
Chapter 18

Multicomponent Polymers

Polymer blends

Copolymers

Multicomponent polymers

= polymers with two or more components

- copolymers ~ different repeat unit
 - 1-phase ~ random, alternating
 - phase-separated ~ block, graft
- blends [alloys] ~ different polymer
 - miscible ~ very few
 - immiscible ~ most
- composites ~ different material [Chapter 24](#)
 - carbons, ceramics, metals

□ for

- cost
- improving property
- special morphology

Polymer blends

- Most polymer blends are immiscible.

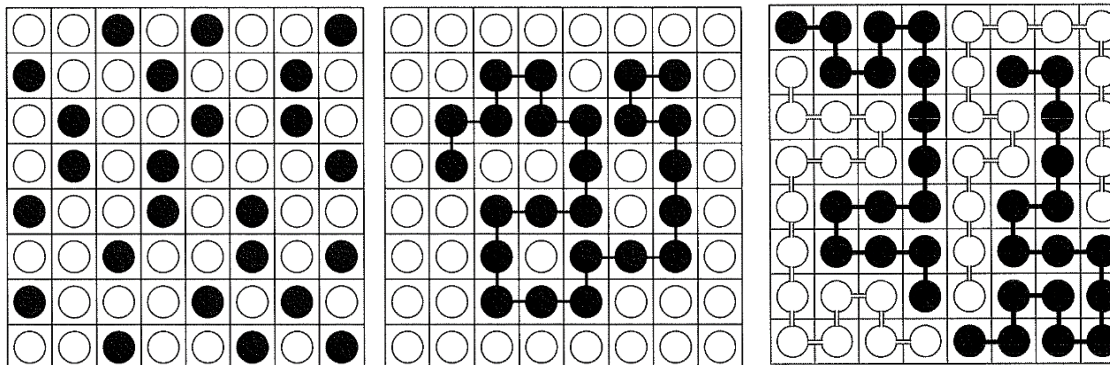
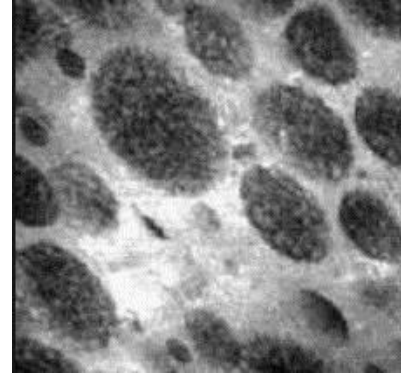
$$\Delta G_m = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + x_1 n_1 \phi_2 \chi]$$

$$\Delta G_m = \Delta H_m - T \Delta S_m$$

$$\phi_1 = \frac{N_1 x_1}{(N_1 x_1 + N_2 x_2)}$$

$$\Delta G_m = \Delta G_m^{\text{contact}} - T \Delta S_m^{\text{comb}}$$

- n_1 and n_2 very small $\rightarrow \Delta S_m (> 0)$ very small (≈ 0)
- ΔG_m dominated by $\chi (> 0)$



Phase behavior

See §14.2 pp310-313 for polymer solution

□ ΔG_m^* vs ϕ_2 at different temp

$$\Delta G_m^* = RT \left[\phi_1 \ln \phi_1 + \left(\frac{\phi_2}{x} \right) \ln \phi_2 + \chi \phi_1 \phi_2 \right]$$

- $\Delta G_m^* = \Delta G_m / (n_1 + x n_2)$
= ΔG_m per mole of lattice [segment]

□ at T_{1b}

- $\Delta G_m^* < 0$ and no inflection point
- ΔG for phase separation > 0
- miscible at all compositions

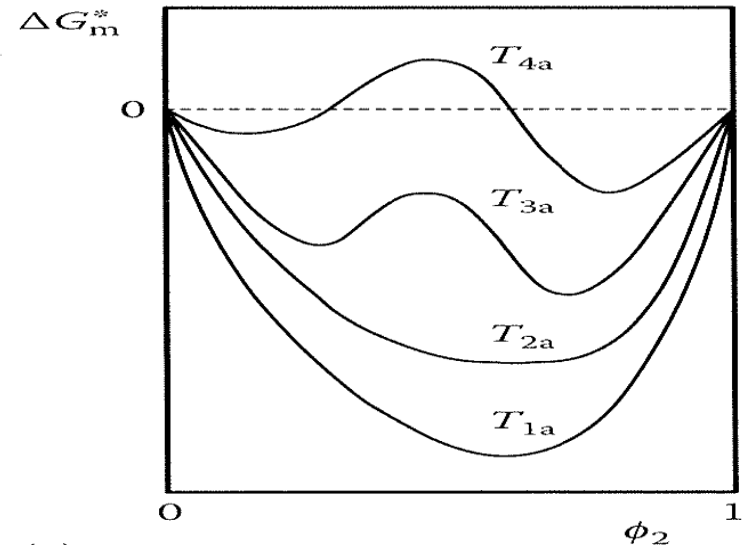
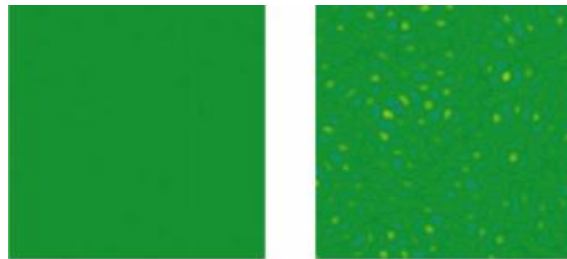
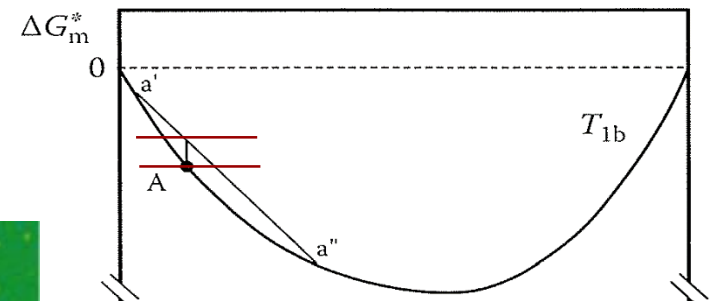
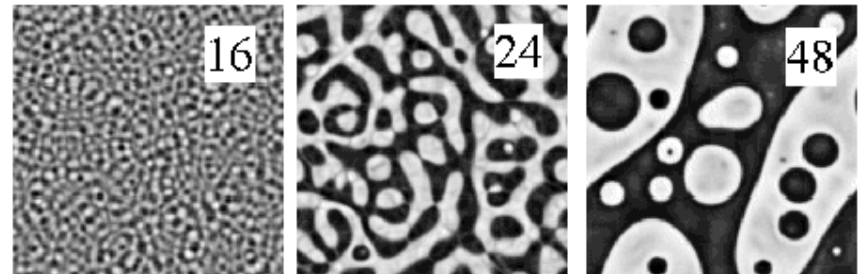
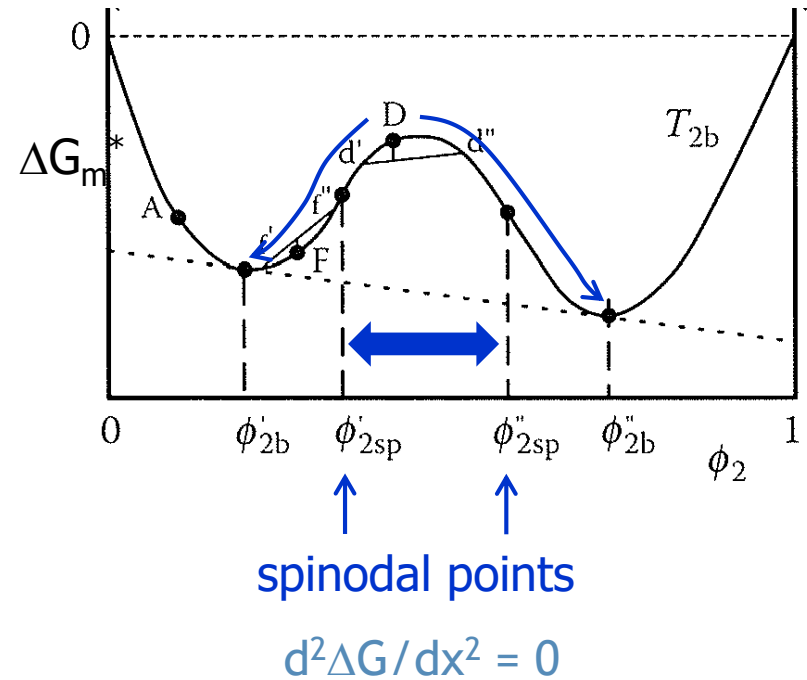


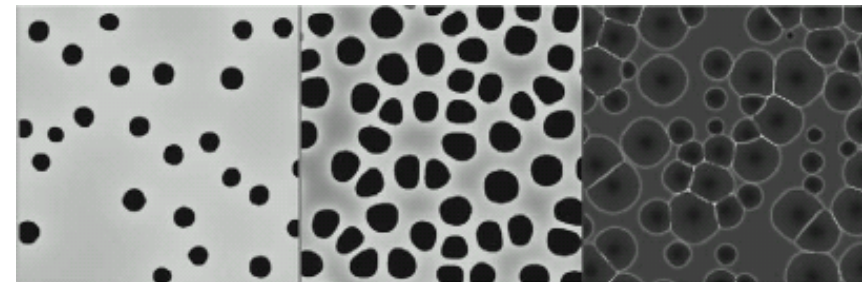
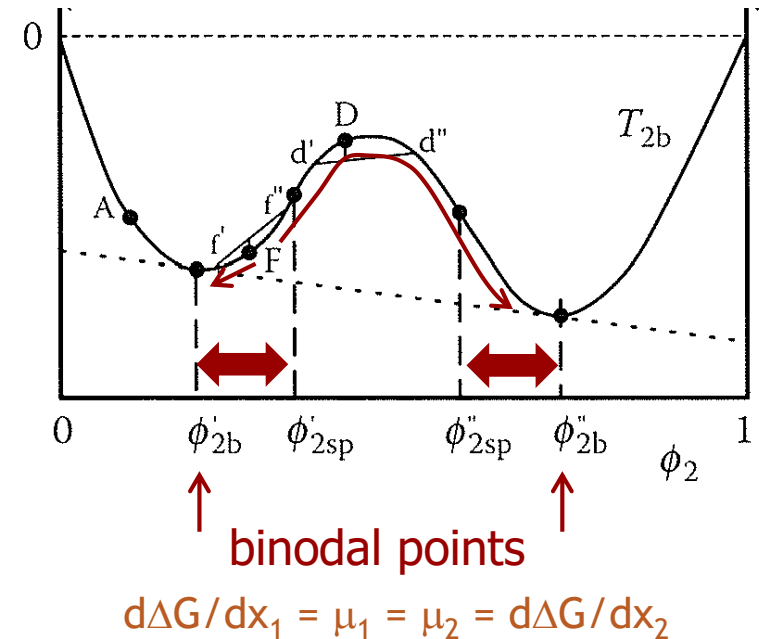
Fig 14.1 p 311



- at T_{2b} between ϕ'_{2sp} and ϕ''_{2sp}
 - between the inflection points
 - local minor composition fluctuation (D to d' and d'')
 - lower the energy [$\partial^2\Delta G/\partial x^2 < 0$]
 - ΔG for phase separation < 0
 - phase **unstable** (to fluctuation)
 - phase-separate to ϕ'_{2b} and ϕ''_{2b}
 - 'spinodal decomposition'
 - co-continuous to discontinuous
 - $\Delta G_m < 0$ but immiscible?
 - necessary but not sufficient
 - $(\partial^2\Delta G_m / \partial \phi_i^2) < 0$
 - $(\partial^2\Delta G_m / \partial \phi_i^2) > 0$ is another requirement for miscibility.

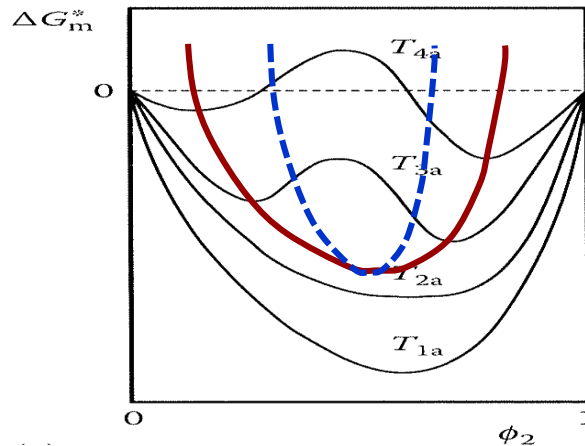


- at T_{2b} in $\phi'_{2b} - \phi'_{2sp}$ or $\phi''_{2sp} - \phi''_{2b}$
 - betw spinodal and binodal points
 - local minor composition fluctuation
 - raise the energy [$\partial^2\Delta G/\partial x^2 > 0$]
 - back to solution
 - phase **metastable** (to fluctuation)
 - ΔG for phase separation (to ϕ'_{2b} and ϕ''_{2b}) > 0
 - need to overcome energy barrier
- major fluctuation like nucleation \rightarrow
 - phase separation
 - to **binodal** composition [ϕ'_{2b} and ϕ''_{2b}]
 - by '**nucleation and growth**'



(Temp-comp) Phase diagram

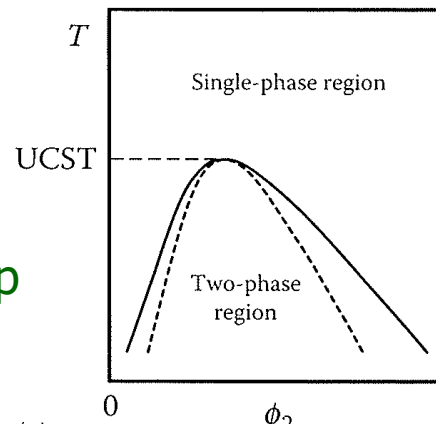
- by connecting **binodal** and **spinodal** points



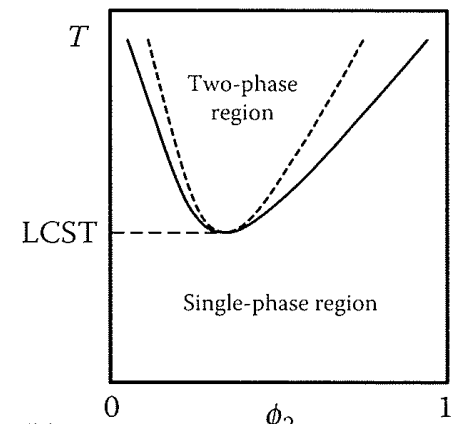
$$\Delta G_m^* = \mathbf{RT} \left[\underbrace{\phi_1 \ln \phi_1 + \left(\frac{\phi_2}{x} \right) \ln \phi_2}_{\text{entropic } [\Delta S_m]} + \underbrace{\chi \phi_1 \phi_2}_{\text{interaction } [\Delta H_m \text{ or } \Delta G_m^{\text{contact}}]} \right]$$

Fig 14.2 p 312

- $\chi = \chi_S + \chi_H = a + b/T$
 - if $b > 0$, $T \uparrow \rightarrow \chi \downarrow \rightarrow \Delta H_m \downarrow$
 - $T_1 > T_2 > T_3 > T_4$
 - UCST = upper critical sol'n Temp
 - if $b < 0$, $T \uparrow \rightarrow \chi \uparrow \rightarrow \Delta H_m \uparrow$
 - $T_1 < T_2 < T_3 < T_4$
 - LCST = lower critical sol'n Temp



(a)



(b)

$b < 0 \leftarrow$ specific interaction (like H-bond)
 $T \uparrow \rightarrow \Delta H_m$ large (-) to smaller (-) to (+)

□ UCST and LCST behavior

□ UCST

- common in solvent/solvent or solvent/polymer blends

□ LCST

- more common in (polymer/polymer) blends
- possible when **specific interaction (like H-bonding)** or
- when ΔV_m (and ΔS_m) < 0

□ at critical point,

$$\left(\frac{\partial^2 \Delta G_m^*}{\partial \phi_2^2} \right) = \left(\frac{\partial^3 \Delta G_m^*}{\partial \phi_2^3} \right) = 0$$

$$\phi_{2c} = \frac{1}{1 + x^{1/2}} \quad \chi_c = \frac{1}{2} \left[1 + \frac{2}{x^{1/2}} + \frac{1}{x} \right]$$

as $x \rightarrow \infty$, $\phi_{2c} \rightarrow 0$ and $\chi_c \rightarrow 1/2$.

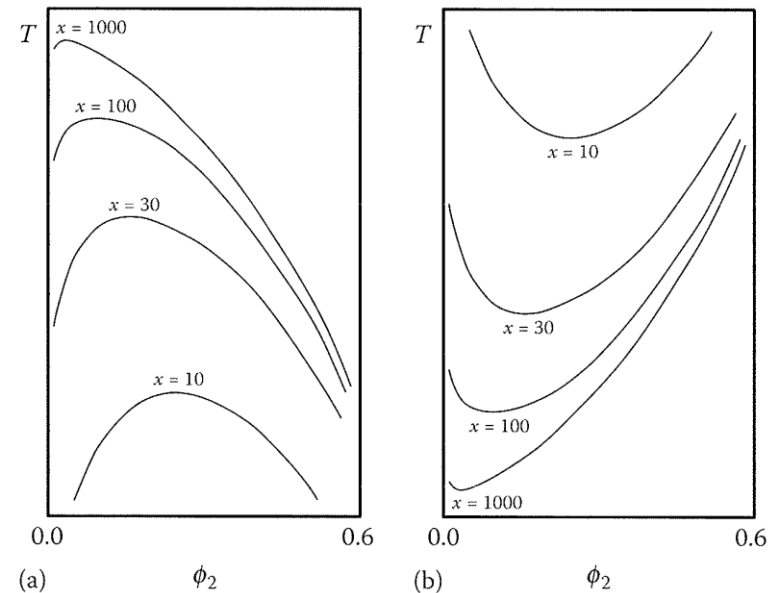


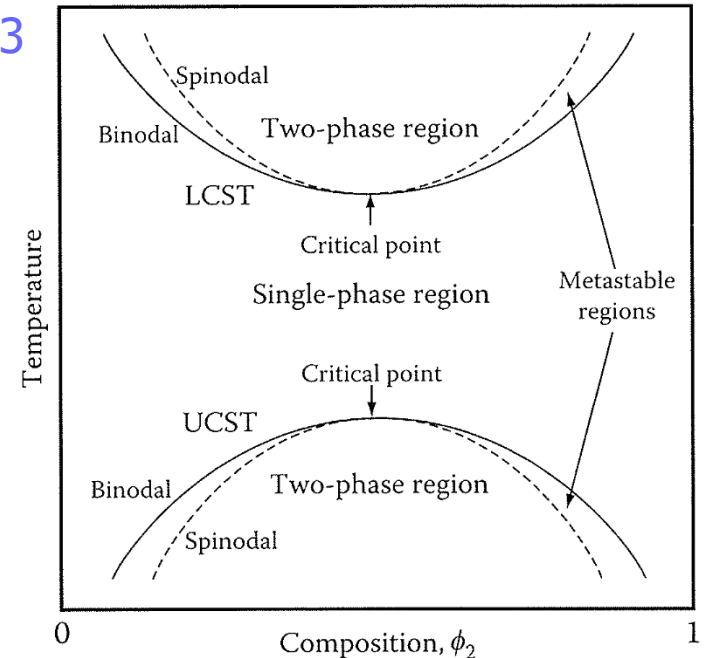
Fig 14.3 p 314

Phase behavior of polymer blends

Ch 18 sl 9

- ❑ close to symmetrical
 - ❑ similar mol wt
- ❑ UCST not usually found
 - ❑ F-H theory predicts UCST only.
- ❑ LCST more common
 - ❑ F-H theory does not consider
 - volume change upon mixing
 - specific interaction
 - ❑ can be explained by equation of state [EOS] model
 - considers $\Delta V_m (< 0)$ with 'free volume'
 - $\Delta H_m < 0$ ($\leftarrow \Delta V_m < 0$) and $\Delta S_m < 0$ [less free volume]
 - at low temp, $\Delta H_m > T\Delta S_m \sim$ miscible
 - at high temp, $T\Delta S_m > \Delta H_m \sim$ phase separates \rightarrow LCST

Fig 18.3 p 453



Miscible polymer blends

- with specific interaction
 - PS/PPO $\sim \pi-\pi$ interaction
 - PEO/PAA \sim H-bonding
- with similarity

Table 18.1 p 311

Polymer 1	Polymer 2	Miscible
Polystyrene	Poly(2,6-dimethyl-1,4-phenylene oxide)	✓
Polystyrene	Poly(vinyl methyl ether)	✓
Poly(methyl methacrylate)	Poly(vinylidene fluoride)	✓
Poly(vinyl chloride)	Poly(butylene terephthalate)	✓
Poly(ethylene oxide)	Poly(acrylic acid)	✓
Polystyrene	Polybutadiene	×
Polystyrene	Poly(methyl methacrylate)	×
Polystyrene	Poly(dimethyl siloxane)	×
Nylon 6	Poly(ethylene terephthalate)	×

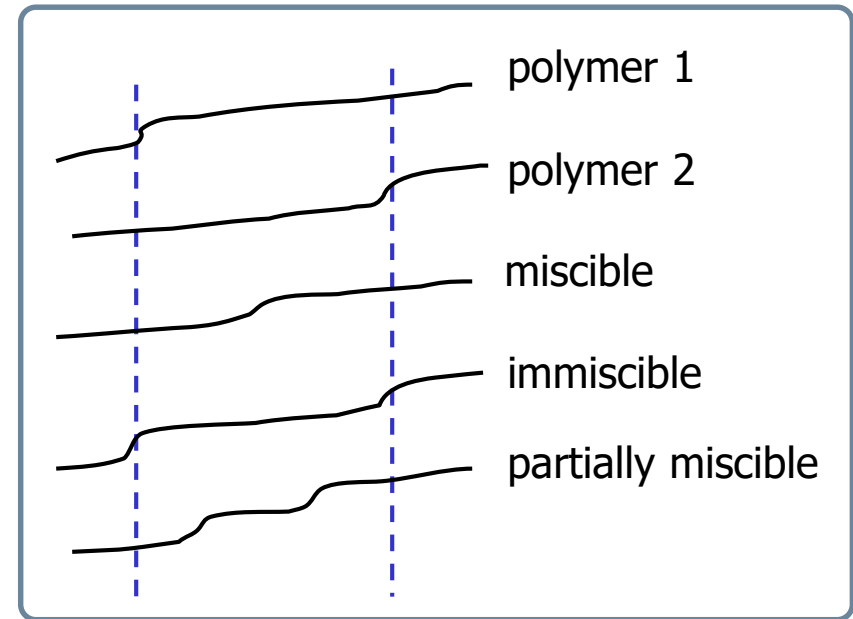
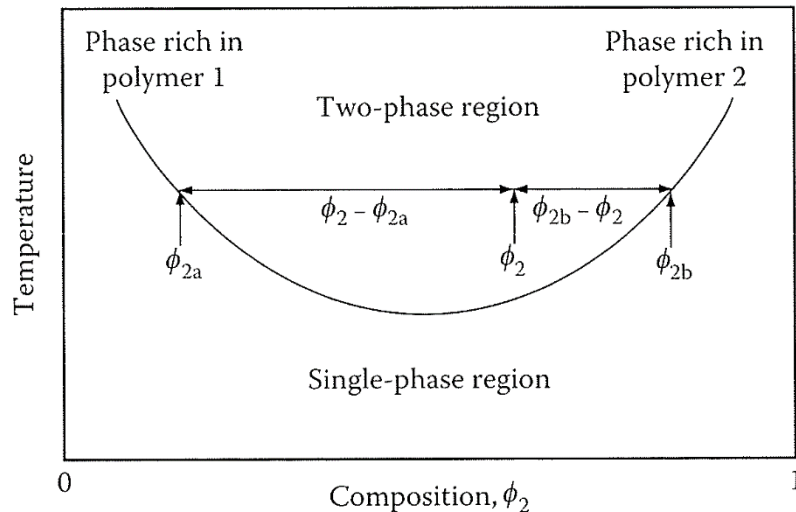
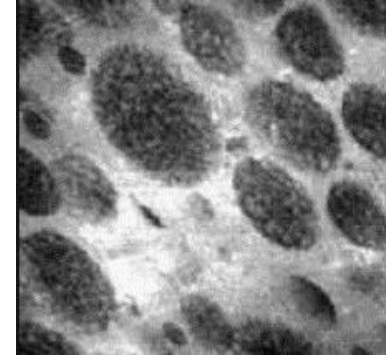
T_g of polymer blend

- miscible [compatible] blends $\sim 1 T_g$

$$\frac{1}{T_g^{\text{blend}}} = \frac{w_1}{T_g^1} + \frac{w_2}{T_g^2}$$

- immiscible [incompatible] blend $\sim 2 T_g$

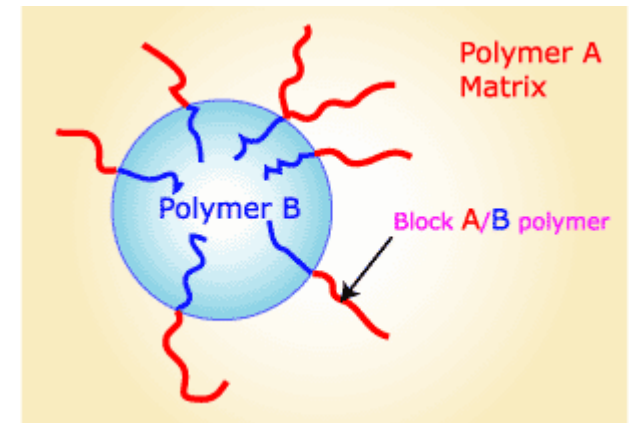
- partially miscible blend



Compatibilization

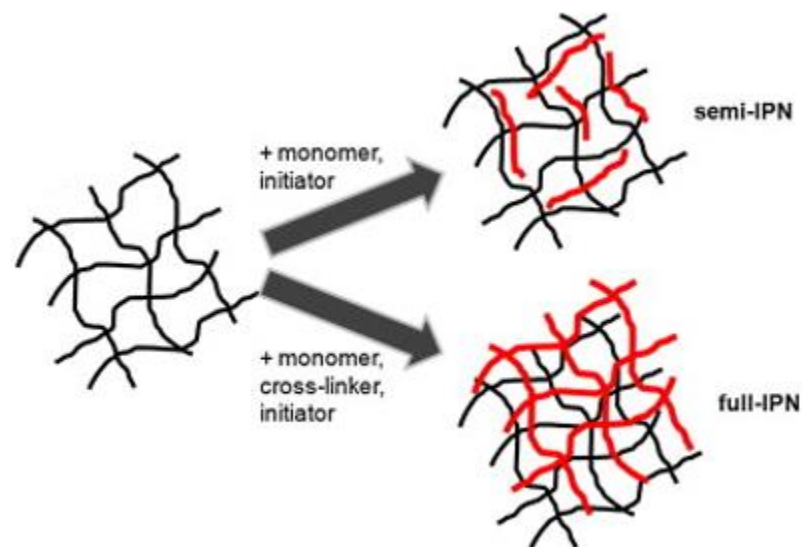
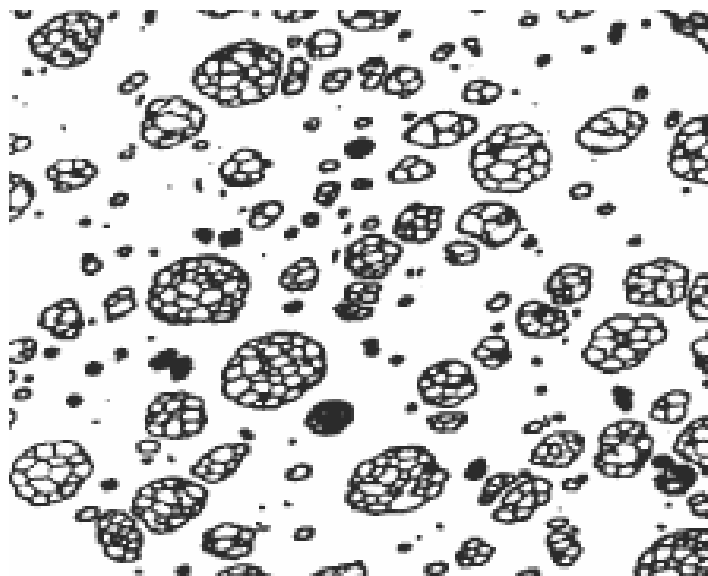


- ❑ alloy = compatibilized blend? no. alloy = blend
- ❑ compatibility = miscibility? no
- ❑ addition of compatibilizer
 - ❑ monomeric
 - ❑ polymeric ~ block or graft copolymer
 - not have to contain A or B
 - not have to be long or much
 - $MM > M_e$ [entanglement mol wt] is enough.
 - A few wt% is enough.



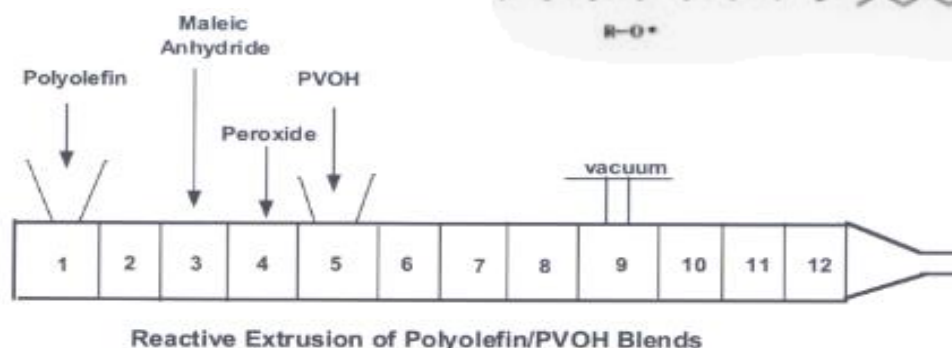
- in-situ polymerization

- HIPS, ABS ~ polym'n of ST or SAN with unsat'd rubber
- interpenetrating polymer network [IPN] ~ crosslinking-polym'n



□ Reactive compatibilization

- compatibilizer [copolymer] formed in situ during mechanical blending
- reactive extrusion



□ through trans reaction

- (polymer-polymer) exchange reaction
- ester exchange betw PEsters, PC, ---
- amide exchange betw PAs
- amide-ester exchange

Block copolymer

□ types

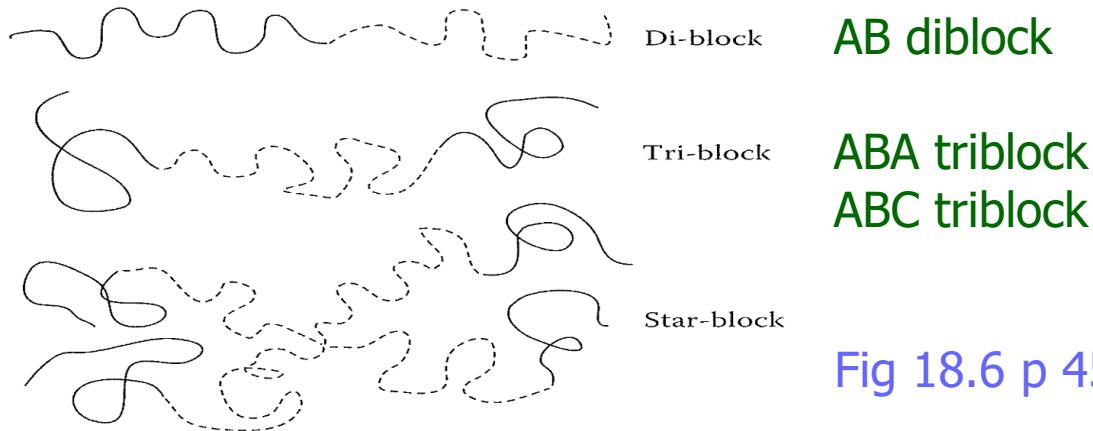


Fig 18.6 p 457

□ order-disorder transition by temperature

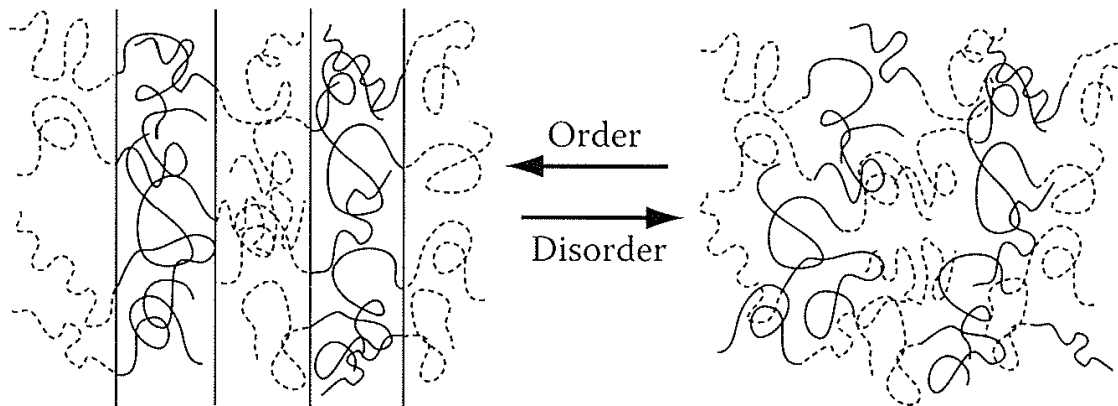


Fig 18.7 p 458

□ phase diagram

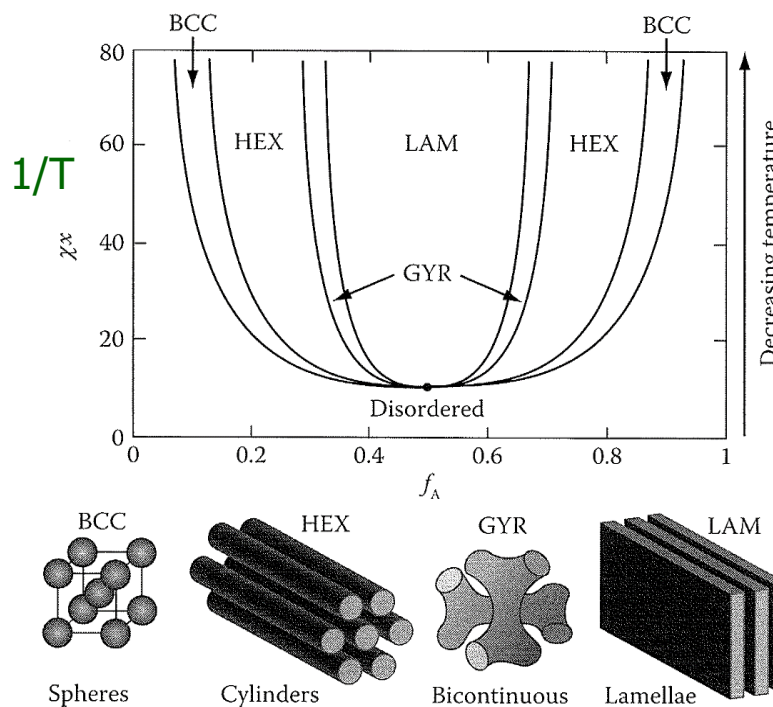


Fig 18.8 p 458

□ morphology

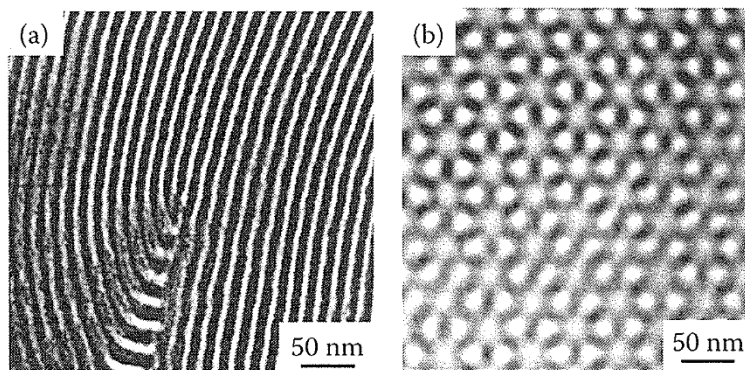


Fig 18.9 p 459
 SBS triblock ($\phi_A = .45$)
 SIS triblock ($\phi_A = .33$)

Thermoplastic elastomers [TPE]

- elastomer = rubber
 - rubber ~ (chemically) crosslinked (→ thermosetting)
 - TPE ~ physically crosslinked → thermoplastic
- (tri)block copolymers
 - SBS, SIS
 - glassy/rubbery block at use temp
 - glassy S domain (physically) crosslinks
 - rubbery/rubbery at high temp
 - thermoplastic ~ processable
- thermoplastic polyurethane [TPU]
 - hard and soft segments
 - urethane (hard) and polyether (soft)

Fig 18.14 p463
SBS with $\phi_A = .2$

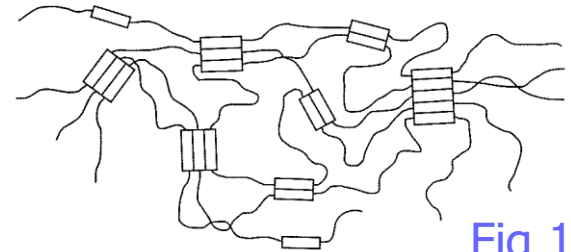
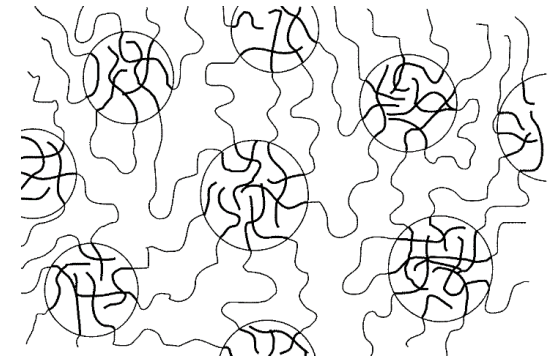


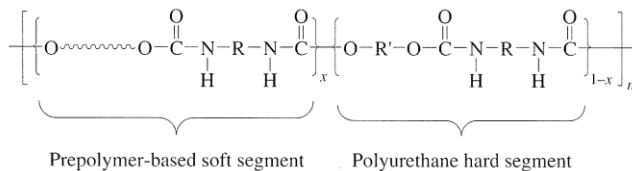
Fig 18.13

Virtually crosslinked/extended network of polymer primary chains

↑ ↓ Heat or solvent



Polymer primary chains



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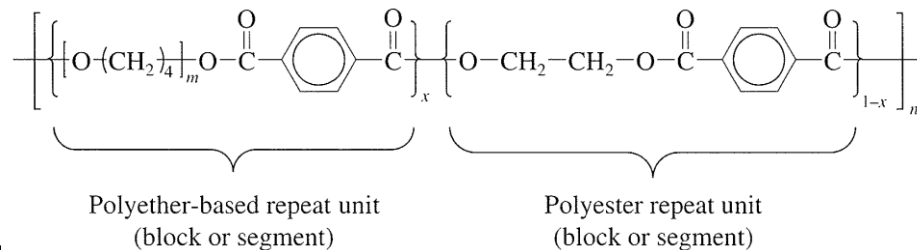
□ TPE with crystallizable block

□ polyester TPE

- polyester/polyether

□ thermoplastic polyolefin [TPO]

- PP/EPDM ~ PP+P crystallize



□ ionic elastomers

□ a type of 'ionomer'

□ EPDM-SO₃⁻ ~ crosslinked by M⁺

