

# Kinetics of the development of supermolecular structures in polymers

## 1. Basic principles of kinetic analysis

- 1940 : the general theory of phase transition kinetics was developed by Avrami
- 1945 : Evans published similar equations for the growth of circles and spheres
- 1950' s : Morgan, Flory and Mandelkern used these principles to the crystallization of polymer
- All crystallization processes consist of nucleation and crystal growth.
  - ① Spontaneous nucleation : On cooling molten polymers to a fixed temperature nuclei appear randomly throughtout the volume of the polymer.
  - ② Time dependence of nucleation : Nuclei can appear instantaneously oncooling or during crystallization in the non-transformed phase. In the firstcase the time dependence is of zero order, in the latter it is a first order quantity, so that  $p=Nt$  where p is the number of nuclei per unit volume at time t, N the nucleus formation constant, the number of nuclei formed in unit time.
  - ③ Nature of the growth process : Growth can proceed in one, two or three dimensions resulting in needles, discs or spheres. Growth stops when neighbouring chains are impinged upon.
  - ④ Time dependence of growth : Linear dimension of growing bodies increase in proportion to the time, and generally the following equation is assumed  $r=Gt$  where r is the relevant linear dimension (for example, in the case of spherical growth the radius of the sphere), G is the growth constant.
  - ⑤ Density of the growing units : The transformed phase is not totally crystalline  $\Rightarrow$  assume : the crystallite content and thus the density of the growing units is constant.  $\rho_L$  – the density of the untransformed liquid phase.  $\rho_s$  – the density of the growing solid phase.
- The Avrami exponent the rate constant and the rate constant can be determined from the Avrami equation
- The Avrami exponent value depends on the dimensionality of the growth process, and on the kinetic order of nucleation.  $\rightarrow$  In most general case, where three-dimensional growth is combimed with first order nucleation, the Avrami exponent (n) :  $3+1=4$
- The equation describing the early stages of growth are simple.(up to 30% conversion)

## 2. Description of the early stages of crystallization.

$$\frac{N * m_0 dx}{\rho_L}$$

Nuclei are formed

$m_0$  : the mass of the crystallizing material at  $t=0$

$N$  : the nucleation rate constant in unit volume

$\rho_L$  : the density of the liquid phase

$$\frac{4r^3 \rho}{3} r_s$$

The mass of each spherulite

$r$  : radius of a spherulite,  $r=Gt$  ( $G$  : the growth constant)

$$dm_s = \frac{4}{3} \rho G^3 x^3 r_s N m_0 \frac{dx}{\rho_L}$$

$dm_s$  : the total mass of spherulitic material, present at time  $x$ , and grown from the nuclei formed in the time interval  $dx$

$$m_s = \int_{x=0}^{x=t} \frac{4\rho N G^3 m_0 r_s x^3}{3\rho_L} dx \quad \Rightarrow \quad \frac{m_s}{m_0} = \frac{\rho N G^3 r_s t^4}{3\rho_L} \quad \frac{m_L}{m_0} = 1 - \frac{m_s}{m_0} = 1 - \frac{\rho N G^3 r_s t^4}{3\rho_L}$$

$m_s$  : the total mass of spherulitic material formed after time  $t$

## 3. Description of the total crystallization process including collision.

- There are two main methods in order to describe the later stage of crystallization where the growing bodies meet or collide  $\rightarrow$  differences between results obtained by the two methods are small.

① Evan's method : assume that the centres of growing discs or spheres are fixed  $\rightarrow$  not valid for continuously shrinking systems.

② The treatment proposed by Flory and Mandelkern  $\rightarrow$  more exact result.

- $(1 - m_s/m_0) = (m_L/m_0)$  : the proportionality constant.

$dm_s$  : the mass of crystallizing material in  $dx$

$dm'_s$  : the mass which would crystallize in a absence of collisions

$$dm_s = \left(1 - \frac{m_s}{m_0}\right) dm'_s$$

$\rightarrow$  At the beginning of crystallization : the probability of collisions is small,

the value of the proportionality factor is close to 1

→ As transformation proceeds : the probability of collisions increase continuously  
the proportionality constant approaches zero  
 $dm_s/dm'_s$  is zero when crystallization is complete

• The assumed amount of crystallized material without collisions

$$dm_s = \frac{4}{3} \rho G^3 x^3 r_s N m_0 \frac{dx}{r_L}$$

when impingement is taken into account

$$dm_s' = \frac{dm_s}{\left(1 - \frac{m_s}{m_0}\right)} \Rightarrow \frac{dm_s}{m_0 \left(1 - \frac{m_s}{m_0}\right)} = \frac{4 \rho N G^3 r_s x^3 dx}{3 r_L}$$

Integrating between  $x=0$  and  $x=t$

$$\ln\left(\frac{m_0 - m_s}{m_0}\right) = \frac{-\rho N G^3 r_s t^4}{3 r_L}$$

$$\therefore \frac{m_L}{m_0} = \exp(-z t^4)$$

$$\text{where, } z = \frac{\rho N G^3 r_s}{3 r_L}$$

→ This is the Avrami equation.

#### 4. Analysis of dilatometry data.

The crystallinity ratio is

$$\frac{m_0 - m_L}{m_0}$$

Whereas the total volume at time  $t$  is

$m_0$  : the initial mass of the system is constant,

$V_\infty$  : Final volume ( $= m_0/\rho_s$ ) →  $\rho_s$  is the density of the growing spherulite, and the final density

$$V_t = \frac{m_L}{r_L} + \frac{m_0 - m_L}{r_s} = \frac{m_0}{r_s} + \frac{m_L}{r_L} - \frac{m_L}{r_s}$$

$$V_t = V_\infty + m_L \left( \frac{V_0}{m_0} - \frac{V_\infty}{m_0} \right)$$

$$V_t - V_\infty = \frac{m_L}{m_0} (V_0 - V_\infty)$$

$$\frac{m_L}{m_0} = \frac{V_t - V_\infty}{V_0 - V_\infty} \cong \frac{h_t - h_\infty}{h_0 - h_\infty} = \exp(-zt^4)$$

$$\frac{h_t - h_\infty}{h_0 - h_\infty} = 1 - X_t = \exp(-zt^n)$$

$$\ln \left( \frac{h_t - h_\infty}{h_0 - h_\infty} \right) = \ln(1 - X_t) = -zt^n$$

$$\ln \left[ -\ln \left( \frac{h_t - h_\infty}{h_0 - h_\infty} \right) \right] = \ln[-\ln(1 - X_t)] = \ln z + n \ln t$$

$X_t$ : relative crystallinity.  $n$ : the Avrami exponent.

→  $n$  can be calculated from the slope.

The intercept gives the rate constant ( $\ln z$ ).

$$X_t = \frac{\int_0^t \left( \frac{dH_c}{dt} \right) dt}{\int_0^{t_\infty} \left( \frac{dH_c}{dt} \right) dt} : \text{isothermal}, \quad X_t = \frac{\int_{T_0}^T \left( \frac{dH_c}{dT} \right) dT}{\int_{T_0}^{T_\infty} \left( \frac{dH_c}{dT} \right) dT}, \text{non-isothermal}$$

$$t_{1/2} = \left( \frac{\ln 2}{z} \right)^{1/n}, \text{ for } (m_L / m_0 = 0.5)$$

**Table 6.1**

Exponents  $n$  of the Avrami equation for different nucleation and growth mechanisms

$n$	
$3 + 1 = 4$	Spherulitic growth + random nucleation
$3 + 0 = 3$	Spherulitic growth + instantaneous nucleation
$2 + 1 = 3$	Disc-like growth + random nucleation
$2 + 0 = 2$	Disc-like growth + instantaneous nucleation
$1 + 1 = 2$	Rod-like growth + random nucleation
$1 + 0 = 1$	Rod-like growth + instantaneous nucleation

After Sharples 1966.

5. Experimental data.

- 1954 : Keller, Flory and Mandelkern proved that crystallization proceeds in accordance with the Avrami equation
- Fig 6.1 shows the crystallization of PET as a function of time at three different temperatures  
 → continuous curves are calculated from the Avrami equation assuming.  
 $n = 2$  at  $110\text{ }^{\circ}\text{C}$   
 $n = 4$  at  $236$  and  $240\text{ }^{\circ}\text{C}$

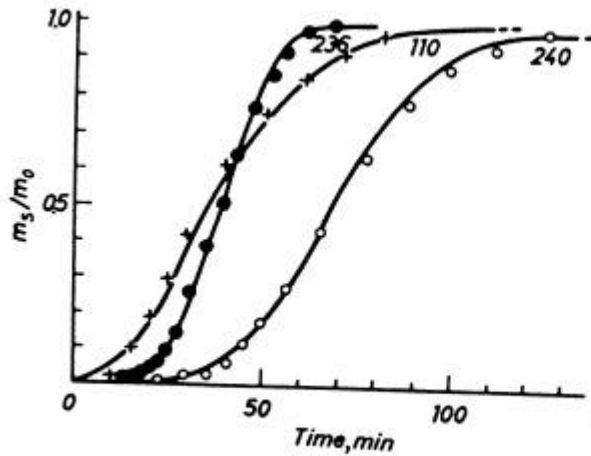


Fig. 6.1. Crystallization isotherms of poly(ethylene glycol terephthalate). (After Keller et al. 1954.)

- Fig 6.2 shows the crystallization of fractionated poly(ethylene adipate) after Takayanagi (1957), plotting  $\ln(-\ln m_t/m_0)$  versus  $\ln t$

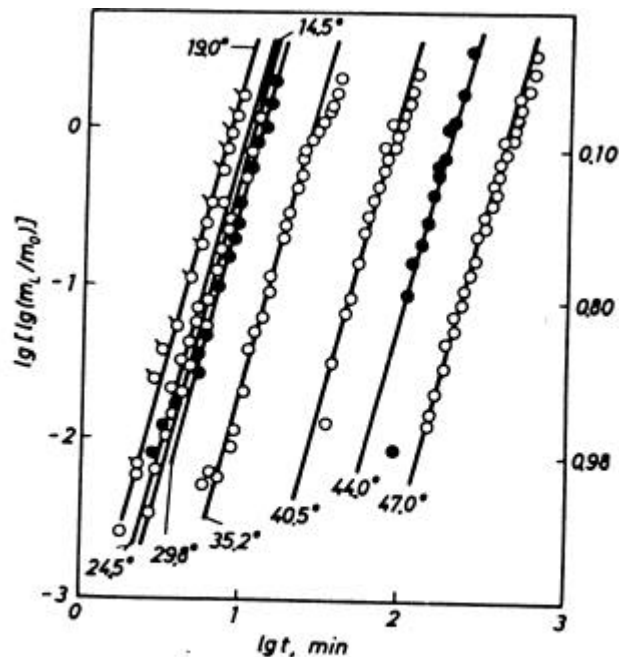


Fig. 6.2. Avrami plots of fractionated poly(ethylene adipate) samples. Crystallized at different temperatures. (After Takayanagi 1957.)

6. Deviation from the Avrami equation.

- Complications appear with systems where  $n$  is non-integer.

→ Such an example is poly(decamethylene terephthalate) shown in Fig. 6.5.

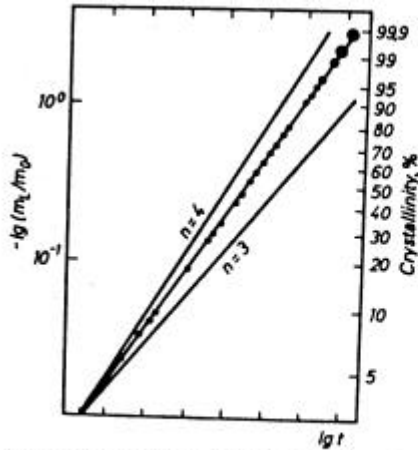


Fig. 6.5. Crystallization of poly(decamethylene terephthalate) at 112.95°C. The Avrami equation seems to be valid, but with fractional exponent  $n = 3.587 \pm 0.008$ . (After Banks et al. 1964.)

- Deviations from the Avrami equation can originate from :

- ① the simultaneous appearance of different growth mechanisms (for example needle- and disc-like)
- ② impurities influencing crystal growth
- ③ the density of the growing phase not being uniform (higher in internal region) so that it is time dependent.

→ The Avrami equation must be modified by a term taking into account the time dependence of  $\rho_s$

$$\frac{m_L}{m_0} = \exp(-zt^4 At^{-m})$$

where  $At^{-m}$  describes the time dependence of  $\rho_s$

- ④ molecular mass distribution can influence crystallization kinetics.

- 1969 : poly(ethylene oxide) were repeated by Hay

→ Avrami exponent can be altered by fractionation.

→ Values of  $n = 2, 2.5,$  and  $3$  were obtained

→ The existence and significance of such fractional exponent is still unexplained.

- The Avrami analysis yields interesting results concerning the time dependence of the crystallization process
- The Avrami analysis is applicable even when the growing units cannot be observed by microscope.

## 7. Secondary crystallization.

- Crystallization does not always end as predicted by the Avrami equation.
- The Avrami equation can only be primary crystallization
- After this process there occurs a secondary crystallization which lasts for a considerable period of time
- Fig 6.6 demonstrates a secondary crystallization process of this kind, where Avrami plots are presented versus time for 4 polyethylene samples.

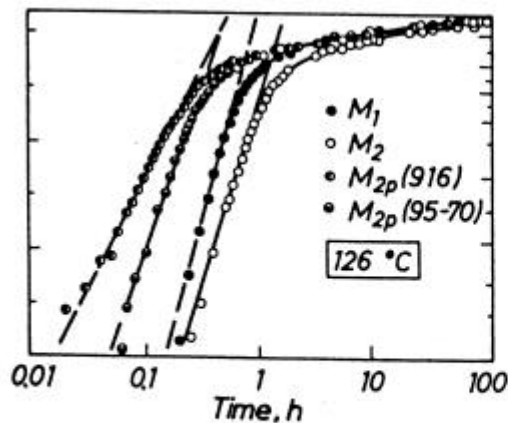


Fig. 6.6. Crystallization of various polyethylene samples as a function of time. Deviation from the Avrami equation can be seen in the final stage of transformation. (After Rabesiaka and Kovács 1961.)

- In the case of secondary crystallization the crystallinity-time relationship

$x$  : crystalline mass fraction at time  $t$ ,

$$\rightarrow x = C + D \ln(t-t_0) \quad t_0 : \text{the beginning of the secondary crystallization process}$$

$C, D$  : empirical constants

- No secondary crystallization occurs : PET, poly(ethylene adipate)
- Secondary crystallization takes up almost one half of the total crystallization process  
 $\rightarrow$  polyethylene or polyamides

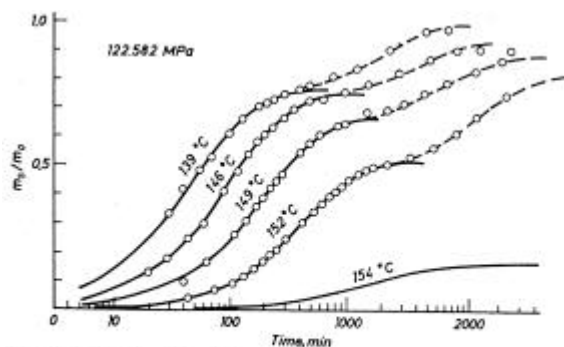


Fig. 6.7. Crystallization of polyethylene at elevated pressures. (After Matsuoka 1960.)

8. Nucleation.

- Two types of nucleation have been observed
  - ➔ Homogeneous
  - ➔ Heterogeneous

① Homogeneous nucleation

- ♥ Polymer chains can aggregate spontaneously below the melting point.
- ♥ Distribution of these nuclei is random.
- ♥ The generation of nuclei is usually a first order function of time. ( $p = Nt$ )
- ♥ Size of growing units

$$\Phi = \left( \frac{G}{N} \right)^{3/4}$$

$\Phi$  : the final average volume crystallized units.     $G$  : the growth constant

$N$  : the nucleation constant per unit volume

- ♥ The relationship between nucleation rate and temperature according to Turnbull and Fischer

$$N = N_0 \exp\left(-\frac{E_D}{kT} - \frac{\Delta G^*}{kT}\right)$$

$E_D$  : the activation energy at the surface of the nucleus

$G^*$  : the Gibbs energy needed for the formation of critical nuclei

→  $\Delta G^*$  is proportional to  $T_m^2/\Delta T^2$  where  $T_m$  is the melting point,  $\Delta T$  is the overcooling (nucleation rate increase with increases with increasing overcooling)

$N_0$  : material constant,     $k$  : the Boltzmann constant,     $T$  : the absolute temperature.

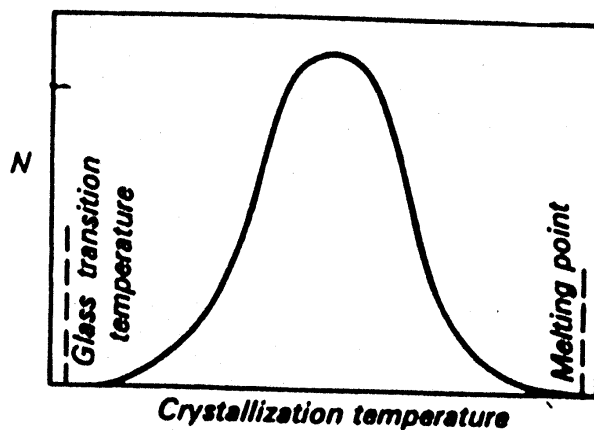


Fig. 6.8. Dependence of nucleus formation rate on the degree of undercooling.



→ At low temperature  $E_D/kT$  becomes dominant

The activation energy( $E_D$ ) decreases in proportion to temperature : nucleation slows down

Fig 6.8 shows the rate of nucleation as a function of temperature.

② Heterogeneous nucleation

♥ Heterogeneous nuclei start from impurity(distributed in the polymer, located at surface and the wall of container)

♥ Nuclei form simultaneously as soon as the sample reaches the crystallization temperature.

♥ Time dependence of nucleation is a zero order function.

♥ In case of fibre-forming polymer, such as polypropylene and polyamide.

♥ Size of growing units

$$\Phi = \frac{V_{\infty}}{N'V_0} \approx \frac{1}{N'}$$

$\Phi$  : the final average volume crystallized units.

$N'$  : the number of nuclei per unit volume

9. The growth process during crystallization.

- Crystal growth of low molecular material.

$$growth, rate = \exp\left(-\frac{A}{T} - \frac{B}{T\Delta T^m}\right)$$

Where  $m=1$  if nucleus formation is two-dimensional.

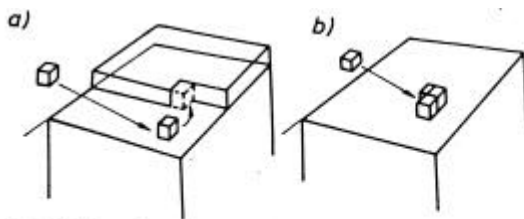


Fig. 6.11. Crystal growth process in a low molecular material. *a* The molecule diffuses to the growing surface then migrates to the low free energy points; *b* those molecules which are to form a new, secondary nucleus, before the new growing step begins. (After Mullin 1961.)

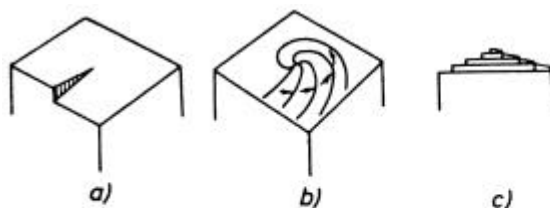


Fig. 6.12. Spiral form crystal growth by screw dislocation mechanism. *a* Crystallization starting at crystal defects; *b* molecules crystallizing in a spiral form (top view); *c* spiral growth (side view). (After Mullin 1961.)

- Spiral form crystal growth by screw dislocation.

$$\text{growth, rate} = A\Delta T^2$$

Where A is a material constant.

♣ Reference

1. Bodor, "Structural investigation of polymers", Ellis Horwood
2. Young, "Introduction to polymers", Chapman & Hall

♠ Ozawa

→ Avrami

(C)

$$X_t = 1 - \exp\left(\frac{-K(T)}{C^m}\right)$$

$$\log[-\ln(1 - X_t)] = \log K(T) + m \log C$$

m : Ozawa