Looking at polymer crystallization with SALS

Looking at Polymer Crystallization with SALS

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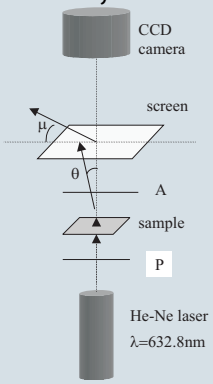
Introduction

Crystallization of polymers during processing affects the properties of the final products. Recently, nucleation phenomena is subjected to an increasing interest. One of the promising techniques to study the evolution of the early stages of crystallization is Small Angle Light Scattering (SALS) [1, 2].

Method and analysis

Samples of isotactic polypropylen iPP HD120MO (Borealis) with thickness of $40\mu m$ are inserted in a LINKAM hot-stage at a certain temperature $T_{cr}(125^0C - 145^0C)$ and the crystal development during isothermal crystallization at T_{cr} is observed by SALS.



parallel mode Vv: $P||A$
crossed mode Hv: $P\perp A$

Debye-Bueche approach:

$I(q) = 1/(A + Bq^2)^2$ (1)

I - scattering intensity

$q = (4\pi/\lambda)sin\theta/2$ - scattering vector

For crystallization kinetics [1] :

$Q_\delta = \int_0^{+\infty} I_{Hv} q^2 dq$ (2)

$Q_\eta = \int_0^{+\infty} (I_{Vv} - \frac{4}{3} I_{Hv}) q^2 dq$ (3)

density fluctuations $< \eta^2 > \propto Q_\eta$

orientation fluctuations $< \delta^2 > \propto Q_\delta$

Figure 1. *Small Angle Light Scattering set-up.*

Parameters to obtain:

$\Rightarrow$ time evolution of Q_η and Q_δ

$\Rightarrow$ R_{sph} - from θ at which I_{Hv} has a max

$\Rightarrow$ correlation length $\xi = \sqrt{(B/A)}$ - from eq.(1)

Experimental observations and Results

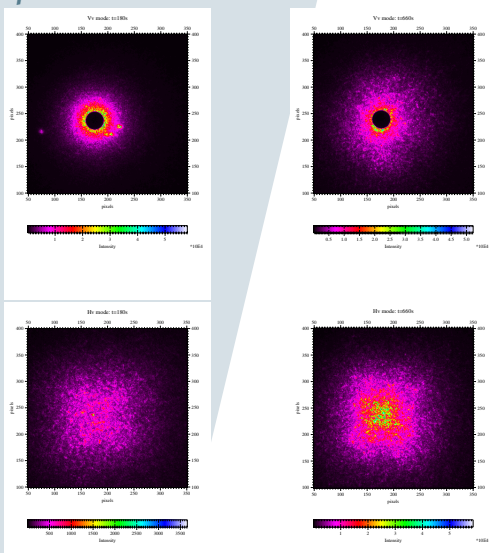


Figure 2. *Scattering patterns obtained by P||A (top) and by $P\perp A$ mode (bottom) at $T_{cr} = 135^oC$; q-scale:$100pixels = 1.5\mu m^{-1}$.*

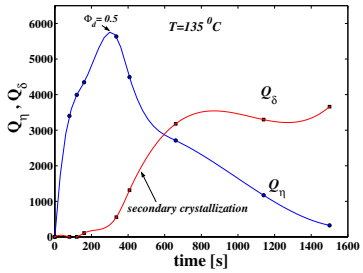


Figure 3. *Time evolution of Q_δ (for $\mu = 45^o$) and Q_η (for $\mu = 0^o$) invariants during crystallization of iPP at $T_{cr} = 135^oC$.Φ_d is the volume fraction of growing crystals.*

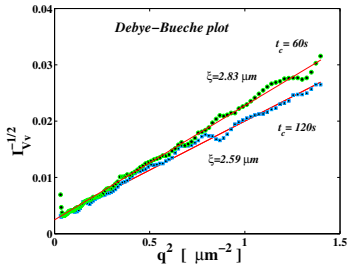


Figure 4. *Debay-Bueche plots for parallel mode Vv at different times for $T_{cr} = 135^oC$, and calculated values of the correlation length ξ .*

Table 1. *Spherulite radius R_{sph} of iPP obtained by two techniques - SALS and hot-stage microscopy at different temperatures T_{cr} for a crystallization time of 360sec.*

	R_{sph}, $[\mu m]$	
T_{cr}, $[^\circ C]$	SALS	hot-stage microscopy
125	43.1	44. 4
135	27.9	31.6
140	12.5	-

Conclusions

- The SALS patterns show the expected 2-fold (for parallel Vv mode) and 4-fold (for crossed Hv mode) symmetry.
- Density fluctuations $< \eta^2 >$ appear prior to crystal development and reach a maximum when volume filling Φ_d is 0.5.
- Secondary crystallization is observed after spherulite impingement.
- The good approximation of $I^{-1/2}(q^2)$ with a linear fit confirms the validity of Debye-Bueche approach to evaluate the data from SALS.
- SALS technique could be a very usefull method for future investigations of flow-induced crystallization, where enhancement in crystal nucleation is expected.

References:

[1] Stein, R.S., Cronauer, J., Zachmann, H.G.: *Journal of Molecular Structure*, 1996, 383, 19

[2] Kumaraswamy, G., Kornfield, J.A., Yeh, F., Hsiao, B.S.: *Macromolecules*, 2002, 35, 1762

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