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Supporting information for article:

Nanoscale Element Behaviors in a Continuum

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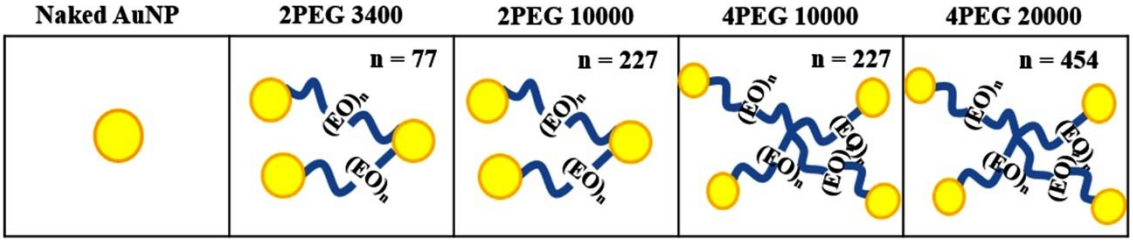
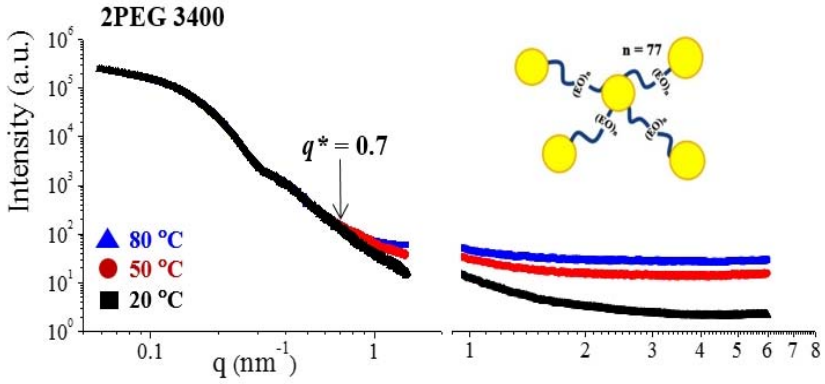
Figure S1. (A) Binary and quaternary thiol end-capped functional PEG molecules are incorporated for AuNP interconnection. Molecular weight between the junction point (M_p) is controlled by their characteristic structures: 2PEG3400 has M_p = 3400, $(EO)_n$, n=77 and 2PEG10000 has M_p = 10,000, $(EO)_n$, n=227, for binary-functional PEGs. Meanwhile, 4PEG10000 has M_p = 10,000, $(EO)_n$, n=227 and 4PEG20000 has M_p = 20,000, $(EO)_n$, n=454, for quaternary-functional PEGs. In addition, the number of incorporated PEG molecules is controlled to 5 times of the number of AuNPs for each system (×5), considering the multi-reactive sites on a single AuNP.



(**B**) The formed nanocomposite networks exhibit characteristic spectra in SAXS. Beyond the critical *q** value the systems are responsive to temperature, while below that *q** value all the systems are stable. Under the given synthetic condition, only 2PEG 10,000 and 4PEG 10,000 exhibit detectable structures. To get broad *q* range, two sample-to-detector distance conditions in different *q* regions are combined. The observed *q* region is broad from gold nanoparticle region to polymeric structure region. The main changes happen in the region of polymeric structural change.



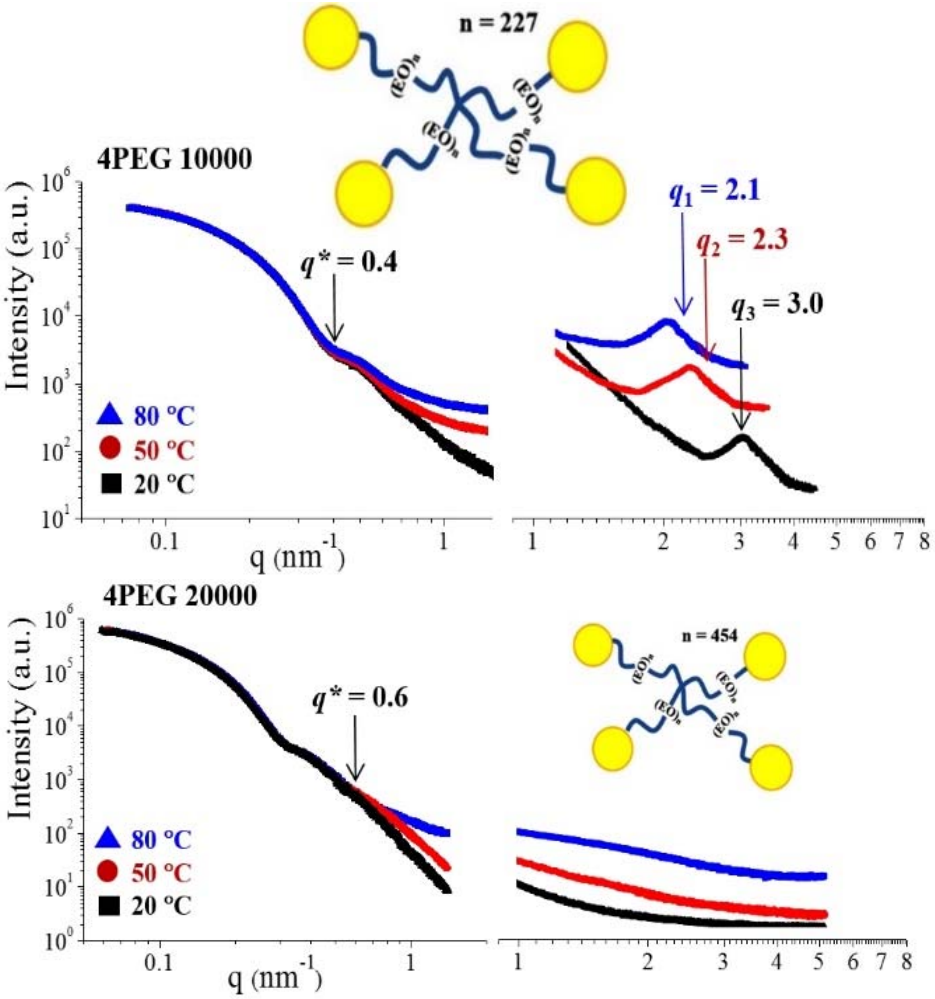
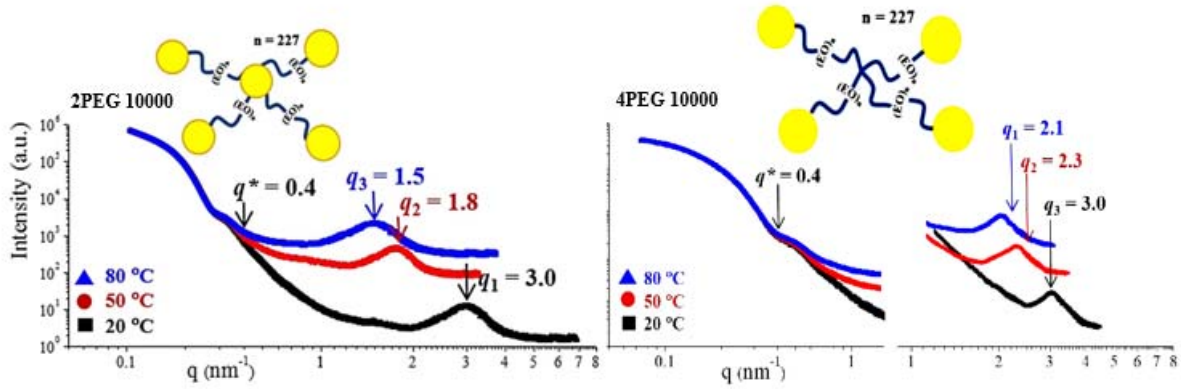
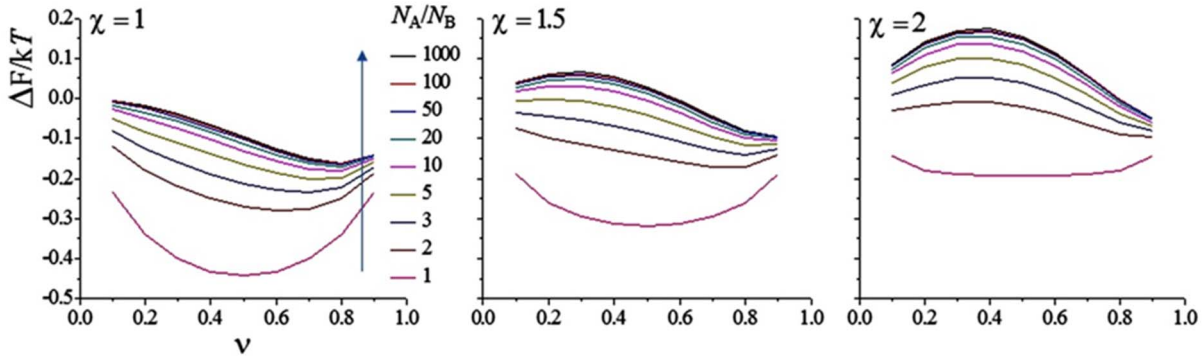

n = 227
4PEG 10000
Intensity (a.u.)
q* = 0.4
q1 = 2.1
q2 = 2.3
q3 = 3.0
80 °C
50 °C
20 °C
q (nm-1)
4PEG 20000
n = 454
Intensity (a.u.)
q* = 0.6
80 °C
50 °C
20 °C
q (nm-1)

Figure S2. The surface-modified AuNP aqueous stock solutions are adjusted to have a concentration of 2.4×10^{21} AuNPs/m^3 in consideration of the AuNPs in average 2 nm diameter and the $HAuCl_4$ concentration of 1 mmol/L. For the standard concentration of the AuNP stock solution of 1 mmol/L, the concentration of the ligand stock solution is varied as ×5, ×10 and ×20 of AuNP number. Depending on these number ratio of the ligands to the AuNP, the q values obtained by SAXS are diversified.



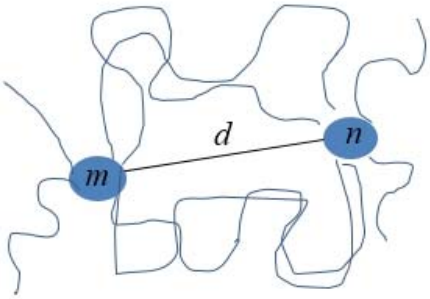
		q_*	q_1	q_2	q_3
× 5	2PEG 10000	0.4	1.5	1.8	3.0
	4PEG 10000	0.4	2.1	2.3	3.0
× 10	2PEG 10000	0.45	1.7	2.0	3.2
	4PEG 10000	0.45	2.3	2.5	3.3
× 20	2PEG 10000	0.5	1.9	2.2	3.4
	4PEG 10000	0.5	2.5	2.6	3.6

Figure S3. Helmholtz free energy (ΔF) evaluation at different dimensionless interaction parameter (χ) 1, 1.5 and 2 according to the increase in the connectivity of a component A in a medium B (N_A/N_B) from 1 to 1000.



Network models

Fluctuation of two junctions separated by several chains are expressed by using the notation of Flory (*R. Soc. London, Ser. A.* 1976, 351, 351) and Pearson (*Macromolecules* 1975, 10, 696),



γ : crosslinking index
ϕ : functionality
d : number of other chains between the junctions m and n

r : end-to-end vector
R_m and R_n : position vectors of junctions m and n.

For the condition of the average fluctuations for t $\rightarrow\infty$,

$$\begin{bmatrix} \langle(\Delta R_m^2)\rangle & \langle\Delta\mathbf{R}_m\cdot\Delta\mathbf{R}_n\rangle \\ \langle\Delta\mathbf{R}_m\cdot\Delta\mathbf{R}_n\rangle & \langle(\Delta R_n^2)\rangle \end{bmatrix} = \frac{3}{2}\begin{bmatrix} (\Gamma^{-1})_{mm} & (\Gamma^{-1})_{mn} \\ (\Gamma^{-1})_{nm} & (\Gamma^{-1})_{nn} \end{bmatrix} = \frac{3}{2\gamma}\begin{bmatrix} \dfrac{\phi-1}{\phi(\phi-2)} & \dfrac{1}{\phi(\phi-2)(\phi-1)^d} \\ \dfrac{1}{\phi(\phi-2)(\phi-1)^d} & \dfrac{\phi-1}{\phi(\phi-2)} \end{bmatrix}$$

The mean square fluctuations of the distance, r_{mn}

$$\langle(\Delta r_{mn})^2\rangle = \langle(\Delta\mathbf{R}_m - \Delta\mathbf{R}_n)^2\rangle = \frac{2}{\phi(\phi-2)(d+1)}\,\frac{(\phi-1)^{d+1}-1}{(\phi-1)^d}\langle r_{mn}^2\rangle_0$$

In the limit as $d \rightarrow \infty$,

$$\lim_{d\rightarrow\infty}\langle(\Delta r_{mn})^2\rangle = \frac{2(\phi-1)}{\phi(\phi-2)}\langle r_{12}^2\rangle_0$$

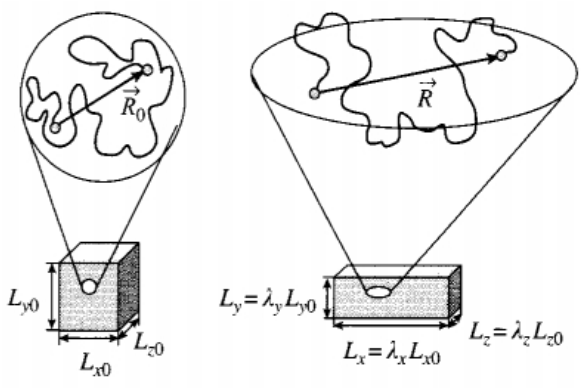
Junctions m and n are separated by one chain only then, $d = 0$

$$\langle(\Delta r_{ij})^2\rangle = \frac{3}{2\gamma}\,\frac{2}{\phi} = \frac{2}{\phi}\langle r_{ij}^2\rangle_0$$

Relative value of the fluctuation $(<\Delta r_{mn}>)^2$ to the distance $<r_{mn}^2>_0$ becomes,

$$\frac{\langle(\Delta r_{mn})^2\rangle_{d=\infty}}{\langle(\Delta r_{mn})^2\rangle_{d=0}} = \frac{(\phi-1)}{(\phi-2)}$$

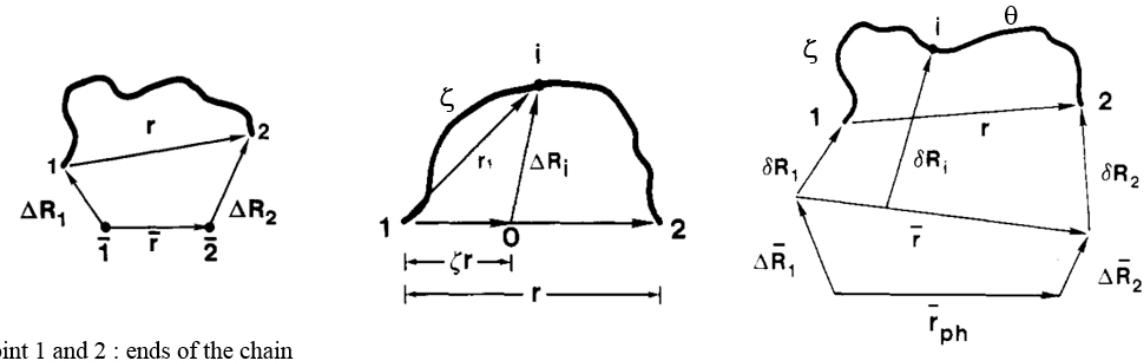
The deformation of the network structures is described by introducing the deformation factor λ,



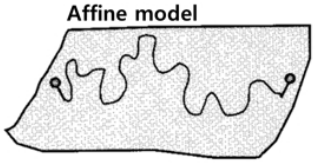
For isotropic deformation
$\lambda_x \lambda_y \lambda_z = 1$: volume of a network remains constant
For uniaxial deformation at constant volume
$\lambda_x = \lambda$, $\lambda_y = \lambda_z = 1/\sqrt{\lambda}$: stretched ($\lambda > 1$) or compressed ($\lambda < 1$) in *x* direction

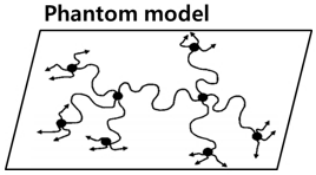
Affine and Phantom model and chains of various k values

Two theoretical models of Affine and Phantom models and real chain are compared.



Point 1 and 2 : ends of the chain
Point $\bar{1}$ and $\bar{2}$: time averaged position
r : instantaneous end-to-end vector
$\bar{r}$: time averaged end-to-end vector
ΔR_1 and ΔR_2 : instantaneous fluctuation from mean position



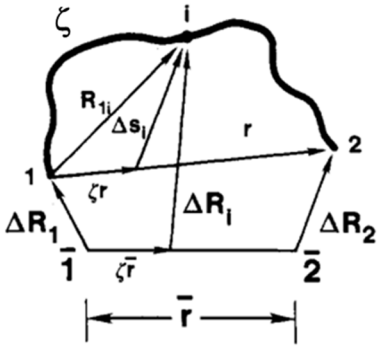


$\boldsymbol{r}_{ij}$: = $\hat{\boldsymbol{r}}_{ij} + \Delta \boldsymbol{r}_{ij}$
$\boldsymbol{r}_{ij}$: vector which joins two point *i* and *j* on the chain [by Pearson's law]
$\hat{\boldsymbol{r}}_{ij}$: mean separation between point *i* and *j* on the chain
$\Delta \boldsymbol{r}_{ij}$: instantaneous fluctuation of this distance

$\hat{\boldsymbol{r}}_{ij} = \lambda \hat{\boldsymbol{r}}_{ij,0}$
$\hat{\boldsymbol{r}}_{ij,0}$: initial mean separation between point *i* and *j* on the chain

ζ : Fractional distance from the junction position between the point *i* and *j*.
$\langle \Delta X_i^2 \rangle$: Ensemble average of the mean-square fluctuations between the point *i* and *j* at a certain ζ.
$\langle x_0^2 \rangle$: Ensemble average of mean-square fluctuations of the end-to-end distance.

The extent of junction fixation is fixed in Affine model ($\kappa=\infty$) while it fully moves in Phantom model ($\kappa=0$). In real chain the degree of fluctuation designated as κ ranges between two ideal model systems.



κ : extent of fluctuation
ϕ : functionality

Phantom Model
$\langle(\Delta X_i)^2\rangle/\langle x^2\rangle_0 = \zeta(1-\zeta)(1-2/\phi)\lambda^2 + (\phi-1)/(\phi(\phi-2))$

For $\phi \rightarrow \infty$ condition, it goes to Affine model
$\langle\Delta X_i)^2\rangle/\langle x^2\rangle_0 = \zeta(1-\zeta)\lambda^2$

By introducing extent of fluctuation, κ Real chain is described by
$\langle(\Delta X_i)^2\rangle/\langle x^2\rangle_0 = [\lambda^2/\lambda^2 + \kappa]\,[(\phi-1)/(\phi(\phi-2))] + \zeta(1-\zeta)[(1-2/\phi)\lambda^2 + (\kappa\lambda/(\lambda^2+\kappa))^2(2/\phi)]$

Theoretical Analysis

Monte Carlo simulation is carried out for a system consisting of 500 nanoparticles by assuming that each nanoparticle is independent but with uniformly grafted polymer chains in a solvent. Each nanoparticle is assumed as a sphere of diameter, d. The polymer chains are modelled as lines of beads with diameter of d, and adjacent lengths between them are in the range of 1.01–1.5d. A square-well potential is used to represent the interaction between two NPs,

$$U(r) = \infty \ (r < d)$$

$$= -\alpha \ (d \le r < \kappa d)$$

$$= \xi \ (r \ge \kappa d)$$

where α is the attractive well depth and κ is the attraction range. If the NPs are completely independent, $U(r) = 0$ ($r \ge \kappa d$) is supposed to be satisfied. However, considering networked structure this term is not considered in this study, ξ is instead considered as a fully stretched correlation length of a network. NP–NP and NP–polymer interactions are modelled with hard-sphere potentials. Canonical ensemble (NVT) simulations are performed using the Metropolis algorithm. The number density fraction of the NPs is 0.005. The simulation box is a cube with periodic conditions. Five types of Monte Carlo attempted with a probability (0.3:0.1:0.4:0.1:0.1), are translation and rotation of grafting NPs, translation of polymers and translation and rotation of grafting NP cluster, respectively. The simulation temperature is set as $T^* = k_B T/\varepsilon = 0.1$. Each simulation is at least 10 million Monte Carlo steps of equilibration followed by 100 million Monte Carlo steps. A series of systems with a polymer chain length range from 5 to 50 are investigated. Five independent runs are carried out for each case. With increasing the length of grafted chains, the particle assemblies are observed to change from spheres to cylinders, and further sheets. These structures seem to correspond to the self-assembly of phase-separated NPs. The sheets in these two categories denote local particle packing. For even longer chains, the particles are no longer phase-separated from the solvent, rather they self-assemble into linear chains. Beyond this, the NPs are free from each other within a size of the stretched network.