

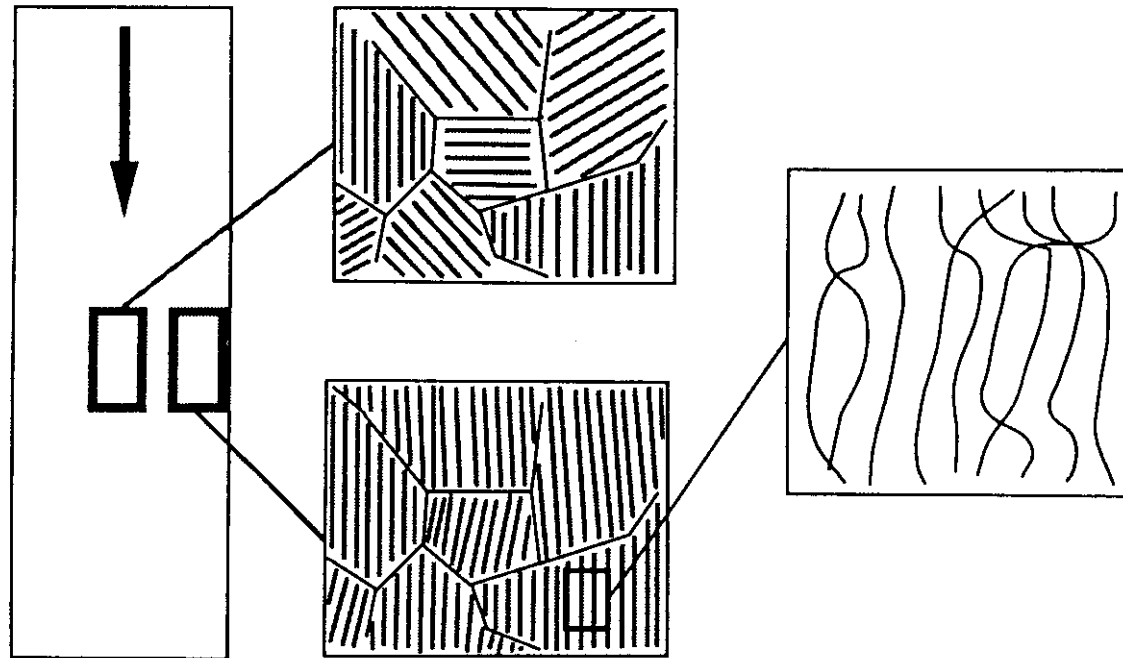
# Chapter 9. Chain orientation

## 9.1 Introduction

Anisotropic property of polymer :

strong covalent bonds along the chain axis

weak secondary bonds in the transverse directions



## 9.2 Definition of chain orientation

Average end-to-end distance

$$\langle r \rangle_0 = C \sqrt{n} l$$

$C$  : constant depending on the segmental flexibility

$l$  : bond length

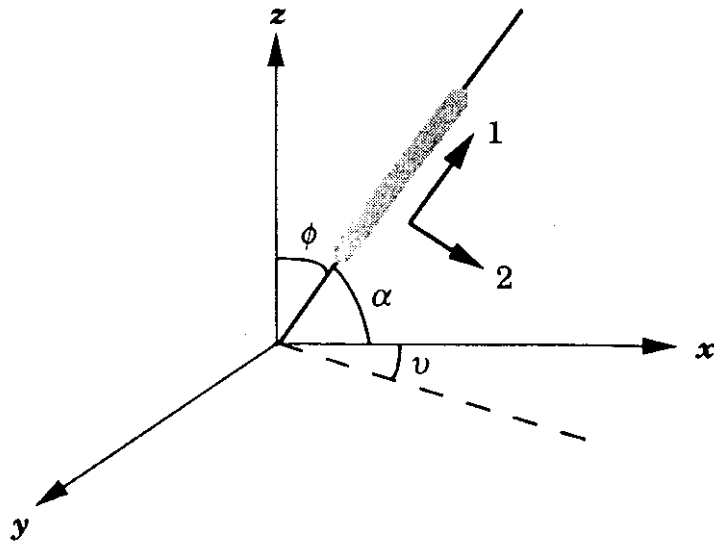
$n$  : number of bonds

Fully oriented molecule,  $r_\infty = nl$

$\therefore$  Strain to reach the completely aligned state

$$\lambda = \frac{r_\infty}{\langle r \rangle_0} = \frac{\sqrt{n}}{C} \Rightarrow \lambda \uparrow \text{ with } \sqrt{M}$$

\* *Hermans orientation function,  $f$*



**Figure 9.4** Chain segment and coordinate system.

Polarizability :

$$p_{zz} = p_1 \cos^2 \phi + p_2 \sin^2 \phi$$

$$p_{xx} = p_2 + (p_1 - p_2) \sin^2 \phi \cos^2 \nu$$

Lorentz-Lorenz equation :

$$\frac{n_{ij}^2 - 1}{n_{ij}^2 + 2} = \frac{4\pi}{3} p_{ij}$$

$p_{ij}$  can be converted to  $n_{ij}$

$p_{ij}$  : polarizability tensor

$n_{ij}$  : refractive index tensor

Birefringence ( $\Delta n$ ):  $\Delta n = n_{zz} - n_{xx}$

Average refractive index  $\langle n \rangle$ ,  $\langle n \rangle = \frac{1}{2}(n_{xx} + n_{zz})$

$$\Rightarrow \dots \Rightarrow \Delta n = \frac{(\langle n \rangle^2 - 2)^2}{6\langle n \rangle} \frac{4\pi}{3} (p_1 - p_2) \left( 1 - \frac{3\langle \sin^2 \phi \rangle}{2} \right)$$

Hermans orientation function :

$$\begin{aligned} f = \frac{\Delta n}{\Delta n_0} &= \frac{3\langle \cos^2 \phi \rangle - 1}{2} \quad \leftarrow \text{for 3-dimensional} \\ &= 2\langle \cos^2 \phi \rangle - 1 \quad \leftarrow \text{for 2-dimensional} \\ &= \frac{2}{n} \sum_{i=1}^n \cos^2 \phi_i - 1 \end{aligned}$$

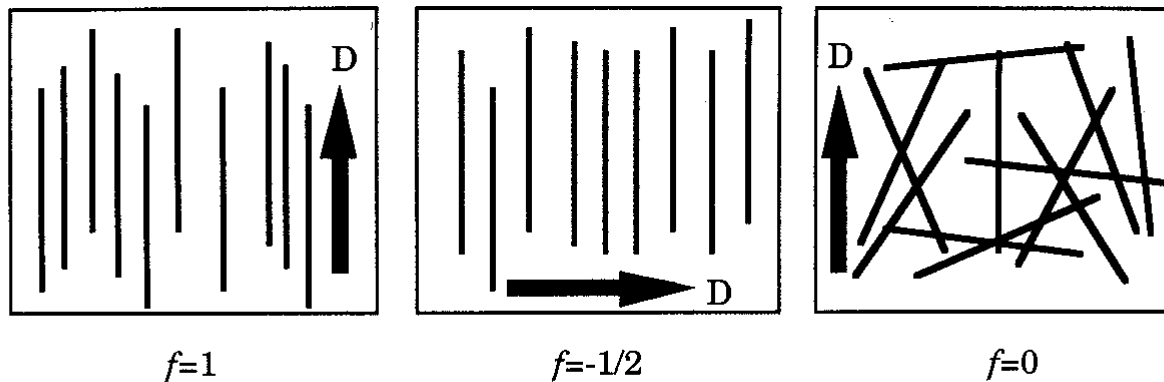
$\Delta n_0$  : maximum birefringence

※ For 3-dimensional orientation,

$f = 1$  (parallel),  $-0.5$  (perpendicular),  $0$  (random)  $\rightarrow$  Fig. 9.5

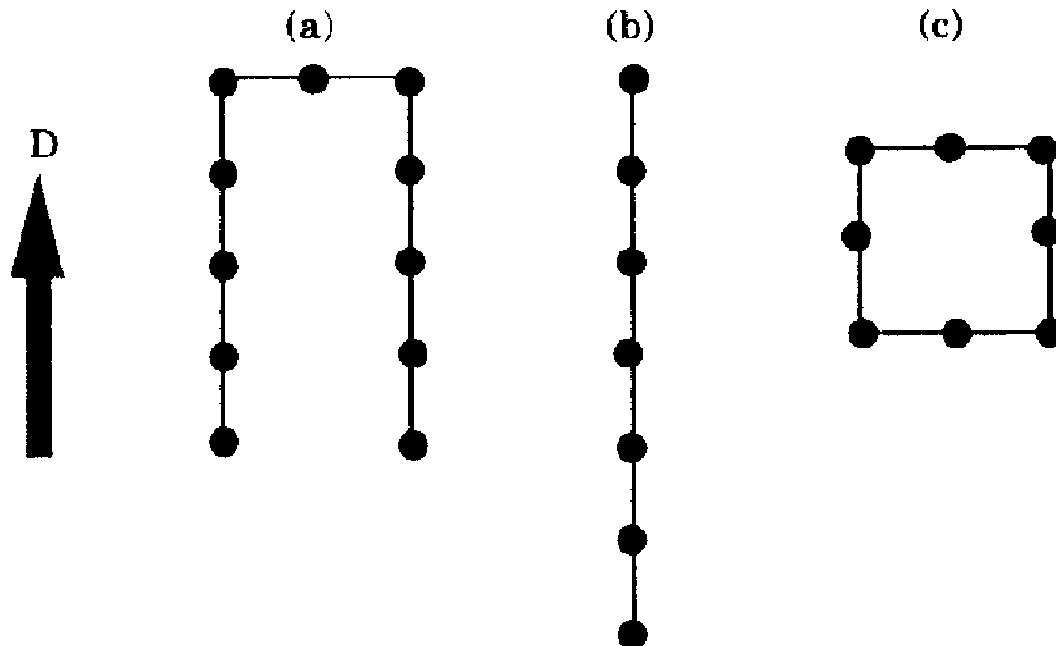
For 2-dimensional orientation,

$f = 1$  (parallel),  $-1$  (perpendicular),  $0$  (random)



**Figure 9.5** Values for the Hermans orientation function for three simple cases. The director (D) is shown for each case.

Ex)



two-dimensional orientation, (a)  $f = 0.6$ , (b)  $f = 1$ , (c)  $f = 0$

\* **Birefringence**

$$\Delta n = \Delta n_f + \Delta n_d + \Delta n_c + \Delta n_a$$

where,  $\Delta n_f$  : form birefringence (occurs only in multiphase systems)

$\Delta n_d$  : deformation birefringence (may cause stresses in bonds)

$\Delta n_c + \Delta n_a$  : orientation-induced birefringence (originating from the crystalline and the amorphous components)

If orientation is uniaxial & both form and deformation birefringence can be neglected,

$$\Delta n = \Delta n_c + \Delta n_a = \Delta n_0 [w_c f_c + (1 - w_c) f_a]$$

$w_c$  : crystallinity

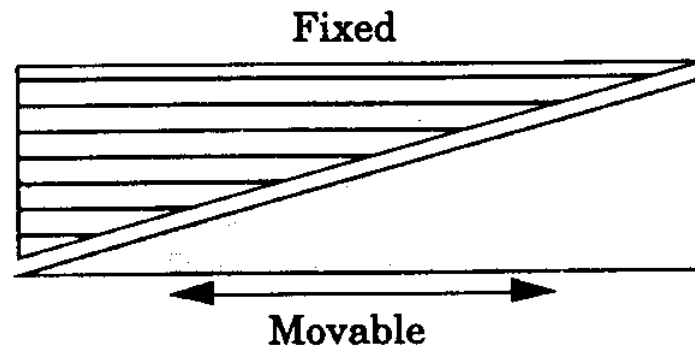
$f_c, f_a$  :  $f$  of crystalline and amorphous components

Birefringence measurements

⇒ " *polarized light microscope* "

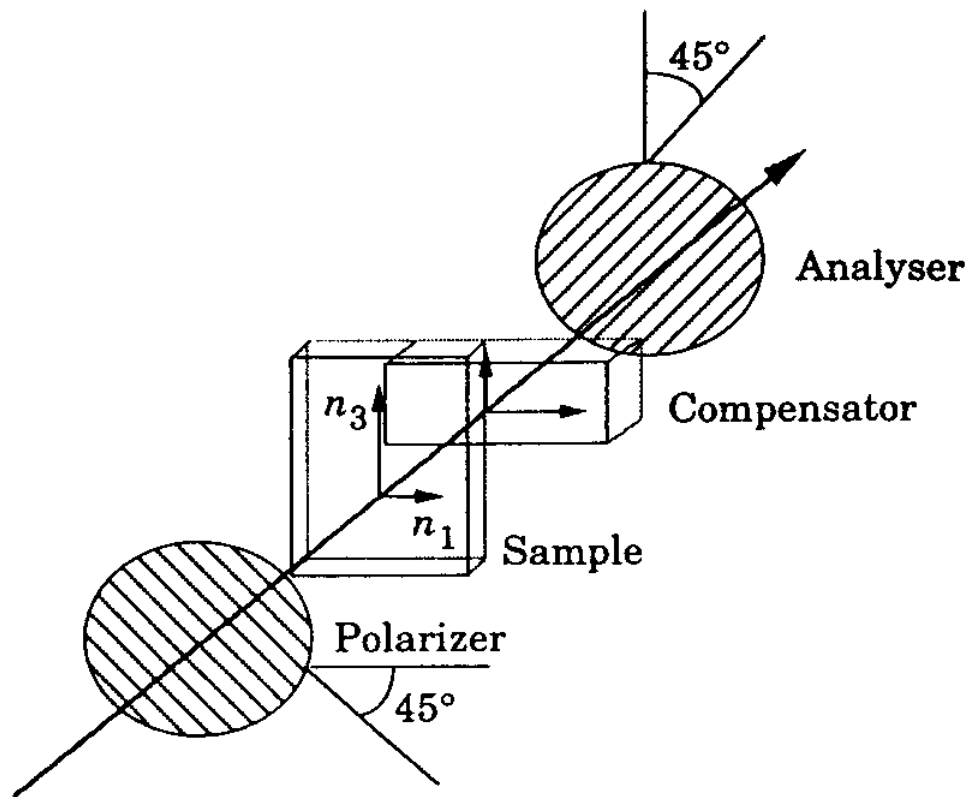
Compensator

-- optical retardation ( $R_{31}$ )



**Figure 9.8** Babinet compensator which consists of two quartz wedges with crossed optical axes.





**Figure 9.9** Optical system for the measurement of orientation in the plane.

In-plane birefringence ( $\Delta n = n_3 - n_1$ ),

$$\Delta n = \frac{R_{31}\lambda}{d}$$

$\lambda$  : wavelength of the light

$d$  : sample thickness

Thinner sample ( $< 100 \mu m$ ) can be measured by white light source

(visible light : wavelength from 400 nm (violet) to 750 nm (red))

← semicrystalline polymers

Clear amorphous polymers → thick sample도 가능

Color as a function of optical retardation ⇒ "*Michel-Levy chart*"

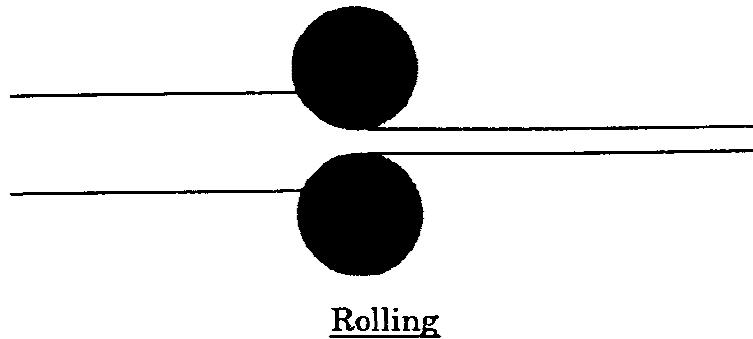
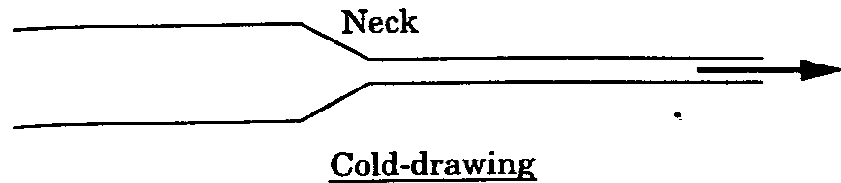
보다 두꺼운 sample (ex, mm 두께의 PE) – far infrared interferometry로 관찰

## 9.5 Chain orientation by processing

\* **Solid-state processes**

- Cold-drawing
- Solid-state extrusion
- Rolling

$$\lambda = \frac{L}{L_0} \approx \frac{A_0}{A} : \text{draw ratio}$$



For semicrystalline polymers,

- deformation of spherulite structure
- spherulite  $\rightarrow$  fibrillar structure
- plastic deformation of the fibrillar structure

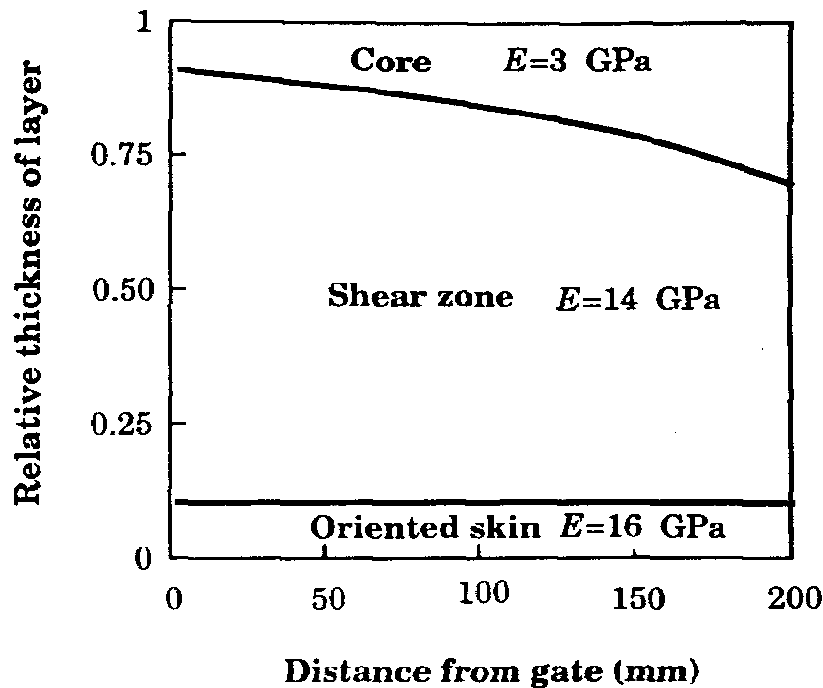
Crystal thickness ( $L_c$ ) of the fibrous polymer

$$L_c = \frac{C_1}{\Delta T} + C_2$$

$\Delta T$  : degree of supercooling

\* **Liquid processes**

- molding (Fig. 9.19 : microstructural layer of a 3 mm thick injection molded ruler)
- spinning (melt-spinning, solution-spinning), etc.



" shear flow "

&

" elongational flow "

=> Relative thickness of microstructural layers of a 3mm thick injection-molded ruler of a liquid-crystalline polymer

## 9.6 Properties of oriented polymers

Axial elastic modulus for a few polymers

**Table 9.1** The maximum elastic modulus at room temperature of a few selected polymers

Polymer	Elastic modulus (GPa)
Polyethylene	240–360
Isotactic polypropylene	42
Polyoxymethylene	54
Poly(ethylene terephthalate)	140
Polyamide 6	250
Diamond	800

Elastic deformation (comparative values) of a single molecule occurs by

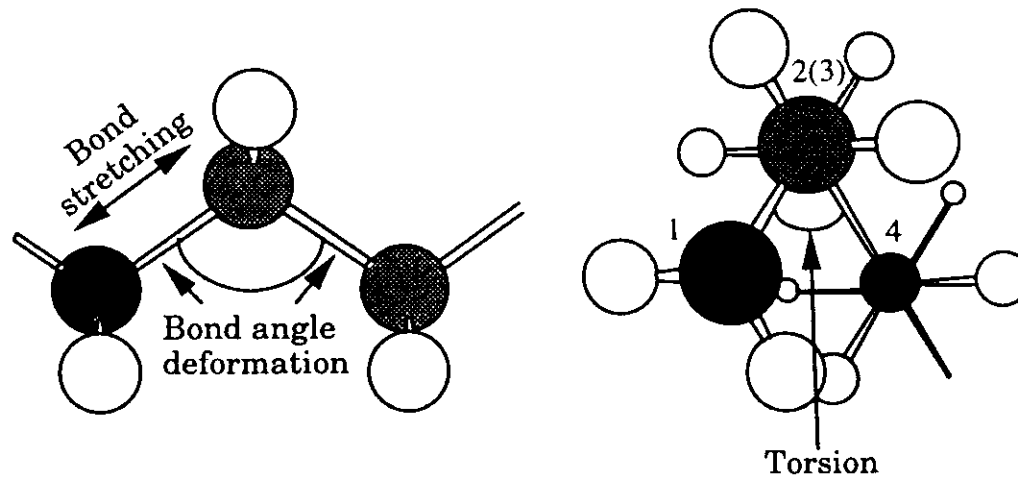
- bond stretching                      100
- bond-angle deformation            10
- torsion about a  $\sigma$  bond        1

ex.)

Diamond : 3-dimensional covalent-bond structure   ← stretching

PE, PA6 : all-trans form (fully-extended)   ← stretching and deformation

IPP, POM : helical conformations   ← stretching, deformation and torsion



**Figure 9.20** Deformation of a polyethylene molecule by bond stretching, bond angle deformation (both left-hand side) and torsion about the  $\sigma$  bond linking carbons 2 and 3 (right-hand side).



**Table 9.2** Summary of relationships between chain orientation and a few selected properties

Property	Relation	Other relations
Birefringence ( $\Delta n$ )	$\Delta n = \Delta n_0 f$ Uniaxial orientation <sup>a</sup>	$n_3 - n_1 = \Delta n_0 \left( f - \frac{g}{2} \right)$  $n_3 - n_2 = \Delta n_0 \left( f + \frac{g}{2} \right)$  $n_1 - n_2 = \Delta n_0 g$ Biaxial orientation <sup>b</sup>
Thermal expansivity ( $\alpha$ )	Linear expansivities: <sup>c</sup> $\alpha_{\parallel} = \alpha_0 - \frac{2}{3}(\alpha_2 - \alpha_1)f$ $\alpha_{\perp} = \alpha_0 + \frac{1}{3}(\alpha_2 - \alpha_1)f$ Uniaxial orientation	Volume expansivity: $\alpha_v = \alpha_{\parallel} + 2\alpha_{\perp} = \text{const.}$
Thermal conductivity ( $\lambda_c$ )	$\frac{1}{\lambda_{c\parallel}} = \frac{1}{\lambda_{c0}} - \frac{2}{3} \left( \frac{1}{\lambda_{c2}} - \frac{1}{\lambda_{c1}} \right) f$ Uniaxial orientation <sup>d</sup>	$\frac{1}{\lambda_{c\perp}} = \frac{1}{\lambda_{c0}} + \frac{1}{3} \left( \frac{1}{\lambda_{c2}} - \frac{1}{\lambda_{c1}} \right) f$ Uniaxial orientation
Elastic compliance ( $J$ )	$\frac{J_{\parallel}}{J_0} = 1 - f$ Uniaxial orientation simplified formula; small/medium $f$ values	For ultra-oriented polymers: good correlation only with draw ratio