Flow Induced Conformation Ordering, Density Fluctuations and Crystallization of Cross-linked Isotactic Polypropylene

Fengmei Su

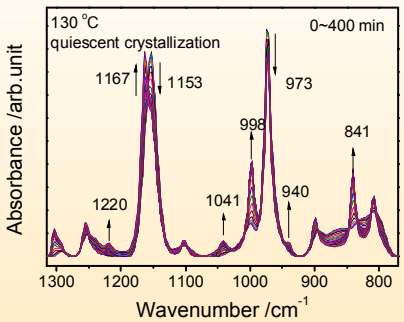
National Synchrotron Radiation Lab (NSRL) & School of Nuclear Science and Technology
Department of Polymer Science and Engineering & CAS Key Lab of Soft Matter Chemistry
University of Science and Technology of China (USTC), Hefei, China

Introduction

Polymer materials are most often processed in the molten state and therefore subjected to (strong) flow fields when shaped into final products. It is well-known that flow fields not only can accelerate crystallization kinetics but also can radically change the crystalline morphology from isotropic spherulites to highly oriented shish-kebab crystals. Such a morphological transition is important since these building blocks determine the final (mechanical and other) properties of products. Therefore, a full understanding of the relation between flow fields, crystallization kinetics, and the resulting morphology is required to design processing procedures for optimal properties. In order to figure out the effect of flow on the polymer melt during flow, extension flow in cross-linked isotactic polypropylene were combined with in-situ FTIR, synchrotron radiation small and wide angle X-ray scattering to follow the conformation evolution, density fluctuations and crystal formation process.

Experiments and data

It has been well established that specific regularity bands are related to the different critical length "n" of isotactic sequences. The minimum n values for appearance of bands at 973, 998, 841, and 1220 cm^{-1} are 5, 10, 12, and 14 monomer units in helical sequences, respectively. Apparently, the larger the value of n, the higher the degree of order of the correspondent regularity bands. FTIR spectroscopy has been used to determine the degree of order of various regularity bands.



A ordering parameter (S) was proposed to present the order degree of the melt, which is absorbance ratio of 998 and 973 cm^{-1}. $S=I_{998}/I_{973}$.

Fig 1. FTIR spectrum of iPP samples during crystallization of iPP sample at 130 °C.

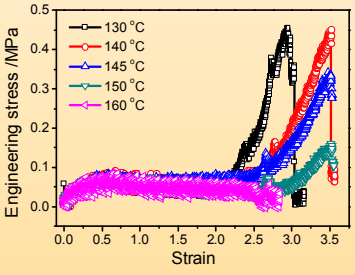


Fig 2. Engineering stress-strain plot of extensional flow with a rate of 0.02 s^{-1} at different temperature.

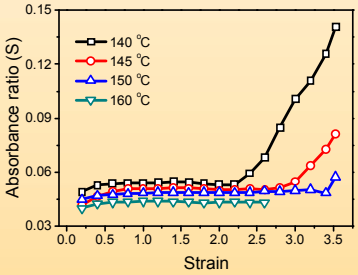
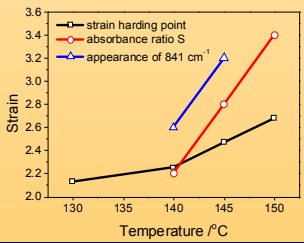


Fig 3. Evolution of absorbance ratio S during extensional flow at different temperature.



The rapid increase of absorbance ratio S represents development of order degree of the melt. The corresponding strain of strain-harding and rapid increase of S different at different temperature.

Fig 4. Strain harding and inflection point of absorbance ratio S, and corresponding strain of appearance of 841 cm^{-1}.

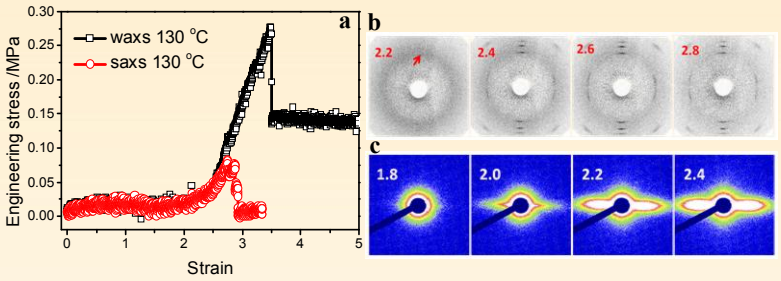


Fig 5. (a)Engineering stress-strain at 130 °C for waxs and saxs experiment; (b) and (c) are waxs and saxs patterns during extensional flow with rate of 0.02 s^{-1}.

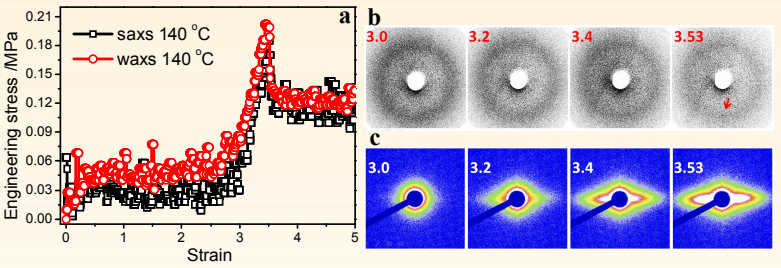


Fig 6. (a)Engineering stress-strain at 140 °C for waxs and saxs experiment; (b) and (c) are waxs and saxs patterns during extensional flow with rate of 0.02 s^{-1}.

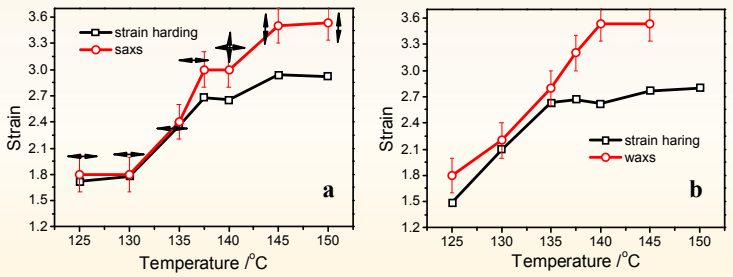


Fig 7. Appearance of saxs (a) and waxs (b) signal at different temperatures.

At temperatures of 135 °C or lower, streaks at meridian direction on saxs pattern and crystalline signal at waxs patterns appear right at strain-harding point; at temperature of 140 °C, streaks at both meridian and equator direction, while at higher temperature than 145, no crystalline signal appears on waxs patterns though steaks appears on saxs patterns.

Discussion and Conclusion

The experiment results put forward the question that what structure forms and what sustain tension when stretching the iPP network? According to results, three regions can be divided.

(i) At the first region (125~135 °C), crystallization appears at the strain-harding point and no shish forms before crystallization which due to high super-cooling degree and crystallization is rather easy.

(ii) At the second region (137.5~140), shish and lamella forms at the same time, it means that at this region, the lamellar crystal can't sustain tension and the network was stretched which induces the formation of shish.

(iii) At region 3, lamellar doesn't form before shish, this may due to the low super-cooling degree, and the iPP network sustain tension. Combine the FTIR result, it can be fond out that, coil-helix transition takes place at this region.

Publication

Fengmmei Su, Weiming Zhou, Xiangyang Li*, Youxin Ji, Kunpeng Cui, Zeming Qi and Liangbin Li*. *Flow-Induced Precursors of Isotactic Polypropylene: An in Situ Time and Space Resolved Study with Synchrotron Radiation Scanning X -ray Microdi ffraction.*
Macromolecules 2014, 47, 4408-4416

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