Dynamic and Static Structure Analyses of Super-homogeneous Tetra-PEG gel

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A series of model networks consisting of polyethylene glycol (PEG), Tetra-PEG gels, have been prepared and their structure and dynamics have been investigated by small-angle neutron scattering (SANS), Static light scattering (SLS) and Neutron Spin Echo (NSE). The Tetra-PEG gels were prepared by cross-end coupling of two types of tetra-arm PEG macromers with the molecular weights, M_w, of 5 to 40×10^3 g/mol. In SANS regime, the structure factors of both as-prepared and swollen gels can be represented by Ornstein-Zernike type scattering functions and be superimposed to single master curves with the reduced variables, ξq and $I(q)/\phi_0\xi^2$, irrespective of the molecular weight of tetra-PEG, where q, ξ, $I(q)$, and ϕ_0 are the magnitude of the scattering vector, the correlation length, the scattering intensity, and the polymer volume fraction at preparation, respectively. In SLS regime, however, a power-law type upturn was observed, indicating the presence of PEG chain clusters. Interestingly, these inhomogeneities disappear by swelling.// The following facts are disclosed: (1) The TAPEG macromer solutions, consisting of tetra-arm polymer chains, are not interpenetrable due to the presence of end groups, and the individual chains behave as hard spheres. Hence, the radius of gyration, R_g scales with $\phi_0^{-1/3}$. (2) The structure factors of both as-prepared and swollen gels in SANS regime can be represented by Ornstein-Zernike type scattering functions and be superimposed to single master curves, irrespective of the molecular weight. (3) However, in SLS regime, a steep upturn was observed in SANS curves in as-prepared Tetra-PEG gels, indicating the presence of PEG chain clusters or defects. A master-curve relationship holds also in SLS regime for a gel having the same molecular weight, indicating a self-similar network structure in Tetra-PEG gels. (4) The upturn in scattering intensity is assigned to be a clustered structure as is often observed in PEG in water and/or network defects. The upturn is suppressed by increasing M_w due to a formation of more regular network structures with less inhomogeneities. It is concluded that Tetra-PEG gels have no noticeable entanglements, but have self-similar structures with respect to M_w, and form ideal tetrafunctional polymer networks, provided that M_w is high enough ($\approx 40 \times 10^3$).

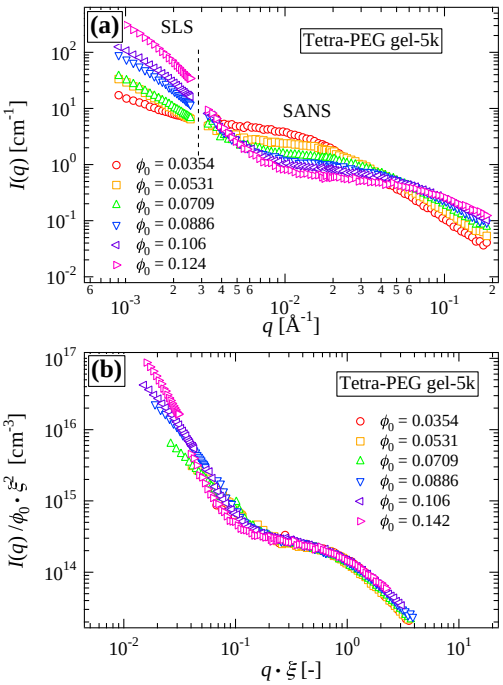

Fig. 1. (a) SANS as well as SLS intensity functions for Tetra-PEG gel-5k prepared at various concentrations, ϕ_0 s. The missing q region is indicated by the vertical dashed line. (b) Scaled plots, $I(q)/\phi_0\xi^2$ and ξq.