Structure and Dynamics in Polyacrylami de Hydrogels With and Without Probe Particles: A Light Scattering Study

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Polymer hydrogels are one among the complex systems that exhibit slow dynamics or incomplete relaxation (non-ergodicity). Because of this, dynamic light scattering (DLS) from polymer gels is complicated by the fact that scattered intensity and intensity-intensity correlation function (ICF) change as different parts of the sample are explored. Past studies on chemically cross-linked polyacrylamide (CPA) hydrogels with and without the probe particles [1-3] have shown that the gel systems exhibit non-ergodic features, implying that the time averaged ICF, the quantity obtained from a single DLS experiment, is not equal to the ensemble-averaged ICF. However no DLS studies exist on photo polymerized polyacrylamide (PPA) hydrogels and they are of current interest as they can be used for immobilizing colloidal crystal [4].

There exist two models to describe the dynamics in hydrogels. In one model, known as gel modes plus inhomogeneties (GMPI) where the gel is viewed as an elastic medium with frozen structures (inhomogeneties), can describe the initial decay of the intermediate scattering function (ISF), $f(q,t)$ and its saturation at long time, $f(q,\infty)$ [3]. Harmonically bound Brownian particles (HBBP) model also found to describe equally well the dynamics in gels [3]. The applicability of these models can be tested by studying the scattering wavevector, q dependence of ISF. DLS data by Xue et al., [3] on CPA gels obeyed GMPI model whereas that by Joosten et al., [1,2] follows HBBP model. Thus there exists a dispute.

In order to resolve this debate as well as to test the validity of these models for describing the dynamics in gels with particles, we have prepared 2.5wt% dust free CPA gel and a PPA gel. Here we report static light scattering (SLS) and DLS studies on CPA, PPA gels and also 2.5wt% PPA gel with polystyrene particles of 93 nm in diameter. Tetramethylethylenediamine and ammonium persulfate are used as initiator and activator respectively for preparing CPA gel. 2-2'azobis [2- methyl-N-[2-hydroxyethyl]propionamide, a UV curable initiator is used for preparing PPA gel. A Malvern (UK) 4700 system has been used for our studies. All samples exhibited nonergodicity and the ISF is obtained by adopting Pusey and van Megen method [5].

If the dynamics of the gel is describable by GMPI model, then ISF obtained for different values of q, when expressed in scaled form i.e. $[f(q, t)- f(q,\infty)]/[1- f(q,\infty)]$ should exhibit collapse with a single characteristic time and $f(q,\infty)$ should be independent of q. If the dynamics in gels obey HBBP model, the above scaled function should not exhibit collapse and $f(q,\infty)$ should show q dependence. The DLS data for PPA and CPA gel obeys GMPI model. These observations imply that pure gels have frozen structures formed during the gelation process. We further confirmed the existence of frozen structures by performing SLS measurements before and after the gelation process. The scattered intensity as a function of q measured for the pre-gel solution showed no q dependence whereas that measured for gels showed extra scattering in the low q regime. Unlike in pure gels, the scaled function obtained from DLS data for PPA gel with particles exhibited no collapse and $f(q,\infty)$ showed q dependence implying that the dynamics of particles immobilized in hydrogel obey HBBP model. Thus our light scattering studies unambiguously prove that the dynamics in pure gels is describable by GMPI model. We have also shown for the first time that the dynamics in PPA gel follows the GMPI model.

References

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