Experimental report

05/02/2016

Proposal: **9-11-1678** **Council:** 4/2014

Title: Dynamics of Star Polymers Tetheredon Hard Cores

Research area: Materials

This proposal is a new proposal

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Samples: C60-PS $(C8H8)n$

Instrument	Requested days	Allocated days	From	To
IN16B	6	4	21/11/2014	25/11/2014

Abstract:

The behavior of branched polymers is rather complex, making the use of model architectures particularly powerful for understanding the behavior of these systems. We have recently synthesized star-polymers with a hard fullerene-core which contain 6 polystyrene arms covalently bound to the core. Their Tg behavior even for very short arm molecular weights, appears to be the same as infinite molecular weight linear PS and therefore does not follow theoretical predictions. Clearly molecular motion of these hard cored stars are intriguing and in this proposal we wish to determine the dynamics of the arms for two different polystyrene-arm molecular weight stars using QENS.

Dynamics of Star Polymers Tethered on Hard Cores

Introduction

The performance of entangled polymers is of great importance to understand their fundamental behaviour and for industrial applications, as it provides insight into mechanical properties as well as polymer processing. Whilst the dynamics of linear chains is well understood through the tube model and concept of reptation introduced by de Gennes and Doi and Edwards[1,2], the same is not true for branched polymers. Progress in this area has been relatively slow due to lack of precisely defined model systems. Star polymers offer a means to control the number and molecular weight of the arms, providing model systems to carry out dynamic and structural studies.

The aim of the IN16 experiment was to perform a detailed comparison of the dynamics of fullerene (C60) star polymers and linear polystyrene (PS) chains. Our aim is to use these materials as model systems to understand melt dynamics at long length scales, using neutron spin-echo. However, before undertaking these measurements and to fully understand dynamic and rheological behaviour, it is necessary to characterize the internal (segmental) dynamics above the polymer glass transition, T_g.

Relatively high T_g values were obtained by us for star samples of relatively small molecular weight. These seem at odd with a QENS investigation of PS/C60 nanocomposites reporting that addition of the C60 particles causes plasticization[3]. Contrary to this, using similar star systems to those studied here, Lebedev et al.[4] suggested that the presence of fullerene hinders chain diffusion on a local segmental scale, a result that could support the high T_g values measured by us.

Experimental

PS-fullerene stars were prepared at ORNL according to a procedure published in the literature.. Details of the PS-fullerene star samples and the linear PS chains used for the QENS experiments are given in Table 1 and Table , respectively. The stars have an average of 5.8 arms.

Table 1: Characteristics of the PS-fullerene star samples

Name	HPS or DPS	M_w arm /g mol^{-1}	M_w star /g mol^{-1}
2k HStar	H	2000	12320
16k HStar	H	16000	93520

Table 2: Characteristics of the Linear PS samples

Name	HPS or DPS	M_w /g mol^{-1}
2k HPS	H	2000
16k HPS	H	16000
105k HPS	H	105500

Elastic window scans (EWS) were carried out on the backscattering spectrometer IN16B in the temperature range 1.8 to 573 K. The energy range covered in the experiment was –13 to 13 μeV and the Q range varied from 0.2 to 1.9 Å^{-1} with a resolution in energy of 1μeV.

The EWS measurements on PS-fullerene stars and the corresponding linear polymer chains show that molecular weight has a significant effect on the dynamics of the polystyrene chains. As seen in Figure 1, the two star polymers have different dynamics. This is expected due to differences in glass transition temperature but perhaps more surprisingly, deviations are noticed as low as 100 K. This corresponds to a region where the decrease of the elastic intensity is more pronounced compared to the expected DWF.

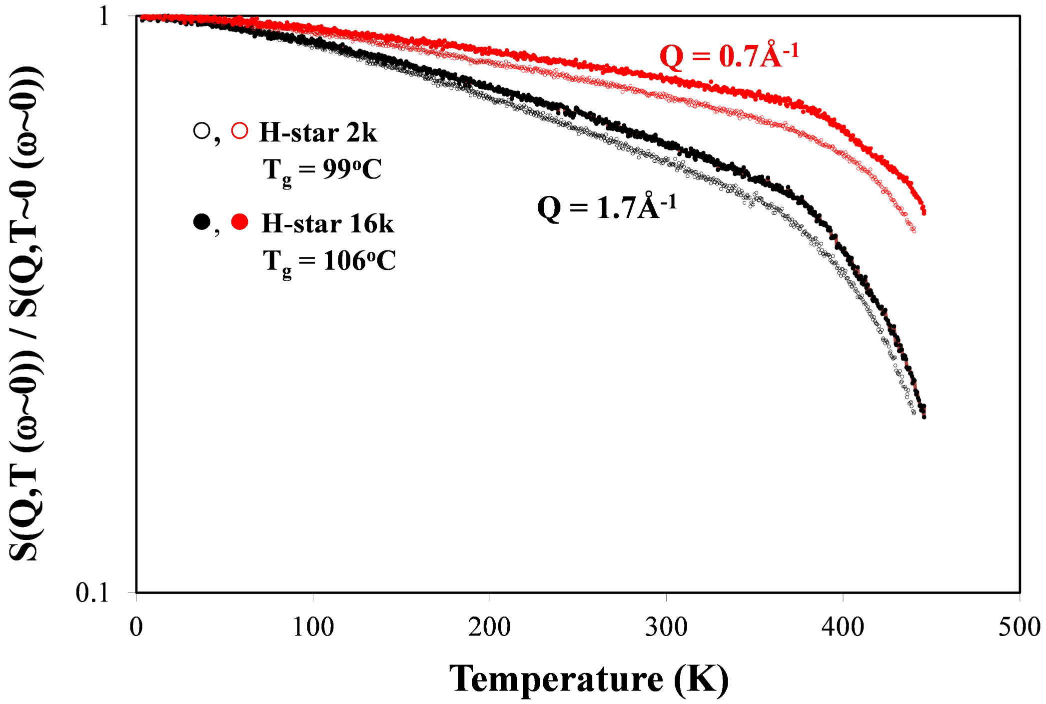

Figure 1: EWS data for the PS-fullerene star polymers of different molecular weights at two different Q values, as indicated.

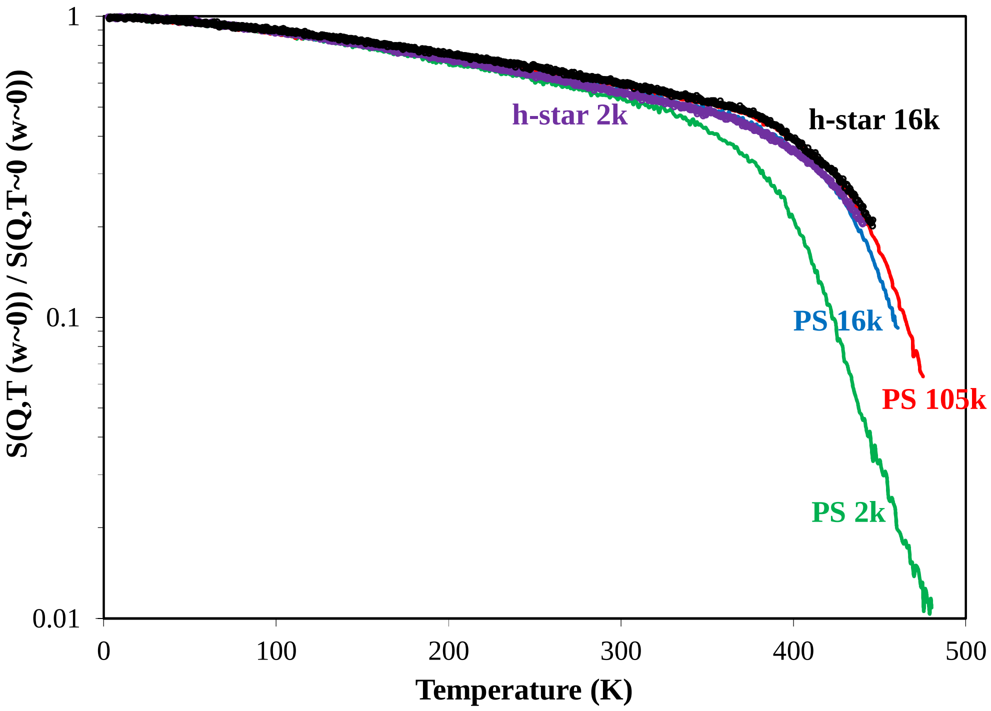

Figure 1: EWS data for all PS-fullerene stars and linear polystyrene chains after subtracting the contribution from the empty cell at Q = 1.7Å^{-1}.

Based on previous studies of PS dynamics in the glassy state[5] and molecular dynamics simulations[6], we attribute the decrease of the elastic intensity above ca 100 K to sub-T_g motions, namely small oscillation of phenyl rings (localised low amplitude motions rather than 180 flips). Increasing molecular weight of both the linear PS and the PS-fullerene star samples seems to hinder both phenyl ring oscillations and segmental dynamics.

A comparison between EWS data of the PS-fullerene stars and the linear polystyrenes is given in Figures 2 and 3. Interestingly, the EWS data of PS-fullerene stars are comparable to those of linear PS chains with molecular weight equal to the total M_w of the star polymers (Tables 1 and 2). Our results show that grafting PS chains onto C60 causes considerable molecular coupling between polymer and hard core: the entire system acts as a single dynamic unit. As a result, chain dynamics depends on the molecular weight of the whole star, rather than that of the arm. Our QENS results are consistent with T_g data, but differ from previous reports that the presence of fullerene hinders chain diffusion on a local segmental scale.[4]

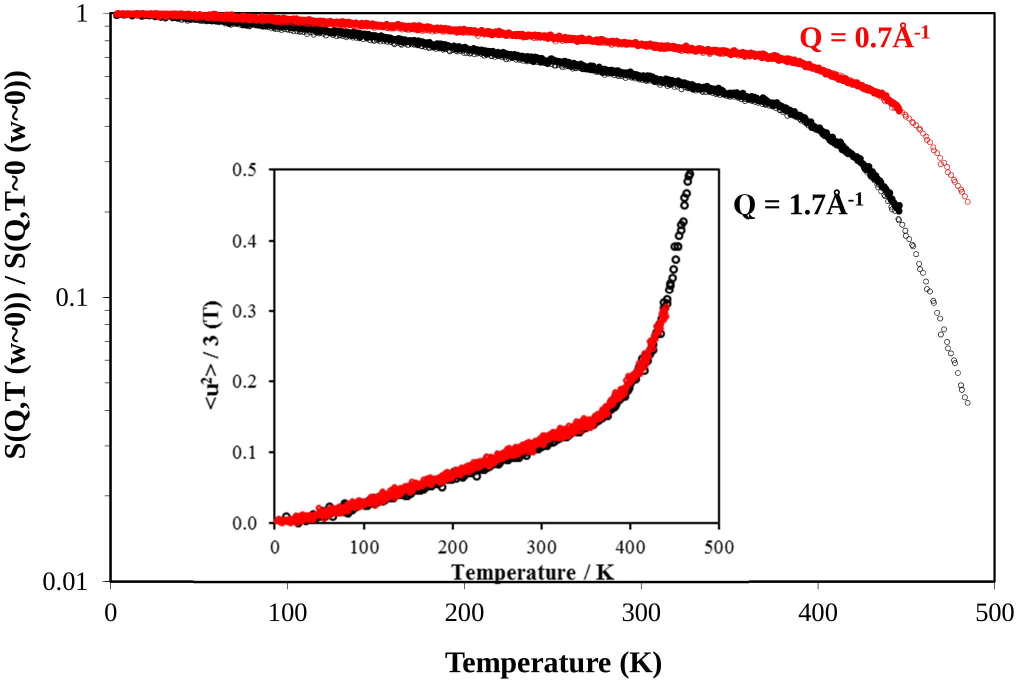

Figure 3: EWS data for 16k HStar (●) and 105k HPS (○) after subtracting the contribution from the empty cell at two different Q values,. Inset: Mean square displacement, <u^2>/3, versus temperature for 16k HStar (O) and 105k HPS (●).

References

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