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# Dynamic light scattering characterization of hard–soft gel phase transition in micellar crystal and comparison with rheological data

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**Abstract.** We report the dynamic light scattering study of polymer dynamics in the broad vicinity of the hard-soft gel phase transition in micellar crystal. Inside the region of micellar crystal phase with increasing temperature the ratio of the magnitudes of two dynamic modes (slow and fast) monotonously decreases below 54 °C in the hard gel. Above 54 °C in the soft gel it is almost independent of temperature, remaining at a minimum. The method provides phenomenon details inaccessible with conventional rheological method, where simple detection of sharp phase transition is available. We show that the diffusion dynamic mode, which is common for a liquid phase, is also present in a micellar crystal despite the obvious difference in the rheological properties of micellar liquid and micellar crystal. This study demonstrates the advantages of the dynamic light scattering method at micro-scale level.

## 1. Introduction

Variety of measurement methods provides different aspects of phenomenon characterization. We discuss the application of dynamic light scattering method in the investigation of a micellar crystal that is already well studied with other conventional methods (neutron scattering, rheology, etc.) Block copolymers PEO-PPO-PEO (polyethylene oxide-polypropylene oxide-polyethylene oxide) are a family of non-ionic surfactants with variation of block length. The patented name of Pluronic and several names associated with trademarks (Pluronic, Synperonic, Proxanols) are well-known. Solubility in water of PEO and PPO blocks is ensured by excess of oxygen atoms, while PPO blocks with additional methyl groups have lower than PEO blocks solubility in water. Aqueous Pluronic systems exhibit variety of phases, depending on parameters such as temperature, pressure and concentration. The presence of different phases in the micellar system is associated with their use in household chemicals, cosmetics, pharmaceuticals, medicine, biotechnology and in other fields. The gel is formed at sufficiently high concentrations, which is a micellar crystal with a cubic lattice well studied by neutron scattering methods (see, e.g., review [1]). While the dynamic light scattering research of liquid phases of Pluronic aqueous systems is reported in numerous papers (see references in [2]), the method was never before applied to Pluronic micellar crystal phase. This might be caused by expected difficulties with dynamic light scattering data interpretation associated with “frozen” fluctuations in gels [3].



New phase transition in the region of Pluronic F127 ( $\text{EO}_{100}\text{-PO}_{65}\text{-EO}_{100}$ ) micellar crystal phase has been reported [4] in rheological research. It was found that the gel region in the phase diagram is divided into two regions of the hard gel and the soft gel with a phase transition between them. The rheological properties of the gel in these regions differ by an order of magnitude. We report the dynamic light scattering study of polymer dynamics in the broad vicinity of the hard-soft gel phase transition in aqueous system with Pluronic F108 ( $\text{EO}_{133}\text{-PO}_{55}\text{-EO}_{133}$ ), which is rather similar to Pluronic F127. In contrast to rheological measurements with generated macroscopic shear stress, the dynamic light scattering method uses fluctuations relaxation at a microscopic scale of the order of wavelength.

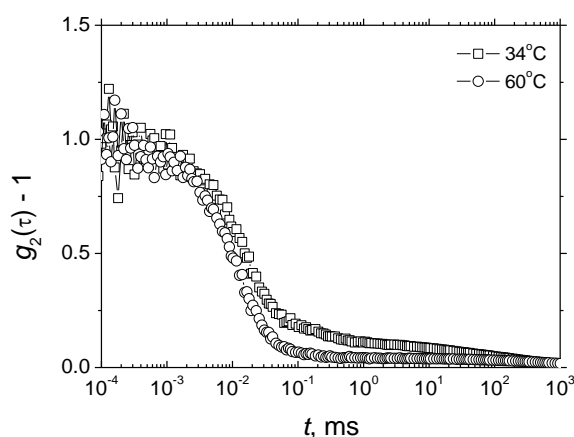
## 2. Results and Discussion

Acquisition of intensity-intensity correlation functions was carried out with Photocor Complex instrument (laser wavelength – 654 nm). The scattering angle for all measurements was set to  $90^\circ$ . Accordingly, the probe distance of about 0.5 micrometer was used in DLS experiments.

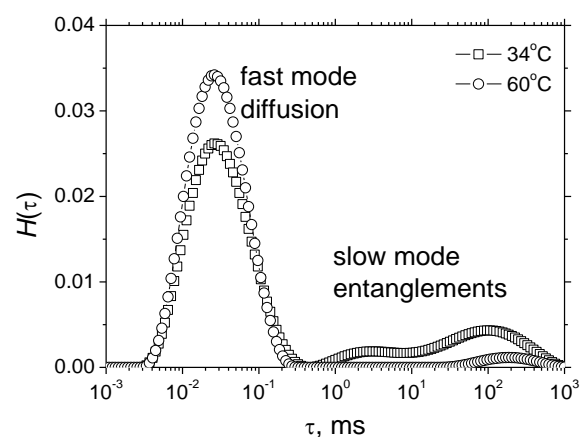
The sample is Pluronic F108 (Sigma-Aldrich) aqueous system at concentration of 20 %. At this concentration the phase of a micellar crystal is detected between  $28^\circ\text{C}$  and  $86^\circ\text{C}$ . Lattice site is a micelle of about 11 nm diameter with less hydrophilic PPO blocks assembled in the core and the chains of PEO blocks flutter in the shell. About four tens of micelles in the micellar crystal lattice correspond to DLS probe distance.

Correlation functions were transformed using the method proposed in [3] for dynamic scattering of light in gels. As a result of this transformation, we obtain the correlation function without distortion caused by the interference contribution from static light scatterers, such as domains borders and defects in the crystal structure. The transformed correlation function is used to find the distribution of correlation times using the procedure CONTIN.

All obtained distributions have two dynamic modes, fast and slow. It is shown in [2] on the basis of data taken outside the phase region of the micellar crystal that the fast mode is diffusive and is associated with the relaxation of concentration fluctuations. Slow dynamic mode in a concentrated polymer solution is associated with polymer chains entanglements, both modes being bound [2, 5]. We found that at the micellar liquid – micellar crystal phase transition the shape of the correlation function and, accordingly, the distribution of correlation times does not exhibit significant transformation.



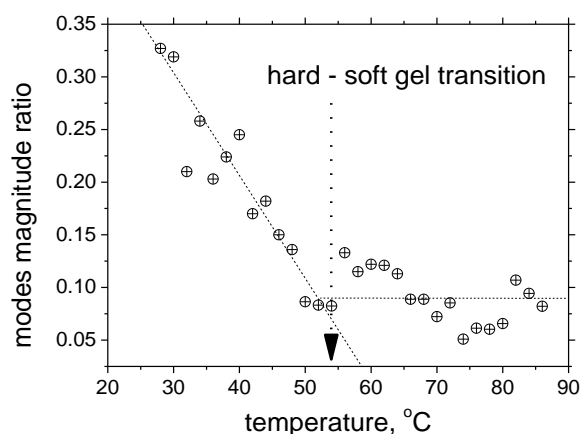
**Figure 1.** Correlation functions for micellar crystal at  $34^\circ\text{C}$  and  $60^\circ\text{C}$ . The angle of scattering is  $90^\circ$ .



**Figure 2.** Distributions  $H(\tau)$  obtained from correlation functions, shown in figure 1 for micellar crystal at  $34^\circ\text{C}$  and  $60^\circ\text{C}$ .

Two correlation functions obtained at temperatures below and above the hard-soft phase transition are shown in figure 1 where the correlation function at 34 °C exhibits the long-time tail that corresponds to slow dynamics of polymer chains. This long-time tail of the correlation function almost vanishes at 60 °C according to figure 1. We see also noticeable difference in the shapes of the long-time tail and the short-time step-like part of the correlation function obtained at 34 °C in the hard-gel phase. This shape of the tail is the evidence of lack of certain characteristic time in the dynamics slowdown by entanglements of the polymer chains. Accordingly, we observe rather broad entanglements mode in distribution, while short-time step-like part of the correlation function corresponds to a narrow diffusion mode. This is completely supported in figure 2.

The ratio of the magnitudes of the slow and the fast modes was calculated as the ratio of the areas under the curves that correspond to modes. Figure 2 shows that the ratio varies significantly with temperature. The dependence of this ratio on temperature is shown in figure 3 for the entire region of the micellar crystal from 28 °C up to 86 °C.



**Figure 3.** The ratio of the magnitudes of slow and fast dynamic modes for the phase region of the micellar crystal as a function of temperature.

Inside the region of micellar crystal phase two noticeable areas are observed. With increasing temperature the ratio of the magnitudes of the dynamic modes monotonously decreases below 54 °C, while above 54 °C it is almost independent of temperature, remaining at a minimum. This behavior can be explained by a monotonic micelle size decrease with heating associated with a gradual change in the interaction of the PEO end blocks with water. Consequently, the overlap area of entanglements of PEO blocks of neighbor micelles gradually reduces. At 54 °C micelle size corresponds to the touch concentration  $c^*$ , where the micelles do not overlap and the engagements of PEO block chains is minimal and is caused by thermal fluctuations. The change in polymer chains entanglements at a temperature of 54 °C corresponds to the phase transition between the hard gel, where neighbor micelles are essentially detained together by entanglements of PEO chains, and the soft gel, where entanglements of PEO chains are minimal.

### 3. Conclusion

Gradual decrease with heating of the micelles size built by PEO-PPO-PEO block copolymer is obtained with dynamic light scattering method. The method with a micrometer probe distance provides phenomenon details inaccessible with conventional rheological method with macro-scale, and where simple detection of sharp phase transition is available. We show that the diffusion dynamic mode, which is common for a liquid phase, is also present in a micellar crystal despite the obvious difference in the rheological properties of micellar liquid and micellar crystal. This study demonstrates the advantages of the dynamic light scattering method at micro-scale level.

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