Integrated polymer spherulites growing from one homogeneous nucleation site in supercritical fluid†

Changming Wang,[ab] Ying Zhao,[a] Jinliang Song,[a] Buxing Han[a] and Dujin Wang*[a]

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Integrated micro-sized spherulites of ultrahigh molecular weight polyethylene (UHMWPE), with one clear homogeneous nucleation site and sheaf-like lamellae, have been successfully prepared from supercritical fluid of ethanol, supplying a propagating stage from sheaf-like dendrite to final spherical crystal.

The concept of spherulites became understood as the rounded crystalline bodies which commonly occur in vitreous igneous rocks.[1] Later, organic, inorganic, and polymeric spherulites were extensively studied.[2] Much attention has been paid to the study of the mechanism of polymer spherulite formation and a mechanism proposed by Keller[3] was confirmed by a modern *in situ* atom force microscopy (AFM) study for the very slow crystallizing polymer system.[4] Lamellae generally self-assemble into spherical superstructures, in which the lamellar sheets grow out radially from the center. In order to keep increasing the surface of the three-dimensional growing spherulite, lamellae have to branch and splay, therefore, a sheaf-like structure dominates the lamellae frame.[1,4,5] In some cases, banded spherulites were also observed due to the twisting of crystalline lamellae.[3b,6]

Understanding the structural characteristics of spherulites is crucial to the ultimate properties of semi-crystalline polymer materials. Chan's observations using modern *in situ* AFM successfully proved the homogeneously and heterogeneously nucleated spherulite growth mechanism that Keller had proposed previously.[3,4] Unfortunately, *in situ* AFM could not be used to observe the spherulite morphology,[4] because the AFM sample is limited to very thin film like several hundreds of nanometres. In such a confined geometry, only sheaf-like dendrites could be finally obtained at the root of spherulite formation in polymers.[1] Therefore, the study of spherulite growth still lacks the propagating stage from the sheaf-like dendrite to the final spherical crystal, and to date the integrated spherulite morphology at the stage of crystallization has not been observed. Although some spherulites of biopolymers were reported,[7] under these solution conditions, spherulites are not stable crystals but unstable aggregates of thin crystal plates.

In the past two decades, the crystallization and solid phase transition of polymers have attracted extensive attention in supercritical fluid, which can act as a reaction medium or processing factor to obtain environmentally-responsible materials because of its gas-like viscosity and liquid-like solubility.[8] Interesting ordered structures of polymers have been successfully prepared based on the unique properties of supercritical fluids.[9] The mechanism of the phase behaviors of polymers in such a critical state, however, has seldom been reported, especially how nucleation occurs and in which way a spherulite grows. Therefore, it is the main aim of this work to explore the correlations between polymer crystallization and soft confinement provided by supercritical fluid in which the supercooled polymer droplets are surrounded by the solvent at high pressure. This special environment may provide an opportunity to probe the homogeneous nucleation in a relatively fast-crystallizing polymer melt, and create the circumstances to prepare a single spherulite as one particle. Here in this investigation, integrated spherulites of ultrahigh molecular weight polyethylene (UHMWPE) were explicitly obtained from supercritical ethanol. The result sheds light on the experimental investigation of the formation mechanism of a surface nucleated polymer spherulite, especially the occurrence of a homogeneous nucleus and the growth of lamellae.

The unique spherulites growing from the nascent UHMWPE powder in supercritical ethanol (SC-EtOH) were characterised by SEM and FTIR. Sphere-like particles were obtained from the ethanol suspension (Fig. 1B), which originate from the irregular-shaped nascent powder (Fig. 1A). The spherulitic morphology exactly confirms the classical polymer crystallization model by Wunderlich, deduced from the observation of the early stage of nylon 6 spherulite development.[1] Well-stacked edge-on lamellae of uniform thickness of *ca.* 10 nm are shown (Fig. 1C and D), in good agreement with the general lamellar thickness reported previously.[4,10] More interestingly, the characteristic feature of spherulite, a pair of "eyes" located at the two sides of a nucleation site, can be observed on the surface of almost all the particles. Furthermore, the classical Maltese cross is shown in the POM image and the sizes of the spherulites correspond to SEM observations (Fig. 2A). After melting, the single spherulite morphology could not be retained by recrystallization (Fig. 2B). Therefore, we conclude from the morphology observation that one particle is a single spherulite with a unique nucleation site.

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[a] *Key Laboratory of Engineering Plastics and Key Laboratory of Colloid, Interface Science and Chemical Thermodynamics, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, PR China. E-mail: djwang@iccas.ac.cn; Fax: +86 10 82618533; Tel: +86 10 62556180*
[b] *Graduate University of Chinese Academy of Sciences, Beijing, 100049, P. R. China*

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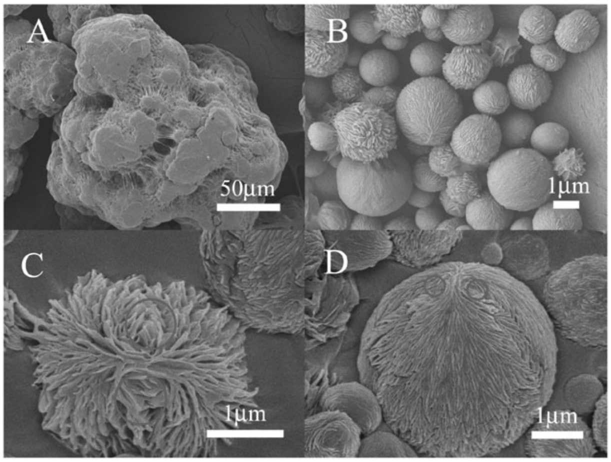


Fig. 1 SEM images of UHMWPE nascent particles (A) and prepared spherulites from SC-EtOH (B, C, D).

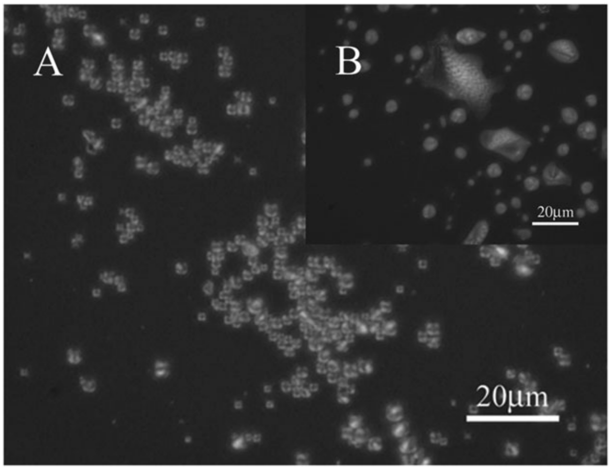


Fig. 2 POM images of spherulites prepared from UHMWPE. A is the directly formed particles on a glass wafer, while inner image B is after melting.

Due to the inadequate amount of polymer particles, micro FTIR spectroscopy was adopted to detect the crystalline variation of UHMWPE before and after being treated with SC-EtOH (Fig. 3). The doublet of 719/730 cm^{-1} is known as the vibrational bands of an orthorhombic crystal in polyethylene, and the stronger absorbance of the 730 cm^{-1} band is indicative of a larger content of orthorhombic crystal.[11] The stronger absorbance of 730 cm^{-1} in spherulites manifestly indicates that UHMWPE crystallizes into an orthorhombic form in SC-EtOH. The relative contents of the orthorhombic phase (intensity ratio of 730/719 cm^{-1}) for spherulite and nascent powder are 0.76 and 0.13, respectively, implying that under supercritical conditions, a stable crystalline phase is formed. The halfwidth of the 719 cm^{-1} peak of spherulites is narrower than that of nascent powder, further indicating the higher crystallinity and more ordered crystal structure of spherulites. Therefore, it is deduced that the polymer chain mobility is greatly promoted in SC-EtOH and it is feasible for the chains to self-organize into a thermodynamically stable structure. There are literature reports of the formation of a metastable hexagonal crystal of polyethylene at extreme high pressure,[6,12] however, SC-EtOH prefers to induce a stable orthorhombic phase.

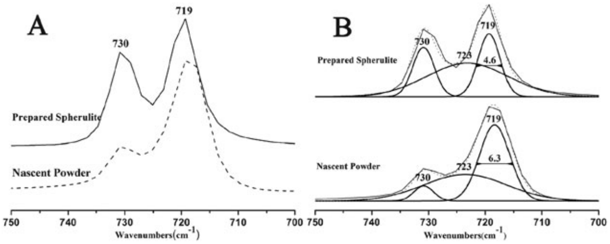
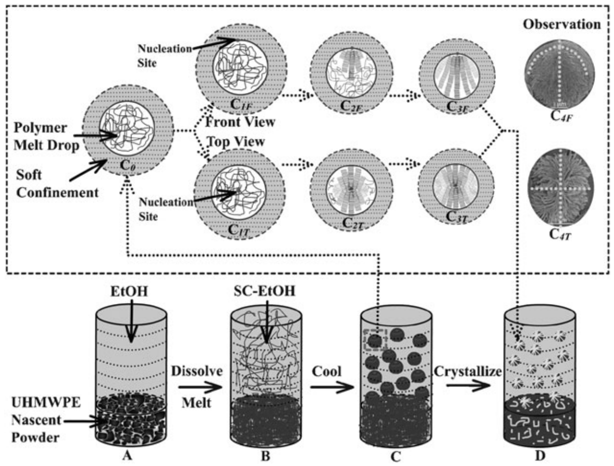


Fig. 3 Micro FTIR spectra of UHMWPE nascent powder (dashed line) and prepared spherulite (solid line). A: original spectra; B: curve-fitting results.

Performing the same experiment on smaller molecular weight polyethylene (see the ESI, Fig. S1†), only spherical particles were produced without a spherulite sheaf-like structure, implying that molecular weight plays an important role in the formation of spherulites. Hu[13] developed the concept of molecular nucleation suggested by Wunderlich and Mehta.[14] It was proposed that shorter chains have a melting barrier lower than the crystallization barrier, and hence will be spontaneously excluded from the crystal growth front, while longer chains survive on the crystal growth front. On cooling from a relatively high temperature, the long-chain fractions of a polydisperse polymer will meet the critical chain length and contribute to the dominant lamellae, while the short-chain fractions meet the critical chain length at lower temperatures, and contribute to the subsidiary lamellar crystals in the spherulite. In the present investigation, there may be no short-chain fractions below the critical molar mass, so only the dominant lamellae contribute to the spherulite frame. The above viewpoint is faithfully confirmed by the present observations, *i.e.*, a separated spherulite frame can be prepared with polyethylene of ultra high molecular weight.

Clarifying the spherulite formation mechanism is a challenging subject because of the difficulty of *in situ* characterization of the crystallization process. We were lucky to obtain the integrated and imperfect spherulites (Fig. 1C and D and more figures in ESI, Fig. S2†), giving a hint for understanding the formation process of spherulites. This is the first time that it has been possible to physically obtain a single spherulite at the stage of polymer crystallization. Fig. 1C and 1D directly show a nucleation site, a pair of "eyes" on a single spherulite, and lamellae orienting as a hyperbola. The gap between two lamellae and the branching phenomenon account for the independent growth of each lamella. A lamellar sheaf propagates from the founding lamella through branching and splaying, and develops into a spherulite with two "eyes" as has been predicted previously.[1,5]

Based on the morphological observations, a mechanism is proposed to interpret the unique spherulite formation in SC-EtOH (Scheme 1). In the heated autoclave, the UHMWPE nascent powder becomes molten as the temperature rises above the melting temperature (141 °C) and ethanol evaporates to gas correspondingly (Scheme 1A). Approaching the vicinity of the ethanol's critical point, the solvency of ethanol increases greatly, owing to its gas-like viscosity and



Scheme 1 Schematic diagram of UHMWPE spherulite formation in SC-EtOH. The lower row describes the experimental procedure, while the upper dashed frame represents the crystallization process from a polymer melt droplet.

liquid-like solubility.[8a,15] Consequently, a certain amount of UHMWPE on the nascent powder dissolves into SC-EtOH, while the bulk UHMWPE melts at the bottom of the container (Scheme 1B). As the temperature starts to decrease, SC-EtOH leaves the supercritical state. When the temperature decreases to below the critical temperature but is still higher than the melting temperature of UHMWPE, the polymer chains separate out to form small melt droplets (Scheme 1C), due to high supersaturation of the polymer chains and the low surface energy of droplets with small size.[8a,15] These UHMWPE melt droplets are confined in the soft confinement of SC-EtOH liquid. With temperature further decreasing, the supercritical state of SC-EtOH gradually vanishes. At the crystallization temperature, the expanded coils will shrink and nucleation occurs, resulting in the formation of the unique integrated polymer spherulites (Scheme 1D).

We argue that the crystallization of UHMWPE starts from homogeneous nucleation in SC-EtOH. One reason is that the nucleation happens within the individual droplets, which disperse in the bulk ethanol. This depresses impurity nucleation by dividing the macromolecular chains into tiny enough portions and most of the droplets will not contain a heterogeneous nucleation site.[16] Turnbull pioneered this study with metal and polymer samples to research the homogeneous nucleation kinetics.[17] Another fact also supports the homogeneous nucleation: with the vanishing of the supercritical state, the impurities dissolved in ethanol will be retained in the solution, while the UHMWPE chains separate out to form melt droplets. Therefore, homogeneous nucleation occurs on the surface of a unique melt droplet (Scheme 1, C_0). The homogeneous nucleation results in the spherulite morphology with two "eyes" (Fig. 1C and D).[1,4] Although the starting mixture is liquid-like in density, its high compressibility allows nucleation to be triggered mechanically (pressure reduction) rather than thermally.[15] The location most sensitive to pressure reduction and temperature decrease is the interface between the polymer melt droplet and ethanol soft confinement. As a result, the concentration of polymer chains will promote the ordered arrangement of chains and overcome the nucleation barrier from the surface free energy of crystallites. Once an embryo has gestated, the nucleation procedure is completed (Scheme 1, C_{1F}, C_{1T}). More specifically, one nucleation site is enough to stimulate the spherulite growth because of the small droplet size of the UHMWPE melt and the fast growth rate of lamellae.

According to Wunderlich,[1] surface-nucleated crystal growth should have its chain axis parallel to the surface for maximum reduction of free energy of nucleation. The direction normal to the surface has the lowest free energy barrier, so the growth rate is the highest. As a result, the kinetics-determined surface nucleation growth morphology is observed in the present research. When a nucleus is formed at the surface, the edge-on orientation is preferred, so a founding edge-on lamella (the longest one in Scheme 1, C_{2F} and C_{2T}) grows at the lateral of the interface from the embryo. The growth of the lamellae will most likely assume the same orientation as the primary nuclei formed at the surface. A lamellar sheaf propagates from the founding one through branching and splaying (Scheme 1, C_{3F} and C_{3T}), and develops into a spherulite with two "eyes" (Scheme 1, C_{4F} and C_{4T}). Conclusively, the formation of unique UHMWPE spherulites from SC-EtOH can be attributed to triple contributions: the surface nucleation, the ultra-high molecular weight, and the softly confined geometry.

We have proved that under the SC-EtOH condition, the combination of large supersaturation and quick nucleation favors the formation of unique spherulites. If given a longer time at 300 °C, the small droplets will coalesce with each other, and bigger spherulites will be formed. This may induce the growth of spherulites from several nucleation sites located on the surface of one droplet. This speculation is successfully confirmed by the experiment of annealing the UHMWPE droplets for another 2 h at 130 °C after melting for 2 h at 300 °C. Fig. 4A and B show a particle with three nucleation sites on the surface. The spherulite boundaries ultimately intersect at one point, implying that the nucleation sites may induce the lamellae growth simultaneously. In this way, an

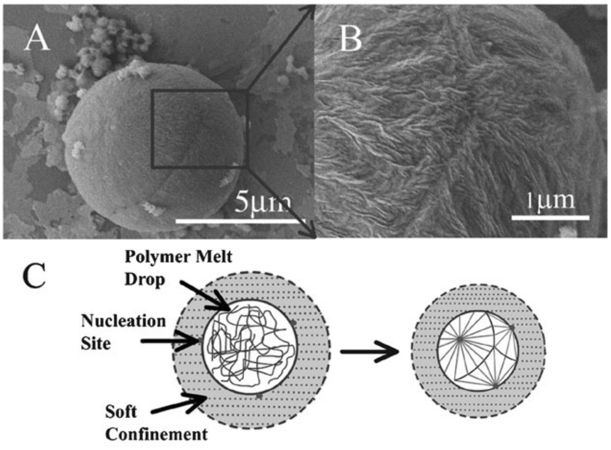


Fig. 4 A, B: SEM images of a spherulite with three nucleation sites on the surface; C: schematic illustration of the formation mechanism of a tri-nuclear spherulite.

UHMWPE particle comprising three spherulites comes into being (Fig. 4C).

In conclusion, we have probed homogeneous nucleation in a relatively fast-crystallizing polymer melt, presenting single spherulite formation in an independent particle of UHMWPE from a softly confined geometry, provided by the supercritical state of ethanol. The unique morphology results from the homogeneous surface nucleation, the ultra-high molecular weight of polyethylene, and the special soft confinement of SC-EtOH. These observations provide the propagating stage from the sheaf-like dendrite to the final spherical crystal, and this stage has been neglected in previous investigations.

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Experimental

Materials and preparation

The UHMWPE (M_w = 3.8 × 10^6 g mol^{-1}, MWD = 6.8) powder is a commercial product of Ticona (Houston, Texas), and ethanol was provided by Beijing Chemical Company. The preparation of the UHMWPE particles was conducted in a custom built high pressure, clamp sealed stainless steel autoclave.[9b] A pre-weighed quantity (0.1 g) of UHMWPE and 4 ml ethanol were added to the autoclave, which was sealed and then heated to 300 °C. A high pressure of 36.0 MPa was reached at this temperature, and the autoclave was kept for 2 h and then cooled down to ambient temperature through water cooling, followed by the releasing of the pressure. A white turbid suspension containing UHMWPE particles was obtained and dried for further characterization.

Characterization

The prepared samples were submitted to scanning electron microscopy (SEM) observation using a JEOL JSM-6700F at an acceleration voltage of 5 kV. Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Nicolet Magna-750 spectrometer equipped with a microscope and a liquid nitrogen cooled MCT detector. IR spectra were recorded at 4 cm^{-1} resolution and 128 scans. Polarized optical microscopy (POM) images were acquired on an Olympus BH-2 instrument equipped with a Panasonic 230 CCD camera. The sample temperatures were controlled with an accuracy of ±0.1 °C using a hot stage (Linkam LTS350) under a nitrogen atmosphere.

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