Polymer 131 (2017) 68–72

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

# Extension decelerated crystallization in γ-irradiated isotactic polypropylene: The role of asymmetric chain relaxation

Jianzhu Ju [a], Fengmei Su [a], Zhen Wang [a], Haoran Yang [a], Xiaoliang Tang [a], Xiaowei Chen [a], Yankun Lv [a], Jie Lu [a], Nan Tian [b, *], Liangbin Li [a, **]

[a] *National Synchrotron Radiation Lab, CAS Key Laboratory of Soft Matter Chemistry, University of Science and Technology of China, Hefei, China*
[b] *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, China*

ARTICLE INFO

*Article history:*
Received 25 May 2017
Received in revised form
16 September 2017
Accepted 26 September 2017
Available online 27 September 2017

*Keywords:*
Isotactic polypropylene
X-ray scattering
Flow induced crystallization

ABSTRACT

Extension induced crystallization of γ-irradiated isotactic polypropylene (γ-iPP) was studied with the combination of extensional rheology and in-situ wide-angle X-ray scattering (WAXS). The high gel content and markedly frequency-dependent storage modulus of γ-iPP indicates the occurrence of slight crosslinking accompanied by formation of free branching/dangling chains during irradiation. With WAXS, it is found that an abnormal slowing down of crystallization occurs when engineering stress passes its maximum. Lamellar network built of parent and daughter crystal also appears in this region, where daughter crystallization is commonly frustrated under such strong flow. Further increasing strain, crystallization is accelerated gradually and the acceleration becomes more significant after occurrence of strain-hardening. Interestingly, the orientation of crystal increases monotonically during this process. It is supposed that the difference in relaxation rate of cross-linked network and free branching/dangling chains is the origin of the abnormal deceleration and unique structure morphology.

## 1. Introduction

Flow-induced crystallization (FIC) of polymer is an important issue in both industry and academia. It has been found that the final properties of products, e.g. modulus, strongly depend on the flow field during processing [1,2]. The widely accepted mechanism is that chain conformation can be modified when relaxation of polymer is slower than the deformation rate, leading to crystals with different orientation, size, crystal forms and morphologies [3–7]. Given the polydispersity of common polymer, an interesting question in FIC is how chains with different relaxation rate response to the flow field and then crystallize.

FIC of polydisperse melt has been intensively investigated for decades, in which the relaxation rate of different chains is still comparable [8,9]. In practice, the polydispersity of polypropylene and polyethylene seldom exceeds 10 and the molecular weight usually is above $10^5$ g/mol. In these systems, shorter chains have to relax synergistically with longer chains [10,11], even though their relaxation time can be as large as two orders of magnitude shorter than the longer ones. These systems are defined as the dynamically symmetric system [12,13]. Long chains are found to accelerate crystallization more effectively for larger deformation during flow and slower relaxation after flow [14]. The final orientation and morphology of crystal can be also changed by adding long chains [15,16].

FIC in dynamically asymmetric systems, where parts of chains relax much faster, has not draw much attention and may provide new ways to tailor the formed structure. One extreme example is the semidilute solution [17–20]. Hashimoto et al. has shown that shish-kebab structure will form in the sheared semidilute solution of polyethylene through stress-concentration coupling induced phase separation [19,20]. In the early stage, solvent is squeezed from polymer coils to release stress for their much faster diffusion. Then domains with higher polymer concentration appear and assemble to form shish-kebab structure. Similar asymmetric relaxation is supposed to happen in partially cross-linked polymer. Irradiation is usually applied to induce crosslinking in polymer and irradiation crosslinking is an effective method to enhance thermal resistance [21]. During irradiation, chain scission and crosslinking

---

[*] Corresponding author.
[**] Corresponding author.
*E-mail addresses:* tiannan@nwpu.edu.cn (N. Tian), lbli@ustc.edu.cn (L. Li).

https://doi.org/10.1016/j.polymer.2017.09.059

can both happen, resulting in coexisting cross-linked network and free chains [22]. For the cross-linked part, relaxation is prevented by chemical bonding [23,24]. Meanwhile, the free chains can disentangle and diffuse freely at long range. It is similar to the semidilute solution, where the free chains play the role of fast solvent and cross-linked strands response as slow polymer chains. However, in partial cross-linked polymer at high temperature, how the crystallization will proceed is an open and interesting problem.

In this work, extension induced crystallization of γ-irradiated isotactic polypropylene (γ-iPP) was investigated. The nucleation rate and final structure are measured by wide-angle X-ray scattering (WAXS). Three regimes can be defined from both stress response and crystallographic results. Based on above results, the structure transition related to chain stretch and asymmetric relaxation is discussed.

## 2. Experiment and materials

### 2.1. Materials and sample preparation

The isotactic polypropylene material was kindly supplied by SABIC-Europe with a number- and weight-average molecular weight ($M_n$ and $M_w$) of 150 and 720 kg/mol, respectively. Chemical grade trimethylolpropane triacrylate (TMPTA) was used as cross-linking agent with an amount of 0.2 mmol in 100 g iPP. Irradiation dose was 10.4 kGy with a dose rate of 0.65 kGy/h.

### 2.2. Material characterization

The gel content was measured with Soxhlet extraction as 61.2%. The Small-amplitude oscillation shear (SAOS) measurements were performed with Anton Paar MCR302 rheometer. Differential scanning calorimetry (DSC) measurement was performed on TA Q2000. The fusion enthalpy is 66.64 J/g, which is much smaller than linear iPP value of 148 J/g [25,26].

### 2.3. Scanning electron microscope (SEM)

Crystallized samples were etched by 3 wt% solution of potassium permanganate in a mixture of sulphuric acid and orthophosphoric acid. Then the samples were covered with a thin layer of gold and observed with a Schottky Field Emission Scanning Electron Microscope, operating at 10 kV.

### 2.4. Extension experiment and X-ray measurement

A home-made extension rheometer was employed to impose extensional flow, which has been described in detail somewhere else [27]. The sample was mounted on two spindles and extension was carried out by rotating the spindles oppositely. The stress during extension was measured by a dynamic torque sensor and recorded simultaneously.

Sample was firstly heated to 210 °C and kept for 10 min to erase the thermal and mechanical histories. Then it was cooled to the crystallization temperature 150 °C with a cooling rate of 2 °C/min. Immediately after reaching 150 °C, extension was carried out with the homemade extension rheometer. The strain rate was kept at a constant of 5 $s^{-1}$ and the strain was changed. Starting and braking time are both limited to around 15 ms, thus the strain rate can be regarded as constant during extension. The structure evolution was monitored by in-situ 2D wide-angle X-ray scattering (WAXS). The experiments were performed at 1W2A SAXS station at Beijing Synchrotron Radiation Facility (BSRF) with X-ray wavelength of 0.154 nm. Time resolution is 30 ms during the extension and 1 s during the crystallization. Ex-situ small angle X-ray scattering (SAXS) experiments was performed at the beamlines BL16B of Shanghai Synchrotron Radiation Facility (SSRF) with wavelength of 0.124 nm.

## 3. Results

SAOS was applied to characterize the chain structure of the γ-iPP, since degradation of iPP is prior to crosslinking during γ-irradiation. The results at 200 °C are shown in Fig. 1(a). For the γ-iPP, it is found that with increasing frequency the storage modulus changes from $1.64 \times 10^4$ Pa to $1.02 \times 10^5$ Pa, much higher than the loss modulus in the whole range. Combining with the measured gel content of 61.2%, it can be concluded that crosslinking network is formed in the system. However, the significant increase of storage modulus is different from the commonly found plateau in a crosslinking network. On the other hand, storage modulus of linear iPP varies between $2.11 \times 10^3$ Pa to $1.59 \times 10^5$, showing a stronger frequency dependence. The value is also close to that of γ-iPP. SAOS results clearly point to a system with low crosslinking density and high content of free/dangling chains.

The engineering stress-strain curve of γ-iPP during extension with strain of 2.9 is presented in Fig. 1(b). The stress increases linearly at first and passes a maximum at strain around 0.5. Then the stress begins to decrease slowly with strain. The decline stops at strain around 1.9, where a total decrease of 0.1 MPa is found. Further increasing strain, strong strain hardening happens and the stress increases rapidly to 1.4 MPa. Based on the stress response, the extension process can be divided into three regimes, corresponding to the initial increase of stress (regime I), the slight decrease of stress (regime II) and the strain hardening (regime III), respectively. Crystallization can be induced during the extension as seen in the WAXS patterns in Fig. 1(c). At the strain of 2.25, highly oriented crystal signal can be discovered, right after strain hardening.

2D WAXS patterns during crystallization are given in Fig. 2(a), where results after extension with strain of 0.25, 0.8, 1.4 and 2.9 are shown as representatives. With a strain of 0.25, weak scattering of crystal can be found at around 400 s. The intensity increases with time, and becomes unchanged at around 1000s. It is clear that the scattering of (040) plane at meridian direction is lower than that at vertical, indicating the formation of oriented crystals. When strain is increased to 0.8 and 1.4, it is interesting to find that the scattering of crystal occurs at around 600 s and 500 s, respectively. Meanwhile, the intensity increase lasts 1500 s and 1800 s, longer than that with strain 0.25. These changes seem to point to a slower nucleation and crystallization, even though larger strain is used. As seen in Fig. 1(c), for strain 2.9, scattering of highly oriented crystal can be found during the extension. The intensity increase is rather rapid, which takes less than 300 s. Clearly, the transition in crystallization kinetics shows a close relation with changes in stress response.

Contrast to the nonmonotonic kinetics, the azimuthal distribution of scattering of (040) continuously concentrates along vertical, indicating a monotonic increase of orientation of crystal. The orientation parameter is shown in Fig. 2(b). Indeed, a monotonic increase with strain is found. On the other hand, the value is high even with the smallest strain of 0.25, which may be induced by the negligible relaxation of cross-linked part during crystallization.

The time evolution of summed WAXS intensity is given in Fig. 3(a). It is clear that crystallization is faster with a strain of 0.25 and 0.4 than that with a strain of 0.8 and 1.4. While when strain enters regime III (strain 2.0 and 2.9), crystallization becomes much faster. To give a quantitative analysis, the half crystallization time ($t_{1/2}$) and induction time are shown in Fig. 3(b). Here $t_{1/2}$ is defined as the time that normalized intensity reaches 0.5 and induction time is defined as the intersection of base line and the tangent of