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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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Keywords: Micromoulding; medical devices; morphology; properties; semi-crystalline.

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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.

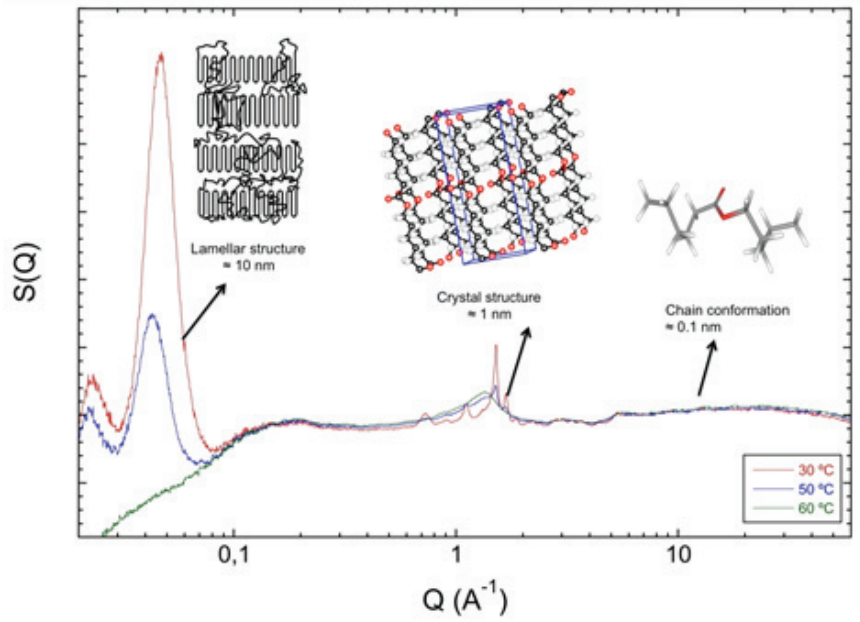

Figure 1 Experimental differential scattering cross sections for a sample perdeuterated poly(ε-caprolactone) in the melt at 60C (green line) and at two states of crystallisation (50C – blue line, and 30C – red line) obtained using the first T Jump cell system. The small inserts illustrate the three critical length scales in this work.

In recent years new neutron instrumentation has been developed, specifically NIMROD [11] at the ISIS Facility which delivers high quality data over extended length scales and in which there is no loss of quality of data due to the combination of length scales. A major advantage of the instrument and the associated data analysis is that due to the need to normalise the data to the incident spectrum the data almost naturally is presented on a single calibrated scale. In other words the vertical scale is in absolute units and can be compared directly with the predictions of models which allows a great level of interpretation to be carried out. The NIMROD instrument produces scattering data which encompass the three critical length scales in the ordering process. In contrast to the typical SAXS/WAXS data sets, the scattering data corresponding to the different length scales are presented on the same vertical scale and hence we can avoid many of the pit falls experienced in some early SAXS/WAXS experiments and their interpretation [12, 13]. An example of the NIMROD output is shown in Figure 1 with a schematic representation of the relevant length scales. The scattering for the melt shows the broad diffuse features which are typical of the disordered state [5]. The data recorded from the semi-crystalline state shows a strong low Q scattering feature which arises from the lamellae while around Q = 1Å-1 there are sharp Bragg peaks arising from the crystalline structure. For Q > 3Å-1 the scattering is dominated by the diffuse features which in effect the scattering from the local structure of polymer chains [14, 15].

Although NIMROD sounds like an ideal instrument for such structural studies the rapidly cooling stage presents a considerable challenge. The design and evaluation of this stage is the focus of this paper.

Neutrons interact weakly with matter, which is a considerable advantage when designing sample enclosures for experiments but this also means that the scattered signal from a sample will be relatively weak [16]. The amplitude of the scattered signal will also be related to the flux of the incident beam. The maximum incident flux for NIMROD is several orders lower than for an equivalent SAXS/WAXS beamline at a Synchrotron radiation source [11]. For example the Dubble Beamline at the European Synchrotron Research Facility facility has an incident flux of up to 10 [11] photons/second [17]. Consequently in order to minimise the measured time-slice we need to

maximise the incident beam so as to yield the highest scattered signal. Therefore we must use the largest beam size available. In contrast to x-ray beams, neutron beams are large16, for NIMROD the largest beam size is 3 x 3cm2. The geometry of the NIMROD instrument [11] is essentially a transmission system using time of flight analysis [16]. Now clearly attempting to rapidly cool a large area (3cm x 3cm) and thin (1 mm) sample, when the only thermal contact possible is through the edges of the sample and the vanadium sample container windows, is naturally a challenging task. In this paper we consider two rather different approaches to this problem and discuss the advantages and disadvantages of both of them.

2. Crystallisation Kinetics

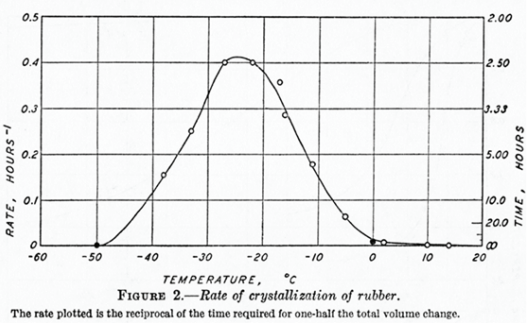

Figure 2 A plot of the rate of crystallization for natural rubber as a function of the temperature. Reproduced from "Controlling the morphology of Polymers" Editors G.R.Mitchell and A.Tojeira 2016 Springer with permission [7]

If a polymer is cooled rapidly enough from the melt, it may not crystallize but may instead form a glass. For polymers in general, the crystallization rate is a function of temperature and passes through a maximum (Figure 2). Crystallization in polymers is principally a nucleation controlled phenomenon: Figure 2 refers to an overall degree of crystallinity. However, if the growth rate of spherulites (A common morphology7) is plotted, the maximum will be moved to somewhat lower temperatures, since nucleation is denser at lower temperatures. The increase in growth rate while cooling from the melt is a thermodynamically based phenomenon. The increase in growth rate with increasing temperature from lower temperatures is a result of a decreasing viscosity [8].

For polymers, which crystallize extremely rapidly, such as polyethylene and iso-tactic polypropylene homopolymers, it may not be possible to cool quickly enough to obtain a glass so the full crystallization curve cannot be obtained for these materials using conventional techniques. The use of fast calorimetry has extended our knowledge in this area [18].

3. Cooling Stage

3.1. T Jump System 1

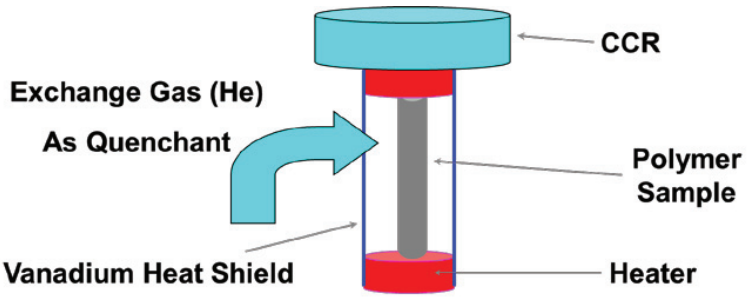

Figure 3 A schematic of the Temperature Jump System 1 see text for description

The first system is based around a closed cycle refrigerator or CCR, which is an electrically driven mechanical device which, by the controlled cyclic compression and expansion of high pressure helium gas can produce temperatures down to 4K. This acts as cold sink. The sample is mounted in a vanadium can, which is attached to copper blocks at the top and bottom of the sample. This assembly is attached to the bottom of the CCR. The whole assembly is mounted inside a vacuum chamber. The heaters and sample stage are enclosed in a vanadium heat shield. This allows the heaters to raise the temperature of the sample in the evacuated vacuum chamber up to above 200ºC. The arrangement is highly stable. To rapidly cool the sample, the heaters are switched off and a small amount of exchange gas (Helium) is introduced in to vacuum chamber. This acts as a coolant through the cold sink provided by the CCR and the sample is rapidly cooled. Temperature sensors at the top and bottom of the sample are used to monitor the sample temperature. Once the sample has reached the lower temperature, the vacuum is re-established and a highly stable system prevails. The rate of cooling depends on the amount of the gas introduced. This system allows a rapid cooling from the melt phase temperature to the crystallization temperature. However, it does require some tuning of the introduction of the exchange gas in order to prevent undercooling of the sample, which must be eliminated in this style of experiment. As the driving force for crystallization increases rapidly with the degree of undercooling, any great extent of undercooling will lead to rapid transformation of the super cooled melt to the semi-crystallized state. These experiments depend critically on rapidly cooling the sample through the maximum in the crystallization curve without any transformation, so that the subsequent crystallization processes proceed relatively slowly dues to the effects of viscosity, which increase on cooling.

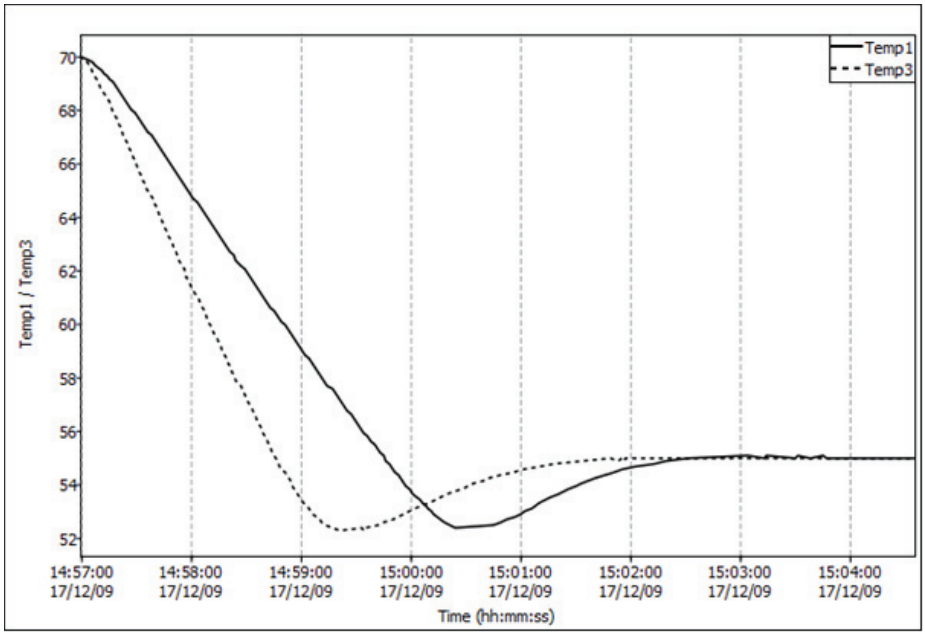

Figure 4 The cooling curves recorded for a temperature jump from 70°C to 55°C at the bottom of the can (broken line) and at the top of the can (solid line). See Figure 3. Time=0 corresponds to the point at which the cooling process was initiated.

Figure 4 shows the cooling curves recorded for one particular T Jump from 70°C to 55°C using the setup shown in Figure 3. We can see that the top cools more quickly as it is close to the cold source with an initial rate of 8.4°C/min whereas the bottom is substantially slower with a cooling rate of 5.4°C/min. The system does not reach a steady state as judged by the sensors until ~300s. The greatest problem is the slight overshoot in the cooling of 2.6°C for the top sensor and 1.5°C for the bottom sensor. The possible temperature gradient within the sample and the overshoot make this a less promising approach although with some fine tuning and automation of the valve system, we anticipate that the overshoot could be eliminated. We checked the outcome of the T jump experiment by examining the neutron scattering patterns for time points corresponding to the temperature change. If the overshoot in cooling had initiated crystallization we might expect to observe some signs of it in the data shown in Figure 5.

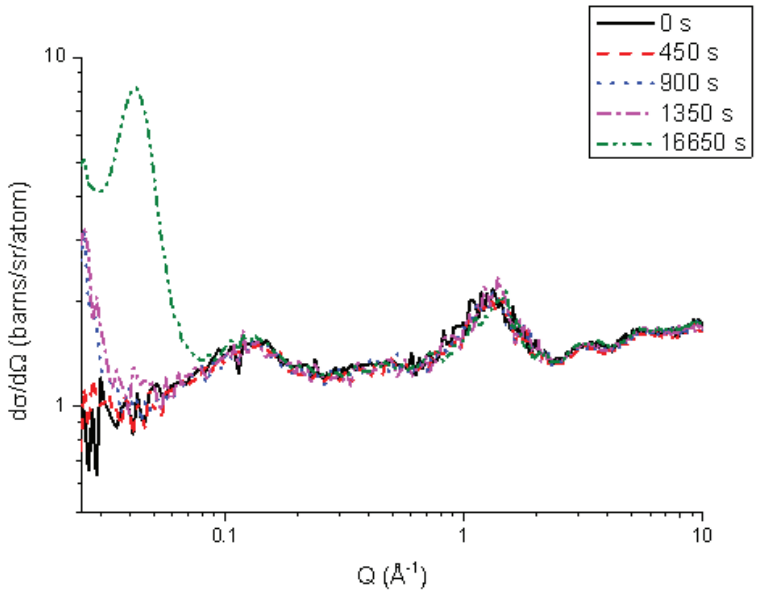

Figure 5 Scattering curves recorded during T Jump experiments from 70°C to 55°C using the system shown in Figure 3. The start times of each data cycle are shown in the key to the figure.

The scattering data in the curve labelled t=0s is typical of the scattering from a polymer melt and corresponds to that expected for a system with only short range order present. The curve labelled t=450s corresponds to the time slice immediately after reaching the crystallization temperature. This curves follows the polymer melt curve and reveals no Bragg peaks arising from the crystalline structure and shows that the quench has been successful without resulting in any crystallization. We also show how the large scale structure develops in some of the following time slices as shown in Figure 5. The curve labelled 16650s shows a well developed low Q peak which is typical of a semi-crystalline polymer [7]. In these experiments the time slices were fixed at 450s to generate curves with adequate signal to noise ratios. The one disadvantage is the limited amount of the incident beam which is employed for this type of stage. The beam was limited to 300mm vertically × 10mm horizontally. This is a consequence of the sample size, it was mounted in a 6mm diameter vanadium can.

3.2. T Jump System 2

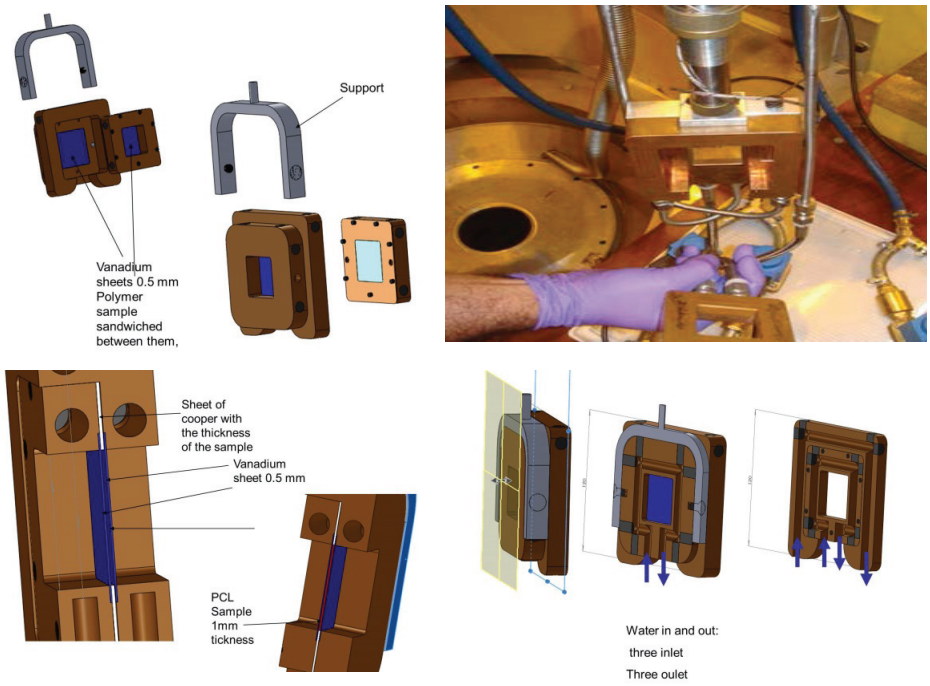

Figure 6 Design images of the Temperature Jump stage 2. Top Left the overall design of the copper blocks; bottom left the sample mounting using copper sheets for thermal contact and vanadium sheets for windows; bottom right shows the internal structure of the copper blocks with the channels for the cooling fluids; top right photograph of the manufactured system mounted on the standard NIMROD candlestick.

To overcome the limitations of the first T Jump system, an alternative approach was employed. This was designed to use a larger area sample and to avoid the undercooling of the sample past the crystallization temperature. It was based on the use of circulating fluids for cooling. Essentially the system consists of 2 large (27L) recirculating fluid baths held at two different temperatures. Each recirculating bath contained a 50:50 mix of ethylene glycol and water which circulated through the copper block at a flow rate of between 22 to 26 litres per minute. The copper block system was connected to the circulating water baths through a series of electrically operated valves (Figure 7) which were controlled using a Arduino microcontroller running a small programme which was able to act on instructions received from the NIMROD control system to switch to high temperature or to switch to low temperature. The arrangement of the valves allows the fluids from both baths to circulate and stabilise the temperature of the water bath, but only one was flowing through the copper block system at any one time. We should note here that the NIMROD sample area was fitted with a secondary enclosure complete with separate vacuum system so that in the event of any leakage of the fluids from the copper block system, the vacuum system for the whole instrument would not be compromised. The experiment proceeded as follows. Both water baths were stabilised at the required temperatures. In the example shown here using a perdeuterated poly(ε-caprolactone) sample, the upper temperature, the melt phase was 68.77ºC and the lower temperature, the crystallisation temperature was 54.27°C. The experiment was controlled via the scripting system available on NIMROD. Data in the melt phase was accumulated and then a sequence of data collections were initiated with a time slice of 100s. The length of the time slice was determined from earlier data collection to ensure that a reasonable signal to noise ratio was obtained in the data so that any small changes associated with the start of crystallisation could be identified. After the collection of 10 time slices in the melt, the valves were switched to initiate cooling. We monitored the temperature of the copper block and the temperatures of both water baths.

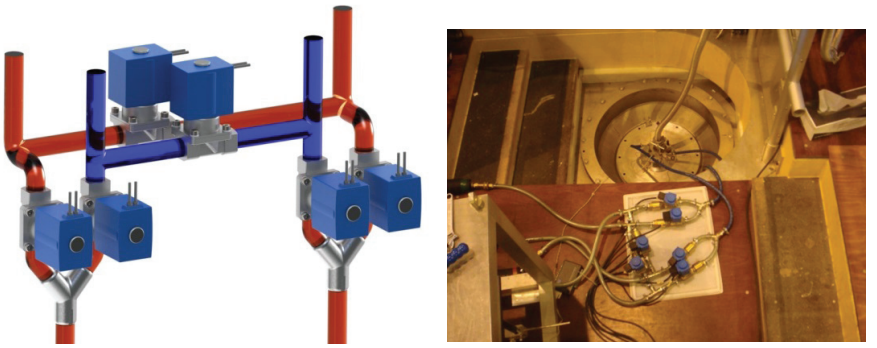

Figure 7 Design image of the valve system used to switch the circulation from one water bath to another together with a photograph showing part of the experimental system used with the second quench stage shown in Figure 6. The stage and the mount are inserted in to the NIMROD system through the aperture at the top of the photograph. The NIMROD instrument is below the floor level. The six electrically operated water valves (centre of photograph) switch the input and return lines from the two water baths

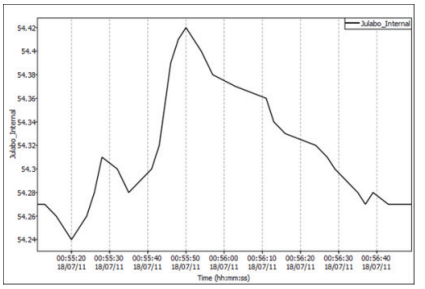

Fig 8 The cooling curves recorded for a Temperature Jump from 68.77°C to 54.27°C using the copper block systems. See Figures 6 & 7. Time=0 corresponds to the point at which the cooling process was initiated.

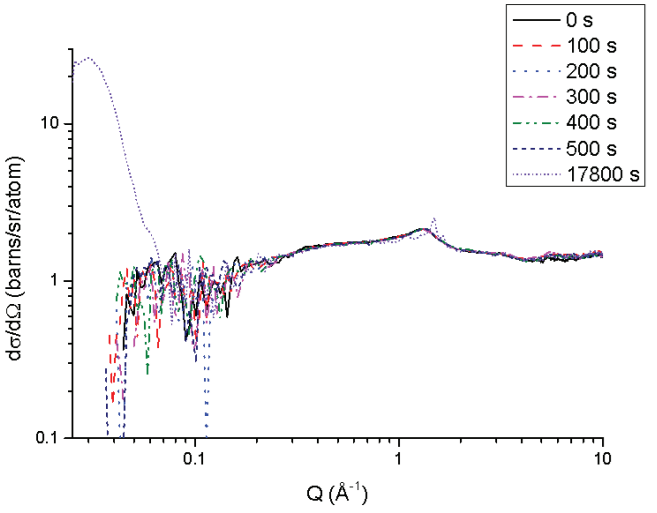

Fig 9 Scattering curves recorded during T Jump experiments from 68.77°C to 54.27°C using the system shown in Figure 6. The start times of each data cycle are shown in the key to the figure.

Figure 8 shows the temperature of the lower temperature water bath during the time of the switchover. We can observe a small rise in the temperature of the fluid which peaks at 0.15°C after 30s. This corresponds to the cooling of the copper block from 68°C to 54°C and the transfer of the heat to the water bath. Monitoring the temperature of the copper block showed that this responded as expected by cooling rapidly at first and then approaching the temperature of the lower bath more slowly. In any event, the crystallization temperature is reached by the block within one time slice. In order to determine what the state of the sample is, we used the neutron scattering data recorded during this cooling period. Selected curves are shown in Figure 9. The curve for the sample prior to cooling is typical of a melt polymer. The series of curves taken during the cooling period follow the melt phase. At low Q a certain level of noise is observed. This is a consequence of the low scattered signal in this region and the short time slice selected. However it is clear that all curves are superimposed and we process the data in the future analysis using a longer time slice by combining data. It is clear that in the region of Q = 1-2$Å^{-1}$ there are no sharp Bragg peaks corresponding to the crystalline structure. Despite the noise it is clear that there is no corresponding increase in the low scattering corresponding to the formation of chain folded lamellae or other inhomogenities. The curve labelled 17800s is obtained for the sample when it iscrystallized and we can easily see the feature at low Q and at Q = 1-2$Å^{-}$ 1resulting from the crystallization. We can conclude that the T Jump was successful in rapidly cooling the sample to the crystallization temperature without any crystallization at higher temperatures taking place.

4. Conclusions

We have successfully designed a T Jump system for studying phase transitions in polymers using neutron scattering and more specifically which is matched to the characteristics of NIMROD. We have successfully obtained high quality data for a perdeuterated poly(ε-caprolactone) sample and we hope to report on the full analysis of these data in the near future. The cell is easily adaptable to other experimental systems and could be used in a SAXS/WAXS experiment on a synchrotron beam line. In fact the thermal transfer could be greatly improved through the use of smaller beam sizes.

Acknowledgements

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