

## Supporting Information

### **Volume phase transition of electron beam cross-linked thermo-responsive PVME nanogels in the presence and absence of nanoparticles: with a view toward rheology and interactions**

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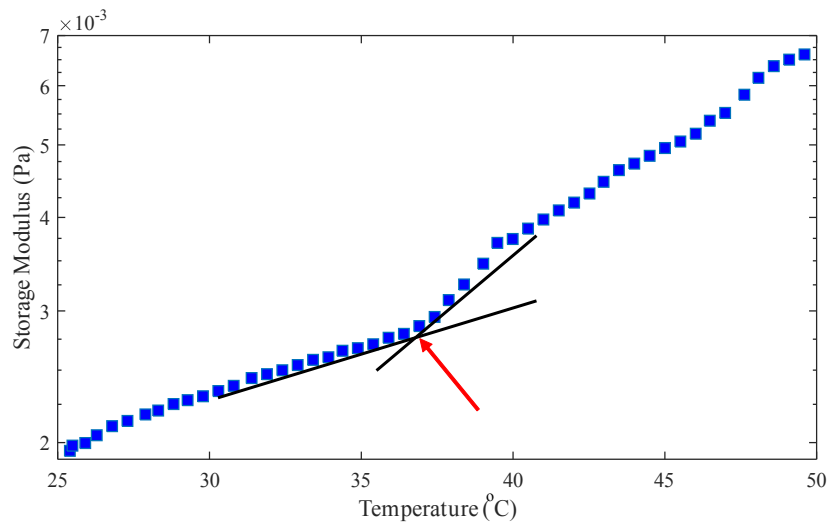
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## S1) Volume phase transition temperature and FT-IR data of the blank sample with no radiation and free of particles

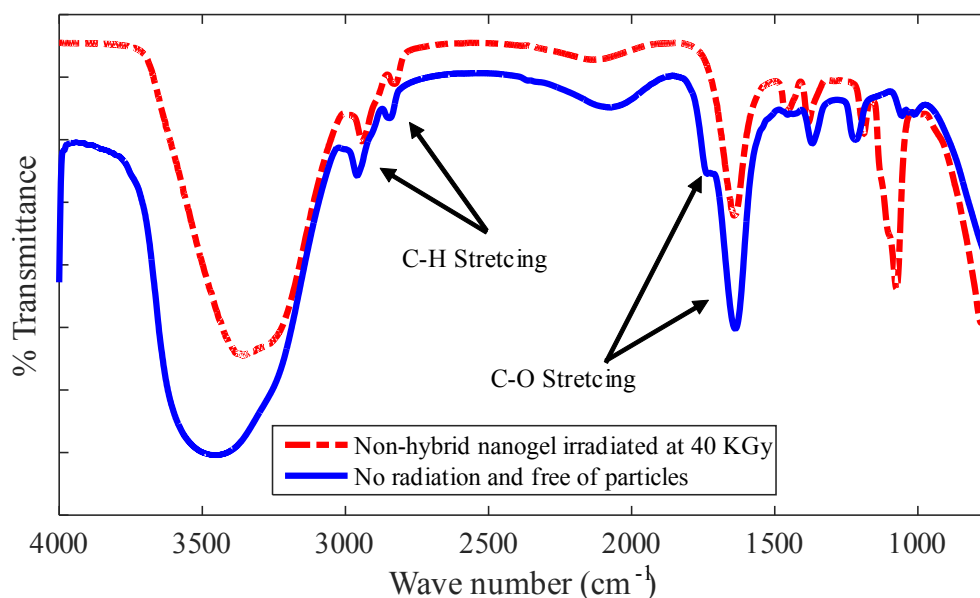
Figure S1 shows the temperature sweep of storage modulus for the aqueous solution of PVME with no radiation and free of particles. As can be seen, phase separation temperature of the blank sample (35.4 °C) is lower than the pure PVME nanogels (36.9 °C for nanogel irradiated at 20 KGy, Figure 1). This indicates that radiation increases the volume phase transition temperature.



**Figure S1.** Isochronal dynamic temperature sweep of storage modulus for the sample with no radiation and free of particles. The rheologically determined volume phase transition temperature is:  $T = 35.4$  °C which is marked with an arrow in the figure. The solid lines represent the slope of the  $G'$  curve before and after phase separation temperature and are guides to the eye.

Figure S2 shows the FT-IR spectra of the blank sample and non-hybrid nanogel irradiated at 40 KGy at the homogeneous state. As can be seen there is a blue shift of the C-O stretching band at  $1050-1150$   $\text{cm}^{-1}$  (which means the breakdown of the hydrogen bonds between macromolecules and water molecules [4]) and a red shift of the C-H stretching band at  $2800-3000$   $\text{cm}^{-1}$  (which means dehydration of the methyl groups of PVME [4]), when the system is

irradiated by electron beam. Therefore, the radiation itself restricts the mobility of the macromolecules.

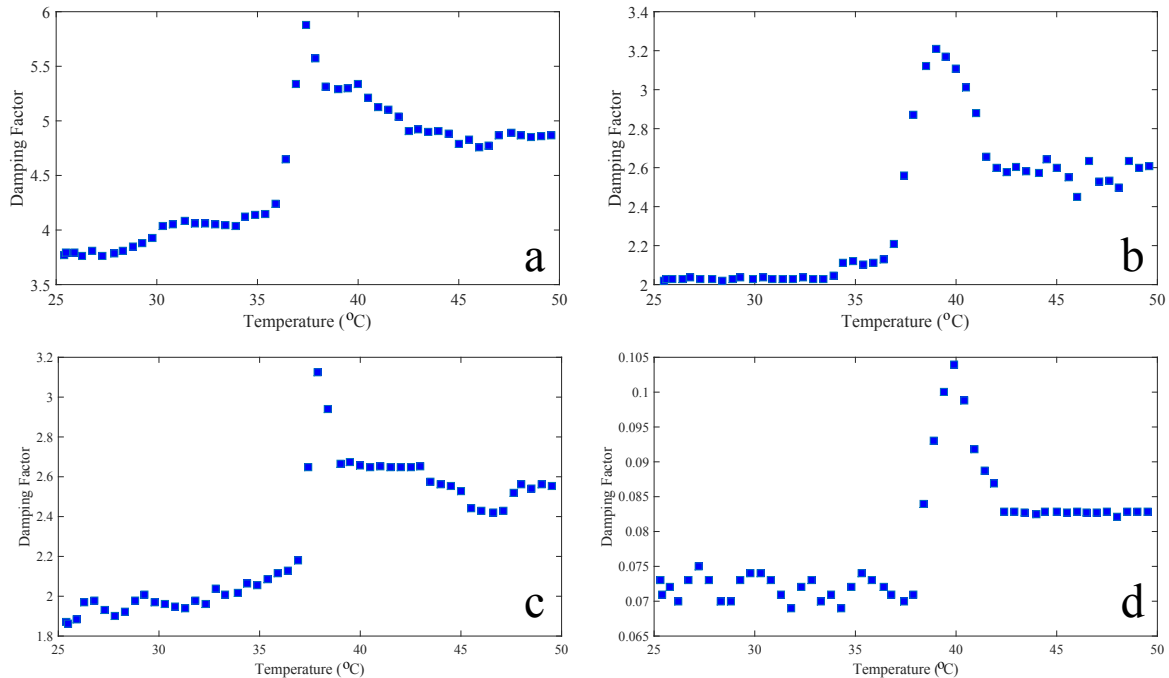


**Figure S2.** FT-IR spectra of the sample with no radiation and free of particles and non-hybrid nanogel irradiated at 40 KGy at temperature of 30 °C.

## **S2) Damping factor vs. temperature curve for the hybrid and non-hybrid nanogels**

Determination of phase separation temperature from dynamic temperature sweep experiment may involve an error in the estimation of slopes. In the manuscript, we tried to draw the slopes carefully (Figure 1) to minimize the error to make a proper comparison between the phase separation temperatures of different samples. To be sure of the data accuracy obtained from Figure 1, we also used another method to determine the phase separation temperature. For determination of the phase separation temperature by rheology the corresponding  $\tan \delta$  (damping factor) vs. temperature curve of the  $G'$  temperature sweep of the samples (Figure 1) can be used.<sup>1</sup> In this curve a peak in  $\tan \delta$  appears at the phase separation temperature. This method is particularly useful in the case where the change in the slope of  $G'$  temperature sweep is subtle.  $\tan \delta$  vs. temperature curves are shown in Figure S3. As can be seen at the

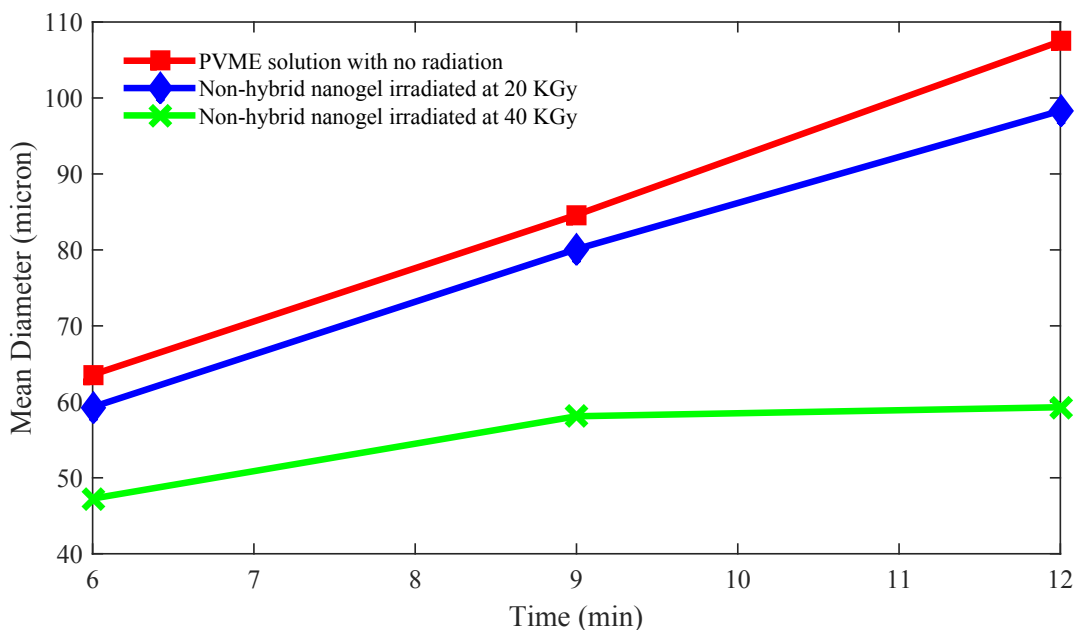
phase separation temperature there is a clear peak which its corresponding temperature is nearly equal to the one obtained from Figure 1.



**Figure S3.** Isochronal temperature sweep of damping factor for a) non-hybrid nanogel irradiated at 20KGy, b) non-hybrid nanogel irradiated at 40 KGy, c) hybrid nanogel irradiated at 20 KGy, and d) hybrid nanogel irradiated at 40 KGy. The peaks position shows the volume phase transition temperature: a)  $T = 36.9\text{ }^{\circ}\text{C}$ , b)  $T = 37.9\text{ }^{\circ}\text{C}$ , c)  $T = 37.4\text{ }^{\circ}\text{C}$  and d)  $T = 38.4\text{ }^{\circ}\text{C}$ .

### S3) Time evolution of domain size for non-hybrid nanogels

Figure S4 shows the effect of radiation on variation of average domain size (PVME-rich phase) with time obtained by image analysis of the optical micrographs using ImageJ software [6] in the late stage of phase separation. As can be seen, radiation considerably decreases the average domain size at the corresponding phase separation times indicating the slowdown of phase separation.

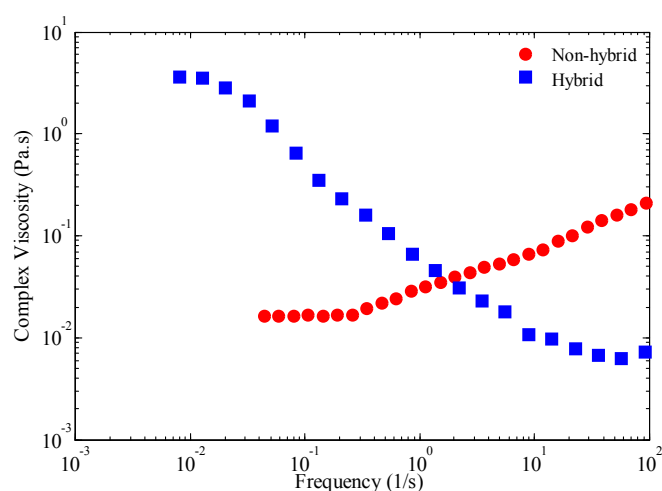


**Figure S4.** Variation of the domain size with time for the PVME solution with no radiation and non-hybrid nanogels irradiated at 20 and 40 KGy at 40 °C.

#### **S4) Comparison of the frequency dependence of the complex viscosity of the hybrid and non-hybrid nanogels**

To further elucidate the intra- and inter-interactions in hybrid and non-hybrid nanogels, we investigate the frequency sweep behaviour of complex viscosity. Figure S5 shows the frequency sweep curve of the complex viscosity for the hybrid and non-hybrid nanogels irradiated at 20 KGy at the homogeneous region (30 °C). Interestingly, non-hybrid nanogel exhibits shear-thickening behaviour. Similar behaviour was observed in sterically stabilized colloidal suspensions.<sup>3</sup> At 30 °C which PVME is soluble in water, hydrophilic ether oxygen groups of PVME macromolecules make H-bonds with the water molecules. This induces a soft repulsive interaction between the particles in non-hybrid nanogels.<sup>3</sup> Therefore, repulsive interactions prevent the nanogels clustering at homogeneous state when the nanogels are at rest. By applying shear, nanogels arrange along the stress axis and overcome the repulsive interactions by formation of intermolecular H-bonds. Thus, hydroclusters are formed which

induces shear thickening behavior.<sup>4</sup> However, nanogels containing nanoparticles dramatically shear thinned against dynamic flow. The added silica nanoparticles disrupt the interactions between the PVME macromolecules and water molecules, due to the adsorption of polymer chains on the nanoparticles surface.<sup>5</sup> Therefore, applying shear induces shear thinning behavior as in colloidal suspensions.<sup>6,7</sup> These results agree FT-IR measurements that with addition of nanoparticles the majority of H-bonds between nanogels and water are broken and replaced with the H-bonds between nanogels and nanoparticles.



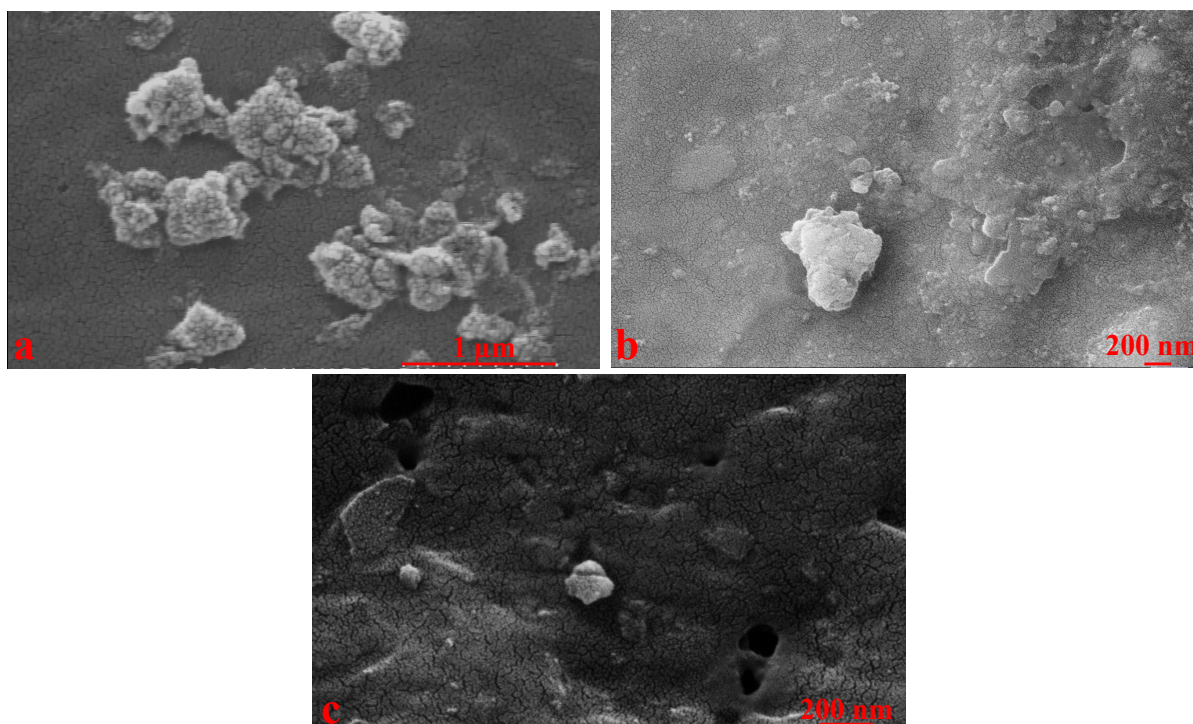
**Figure S5.** Frequency dependence of complex viscosity for non-hybrid and hybrid nanogels irradiated at 20 KGy at homogeneous state, 30 °C.

### **S5) FE-SEM observations of the non-hybrid nanogels**

In order to investigate the morphology and aggregate structure of the hybrid nanogels, field emission scanning electron microscopy (FE-SEM) observations were carried out (Hitachi S-5000, in-lens type). The samples were prepared as described in ref. 8.

Figure 6S shows the morphology and aggregate structure of hybrid nanogels irradiated at 40 KGy at the swollen state. It can be seen that nanogel particles are isolated with a globular-like structure and mean diameter of 150-200 nm. The background of FE-SEM images represents the structure of the carbon coating of the sample for the experiment. FE-SEM micrographs

show that there is no macroscopic network of the silica nanoparticles which is in good agreement with the DLS results.



**Figure 6S.** FE-SEM micrographs of the hybrid nanogels irradiated at 40 KGy at the swollen state at 25 °C with different magnifications.

#### References:

- 1- D. Chopra, M. Kontopoulou, D. Vlassopoulos, & S. G. Hatzikiriakos, *Rheol acta*, 2002, 41, 10-24.
- 2- E. M. Herzig, K. A. White, A. B. Schofield, W. C. K. Poon, & P. S. Clegg, *Nature materials*, 2007, 6(12), 966-971.
- 3- D. Heyes and A. Brańka, *Soft Matter*, 2009, 5, 2681-2685.
- 4- J. Kaldasch and B. Senge, *Colloid. Polym. Sci.*, 2009, 287, 1481-1485.
- 5- A. Gharachorlou and F. Goharpey, *Macromolecules*, 2008, 41, 3276-3283.
- 6- R. Krishnamoorti, R. A. Vaia and E. P. Giannelis, *Chem. Mater.*, 1996, 8, 1728-1734.
- 7- H. Senff and W. Richtering, *Colloid. Polym. Sci.*, 2000, 278, 830-840.
- 8- K.-F. Arndt, T. Schmidt and R. Reichelt, *Polymer*, 2001, 42, 6785-6791.