Crystallization of polycaprolactone with reduced entanglement

Nan Tian[a,∗], Dong Liu[b], Hanghang Wei[c], Yanping Liu[c,∗], Jie Kong[a]

[a] *MOE Key Laboratory of Space Applied Physics and Chemistry, Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Science, Northwestern Polytechnical University, Xi'an 710072, PR China*
[b] *Key Laboratory of Neutron Physics and Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, 621999 Mianyang, PR China*
[c] *National Center for International Research of Micro-Nano Molding Technology & Key Laboratory for Micro Molding Technology of Henan Province, Zhengzhou University, Zhengzhou 450002, PR China*

ARTICLE INFO

ABSTRACT

Structure of polycaprolactone (PCL) crystallized in a wide concentration range was investigated to correlate entanglement content with the formed structure. Mixed solvent constituted by good solvent chloroform and nonslovent ethanol was used to control the concentration crystallization started (c_{onset}, weight fraction), which varied from 0.13 to 0.53. Crystallization at higher c_{onset} was achieved by electrospinning and melt crystallization. The concentration correlates with entanglement number (N) by the scaling law $N/N_0 = \phi^{1.3}$ with ϕ the volume fraction of polymer in solution. In this work, the scaling law was modified as $N/N_0 \approx c_{onset}^{1.3}$ as an approximation. Thickness of amorphous region (l_a) and fusion enthalpy (ΔH) were obtained through small angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC). It is found that l_a increases monotonically with $c_{onset}^{1.3}$ from 4.5 nm to 10.2 nm, and ΔH decreases monotonically from 92 J/g to 50 J/g. The smooth change of l_a and ΔH with $c_{onset}^{1.3}$ indicates increased entanglement leads to thicker amorphous region and lower crystallinity, which is valid even when the entanglement number is as low as one-tenth of that in melt. Moreover, changes in lamellae thickness (l_c) is also discussed.

1. Introduction

Crystallization of polymer is different from the small molecules for its long chain structure. The most striking change is that polymer can hardly crystallize completely [1–3], especially in the commonly used molecular weight range [4–8]. Entanglement has been considered as an important origin of the semi-crystalline character, which restricts the adjustment of segments during crystallization. Meanwhile, products with different entanglement content also show distinctly different properties [9,10]. For example, the nascent ultra-high molecular weight polyethylene (UHMWPE) with less entanglement can be drawn more than 150 times at 120 °C, while the common UHMWPE can be drawn only several times [11]. Since the structure of lamellae is the same, change in the drawability implies that entanglement affects the organization of amorphous region as well [12,13]. Clearly, entanglement plays an important role in crystallization of polymer [2,14]. However, quantitative information about this effect is still lacking. For example, if the entanglement number is reduced to a half of that in melt, how much the crystallinity will increase? How the organization of amorphous part will change? To answer these questions, more effort and also new approach are needed.

The effect of entanglement on crystallization has been investigated by using disentangled polymer melt, while mostly the focus is changes in crystallization kinetics. In the widely used Lauritzen and Hoffman (L-H) theory [15], entanglement is taken into account by considering chain diffusion along the reputation tube constituted by entangled chains, which is described as "reeling in" process. At low and moderate undercooling (regime I and II), entanglement induced slowing down of growth rate can be well described. Based on this theory, it is easy to deduce that reduced entanglement will lead to faster crystallization. Though the conclusion is simple, experimental verification is difficult. In polymer melt, the conformational entropy will drive polymer chains to interpenetrate with each other, thus entanglement will spontaneously form. To reduce content of entanglement, freeze-drying of dilute solution [16–18], crystallization from solution [19,20], crystallization under high pressure [21] and also polymerization with special catalytic [22–24] have been used. The obtained polymers with reduced entanglement are melted at relatively low temperature, during which recovery of entanglement is limited. The content of entanglement can be further tuned by melting time qualitatively. During crystallization, the growth rate of spherulites is usually measured. With increasing melting time (more entanglements), the growth rate slows down

towards the value of well entangled melt [16,19]. The qualitative agreement between theory and experiment indeed reflects the influence of entanglement in crystallization kinetics. Nevertheless, low-temperature melting may result in incomplete destruction of crystal, which is also reported to enhance the growth rate [25]. More importantly, the crystallinity change in disentangled sample is seldom considered [26]. This overlook may come from the high crystallization temperature used, which leads to relatively slow growth and fast chain relaxation.

Compared to melt, crystallization in solution provides a better chance to reveal the topological effect of entanglement. As mentioned above, the spontaneous recovery of entanglement [18] during melting makes control of entanglement content severely restricted. One promising way is slow melting induced heterogeneous distribution of entanglement, while it seems restricted in UHMWPE at present [27,28]. When considering solution, this problem is easier to resolve. In solution, the possibility of interpenetration between different chains is reduced by dilution, thus entanglement becomes less at lower concentration. For most used polymers, the critical concentration for occurrence of entanglement is within 10% [29,30]. The low critical concentration makes it possible to change entanglement number in a rather wide range. Meanwhile, in solution polymer chains are separated by large amount of solvent. The interaction with solvent and entropy gain from mixing lead to a stable state with reduced entanglement [31]. These two advantages are favorable to investigation of influence of entanglement in a wide range of entanglement content.

The entanglement content in solution can be estimated theoretically, thus a semi-quantitative relation between entanglement and crystallization can be established. If entanglement is considered as transient crosslinking point, its content can be estimated by the plateau of storage modulus [32,33], similar to that in rubber elastic theory. In solution, the interpenetration of polymer chains is reduced by solvent and less entanglement is expected. However, direct measurement of entanglement content, e.g. by small amplitude oscillation shear, is usually difficult for crystallizable polymer. The difficulty lies in the fact that fast chain relaxation in solution requires measurement at low temperature, especially for the commonly used polymers with a molecular weight of order of 10^5 g/mol. Under this condition, crystallization will happen and prevent precise rheological measurement. Fortunately, the reduction of entanglement in solution can be described by a power law

$$N(\phi) = N_0 \phi^{\alpha} \tag{1}$$

where N_0 is the entanglement number in melt, ϕ is the volume fraction of polymer in solution and α is the dilution exponent. Though the value of α changes with used model, the power law is still valid [14]. This equation bridges the concentration of solution with entanglement number [31]. Note that entanglement number also depends on solvent quality. For θ and good solvent, the entanglement number has been predicted to be proportional to $\phi^{1.3}$ in both semi-dilute and concentrated solution [34,35]. With this universal scaling law, a semi-quantitative correlation between entanglement content and crystallization behavior can be established approximately.

In this work, crystallization of PCL with different entanglement content was investigated. Ethanol was used as a non-solvent to tune the concentration crystallization starts (c_{onset}). Electrospinning and melt crystallization were used to further expand the concentration range. The changes in thickness of amorphous region and fusion enthalpy were analyzed, and entanglement number was estimated by scaling law $N/N_0 \approx c_{onset}^{1.3}$ approximately. Based on the information, a phenomenological relation between concentration determined entanglement number and structure parameters was established.

2. Experimental section

2.1. Material

Polycaprolactone (PCL) was purchased from Sigma-Aldrich, which has a number-averaged molecular weight of 80,000 g/mol. Chloroform ($CHCl_3$) and ethanol (EtOH) were used as received.

2.2. Sample preparation

PCL solution with a concentration of 0.15 g/ml (15% w/v) was first prepared at room temperature (25–27 °C). The solvent used was a mixture of ethanol and chloroform, of which the volume ratio of ethanol to chloroform is 1.9:1, 1.4:1, 1.0:1, 0.5:1, 0.3:1 and 0:1, respectively. The highest ratio 1.9:1 was selected since for 15% (w/v) solution slightly higher ethanol content will lead to precipitation of PCL, thus this ratio gives the lowest c_{onset} at room temperature. For other ratios, ethanol content was reduced so c_{onset} gradually increases. The corresponding weight fraction of PCL in solutions with deceasing ethanol content ranges from 0.13 to 0.09. After addition of PCL granule, the mixture was stirred for two days to ensure full dissolution, during which evaporation of solvent was prevented by sealing with a rubber gasket.

For slow evaporation, 5 mL solution was put in a bottle with 24 mm diameter to evaporate the solvent at room temperature (25–27 °C). Depending on the content of ethanol, crystallization of PCL began within several hours to two days, which was determined by appearance of white precipitation of PCL. The weight loss was recorded to calculate the weight fraction of PCL at the beginning of crystallization, which will be referred to as c_{onset} hereafter. After most solvent was removed, the obtained samples were further dried in vacuum for three days at 35 °C. These samples will be referred to as PCL1.9, PCL1.4, PCL1.0, PCL0.5, PCL0.3 and PCL0.0, respectively. Note that the actual ratio of ethanol to chloroform at c_{onset} is different from the initial value. Here the names PCL1.9-PCL0.0 are used just for convenience of description.

Electrospinning at room temperature was carried out for the sake of rapid evaporation. During electrospinning, a 2 mL syringe and a blunted 21-G needle was used. The flow rate was set as 400 μl/h. A positive 10 kV was imposed to the solution and a negative 2 KV was added to the collecting plate. The distance between needle and the plate was 15 cm. The obtained samples were dried under vacuum at 35 °C for two days. These samples will be referred as PCL1.9-ES, PCL1.4-ES, PCL1.0-ES, PCL0.5-ES, PCL0.3-ES and PCL0.0-ES, respectively. Similarly, the names are used just for convenience of description.

Melt crystallized PCL (PCL-mc) was prepared by melting PCL at 100 °C for 10 min and then cooling it to room temperature with Linkam HFSX350 hot stage. The heating and cooling rate was 10 °C/min.

2.3. Characterization

2.3.1. Differential scanning calorimetry (DSC)

DSC measurements were carried out on DSC Q2000 (TA Instruments). The samples were first melted at 100 °C for 10 min to erase the thermal history. After that the samples were cooled to −20 °C and held for 5 min for completion of crystallization. In all the measurements, the heating and cooling rate was 10 °C/min. The fusion enthalpy of PCL with 100% crystallinity was taken as 136 J/g [36].

2.3.2. Small-angle X-ray scattering (SAXS)

SAXS was conducted in the beamline of BL16b of Shanghai Synchrotron Radiation Facility [37]. The wave length was 1.24 Å. A Mar-165 CCD was used as detector, which has 80 × 80 μm pixel. The sample-to-detector distance was calibrated as 2070 mm. Lorentz correction was applied to all the one-dimensional (1D) intensity profile. Scattering invariant Q was calculated by Eq. (2):