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Shear Suppression of Crystal Nucleation in a Low Molar Mass Compound / Polymer Solution

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Abstract

The transformation of a super cooled fluid to a solid ordered structure via crystallisation is a basic building block of materials science. From a practical point of view crystallisation usually takes place in a perturbed state such as a thermal gradient or flow field. The influence of flow or more specifically shear flow has widely studied especially via simulation techniques on colloidal systems. Experimental work dates from studies by Mullin et al some 45 years ago on the nucleation of inorganic salts from an agitated aqueous solution but these were inconclusive. We explore the crystallisation of a low molar mass molecular systems, dibenzylidene sorbitol at low concentrations in a polymeric solvent with and without shear flow. The polymeric nature of the solvent reduces the diffusion rates of the solute molecules. We show that the nucleation of this specific low molar mass compound and polymeric solvent can be inhibited by up to 80°C of supercooling using modest shear flow and then recovered on cessation of shear flow. We discuss the possible models for this striking behavior.

Keywords

Crystallisation; Nucleation; Growth; Shear flow

Introduction

Crystallisation from solution is core to much of the chemical industry [1] and it is the critical step in many scientific programmes including structural studies of proteins [2] and the development of pharmaceutical compounds [3]. Crystallisation is generally seen as involving distinct nucleation and growth stages but the process of nucleation by which embryonic crystals form within a supersaturated solution remains largely unexplained. In classical nucleation theory, there is a kinetic factor and a barrier to nucleation in which the volume excess free energy of the nuclei at a critical radius balances the surface excess free energy; nuclei larger than this critical radius grow, smaller entities dissolve back in to the solution [4]. Recently other pathways of transformation have been proposed theoretically in which structural and density fluctuations are separated [5]. In parallel, the intense interest in the nucleation and growth of protein crystals [6] and the emerging area of colloidal crystals [7] has raised again the possibility that nucleation may be enhanced or suppressed by the application of flow fields. The earliest experimental reports date back to studies by Mullin et al. [8, 9] some 45 years ago on the nucleation of inorganic salts from an agitated aqueous solution but were inconclusive. We show experimentally that the nucleation of a specific low molar mass compound can be inhibited by up to 80°C of super cooling using modest shear flow through the use of a polymeric solvent and then recovered on cessation of shear flow. We propose that this striking behaviour arises from a shear flow induced reduction

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in the effective collision cross-section of the embryonic nuclei thereby limiting the growth of the nuclei to below the critical size. This arises from the symmetry breaking consequence of the imposed flow field and the asymmetric nature of the nuclei.

Experimental

Solutions were prepared containing 0 to 9.1% w/w dibenzylidene sorbitol (DBS) (mp 220°C, molecular weight 358 Da) as the solute and poly(ε-caprolactone) (PCL) (Mw 80,000 Da. mp ~ 60°C) as the solvent. DBS is used industrially as a clarifying and nucleating agent for isotactic polypropylene. Small-angle neutron scattering (SANS) experiments using LOQ at ISIS (UK) exploited a partially deuterated PCL (Mw=13620 Da, mp55°C). The solutions were subjected to a shear flow field using a parallel plate cell [11] which allows both neutron and x-ray scattering data to be measured during flow. The beam probed material subjected to a narrow range of shear rates. Time resolved x-ray scattering experiments were performed on beam-line 16.1 at the Dares bury SRS and 2-D SAXS data (|Q|~ 0.01 to 0.2 Å-1, where $|Q| = 4\pi\sin\theta/\lambda$, λ is the incident wavelength, and 2q is the scattering angle) were recorded using a RAPID detector with a data cycle of 10s and 2-D wide-angle x-ray scattering (WAXS) data were obtained using the same flow system coupled to a Photonic Science CCD camera with a |Q|max~ 2Å^{-1}.

Results

Figure 1 shows part of the phase diagram for the DBS/PCL system constructed from the scattering data and differential scanning calorimetry data. At higher temperatures the SANS data (Figure 2) show a single phase solution. For each measured scattering curve (I (Q) we have calculated the invariant, Ω given by [10] :

$$\Omega = \frac{1}{2\pi^2}\int I(\underline{Q})d\underline{Q} = \left\langle \rho^2 \right\rangle V \qquad (1)$$

Where ρ is the fluctuation in the scattering length density and V is the scattering volume. If the scattering length density difference between crystal and liquid is constant, Ω is proportional to the fraction of crystals in a dilute system. The curves (inset Figure 2) show that Ω for the 2% DBS solution reduces with temperature and reaches a minimal steady value at ~ 110°C commensurate with a homogenous solution; for the 2.9% DBS solution the equivalent point is ~ 120°C. At lower temperatures there is a biphasic region which contains DBS crystals [12]. We can use shear flow to align these crystals to reveal their highly anisotropic nature without altering their structure [12]. Application of a low shear rate, $\dot{\gamma}$, of 10s^{-1} and a shear strain of 1000 shear units (shear units = shear rate x elapsed time) aligns the crystals as shown by the crystalline spots in the WAXS pattern (Fig 3a) and the horizontal streak in the SAXS pattern (Figure 3b). Analysis of the SAXS data gives a fibril diameter of 140Å and a length of over 500Å [13]. Clearly the DBS crystals are aligned preferentially parallel to the flow direction. Measurements as a function of temperature show that the crystalline features progressively reduce to zero at the point corresponding to the liquidus line in Figure 1. The biphasic region is terminated at lower temperatures by the solidification of the PCL. As is typical for polymers, the solvent can be supercooled below its melting point; the extent of supercooling is dependent on the fraction of the DBS as it acts as a nucleant [11] for the PCL in this circumstance. On heating, all compositions melt at the same temperature indicating that no DBS was incorporated in the PCL crystals.

Figure 1: Part of the phase diagram for the DBS/PCL system obtained using a combination of in-situ small-angle neutron and x-ray scattering techniques together with differential scanning calorimetry. Redrawn from [8].

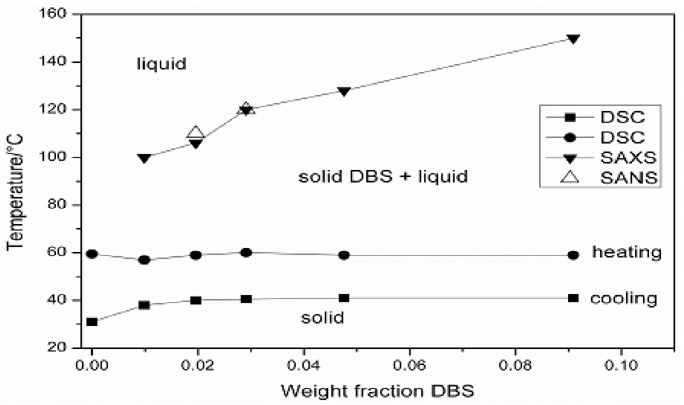

Figure 2: SANS curves I(Q) for a sample of 2% DBS in PCL at 80, 90, 100, 110, 120, and 130°C. The inset shows plots of the invariant Ω calculated from scattering curves recorded at different temperatures for 2.0% (■) DBS and 2.9% (o) DBS solutions.

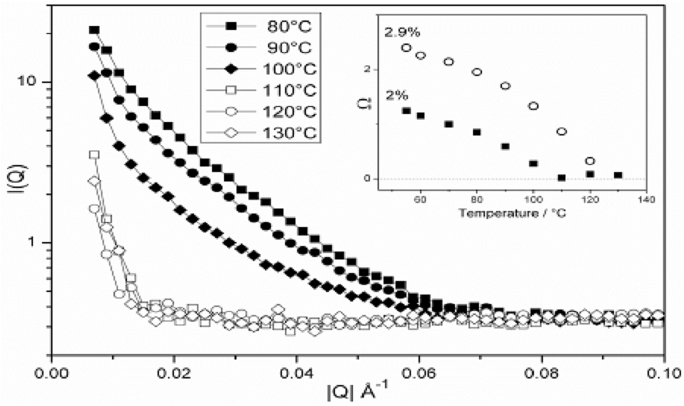

Figure 3(a): Wide-angle x-ray patterns of a 3% DBS/PCL system subjected to shear flow at 80C and **(b)** Small-angle x-ray scattering pattern on the same samples and conditions the central black shadow is formed by the beam-stop, much of the vertical scattering features arises from the mica windows in the shear cell as does the sharp ring. The maximum value of |Q| in the WAXS pattern is ~ 2Å^{-1}.Figure 4 A plot of the invariant derived from SAXS patterns recorded at different temperature for a sample of 2.9% DBS in PCL under quiescent conditions (filled circles); subjected to a shear rate of 1s^{-1} (full line) and a shear rate of 10s^{-1} (open circles). The temperature rate was 10°C/min.

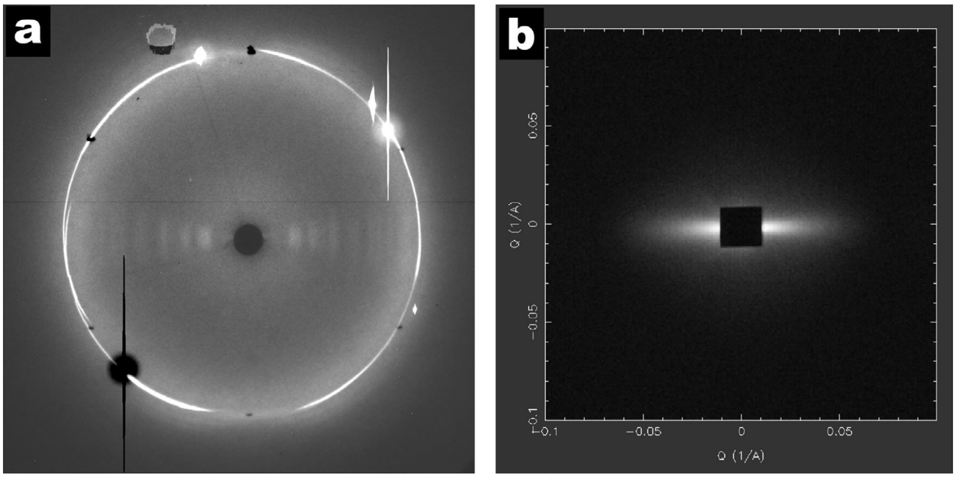

Figure 4: A plot of the invariant derived from SAXS patterns recorded at different temperatures for a sample of 2.9% DBS in PCL under quiescent conditions (filled circles); subjected to a shear rate of 1s^{-1} (full line) and a shear rate of 10s^{-1} (open circles). The temperature rate was 10°C/min.

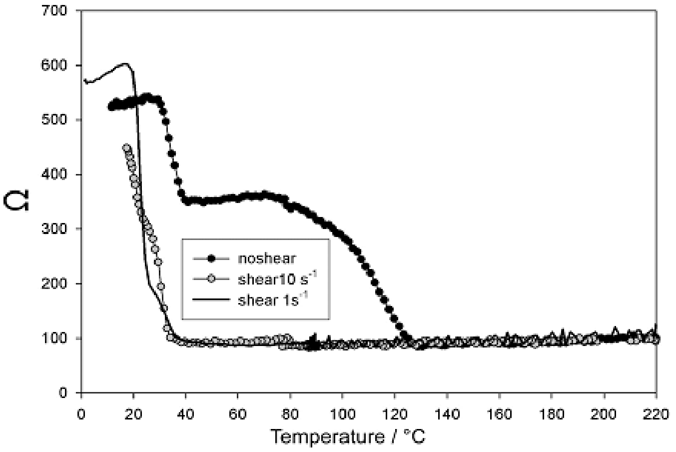

Figure 4 shows (filled circles) the invariant, Ω derived from SAXS data for a 2.9% solution cooled from the single phase region at 220°C at 10°C/min under quiescent conditions. At ~120°C the invariant increases steadily until ~ 80°C which we relate to the crystallisation of the DBS as the sample moves through the biphasic region. The rate of crystallisation appears as fast as the cooling rate. At ~ 40°C, there is a further upturn in the invariant which corresponds to the solidification of the PCL. Figure 4 shows two further experiments which repeat these measurements, but now the solutions are subjected to a shear flow field of $10s^{-1}$ or $1s^{-1}$. Both curves show no increase in the invariant until a temperature of ~ 30°C is reached. We attribute this dramatic difference to the fact that the DBS has not crystallised and has remained in solution until the temperature at which the solvent solidifies. We can confirm the absence of the DBS crystals in the solution as the crystallisation temperature is equivalent to that of the PCL without DBS. In contrast, the sample cooled without shear flow shows crystallisation at a higher temperature due to the nucleating effect of the DBS crystals. If we cool a solution from 220°C to 80°C and halt the shear flow, crystallisation of the DBS takes place within 300s; the crystals which form have no preferred orientation with respect to the previous flow direction. Fig 3b shows that the DBS crystals once formed in the biphasic region are stable under shear flow.

We have shown that modest shear flow inhibits the nucleation and crystal growth of DBS such that a quench of at least 80°C is possible. The crystallisation process starts with nucleation of an embryonic DBS crystal from the fluctuations in the solution and at the simplest level our observations suggest that either the flow is breaking up these embryos or damping out the fluctuations of order, or that flow in some manner does not favours the formation of those nuclei. In classical nucleation theory a single order parameter, namely density, is involved, but clearly the formation of crystals from a saturated solution involves both density *i.e.* phase separation, and structure, namely crystallisation;[5]a number of approaches have explored theoretically the interplay between these two processes [19]. It is well established that shear flow can depress the cloud point of a mixture of two liquids [20, 21] with a form for the shift of $a\dot{\gamma}^k$ where k has a universal value of 0.5 and a is strongly dependent on the nature of the 2 liquids [22]. The shifts observed for polymer/compound mixtures are small compared with that observed here and so we rule out the possibility of a liquid-liquid phase separation at the heart of the current process. Polymer matrices have been widely exploited to control the growth of nanoparticles. The higher viscosity limits diffusion and the polymer may interfere in the attachment process at the crystal/solution interface [23] but it seems unlikely that these processes are shear rate dependent.

Simulations of colloidal melts have observed the suppression of the nucleation of crystals by shear flow [14, 17, 18]. In classical nucleation, theory the Gibbs free energy depends on the relative strengths of γ_S, the interfacial free energy and β, the product of the density of the nuclei and the difference in chemical potential between the nucleus and the liquid phase. Blaak et al [17, 18] proposed that the surface and volume energy parameters γ_S and β could be expanded in even powers of the shear rate. Truncating the expansion at the first two terms leads immediately to expressions for the critical radius and the barrier height which have a quadratic dependence on the shear rate. The critical radius, r_c is:

$$r_c = \frac{2\gamma_S(1+a_0\dot{\gamma}^2)}{\beta(1+b_0\dot{\gamma}^2)} \qquad (2)$$

Where a_0 and b_0 are coefficients; the expression reduces to the classical form if $\dot{\gamma}$ is zero. Blaak et al found good agreement between Equation 2 and the results of their simulation. Although a useful approach it does not identify the microscopic origin of the shear rate dependence of the energy terms. Moreover, such an expansion of the free energy can only be considered appropriate at conditions close to the quiescent state and we are clearly not in that regime.

Shear flow modifies transport and the nucleation rate is directly related to the attachment rate of molecules to the embryonic cluster and this in turn is approximately proportional to the diffusivity of the solute molecules [15]. Mura et al [16] have considered these factors and the effect of shear flow on flow induced nucleus straining which lowers the nucleation rate as observed in this work. Their interesting theoretical predictions are restricted in their application to this work due to the limitations of the hard sphere colloidal model used. The impact of the shear rate on the diffusivity increases as the viscosity increases and clearly this will be greater for a polymeric solvent. In the case of PCL, the glass transition is ~ -60°C and hence variations of the viscosity with temperature will be limited. Although such factors may have a part to play, we propose that it is the symmetry breaking inherent in the flow which is the major cause of the effects observed. The crystalline form of the DBS is in the form of highly extended fibrils which means that the growth rates in the fibril direction are substantiaally greater than in the perpendicular and we anticipate such differences will be reflected in the attachment rates of DBS molecules to the embryonic nucleus. Although the attachment probability may be anisotropic, in the quiescent state, the distribution of embryonic nuclei is random and in a time/spatial-averaged manner, diffusing solute molecules will be captured by an embryonic nucleus aligned such that a suitable face of the nucleus is normal to the trajectory of the molecule. We propose that the embryonic nuclei are anisotropic in form and have a preferential alignment with respect to the shear flow direction. If we assume that at the modest shear rates employed, the diffusion of the DBS solute remains largely isotropic, there will be a reduced number of nuclei which have their high growth rate faces suitably aligned for attachment of solute molecules. The alignment of the embryonic nuclei in the flow field depends on the embryo aspect ratio; the latter in turn defines the reduction in attachment probability. It is straightforward to identify embryonic forms which would lead to a reduction of attachment rate by an order of magnitude. Moreover any growth of embryonic nuclei which does takes place will increase the aspect ratio, thereby increasing the alignment and hence decreasing the probability of further growth. Cessation of shear flow leads rapidly to an isotropic distribution of embryonic nuclei as they continually form and redissolve and this leads to a recovery of the nucleation rate as observed experimentally. This mechanism will be applicable over the wide range of temperature observed. This mechanism will most marked in crystallising systems with anisotropic growth rates and in part explains why such effects have not been observed in previous studies, although systems with extended external form are not uncommon; we anticipate at low shear rates, a polymeric solvent will be essential to the effect. McBride et al. [24] have identified the importance of shear induced mixing in the observation of a maximum in the nucleation rate of the formation of amyloid aggregates with shear rate. We know from previous work that the DBS crystals are sensitive to shear flow [25] and that clearly there is a strong differentially growth rate for the anisotropic crystals [26]. These results underline the need to incorporate the tensorial nature of diffusion in to theories of crystal nucleation and this opens a new approach to the control of structure formation in dispersions.

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