

Trans-States-Repulsion Scenario of polymer crystallization

S. Stepanow

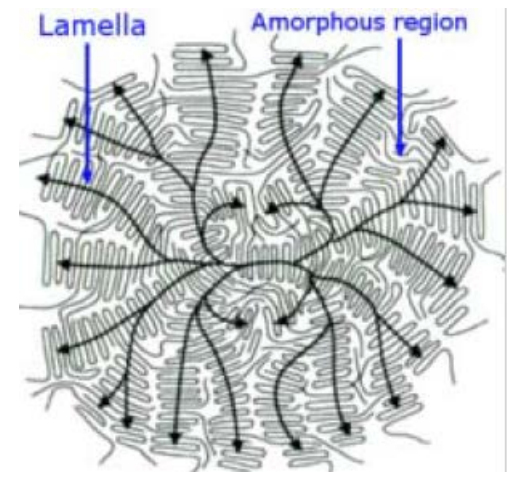
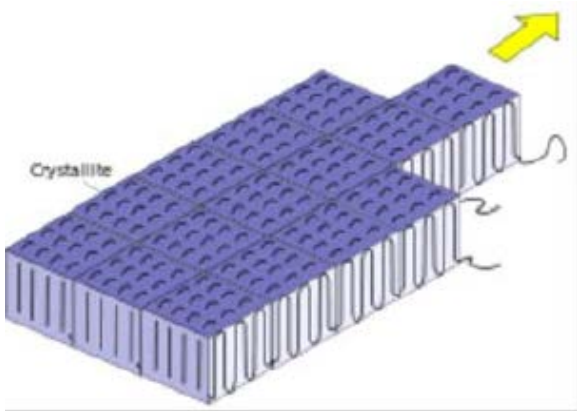
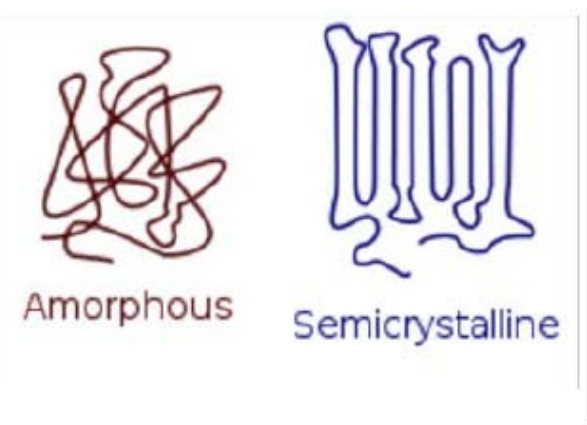
University of Halle, Dept. Phys., D-06099 Halle, Germany

Outline

1. What is polymer crystallization?
 - 1.1 Nucleation theories
2. The trans-states-repulsion (TSR) scenario
 - 2.1 Qualitative idea
 - 2.2 Quantitative consideration, **calculation of lamellae thickness**
 - 2.3 Secondary crystallization, **growth rate**
 - 2.4 Scattering intensity at early (induction) times
3. Summary

1. What is polymer crystallization?

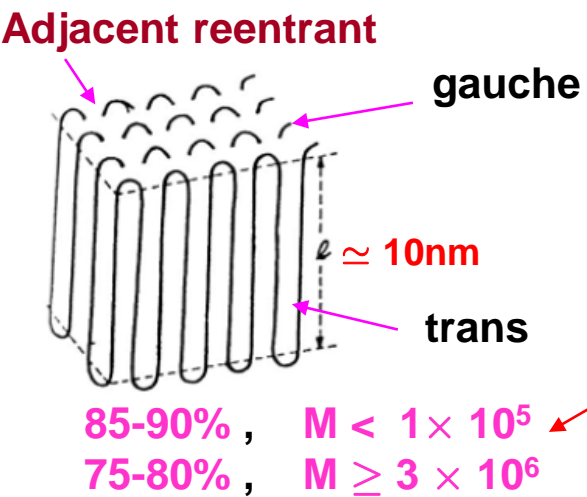
Formation of crystalline regions with thickness $\approx 10\text{nm}$ in supercooled polymer melts



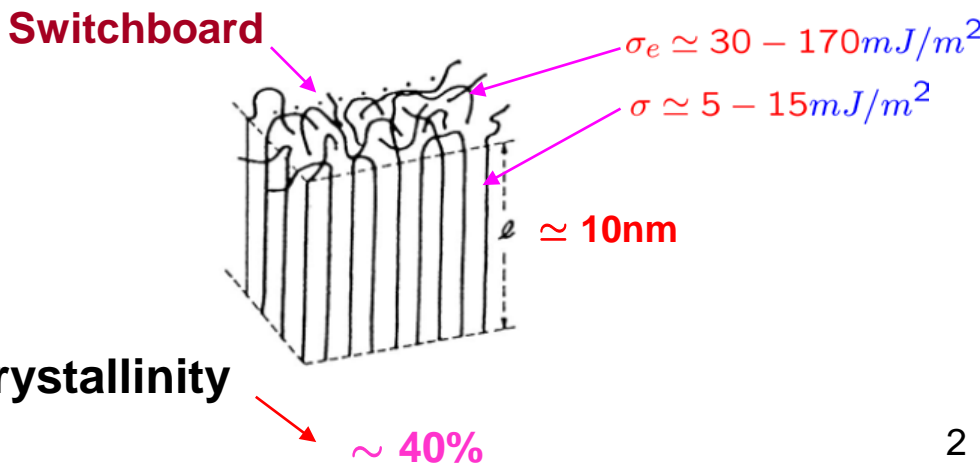
Schematic model of a spherulite

The lamellae are separated by amorphous regions

Crystallization from solution:



Crystallization in melt:

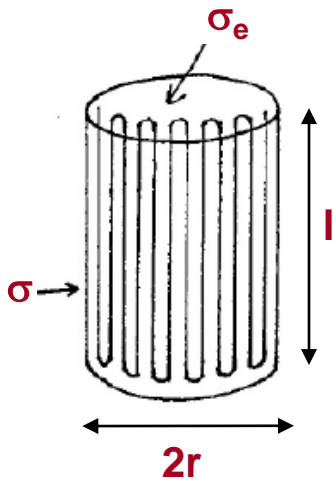


Degree of crystallinity

1.1 Nucleation theories, primary nucleation, crystallization rate

Development of the crystalline phase:

- formation of primary nuclei
- growth of nuclei/ secondary cryst.



$$\Delta G = 2\pi r l \sigma + 2\pi r^2 \sigma_e - \pi r^2 l \Delta g \quad \frac{\partial \Delta G}{\partial l} = 0, \quad \frac{\partial \Delta G}{\partial r^2} = 0$$

Extremum

Critical crystal thickness

Critical crystal area

$$l_1^* = \frac{4\sigma_e}{\Delta g}$$

$$(\pi r^2)^* = \frac{4\pi \sigma^2}{\Delta g^2} \equiv \nu a^*$$

Free energy barrier for critical size nucleus $\Delta G_1^* = \frac{8\pi \sigma^2 \sigma_e}{\Delta g^2}$

Crystallization rate and supercooling

Critical nucleus size $\Delta G_1^* = \frac{8\pi \sigma^2 \sigma_e}{\Delta g^2} \longrightarrow \Delta g = \Delta h \left(1 - \frac{T_m}{T_m^0}\right) = \Delta h \frac{\Delta T}{T_m^0}$

Turnbull and Fisher

$$N = N_0 \exp\left(-\frac{E}{k_b T} - \frac{8\pi \sigma^2 \sigma_e T_m^0}{k_B \Delta h^2 T \Delta T^2}\right)$$

Heterogeneous nucleation: $(\Delta T)^{-2} \rightarrow (\Delta T)^{-1}$

Shortage of nucleation theories: do not explain the lamellae thickness

l_1^*, l_2^* : critical sizes

2. The trans-states-repulsion (TSR) scenario

2.1 Qualitative idea: preferential occupation of **trans states** below T_m



Formations of **stems**



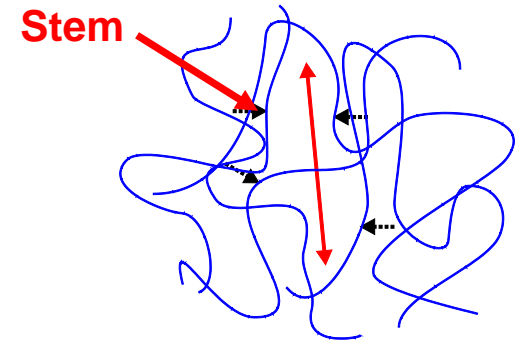
Increase of **repulsion** between the monomers



Orientation of **stems** along one direction: **minimization of the excluded volume** similar to isotropic-nematic transitions in liquid crystals, **Onsager**



Difference to the isotropic-nematic transition: the stems in the case of polymer crystallization do not exist from the beginning, **but emerge due to occupation of trans states, and orient and grow due to repulsive interactions**



2.2 Quantitative consideration, **calculation of lamellae thickness**

Lamella thickness: set equal the formation time of stems τ_s to the **Rouse time** of the piece of the polymer with arc length d_l

$$\tau_s = \frac{d_l}{v_0 + c\Delta T} \leftrightarrow \tau_{Rouse} = \frac{\zeta d_l^2}{3\pi^2 k_B T_m}$$

ζ : monomer friction coefficient



$T \uparrow \rightarrow T_m$

Balance/Interplay between the **nematic ordering of emerging stems** and the **coil structure of polymers on all scales**
(TSR, one-chain effects)

Relation between the temperature and the lamella thickness:

PE, experiments:

$$\zeta = 4.74 \times 10^{-13} N_s/m$$

$$v_0 + c(T_m - T) = \frac{3\pi^2 k_B T_m}{\zeta} \frac{1}{d_l} \quad \rightarrow \quad T = T_c - \frac{3\pi^2 k_B T_m}{c\zeta} \frac{1}{d_l}$$

Modification of the melting temperature: $T_c = T_m + v_0/c$, $T_c > T_m$ for $v_0 \neq 0$

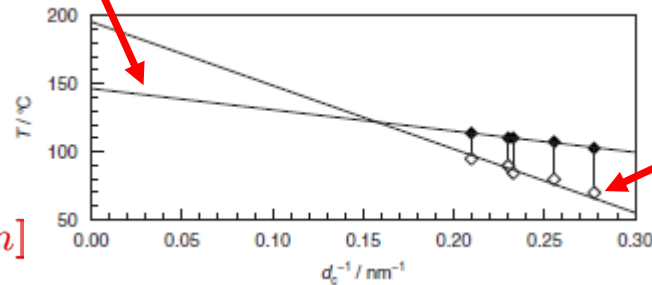
TSR relation:
$$T = T_c \left(1 - \frac{3\pi^2 k_B T_m / T_c}{c\zeta} \frac{1}{d_l} \right)$$

The Gibbs-Thomson relation:
$$T_m = T_m^0 \left(1 - \frac{2\sigma_e / \Delta h}{d_l} \right)$$

Experiments (SAXS, Strobl, ...)

$$\frac{v_0}{c} \simeq 50 \times [K],$$

$$\frac{\partial T}{\partial d_l^{-1}} = -\frac{3\pi^2 k_B T_m}{c\zeta} \simeq -500 \times [K \cdot nm]$$



$$\zeta v_0 = \frac{3\pi^2 k_B T_m}{10} \times \frac{1}{[nm]},$$

$$\zeta c = \frac{3\pi^2 k_B T_m}{500} \times \frac{1}{[K \cdot nm]}$$

2.3 Secondary crystallization, growth rate (TSR, many-chain effects)

Experimental results:

Maximum shifts to the right & decreases with increase of pressure

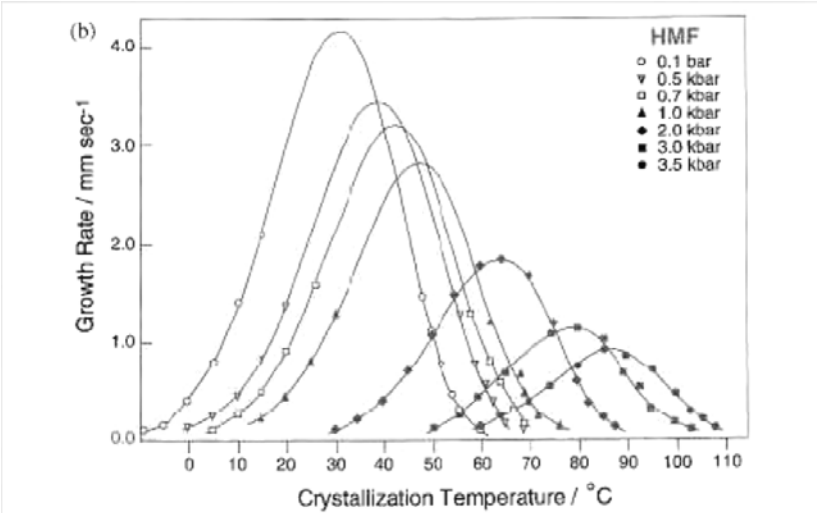


Fig. 12.8 Plot of spherulite growth rates of the low (a) and high (b) melting polymorphs of poly(trans-1,4-isoprene) as functions of temperature at the indicated pressures. (From Davies and Cucarella (40))

Maximum decreases with increase of M_w

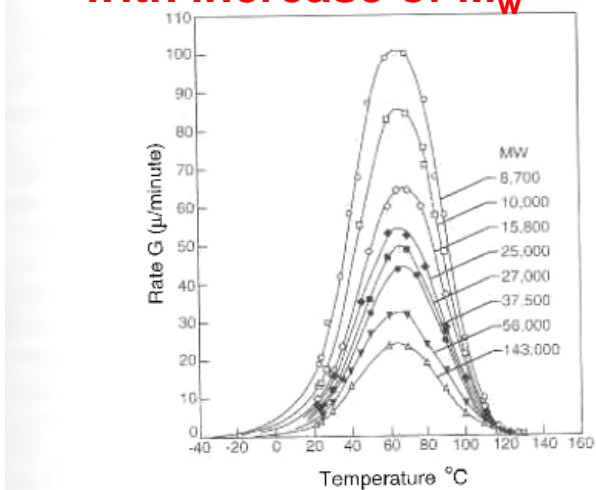


Fig. 9.9 Plot of spherulite growth rates against crystallization temperature for indicated molecular weights. (From Magill (24))

Signature of the TS-Repulsion scenario?

Increase of pressure → increase of the effects of repulsive interactions (frequency of mutual collisions)



Increase of lamellae thickness

↓ $\Delta T > 0$

Multistage/multiscale process (in time) of arrangement of emerging stems at the surface of bundles due to **minimization of the excluded volume**

$$\frac{\partial P(g, t)}{\partial t} = D \frac{\partial^2 P(g, t)}{\partial^2 g} - \frac{\partial}{\partial g} \left(F(g) \frac{\partial P(g, t)}{\partial g} \right) \quad \text{F(g): thermodynamic force}$$

Deposition rate (growth velocity): $\frac{dG}{dt} = -Gvt^{-\alpha}$, $\alpha < 1$, $v \simeq \frac{c}{\Delta T}$ The smaller ΔT , the slower the growth
 $G = \langle g \rangle$

Solution: $G = G_0 \exp \left(-\frac{1}{1-\alpha} \frac{c t_0^{1-\alpha}}{\Delta T} \right)$ t_0 : average time for attachment of a stem

Nonlinear process, compare with: $\delta x \sim t_0$ Ballistic deposition
 $\delta x \sim t_0^{1/2}$ Diffusion

Increase of viscosity with decrease of **T**: $\rightarrow G \rightarrow \exp \left(-\frac{a}{T} \right) G \sim \exp \left(-\frac{a}{T} - \frac{1}{1-\alpha} \frac{c t_0^{1-\alpha}}{T_m - T} \right)$

Degree of crystallinity : $1 - \frac{m_s}{m_0} = e^{-zt^4}$, $z = \frac{\pi G^3 N \rho_s}{3 \rho_L}$
 (The Avrami equation)

2.4 Scattering intensity at early (induction) times

(prior to formation of lamellae)

Temporary contacts of stems



Arising of clusters possessing rigid properties: new phase, order parameter

finite lifetime and a finite size



Modelling: $n \simeq 2$

Consequences for the scattering intensity: $\rightarrow S^{-1}(q) \sim aq^2 + bq^{-n} - \bar{w}(t)$
 Maximum at finite q

$\bar{w}(t)$: average number of consecutively occupied trans states, increases with time

Experiments

- Maximum of $S(q)$ at finite q Imai et al.: $q_{SAXS} \sim 0.1 - 0.2 \text{ nm}^{-1}$
 - Increase of Max. with time Matsuda et al.: $q_{SAXS} \sim 0.3 \text{ nm}^{-1}$
- $q_{SAXS} < q_{WAXS}$

Alternative interpretation: spinodal decomposition, Olmsted et al.

Compare with microphase separation: (de Gennes) polarization of the medium

$\nabla P = \Phi$, Φ : order parameter is the pendant of the charge density



$$b \int P^2 d^3r = b \int \Phi(-q)\Phi(q)/q^2 d^3q \rightarrow \text{The structure factor } S^{-1}(q) \sim aq^2 + bq^{-2} - 2\chi N$$

3. Summary

Repulsions between the monomers, which are due to the increased occupation of trans states below the melting temperature, is considered to be the driving force for polymer crystallization, and is responsible for formation of stems and bundles

Qualitative picture: Balance/Interplay between the nematic ordering of emerging stems and the coil structure of polymers on all scales



✱ Lamella thickness: Formation time of stems = $t_{\text{Rouse}}(d_l)$



Polymer crystallization is of kinetic origin

$T_c > T_m$: minimal supercooling necessary for polymer crystallization

agrees with Strobl's T_{zg}

✱ Growth rate: multistage/multiscale process $\rightarrow G \sim G_0 \exp\left(-\frac{1}{1-\alpha} \frac{c t_0^{1-\alpha}}{\Delta T}\right)$

✱ Scattering intensity: Maximum at $q \neq 0$, and the increase of intensity with time

✱ Kinetic nature of polymer crystallization excludes the nucleation theories !?