Experimental report

16/02/2022

Proposal: 9-10-1639 **Council:** 10/2019

Title: The impact of polymer molecular architecture on lubrication efficacy in non-aqueous media

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: diblock copolymer
d-dodecane
Random Copolymer
Clicked Multiblock
Homopolymer

Instrument	Requested days	Allocated days	From	To
D22	3	0		
D33	3	5	04/09/2020	07/09/2020
			25/03/2021	27/03/2021
D11	3	0		

Abstract:

To relate the lubrication efficacy of oil-soluble copolymers to their molecular architectures, it is necessary to correlate their self-assembly in a hydrocarbon solvent with their interfacial structure and behaviour under shear on a polar substrate. In collaboration with Infineum (a world-leading engine-oil additive company), we propose a small-angle neutron scattering (SANS) study of self-assembly of novel polymethacrylate (PMA) block copolymers as a function of concentration and temperature. Preliminary SANS result from a diblock polymer architecture has revealed a core-shell micelle structure in a model oil (deuterated n-dodecane). Here different polymer architectures will be investigated (multiblock, diblock, random, and homo). The results will complement our ongoing interfacial structure and friction/lubrication studies using synchrotron x-ray reflectivity (XRR) and the surface force apparatus (SFA), respectively, in order to correlate their bulk structures with their surface adsorption behaviour; critically important to their use in Infineum formulation. Such fundamental studies will assist rational design of future polymeric friction-modifying additives.

The impact of polymer molecular architecture on lubrication efficacy in non-aqueous media (9-10-1639)

During the experiment at D33, the bulk structure of various polymeric additives intended for lubrication in engine oils were characterised in deuterated dodecane solvent. Concentration, temperature and water content studies were performed on select additives, and each had a notable impact on the self-assembly of polymers in dodecane. The results of this experiment will be used alongside SANS data gathered from SANS2D, ISIS (2010516) to provide complete cohesive studies on each parameter.

Raw SANS data to demonstrate the distinct difference in self-assembly of the random copolymer (polymer B) as a function of temperature is shown by figure 1. Low Q demonstrates significant change in the clustering of these polymer chains in solution, with increase temperature progressively removing the larger structures in solution. The reversibility of this heating was monitored by performing a cooldown to the initial temperature of 25°C. This showed the formation of larger structures, suspected to be because of an increase in the freedom of movement of the polymer upon heating.

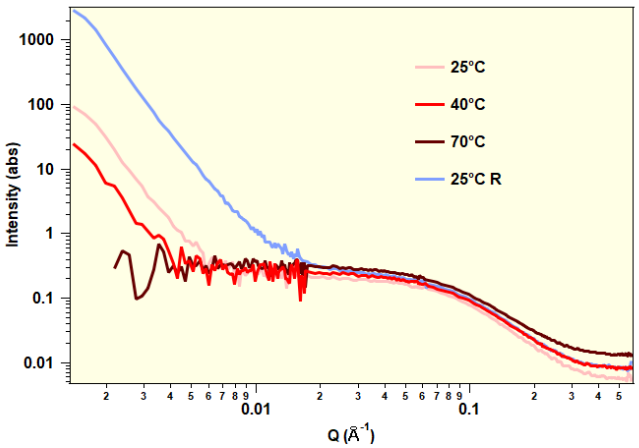

Figure 1. SANS data of the random copolymer (B) absolute intensity as a function of Q shown at 25, 40 and 70°C.

To show the impact of concentration on the bulk structures formed by each polymer architecture, 4 different weight % were measured. Figure 2 shows the raw SANS data for the multiblock architecture (polymer E), whereby free polymer chains in solution are mixed with larger clusters as seen by the uptick from low Q at higher concentration.

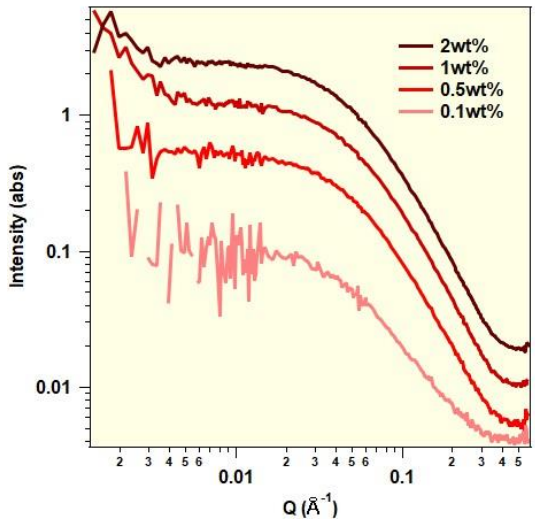

Figure 2. SANS data showing a concentration study of the multiblock copolymer (E) as absolute intensity against Q.

Water contamination is a common occurrence with engine oils and as a result an investigation on how water can impact the performance of lubricant additives was performed by varying the mole ratio of water:polymer. It has been shown by figure 3a and 3b that the diblock polymer architecture incorporates water into its self-assembled structure most likely due to the polar moieties on the sidechains. As a result, you get an increase in the size (as shown by low Q) but also the appearance of a fringe at mid Q seen in 2a at 25°C. Upon heating the polymers at this ratio, the trend in absolute intensity increase is maintained, however the fringe formed at mid Q from the addition of water is completely removed like that of the sample at 25°C with no water added.

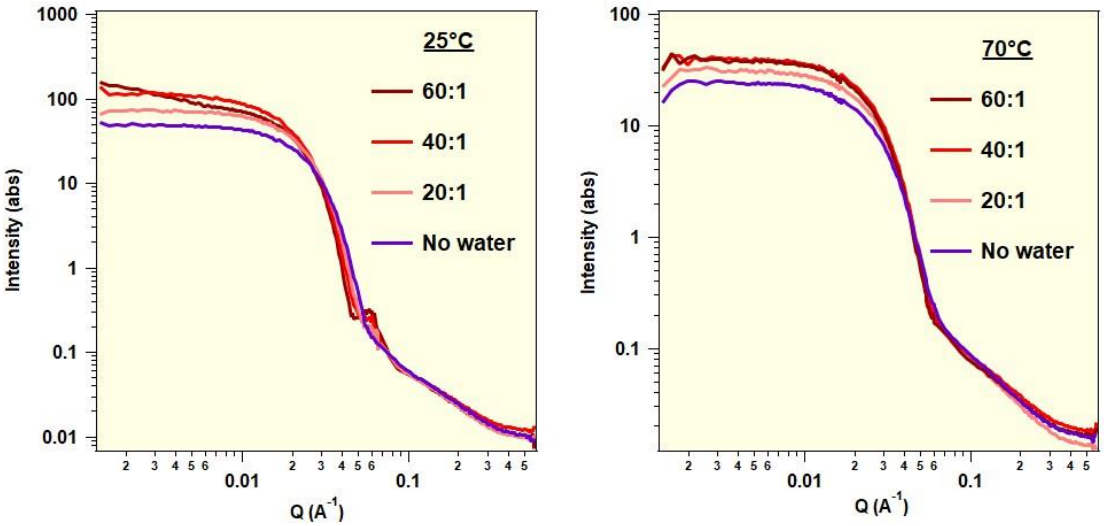

Figure 3. Raw SANS data of the diblock copolymer (a) Varied mol ratio of water:polymer at 25°C (b) Varied mol ratio of water:polymer at 70°C

What will this data be used for?

The data gathered from D33 is intended for publications of polymer self-assembly in non-aqueous media, as well as use in a PhD thesis. Also, it's contribution will lead to understanding mechanisms under confinement when combined with surface force apparatus data. Furthermore, the knowledge gained from this experiment will contribute to the systematic development of novel friction-modifying additives in the engine oil industry.