

Melting of polymer crystals below the melting point

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高分子鎖は折りたたまれて結晶化することにより、非常に薄い板状単結晶として析出する。そこで Gibbs-Thomson 効果により、平衡融点以下の温度で融解する。この融解キネティクスに関して、通常の結晶融解の常識に反する非常に特殊な振る舞いを実験的に見いだした。この振る舞いは高分子性に由来するエントロピー障壁により矛盾なく説明できる。

Our basic understanding of crystal melting is still quite primitive. Since the melting is supposed to proceed without any activation processes, such as nucleation, the kinetics is believed to be limited by thermal diffusion, and hence the investigation of the process is treated as a trivial application of diffusion theory. Then, the melting rate is linearly dependent on the degree of effective superheating, which corresponds to the difference between the set temperature and the temperature at the crystal interface keeping the temperature at the melting point.

Due to the Gibbs-Thomson effect of the thin lamellar crystallites with chain folding, polymer crystals melt below their equilibrium melting points. The melting kinetics can be quite unique because of this characteristic. By thermal analysis, we have previously reported that the superheating dependence of the melting rate must be nonlinear, and hence there should be some activation barrier in this process [1]. We have proposed that the barrier can be due to the excess work for the nucleation of melting hole or due to the entropic barrier caused by the pinning of the melting interface. The distinction needs direct observation of the melting interface, which is the subject of the present report.

We have examined the melting of polyethylene crystals which is prepared by isothermal crystallization and subsequent quenching in advance. The sample was then set in a hot cell at the melting temperature for a certain period of time, and quenched. After the procedure, we obtained the crystallites on the course of melting surrounded by the amorphous and small crystallites portions. By SPM observation of the samples after chemical etching, which preferentially removes those quenched portions, we have concluded that the melting does not need the melting holes and proceeds from the outer edge, as is the case of ordinary crystals. Therefore, it is most probable that the melting kinetics is limited by the entropic barrier caused by the pinning of the melting interface. The conclusion is supported by the direct observation of the melting velocity, which showed an exponential increase with increasing set temperatures. This will be the direct confirmation of the active pinning barrier, which can also be activated in the course of crystallization [2]; the identification in crystallization was almost impossible due to the dependence on supercooling similar to that of surface nucleation process.

[Reference]

[1] A. Toda, M. Hikosaka K. Yamada: *Polymer* **43** (2002) 1667.

[2] D. M. Sadler, *Nature* **326** (1987) 174.

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