Experimental Report

06/02/2013

Proposal: **TEST-2150** **Council:** 4/2012

Title: Polyelectrolyte Dynamics in Interpolyelectrolyte Complexes

This proposal is a new proposal
Researh Area:

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Experimental Team: HOFFMANN Ingo

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Samples: C1016H2378N27O654 JR 400 (cellulose based polyelectrolyte, av. composition)
H-(C2H4O)n-b-(C3H4O2)m-H PEG-b-PAA diblockcopolymer
D20

Instrument	Req. Days	All. Days	From	To
IN15	7	7	05/11/2012	12/11/2012

Abstract:

Experimental Report for: Polyelectrolyte Dynamics in Interpolyelectrolyte Complexes (Exp. No. TEST-2150)

The control of the rheological behaviour of solutions is an important topic in the design of formulations for many applications, e.g. in cosmetics, detergency, and drug delivery. Two different systems, allowing such control have been examined, namely oppositely charged polyelectrolyte (PE)/surfactant systems and microemulsions bridged with hydrophobically end-capped (star) polymers.

Complexes formed by mixing oppositely charged surfactant and PE exhibit rich aggregation behaviour. Furthermore they allow to modify the rheological properties of the corresponding water-based systems largely already at relatively moderate concentrations. Accordingly they have many applications e.g. in cosmetics, detergency, and drug delivery[1]. Typically in the semi-dilute regime a strong increase in viscosity is observed as surfactant is added to the polymer as long as the charge ratio Z between polyelectrolyte and surfactant is larger than 1, i.e. an excess of polyelectrolyte charges is present. It is known, that the increase in viscosity is accompanied by the formation of mixed PE/surfactant aggregates, interconnecting several PE chains. In the case of the system JR 400/SDS the aggregates have been shown to be rodlike and the formation of a structure peak around 0.1 1/nm has been observed[2].

In a previous NSE experiment[3], we had shown that the intermediate scattering function could be described in terms of the diffusion of rods, thereby allowing us to determine the length of the rodlike aggregates, which was impossible using only SANS, as the simultaneous presence of the peak at 0.1 1/nm makes it impossible to see in the static scattering curve. Also, we could observe some evidence for the PE in the aggregates not being tightly bound but being partly free to move. Dynamic light scattering measurements indicate the presence of much larger clusters, comprised of the aggregates observed in SANS and NSE. Therefore, we were complementing our previous measurements to quantify the extent to which the PE in the aggregates is free to move and to which extent the movement of the rods is hindered by the fact that they are part of huge clusters, which should become visible at sufficiently long times.

With the additional measurements we could show, that not all of the PE in the aggregates is tightly bound but a fraction of about a quarter is freely moving. As far as the hindrance of the movement of the rods is concerned, we could show that at long times (t>50 ns) and small q (<0.5 1/nm) the decay is slowed down indeed (which translates into longer effective lengths in Fig 1

Microemulsions (ME) are thermodynamically stable emulsions with droplet sizes up to about 20 nm. Depending on the exact composition, they allow to disperse fairly large amounts of hydrophobic compounds in water, making it possible to use environmentally friendly water instead of organic solvents. However, in some cases, their low viscosity limits their applicability.

An alternative to water soluble polymers as thickeners are hydrophobically end-capped polymers, which can

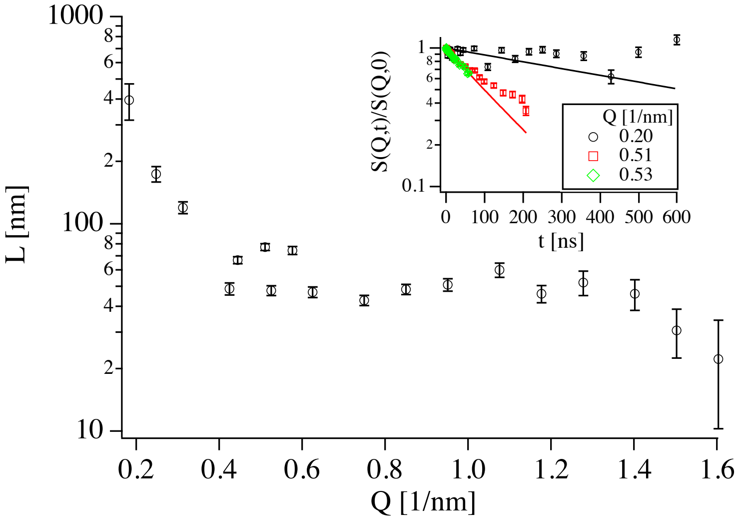

Figure 1: Length of rods obtained for JR 400/SDS at a charge ratio of 3, using parameters from SANS, constant values are found between 0.4 and 1 1/nm; inset: $S(Q,t)$ at 22 Å, 0.2 1/nm (black circles), 16 Å (red squares) and 10 Å (green diamonds), both 0.5 1/nm. Lines are theoretical curves with $L_1 = 48$ nm. While the theoretical curve gives a good description at 0.5 1/nm up to about 50 ns, almost no decay can be observed at 0.2 1/nm on the NSE timescale.

(assuming the ME droplet concentration and the length of the polymers are chosen in a suitable manner) directly bridge the droplets instead of increasing the viscosity of the matrix.

Previously, the performance of different end-capped star polymers and their linear counterparts has been examined by DLS and rheology with SANS showing, that the structure of the ME droplets remains unchanged. A significant increase in viscosity was observed and two additional slow modes from bridged clusters of droplets were observed with DLS[4]. In the present experiment, we were investigating similar samples with NSE. The pure ME shows relaxation stemming from simple diffusion and membrane fluctuations as to be expected from such a system. An additional slow relaxation is observed upon addition of the polymer but it can be shown, that the originally present relaxation from the ME is still present. Thus, we could show that not only the overall size but also the membrane rigidity of the droplets remains unchanged. Interestingly, the NSE measurements show, that the magnitude of the slow relaxation is maximal for linear polymers, while the DLS and rheology measurements showed that the magnitude of the slow relaxation was increasing with the number of arms.

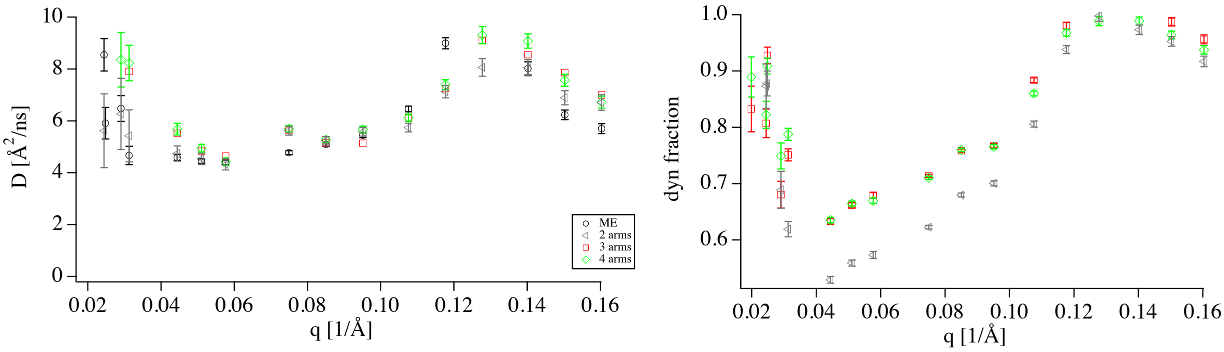

Figure 2: Left: Apparent diffusion coefficient for ME and ME with polymers with different numbers of arms, taking into account the slow contribution separately. The data points almost collapse on a single curve, showing that the dynamics of the individual droplets remain unchanged, including the the peak at 0.14 $1/Å$, which stems from membrane fluctuations. Right: Dynamic fraction as a function of q for different numbers of arms, the linear polymer causes the strongest decrease of the dynamic fraction.

References

[1] J. C. T. Kwak, editor. *Polymer-Surfactant Systems*, volume 77. Marcel Dekker, Inc., 1998.

[2] I. Hoffmann, P. Heunemann, S. Prévost, R. Schweins, N. J. Wagner, and M. Gradzielski. Self-aggregation of mixtures of oppositely charged polyelectrolytes and surfactants studied by rheology, dynamic light scattering and small-angle neutron scattering. *Langmuir*, 27:4386–4396, 2011.

[3] ILL Experimental Report 9-12-273

[4] P. M. de Molina, C. Herfurth, A. Laschewsky, and M. Gradzielski. Structure and dynamics of networks in mixtures of hydrophobically modified telechelic multiarm polymers and oil in water microemulsions. *Langmuir*, 28:15994–16006, 2012.