Time-resolved small angle X-ray scattering and wide angle X-ray diffraction studies on premelting during annealing of gelation crystallized ultrahigh molecular weight polyethylene films

Myung H. Cho and Thein Kyu*
Institute of Polymer Engineering, The University of Akron, Akron, OH 44325, USA

and Jar-Shyong Lin
Center for Small-Angle Scattering Research, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

and K. Saijo and T. Hashimoto
Department of Polymer Chemistry, Kyoto University, Kyoto, Japan
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The phenomenon of melting–recrystallization during annealing below an equilibrium melting temperature (141.6°C) of gelation crystallized ultrahigh molecular weight polyethylene (UHMWPE) films has been investigated by means of time-resolved small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD). Isothermal annealing below 130°C shows that the SAXS long period (periodic distance of successive lamellae) increases, then subsequently levels off with increasing annealing time. At 140°C, the long period increases from 118 to 690 Å without any sign of levelling off. This type of increase in long period has been customarily attributed to lamellar thickening associated with solid state diffusion of intracrystalline chains. Recent synchrotron radiation studies on annealing of single crystal mats of conventional linear polyethylene demonstrated that melting–recrystallization is responsible for the increase in long period. The present time-dependent WAXD studies show a gradual decrease in crystallinity for some initial periods of annealing at 137°C, which slows down with elapsed time. At 140°C, the terminal melting occurs after 15 min. We propose that the increase in long period during annealing of this gelation crystallized UHMWPE near its melting temperature is due to the melting of successive lamellae rather than lamellar thickening.

(Keywords: SAXS; WAXD; annealing; gelation; crystallization; polyethylene)

INTRODUCTION

The phenomenon of premelting is generally inferred by the continuous decrease in crystallinity during annealing below the equilibrium melting temperature of semi-crystalline polymers. It is experimentally established that small angle X-ray scattering (SAXS) revealed an increase in long period with increasing temperature or isothermal annealing[1–3]. There is no agreed opinion on the mechanisms underlying the premelting process. A classical interpretation on premelting is lamellar thickening in which solid state diffusion of intracrystalline chains takes place[1,4–7]. Flory[8], and later Kilian[9] and Pope and Keller[10] attributed the premelting phenomenon to selective melting of small lamellae within the lamellar stacks. An alternative mechanism of melting–recrystallization was proposed by Mandelkern *et al.*[11,12]. Later, Fischer[13] proposed a surface melting mechanism associated with an entropy change in the amorphous regions resulting in an increase in thickness of the interlamellar amorphous region. Strobl and co-workers[14] postulated that premelting is due to a successive melting of the lamellae which is in a reverse sequence of crystallization where a consecutive formation of lamellae occurs in building up the lamellar stacks.

In the past decade, real time SAXS or wide angle X-ray diffraction (WAXD) studies on crystallization and/or premelting transitions have again become of considerable interest because of the availability of synchrotron radiation and high flux X-ray sources[15–17]. It becomes evident that melting and recrystallization takes place during isothermal annealing of linear polyethylene. Kawaguchi *et al.*[15] reported that when a linear polyethylene single crystal was annealed at 122°C, the (1 1 0) WAXD reflection decreased for ~30 s and then increased again while the SAXS long period continuously increased. Grubb *et al.*[16,17] also observed that the

* To whom correspondence should be addressed

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intensities of (1 1 0) and (2 0 0) reflections decreased initially for ~4 s then increased subsequently during annealing at 125–130°C. The initial decrease of the WAXD intensity was attributed to partial melting, while the increase was assigned to recrystallization.

In a previous paper[18], we have investigated the phenomena of melting and crystallization of gelation crystallized ultrahigh molecular weight polyethylene (UHMWPE) using SAXS and WAXD. We observed that the morphology of the gelation crystallized UHMWPE is similar to stacked lamellae of single crystal mats with preferential *c*-axis orientation normal to the film surface. Upon annealing below the melting temperature (T_m), the SAXS long period increases drastically; this has been customarily attributed to lamellar thickening. However, WAXD studies show a remarkable reduction of crystallinity which is inconsistent with the mechanism of lamellar thickening where solid-state diffusion of intracrystalline chains has taken place. We postulated that the increase in long period may be due to an increase in the periodic distance of lamellar structure associated with the partial melting of certain lamellae.

In this paper, we continue our effort to elucidate the phenomenon of annealing based on real time SAXS and WAXD. Isothermal annealing studies were undertaken by conducting temperature (T)-jump experiments from ambient to elevated temperatures around the onset of T_m. The mechanisms which cause the increase in long period during annealing are discussed based on the lamellar thickening and melting–recrystallization models.

EXPERIMENTAL

UHMWPE ($M_w \sim 6 \times 10^6$) was supplied by Himont Co. The method of gelation crystallization of this UHMWPE has been described in detail in previous studies[18,19]. The thickness of the gelation crystallized films was ~300 μm. The films were cut into small pieces 10 mm long and 10 and 2 mm wide for through and edge views, respectively. These pieces were stacked tightly (10 mm long × 10 mm wide × 2 mm thick) for X-ray studies. Real time SAXS isointensity contours were obtained at 60–90 s intervals using the Oak Ridge National Laboratory 10 m SAXS camera equipped with a 20 cm × 20 cm two-dimensional position-sensitive detector. A 12 kW Rigaku X-ray generator, equipped with a Cu target, was operated at 80 mA and 40 kV. The sample to detector distance was 5.12 m to cover a scattering wavenumber (q) range of 0.008–0.10 Å^{-1}, where $q = 4\pi/\lambda \sin\theta/2$ (λ and θ are the wavelength of the X-rays and the scattering angle, respectively). Real time WAXD experiments were carried out using the X-ray facility at Kyoto University. Time dependent 2θ scans were obtained on a Rigaku X-ray generator (18 kW) with the aid of a one-dimensional position-sensitive proportional counter. *T*-jump experiments were undertaken from ambient temperature to 110–140°C by rapidly transferring the specimens to the preset heating blocks. These heating blocks were installed in the vacuum chamber. Because of extremely high viscosity of UHMWPE melts, no cover was needed for the windows of the sample heating blocks. The temperature was measured near the surface of the specimens. The time for equilibrating the specimens at experimental temperatures varied from ~30 to 60 s.

D.s.c. scans were carried out on a DuPont thermal analyser (model 9900) equipped with a heating module (model 910). The heating rate of 10°C min^{-1} was chosen arbitrarily. An indium standard was used for temperature calibration.

RESULTS

Figure 1 shows the WAXD photographs and SAXS contour plots of a gelation crystallized UHMWPE dry film. In the through view (i.e. the incident X-ray is normal to the film surface), there is no preferential orientation of crystals or lamellae. However, the edge view (the incident X-ray is directed parallel to the film surface) manifests the arcs of (1 1 0) and (2 0 0) planes, indicative of crystal *c*-axis orientation in the film normal direction. The corresponding SAXS study[18,19] shows a typical two-point pattern arising from the stacked lamellar structure reminiscent of single crystal mats.

As can be seen in *Figure 2*, the fresh gelation crystallized UHMWPE exhibits a melting endotherm at ~142°C, however, it shifts to a lower temperature of 135°C in the second run. The crystallinity of the gelation crystallized specimen, as estimated from the heat of fusion, is ~85% which reduces to ~50% after cooling to ambient temperature from 200°C. As demonstrated in a previous paper[18], the initial stacked lamellar morphology also transformed to a spherulitic structure during crystallization from 200°C.

Time-resolved SAXS experiments were carried out from ambient temperature to 100–140°C. *Figure 3* shows the typical time evolution of SAXS profiles of the edge view, following a T jump to 130°C. The original peaks of the two-point SAXS pattern gradually shift towards the centre while the intensity increases. This trend is more evident in the plots of intensity *versus* q in *Figure 4a*. The SAXS peak eventually disappears when melting occurs. However, a significant level of scattering persists in the melt which may be attributed to void scattering from the porous UHMWPE melt. This void scattering was subsequently subtracted from the real time scattering data and replotted in *Figure 4b*. The SAXS peaks are very distinct, from which the change of long period with elapsed time has been evaluated. A similar analysis has been undertaken for other T jumps. As shown in *Figure 5*, the long period increases very slightly (~10%) during annealing at 100°C. In the T jumps to 110–130°C,

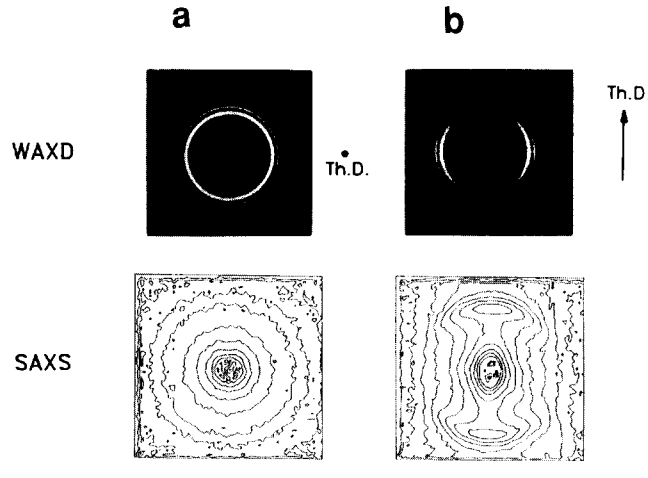

Figure 1 WAXD photographs and SAXS isointensity contours of a gelation crystallized UHMWPE dry film: (a) through view (normal to the film surface); (b) edge view

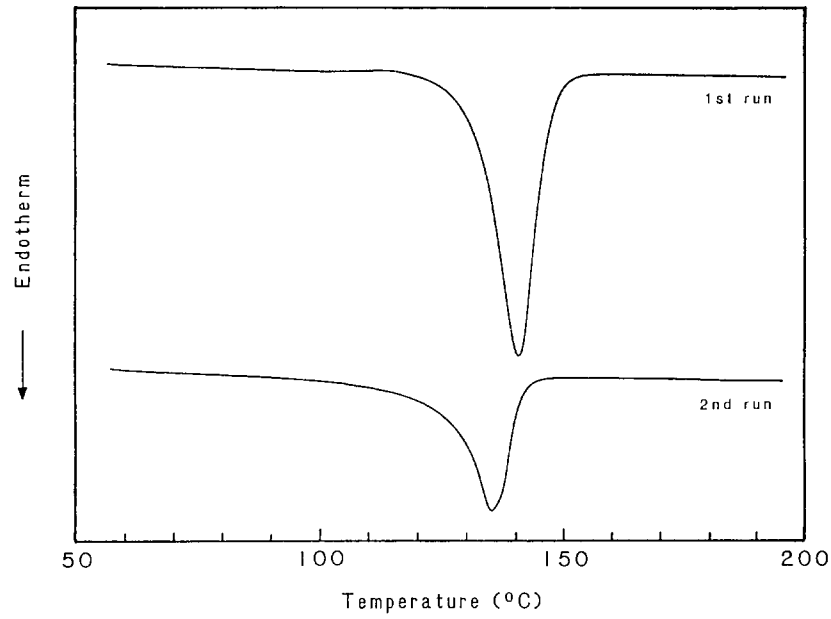

Figure 2 D.s.c. thermograms of a fresh gelation crystallized UHMWPE and a second run after recrystallizing from the melt (heating rate 10°C min^{-1})

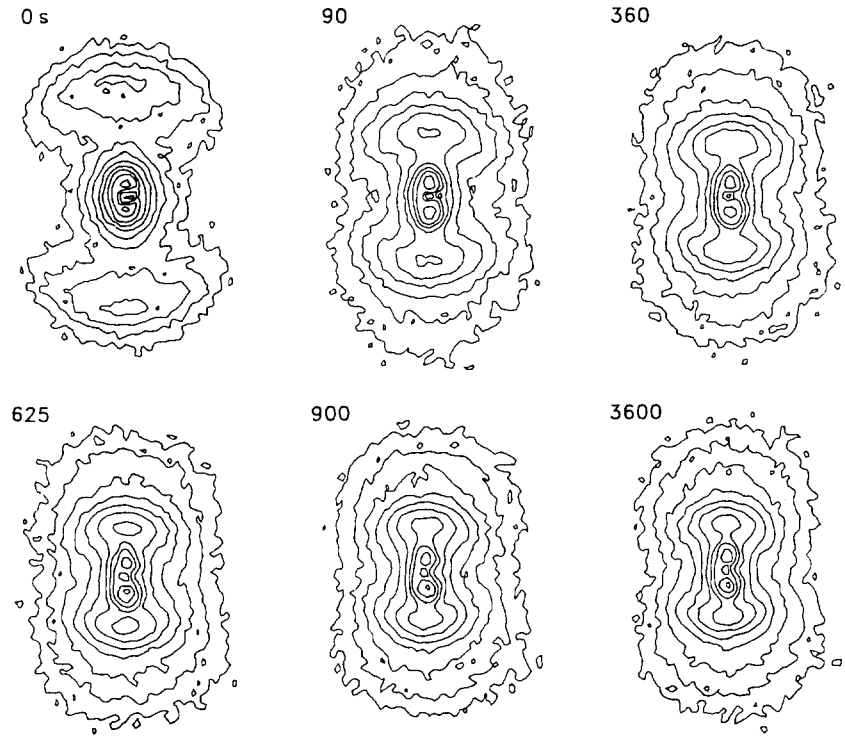

Figure 3 Typical time evolution of SAXS isointensity contour plots following a T jump to 130°C

the long period increases appreciably, i.e. nearly double at 110°C and almost triple at 130°C in 15 min and then levels off. When temperature is increased to 135°C, the long period continually increases without any sign of levelling off within the experimental time-scale. At 140°C, the increase of long period continues for ~15 min, then terminal melting takes place.

WAXD studies during isothermal annealing below 130°C show little or no change in peak intensities of (1 1 0) and (2 0 0) reflections in the equatorial direction. *Figure 6* shows the time evolution of (1 1 0) and (2 0 0) WAXS peaks in the equatorial scans of the edge view for T jumps to 134 and 137°C. At 134°C, the WAXD intensity decreases slightly for some initial periods, then levels off. The decrease in the peak intensities at 137°C is initially clearer, but becomes more gradual with elapsed time. Two possibilities exist to account for the decrease of peak intensity, i.e. premelting and/or crystal reorientation. To clarify this aspect, WAXD scans were acquired in both the equatorial and meridian directions of the edge view at 140°C. As can be seen in *Figure 7*, the peak intensity diminishes drastically in both scanning

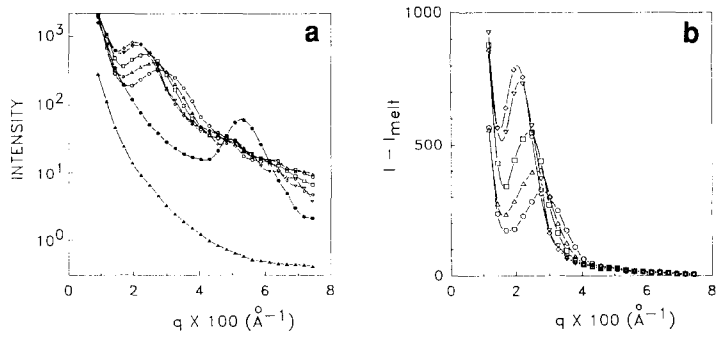

Figure 4 (a) Real time SAXS intensity *versus* scattering wavenumber plots at 130°C and (b) the replots after background subtraction (void scattering): (●) 0 s; (○) 90 s; (△) 180 s; (□) 360 s; (▽) 625 s; (◇) 3600 s; (▲) melt (150°C)

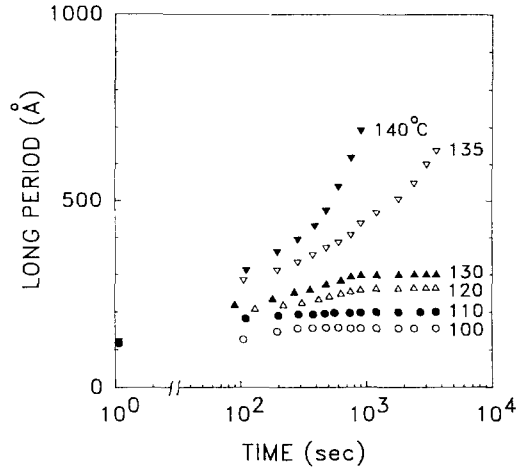

Figure 5 Variation of SAXS long periods for various T jumps

directions, while the amorphous halo concurrently intensifies as time elapses. The two peaks eventually disappear after 15–20 min, suggestive of crystal melting. If the crystal reorientation were to occur during annealing, one would expect to see an increase of the peak intensities of (1 1 0) and (2 0 0) in the meridian direction and a decrease in the equatorial direction. However, both the (1 1 0) and (2 0 0) peaks in the meridian direction simply decrease, thus the contribution of the crystal reorientation process to the X-ray intensities must be negligibly small.

There are two possible mechanisms to account for the premelting behaviour; i.e. the lamellar thickening and the melting–recrystallization. To distinguish between the two mechanisms, it is necessary to know the overall change of crystallinity during annealing. It is, however, cumbersome to calculate the true crystallinity of such oriented specimens as it requires integration of the WAXD intensity over all azimuthal and Bragg angles. Instead the apparent crystallinity was calculated based on the diffracted intensities of the (1 1 0) and (2 0 0) planes of the equatorial WAXD scans which should be sufficient for qualitative comparison with the SAXS results. As shown in *Figure 8*, the apparent crystallinity decreases slightly during isothermal annealing at 134°C and more clearly at 137°C. In the case of a T jump to 140°C, terminal melting occurs in ~15 min.

DISCUSSION

If the lamellar thickening were to occur during annealing, an increase in the crystalline fraction due to an increase in the straight chain lamellar thickness would be expected. The present WAXD studies show no net change in the peak intensities during annealing between 110°C and 130°C. The increase in the SAXS long period at 110–130°C may be associated with the surface melting of crystallites without appreciably perturbing the core crystal stems. At 134°C, there is a slight decrease of crystallinity initially, but it remains unchanged thereafter. This decrease is more pronounced in the annealing at 137°C in the initial period, but it slows down after 20 min. However, this trend certainly continues. At a comparable temperature (135°C), the SAXS long period continues to increase gradually. The initial decrease of WAXD crystallinity at 134–137°C may be due to the partial melting, then melting and recrystallization would occur concurrently such that there is little or no appreciable change in the net crystallinity.

The time resolved WAXD results clearly reveal that the apparent crystallinity decreases during isothermal annealing below T_m, particularly at 140°C, suggesting a premelting transition without recrystallization. The melting–recrystallization phenomenon has been suggested as a plausible mechanism for thickening of lamellae. This phenomenon was observed by Kawaguchi *et al.*[15] in the time-resolved SAXS and WAXD studies of single crystal mats of conventional linear polyethylene. A similar observation was also made by Grubb *et al.*[16,17] in the real time studies of single crystal mats by synchrotron radiation. In both cases, the melting transition was completed within 4–30 s, then recrystallization took place. In the present case, the melting out of successive lamellae must take place in some initial times to reveal a dramatic increase (two- to three-fold) in the SAXS long period. The WAXD crystallinity decreases correspondingly at 134 and 137°C. Then, the melting and recrystallization probably occurs concurrently at later times of isothermal annealing. However, the recrystallization is not detected at 140°C annealing. It should be pointed out that the T_m of the gelation crystallized UHMWPE lamellar crystals was ~142°C, but it reduced to 135°C when it was recrystallized from the melt (*Figure 2*). This seems to suggest that the T-jump temperature (140°C) is evidently beyond the T_m of melt-crystallized UHMWPE and thus may be too high for the molten UHMWPE chains to recrystallize. This

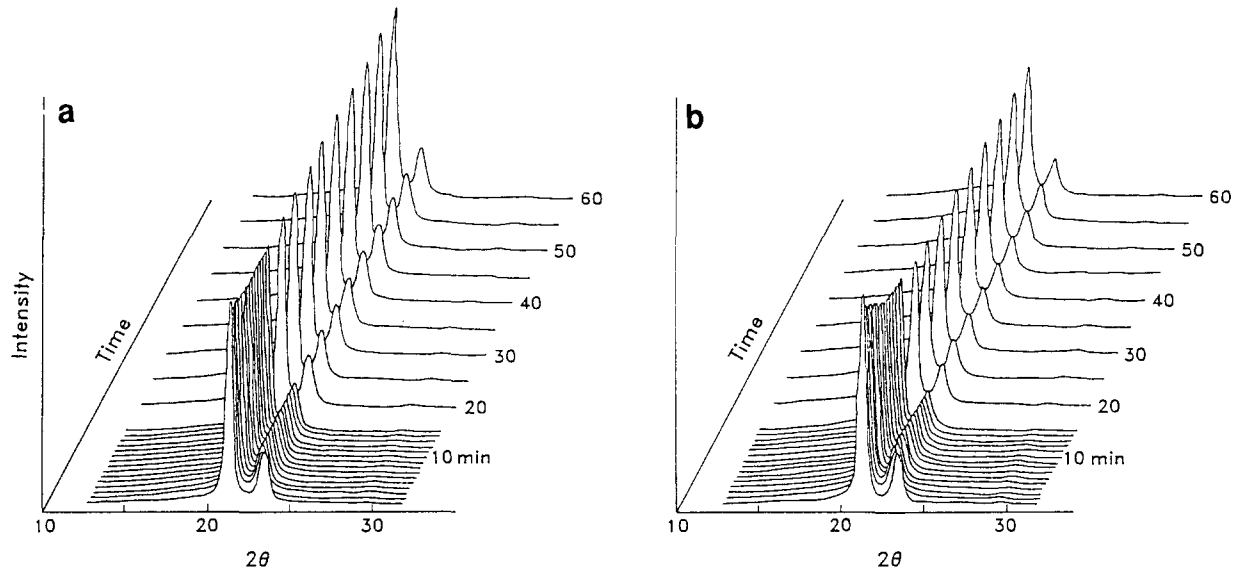

Figure 6 Time evolution of (1 1 0) and (2 0 0) reflections in the equatorial scans of the edge view for T jumps to (a) 134 and (b) 137°C

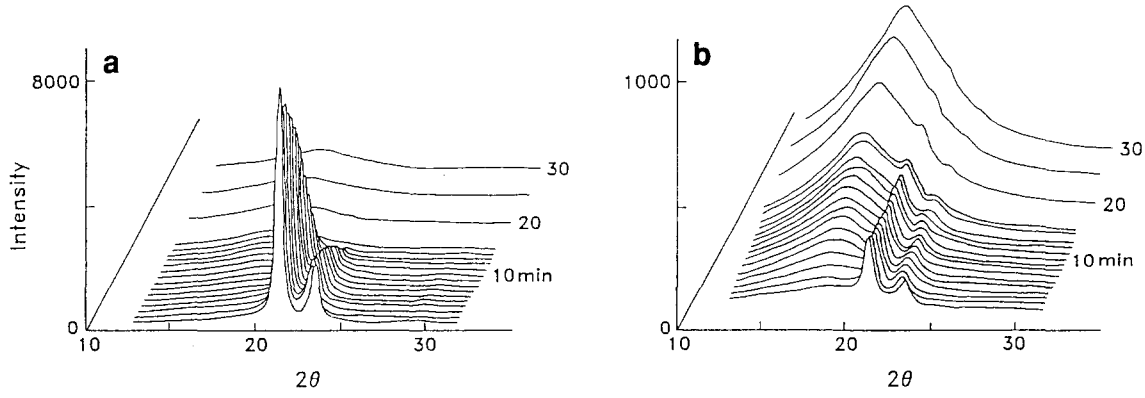

Figure 7 Time evolution of (1 1 0) and (2 0 0) peaks measured in (a) the equatorial and (b) the meridian directions of the edge view at 140°C

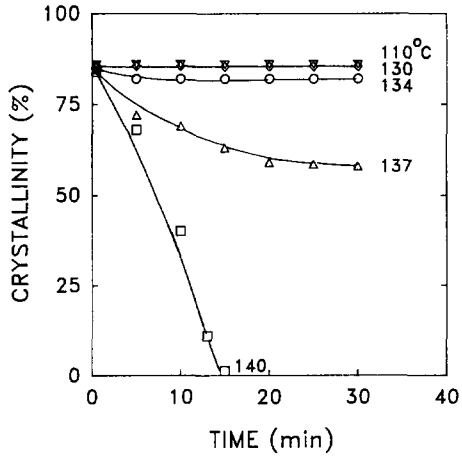

Figure 8 Variation of apparent crystallinity during isothermal annealing for various T jumps

explanation is very simplistic as the epitaxial crystallization, which may have some effect on the T_m, has not been taken into consideration. It is reasonable to conclude from the WAXD results that premelting is the dominant mechanism during annealing near the T_m of UHMWPE.

The increase in the SAXS long period may be simply associated with the melting of neighbouring (or alternate) lamellae, which results in an increase in interlamellar distance. This phenomenon is exactly the reverse sequence of crystallization, where the long period is large at the beginning of crystallization, then reduces as crystallization proceeds. This phenomenon has been explained in terms of a lamellar insertion model[14] or a car parking model[20], in which new lamellae form in the interlamellar spaces. Since melting is a random process, it is likely to have a large distribution of interlamellar periodic distances, which should result in peak broadening during annealing. Unfortunately, this peak broadening could not be observed as the SAXS peak positions were too close to the main beam in the T jumps to 135 and 140°C. In the case of a T jump to 130°C, no peak broadening was noticed (*Figure 4b*); this temperature was obviously too low to observe the random melting of neighbouring lamellae as the long period levelled off after ~900 s (*Figure 5*). Nevertheless, it is reasonable to conclude that the melting of neighbouring lamellae may be responsible for the dramatic increase of the SAXS long period at some initial times of annealing in this gelation crystallized UHMWPE. It should be pointed out that the present observation does not rule out the possibility of lamellar thickening

which might occur concurrently with the partial melting of neighbouring lamellae, particularly at low annealing temperatures. However, the lamellar thickening process alone would be inadequate to account for the drastic increase (three- to six-fold) in the SAXS long period.

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