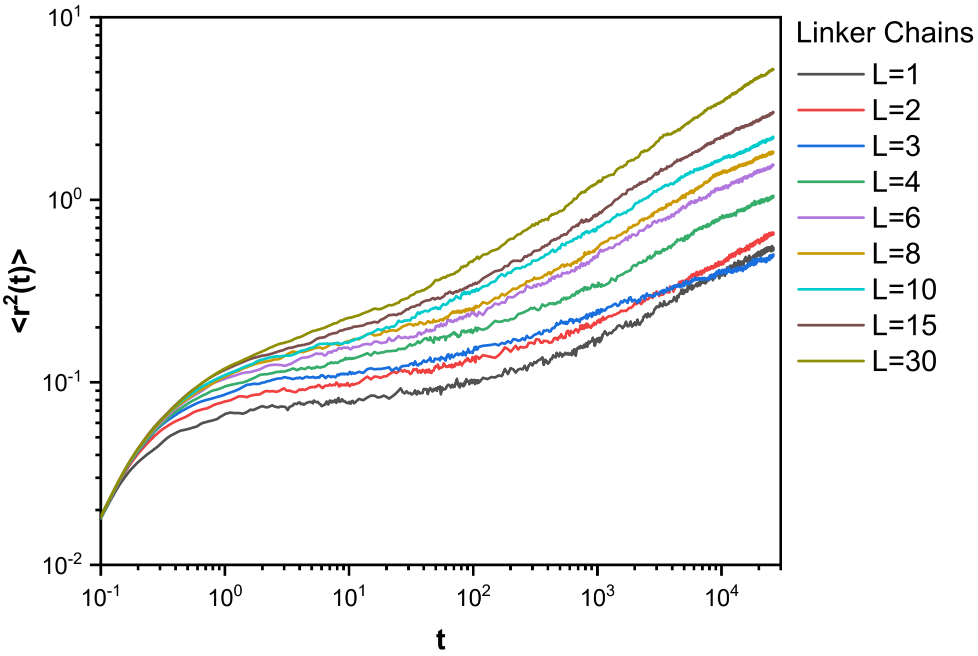

Fig. S12. Mean square displacement of linker chain structure of PolyPOSSs with various linker chain length *L*.

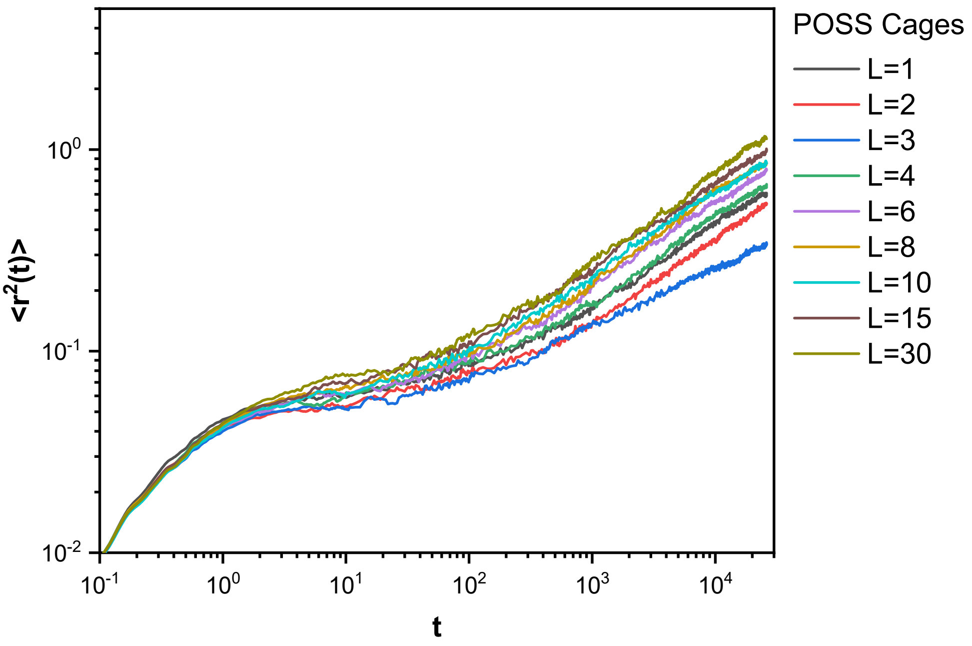

Fig. S13. Mean square displacement of POSS cage structure of PolyPOSSs with various linker chain length *L*.

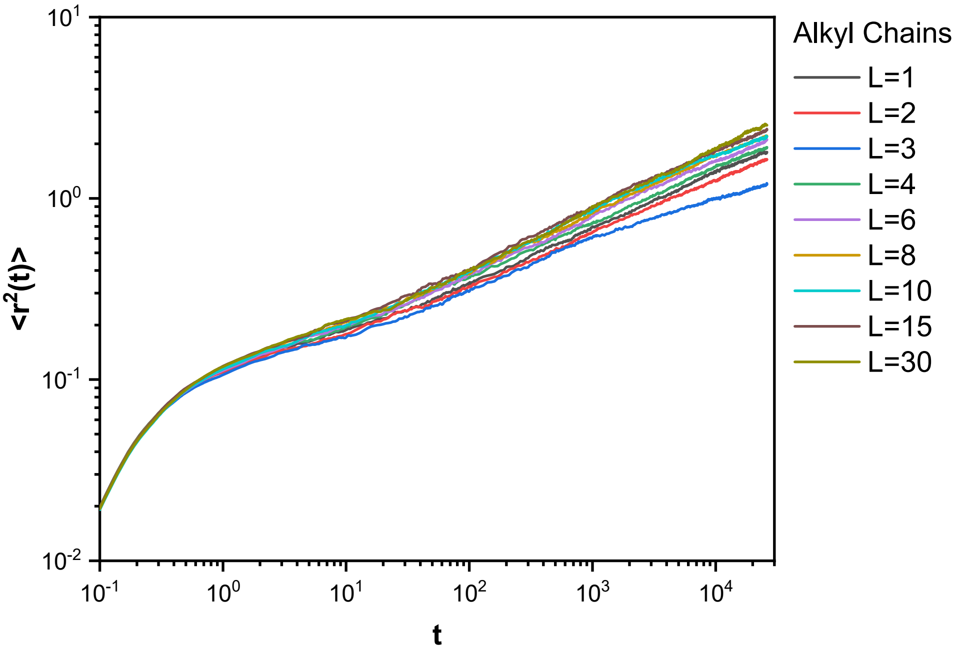

Fig. S14. Mean square displacement of alkyl chain structure of PolyPOSSs with various linker chain length *L*.

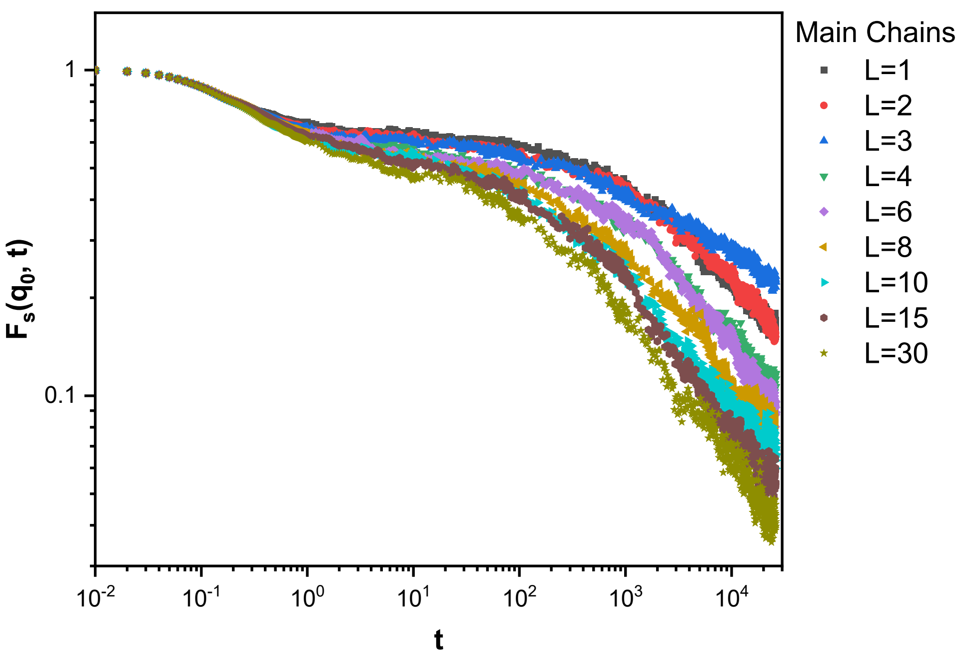

Fig. S15. Self-intermediate scattering function of main chain structure of PolyPOSSs with various linker chain length *L*.

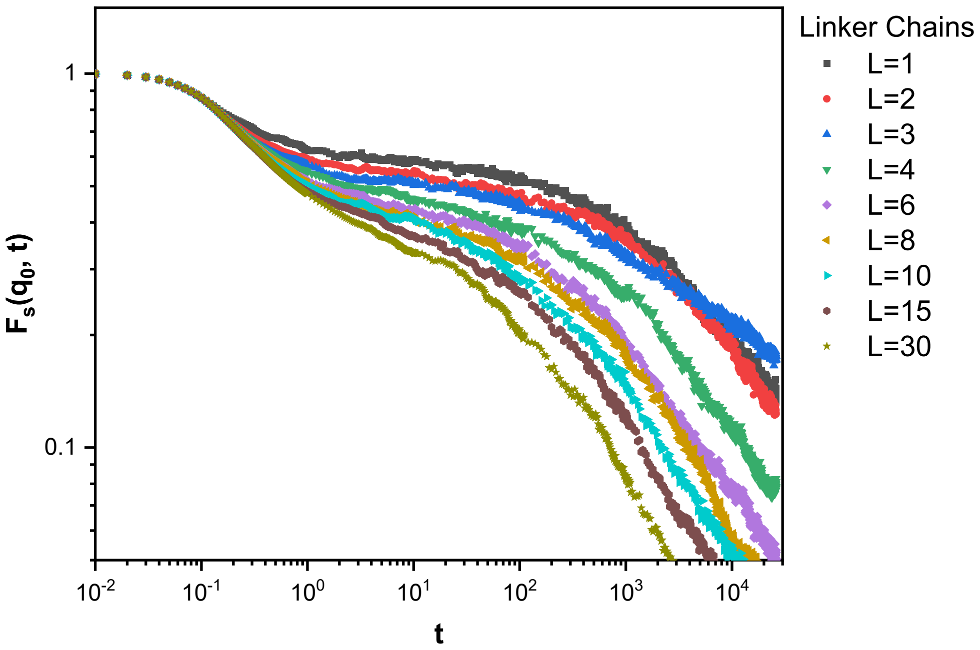

Fig. S16. Self-intermediate scattering function of linker chain structure of PolyPOSSs with various linker chain length *L*.

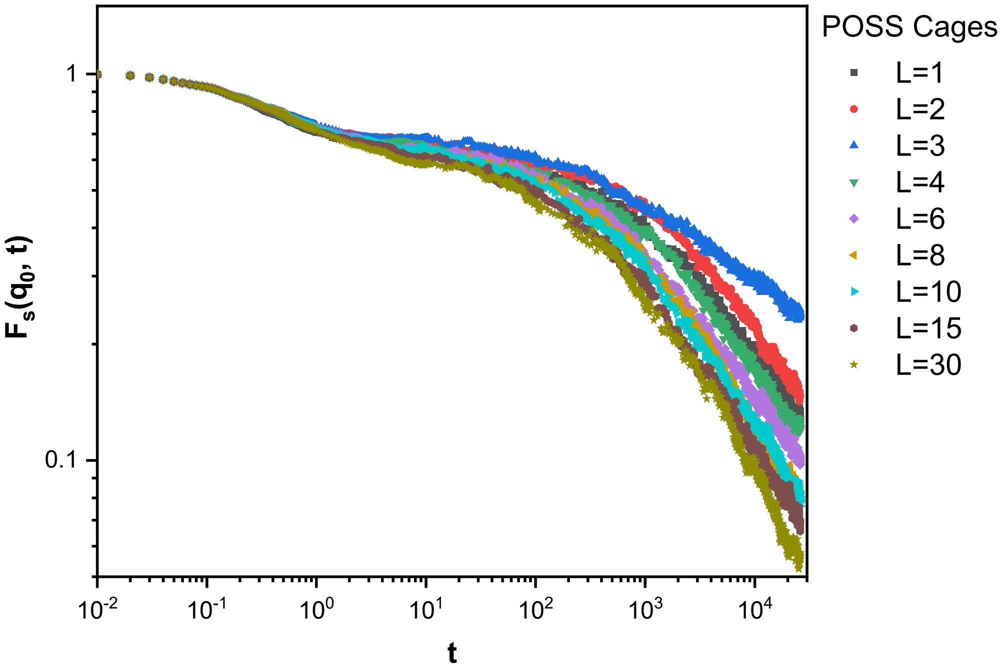

Fig. S17. Self-intermediate scattering function of POSS cage structure of PolyPOSSs with various linker chain length *L*.

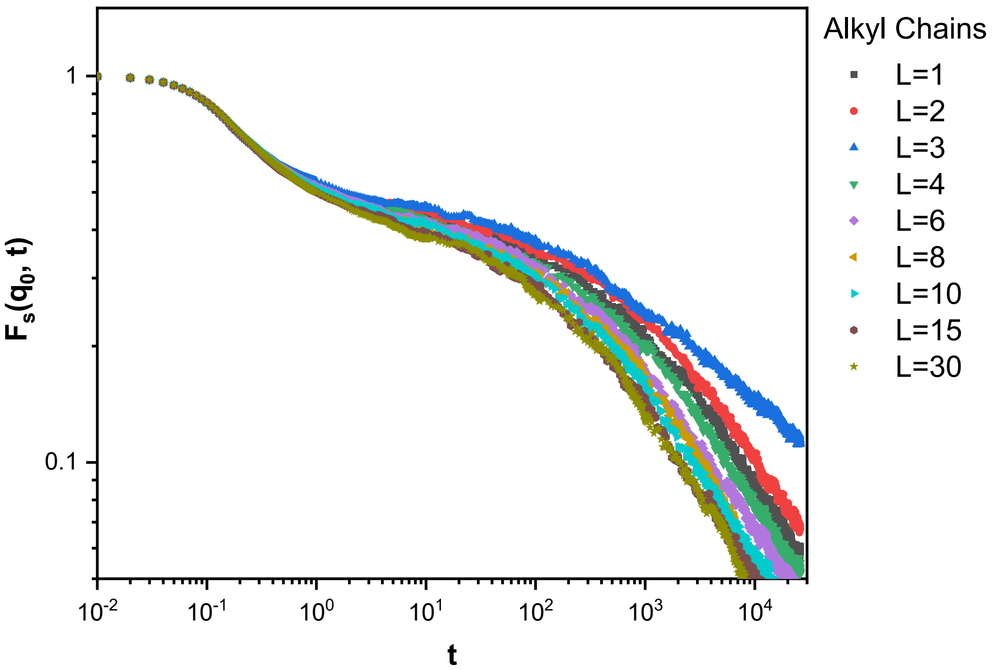

Fig. S18. Self-intermediate scattering function of alkyl chain structure of PolyPOSSs with various linker chain length *L*.

Reference

[1] I. Andricioaei, M. Karplus, On the Calculation of Entropy from Covariance Matrices of the Atomic Fluctuations, J. Chem. Phys. 115(14) (2001) 6289-6292.
[2] J. Schlitter, Estimation of Absolute and Relative Entropies of Macromolecules Using the Covariance Matrix, Chem. Phys. Lett. 215(6) (1993) 617-621.
[3] M. Karplus, J.N. Kushick, Method for Estimating the Configurational Entropy of Macromolecules, Macromolecules 14(2) (1981) 325-332.