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New Tools for Understanding Complex Polymer Behaviour

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Abstract

The process of manufacturing with polymers usually involves shaping in the melt followed by a transition to the solid to preserve that shape and provide the required mechanical properties. The development of an understanding of those transitions is critical to the optimisation of materials and manufacturing technology. For synthetic polymers there are three key length scales in any phase transition such as crystallisation: the first involves the thin (~10nm) lamellar crystals, the second is the crystal planes in the unit cell (~1nm) and the third the regular local chain conformation (~0.1nm). We are using the extended Q range available with NIMROD at the ISIS Facility in the UK to obtain neutron scattering data which follows the transformation pathways of these three length scales simultaneously. We are using computational modelling procedures to analyse these data to develop a firm understanding of the multiscale processes involved in crystallisation. This paper describes the methodology and some of the experimental challenges using data drawn from this study. This work is part of the FCT funded programme UC4EP.

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1. Introduction

Synthetic polymers which exhibit high degrees of regularity are usually crystalline at room temperature. Polymers such as polyethylene, polypropylene, polycaprolactone and polyethyleneterepthlate are examples with particular technological significance [1, 2]. The study of polymer crystallisation dates back to the pioneering experiments of Keller and others who discovered the chain-folded nature of the thin lamellae crystals which are normally found in synthetic polymers [3, 4] The inherent connectivity of polymers makes their process of crystallisation a multiscale transformation. In the melt, polymer chains adopt random configurations with limited short range spatial order [5]. Crystallisation of polymers involves a conformational change to produce segments of the chain with a regular conformation, which form a translationally ordered crystal, which contains chain folded surfaces. There are three key length scales. The chain folded lamellar thickness is ~ 10nm, the crystal unit cell is ~ 1nm and the detail of the chain conformation is ~ 0.1nm. In previous work these different length scales have been addressed using different specialist instrumention or where coupled using compromised geometries. [6,7] Much understanding has been developed over the intervening fifty years but the process has remained something of a mystery. Most recently time-resolved synchrotron radiation based experiments have revealed the possibility of new phenomena in the very early stages of crystallisation. [8] Although there is now considerable doubt on such experiments, it draws attention to the basic question as to the process of crystallisation in long chain molecules and the mechanisms involved. [8] For a simple liquid such as aluminium, it is straightforward to envisage a process by which individual atoms attach to a growth face. For a long chain molecule, in contrast, crystallisation involves conformational rearrangements as well as the development of precise atom positioning. It could be as some have argued, that crystallisation is preceded by conformational changes, perhaps coupled to local density changes to yield an ordered but non-crystalline structure, which subsequently transforms in to crystals. This is the basis of the model of the crystallisation process proposed by Strobl. [8]

Our approach to the experimental study of these transformations is to rapidly cool the sample from the melt to a temperature below that where the sample will crystallise, but to cool the sample sufficiently fast so as to prevent the transformation to the more ordered state [9]. This allows the evolution of the structure to be followed in real time. A key requirement is an experimental stage suitable for the study of the molecular organisation which is able to cool the sample in a fast manner. A second key requirement is the availability of experimental techniques which are able to obtain information rapidly so that structure formation can be followed in real-time. The third and equally important requirement is that the experimental technique for evaluating the molecular organisation can access structural information of all the relevant scales of structure [10]. As highlighted above in the transformation of polymer melts to an ordered structure whether it is semi-crystalline system or a block copolymer it involves nanoscale phase separation in key scales of the order of ~10nm, 1nm and 0.1nm. Traditionally fast processes have been studied using light scattering or using x-ray scattering with a synchrotron source of radiation. Although the combined use of small-angle x-ray scattering which accesses the 10nm scale and wide-angle scattering which accesses the 1nm and possibly 0.1nm scales is now routine, it is the case that one or both of the techniques is seriously compromised and as a consequence misleading information may be obtained [6]. However, it is the case that these data can be obtained using very short time-slices allowing a range of experiments to be performed.