

Experimental report

04/09/2022

Proposal: DIR-242

Council: 4/2021

Title: Direct measurement of entanglement formation in ultrahigh molecular weight polyethylene (UHMWPE)

Research area: Soft condensed matter

This proposal is a resubmission of 9-11-2012

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Samples: (C₂H₄)₁₇₈₅(C₂D₄)₁₇₈₅₇₁
(C₂H₄)₁₇₈₅(C₂D₄)₁₅₆₂

Instrument	Requested days	Allocated days	From	To
D22	1	1	12/10/2021	13/10/2021
IN15	8	5	08/10/2021	13/10/2021

Abstract:

Ultra-high molecular weight polyethylene (UHMWPE) with molecular weights in the order of 10^7 g/mol is characterized by a highly entangled state exhibiting enormous viscosities, which prohibit its melt processability. The single macromolecules form little single crystals containing one molecule only. These molecules naturally are unentangled giving rise to significantly lower melt viscosities. With ongoing time by interdiffusion the unentangled non equilibrium initial state evolves into the equilibrium entangled melt. This process offers the unique opportunity to observe the formation of entanglements as a function of time - after melting the huge molecules gradually entangle with each other, a process that takes several days. Presently, nothing is known about the molecular mechanisms of entanglement formation. NSE is a unique probe to follow this process on the scale of the entanglement itself and addresses the aspects like spatial evolution, heterogeneity. We propose such a study using fully deuterated UHMWPE co-crystallized with shorter hydrogenated PE that will act as a probe. The acquired knowledge will be crucial for designing the spinning process of ultra-strong PE fibers.

Title: Direct measurement of entanglement formation in ultrahigh molecular weight polyethylene (UHMWPE)

Samples: We aimed to study the entanglement formation in the disentangled ultra high molecular weight polyethylene. The sample consisted of the deuterated polyethylene of molecular weight ~ 6 million g/mole blended with hydrogenated polyethylene of molecular weight 40000 g /mole. The hydrogenated polyethylene was dispersed in the deuterated matrix in the ratio 5:95. The samples were prepared in a manner that they are inherently free from entanglements. Therefore, the sample is in the form of single crystal of ultra high molecular weight polyethylene chains. The previously synthesized hydrogenated polyethylene chains are co-crystallized with the deuterated chains during the polymerization of deuterated chains in order to ensure complete mixing. One heating, the crystals melt and polyethylene chains gradually start getting entangled. The hydrogenated chains act as the probe and as the deuterated chains get entangled, we expect to observe the tube formation through the change in relaxation of the hydrogenated chains.

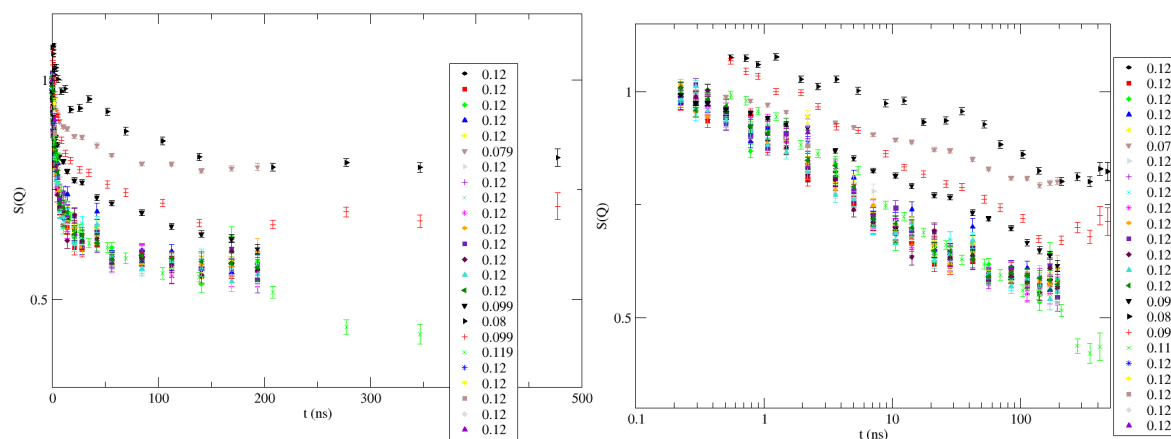
Experiments and results:

Neutron spin echo:

The NSE experiments were performed at the spectrometer IN15. We studied the dynamic evolution during melting of polyethylene blend covering the time range $0.1 < t < 550$ ns.

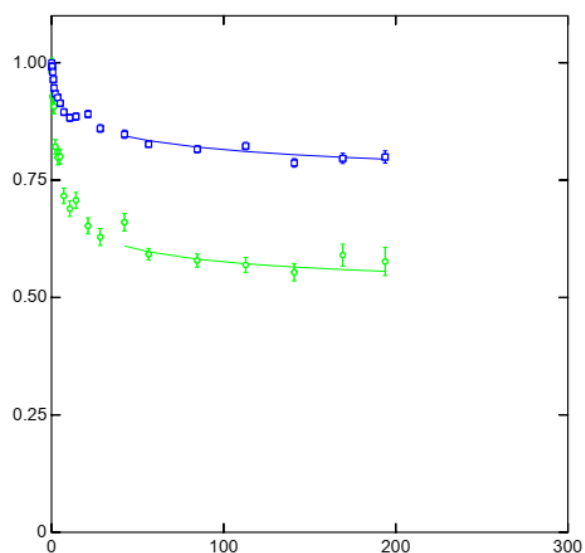
UHMWPE-1:

Ultra high molecular weight polyethylene samples were heated to 438 K and spin echo was performed mostly at $Q = 0.12 \text{ \AA}^{-1}$, 1 scan/30 min starting slightly before the temperature was reached. Following are the scans in linear vs linear and linear vs log plot.



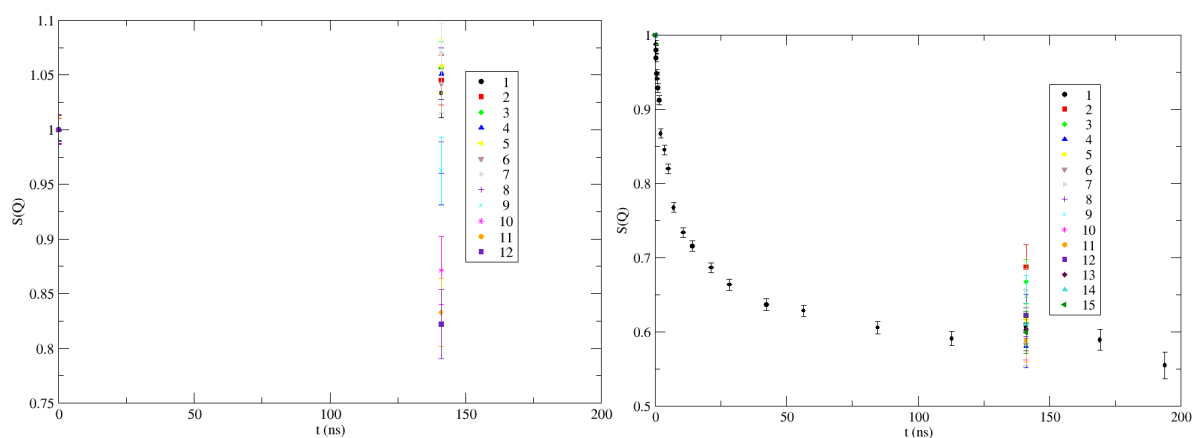
As shown above, we could not notice any change in the decay of structure factor with time. As soon as the sample melt and we perform the first measurement, we reach a plateau at longer Fourier times.

Some of the data was fitted with the De Gennes description of scattering from an entangled polymer. The fits are shown below. The tube diameter obtained from these fits was about $41 \text{ \AA}$, which is close to the known tube diameter for polyethylene chains. This suggested that before we could measure the scattering, the hydrogenated chains were already observing a tube formed by the deuterated chains.



UHMWPE-2:

We measured another sample of same polymer mixture as described in the sample section. Strategy was different than the previous sample. This time the sample was heated from 398 to 415 K and during that spin echo was performed at 1 scan/ 2 min in which a single data points were collected at at $Q = 0.12 \text{ \AA}^{-1}$ and 141 ns. In the following graphs each third data point has been plotted and legend numbers correspond to the sequence:

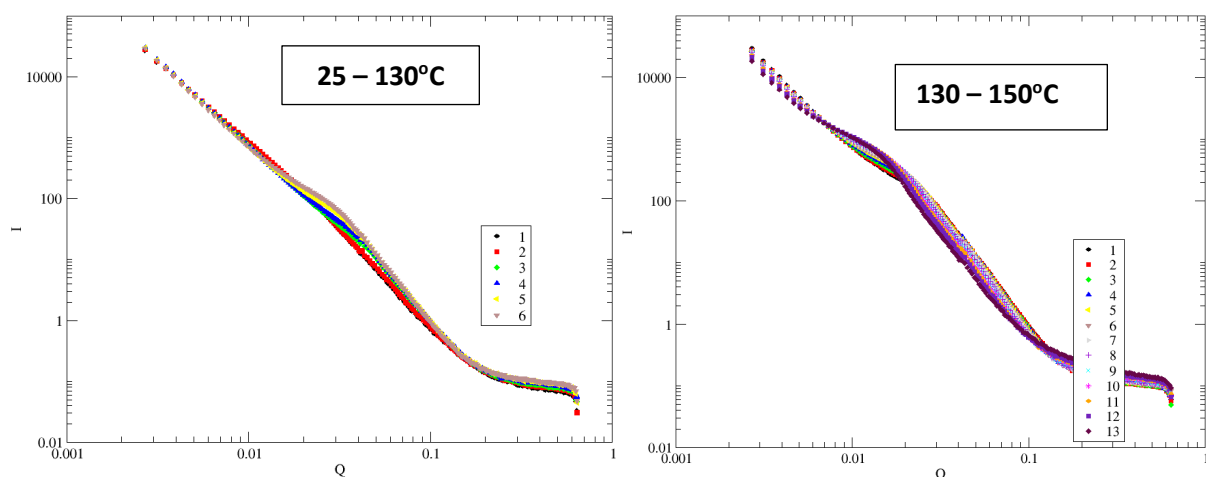


Then the sample was kept at 416 K and again single data points were measured. However as shown above, the echo decreases from 1 gradually to ~ 0.6 (similar to previous run) and then stay constant.

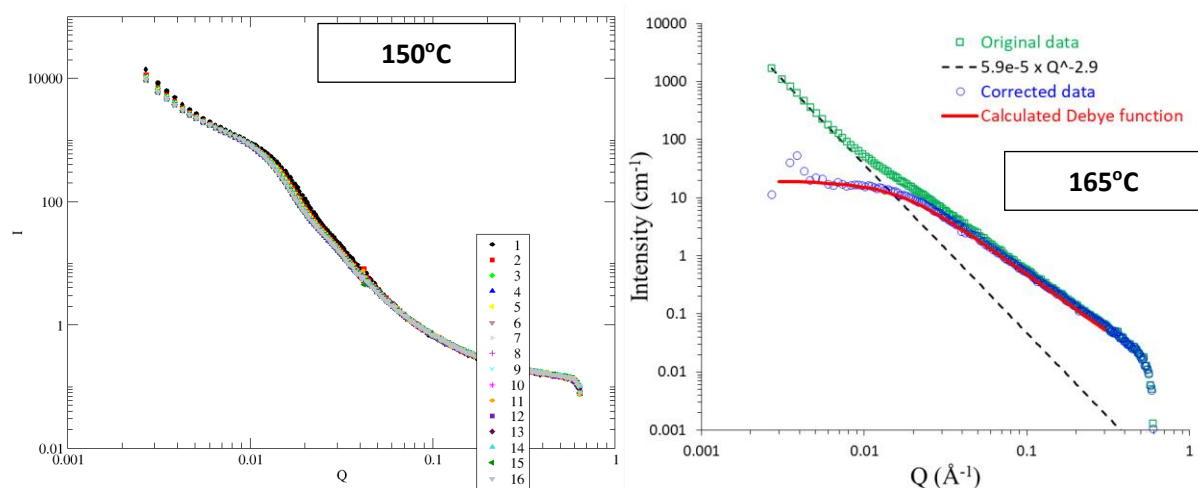
Therefore, even at a scan rate of 1 scan/2 min, we couldn't observe the gradual formation of tube. In order to understand the fate of hydrogenated chains, we performed small angle neutron scattering (SANS) experiments in similar way as NSE on fresh samples.

SANS measurements:

Sample was heated from 298 to 423 K (25 - 150°C). Selective data sets are shown below. We observe a power law and a correlation peak.



Then sample was kept at 423 K (150°C) for 2.5 hours as shown below (left). We do not observe any change during this. Then sample was heated to 438 K (165°C) as shown below (right). Once molten at 438 K, the SANS data corrected for power law follows the calculated Debye scattering



The broad shoulder in the data at 150 °C could either be from the correlation peak from the remaining crystals or could indicate globule formations by the crystals which get molten at that temperature but could not expand into Gaussian conformation due to the elastic matrix of entangled polymer around it. The data at 165 °C indicates that the hydrogenated chains was not aggregated. Therefore, we conclude that as soon as reach the melting temperature, the hydrogenated short chains diffuse into the preliminary entangled regions created by the chain ends. This restricts them to act as probe for the remaining matrix of still disentangled chains. Therefore, we couldn't follow of the kinetics of tube formation over a period of time.

It is suggested that the NSE experiments should be performed on a better sample where this could be avoided. One such suggestion would be to prepare sample with copolymer of hydrogenated and deuterated ethylene dispersed in completely deuterated UHMWPE with same molecular weight. This will decrease the scattering intensity but will allow us to measure the actual kinetics of entanglement formation.