Table of Contents

5

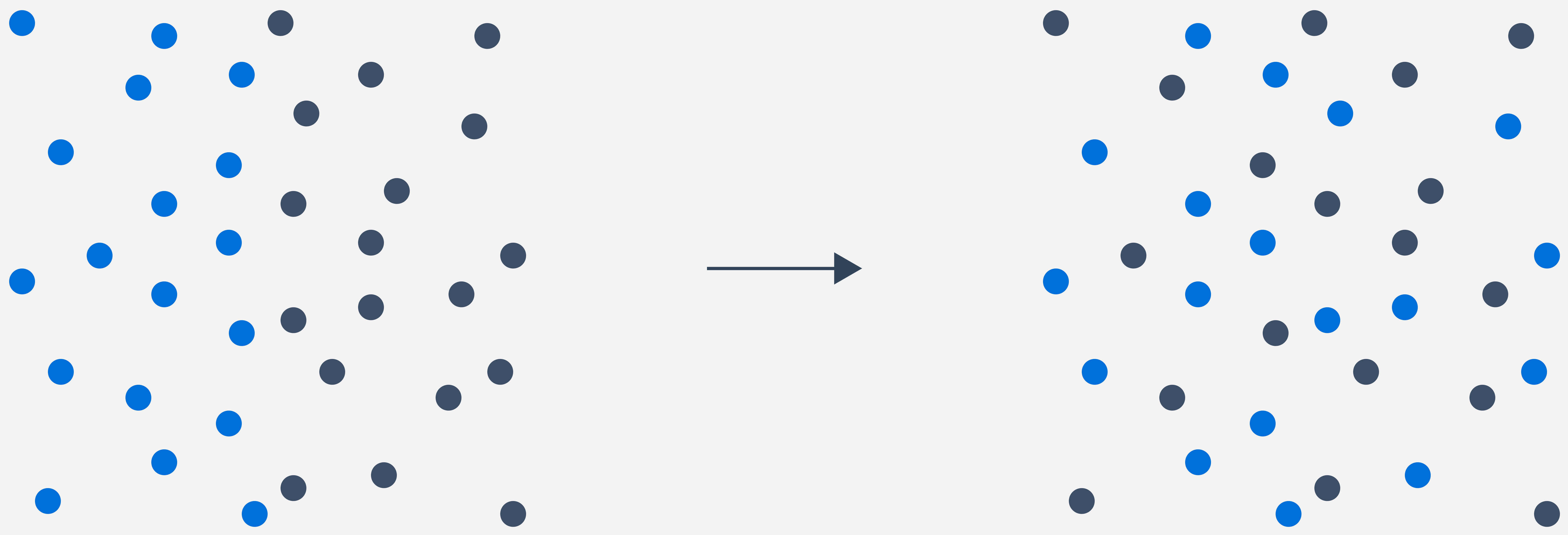
Polymer Mixtures

5.1

Polymer Blends

Thermodynamics of Molecular Mixtures

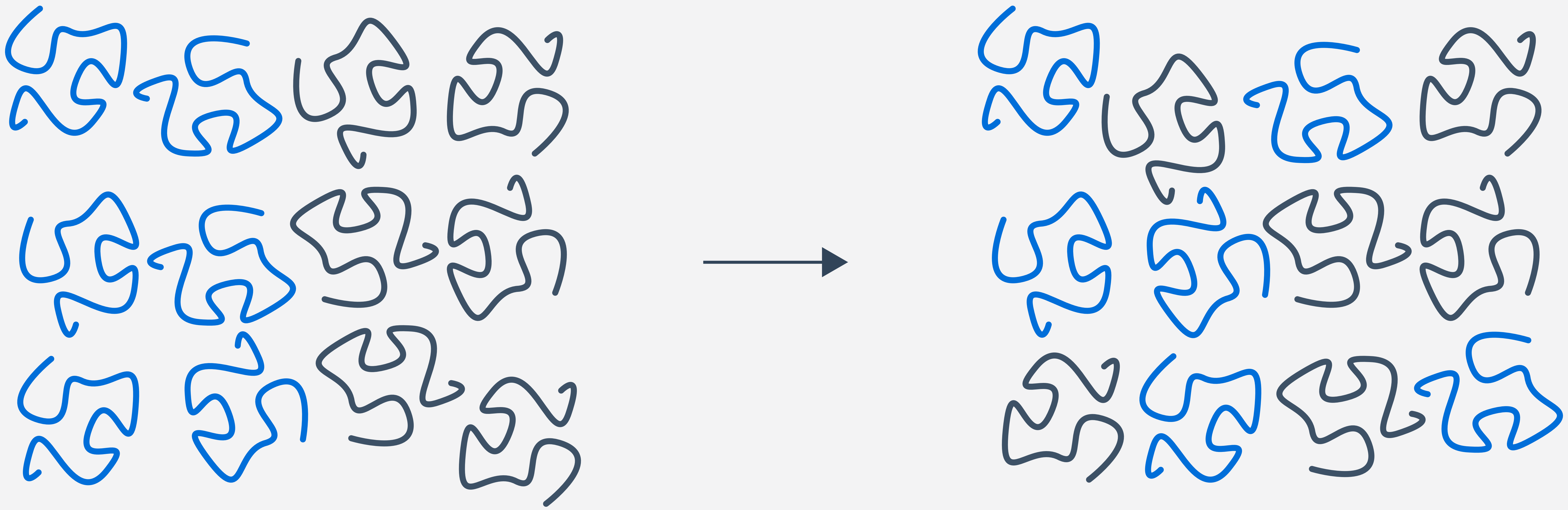
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



- ΔH_{mix} depends on intermolecular interactions between same/different molecules
- ΔH_{mix} is often small and positive, slightly favours demixing
- ΔS_{mix} is typically large and positive, **strongly favours mixing**

Thermodynamics of Polymer Mixtures

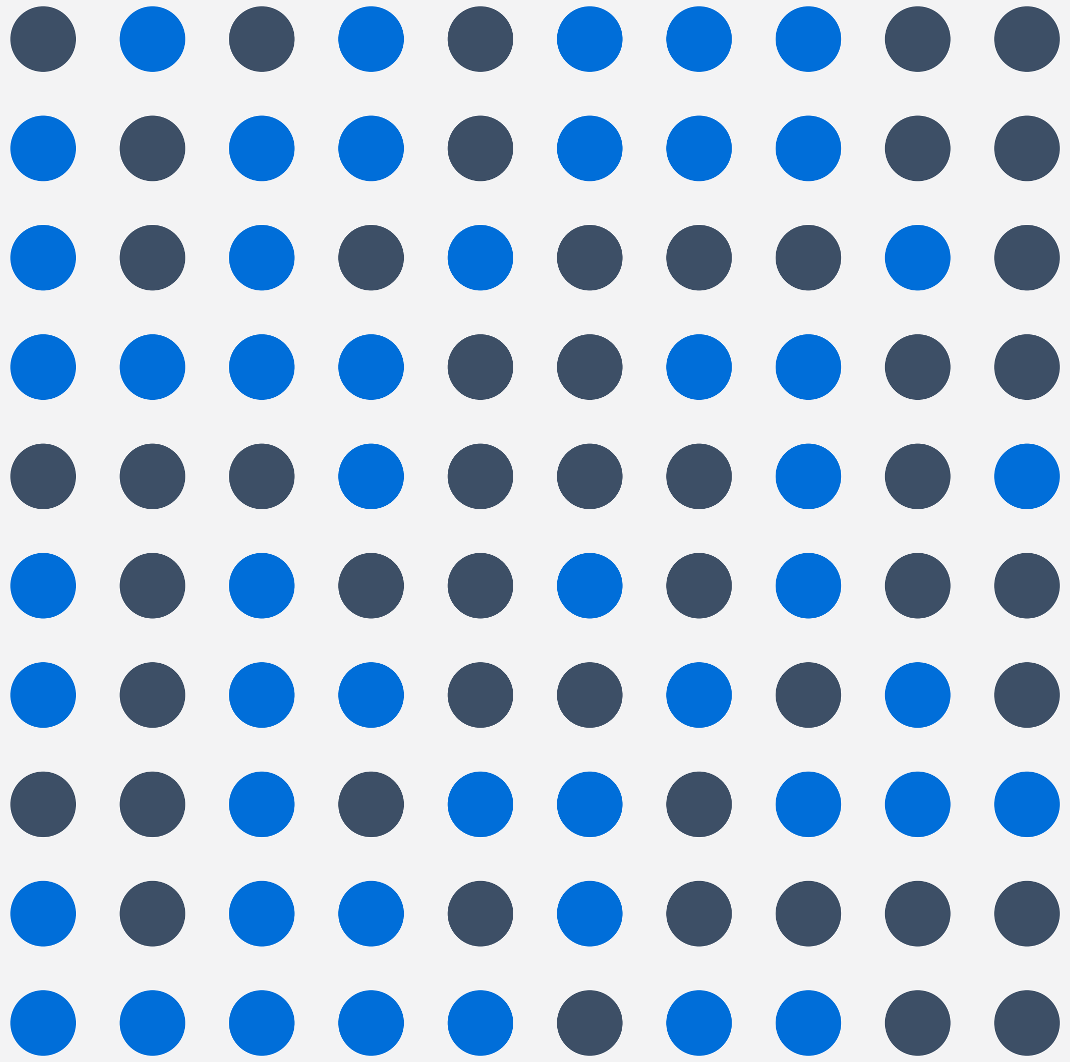
$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$



- ΔH_{mix} depends on intermolecular interactions between same/different molecules
- ΔH_{mix} is often small and positive, slightly favors demixing
- ΔS_{mix} depends on polymer unfolding (unfavorable) and statistics (slightly favorable)
- ΔS_{mix} is typically small and negative, slightly favours demixing

Mixing Entropy for Regular Solutions

- **regular solutions are mixtures of low molar mass species**
- here: n_A blue molecules and n_B grey molecules of identical size distributed in a lattice with n sites



number of states before mixing, Ω_A: $\Omega_A = n\phi_A$ ϕ_A: volume fraction of A

the entropy change of mixing for species A:

$$\Delta S_A = \mathrm{k}\ \ln \Omega_{AB} - \mathrm{k}\ \ln \Omega_A = \mathrm{k}\ \ln\left(\frac{\Omega_{AB}}{\Omega_A}\right)$$
$$= \mathrm{k}\ \ln\left(\frac{n}{n\phi_A}\right) = -\,\mathrm{k}\ \ln \phi_A$$

the entropy of mixing:

$$\Delta S_{\text{mix}} = n_A \Delta S_A + n_B \Delta S_B = -\,\mathrm{k}(n_A\ \ln \phi_A + n_B\ \ln \phi_B)$$

the entropy of mixing per lattice site:

$$\Delta \bar{S}_{\text{mix}} = -\,\mathrm{k}(\frac{\phi_A}{N_A}\ \ln \phi_A + \frac{\phi_B}{N_B}\ \ln \phi_B)$$

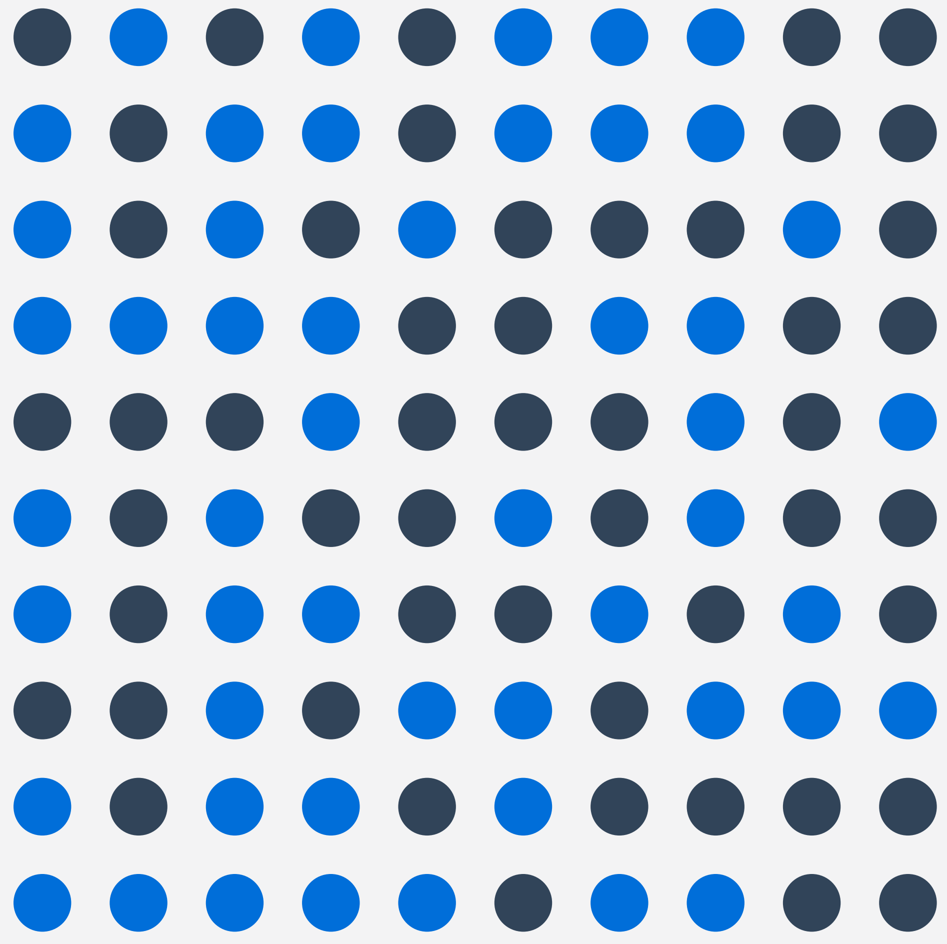
- **for a regular solution the number of lattice sites occupied per molecule** $N_A = N_B = 1$

Mixing Entropy of Binary Mixtures

$$\Delta\overline{S}_{\mathrm{mix}} = -\,\mathrm{k}\left(\frac{\phi_A}{N_A}\;\ln\phi_A + \frac{\phi_B}{N_B}\;\ln\phi_B\right)$$

regular solution

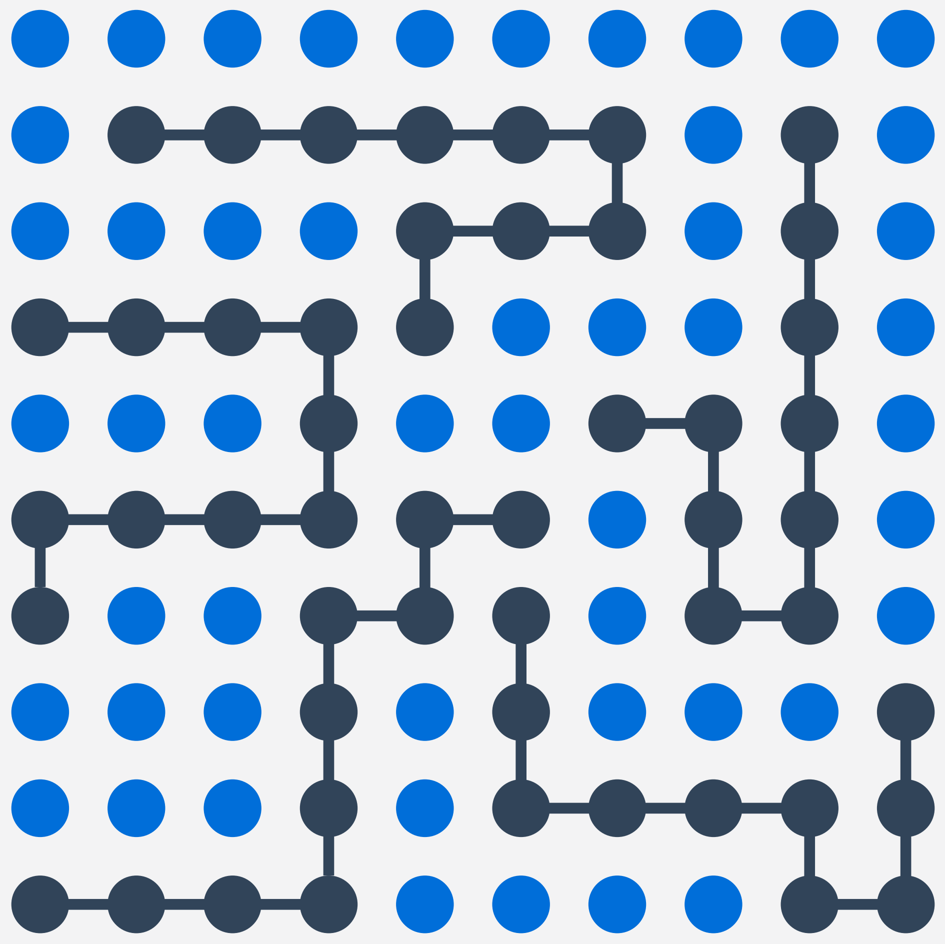
$(N_A = N_B = 1)$



$\Delta\overline{S}_{\mathrm{mix}}/k = 0.69$

polymer solution

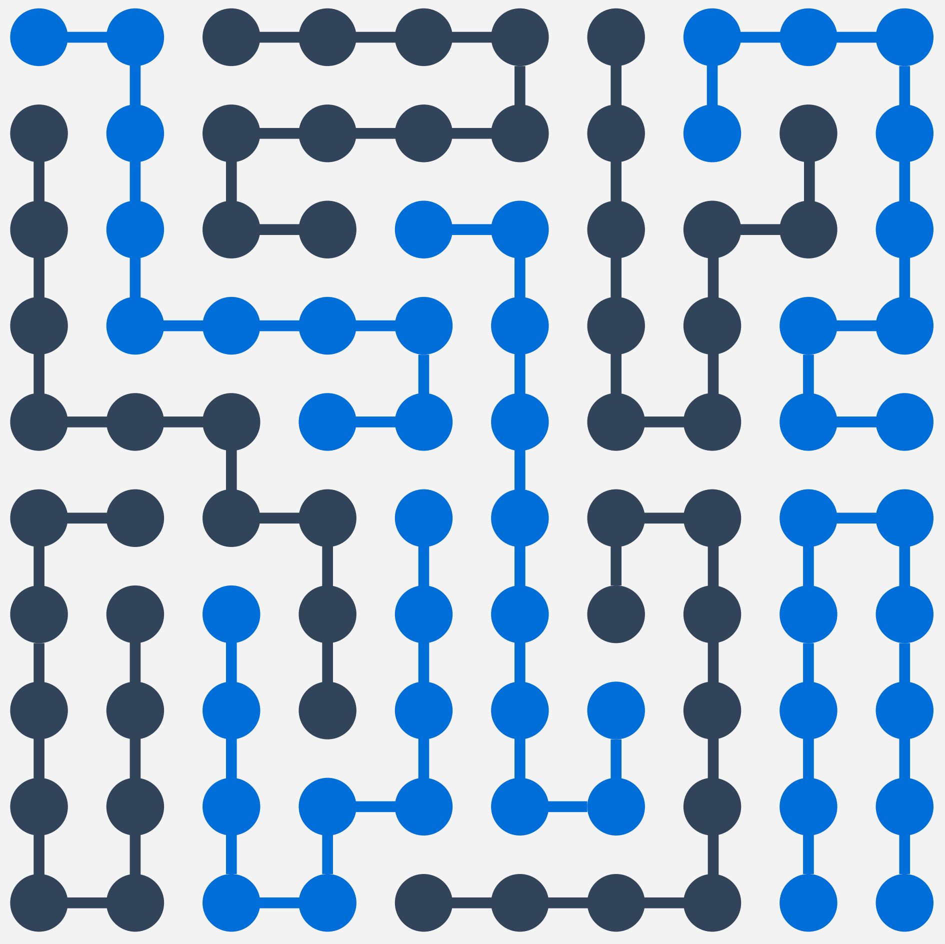
$(N_A = N \quad N_B = 1)$



$\Delta\overline{S}_{\mathrm{mix}}/k = 0.38$

polymer blends

$(N_A \quad N_B)$

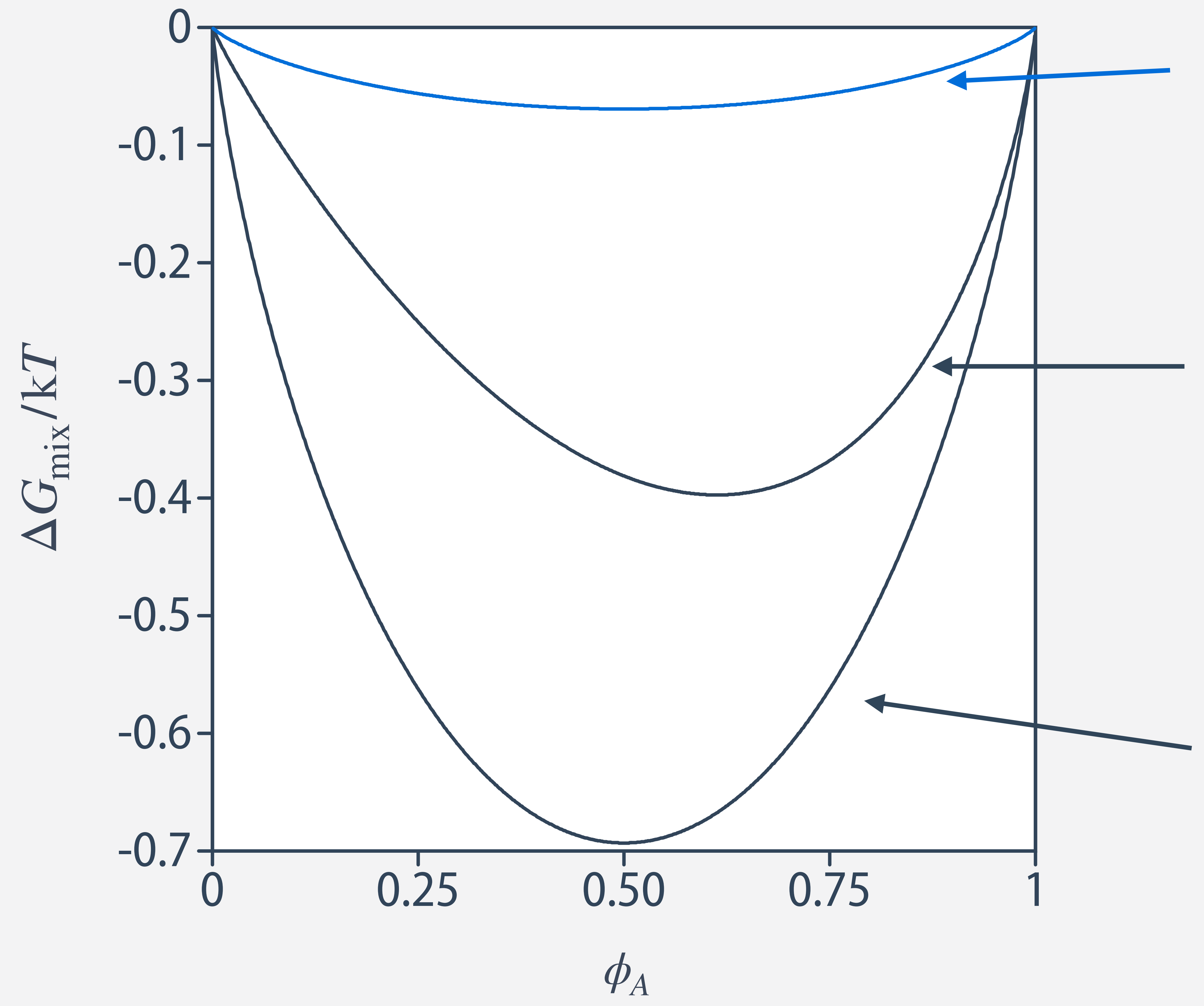


$\Delta\overline{S}_{\mathrm{mix}}/k = 0.069$

- **enormous differences between mixing entropies of regular solutions, polymer solutions, polymer blends**
- **for polymer blends, the mixing entropy is very small**

Ideal Mixtures

- for ideal mixtures, the free energy of mixing is purely entropic (translational entropy)



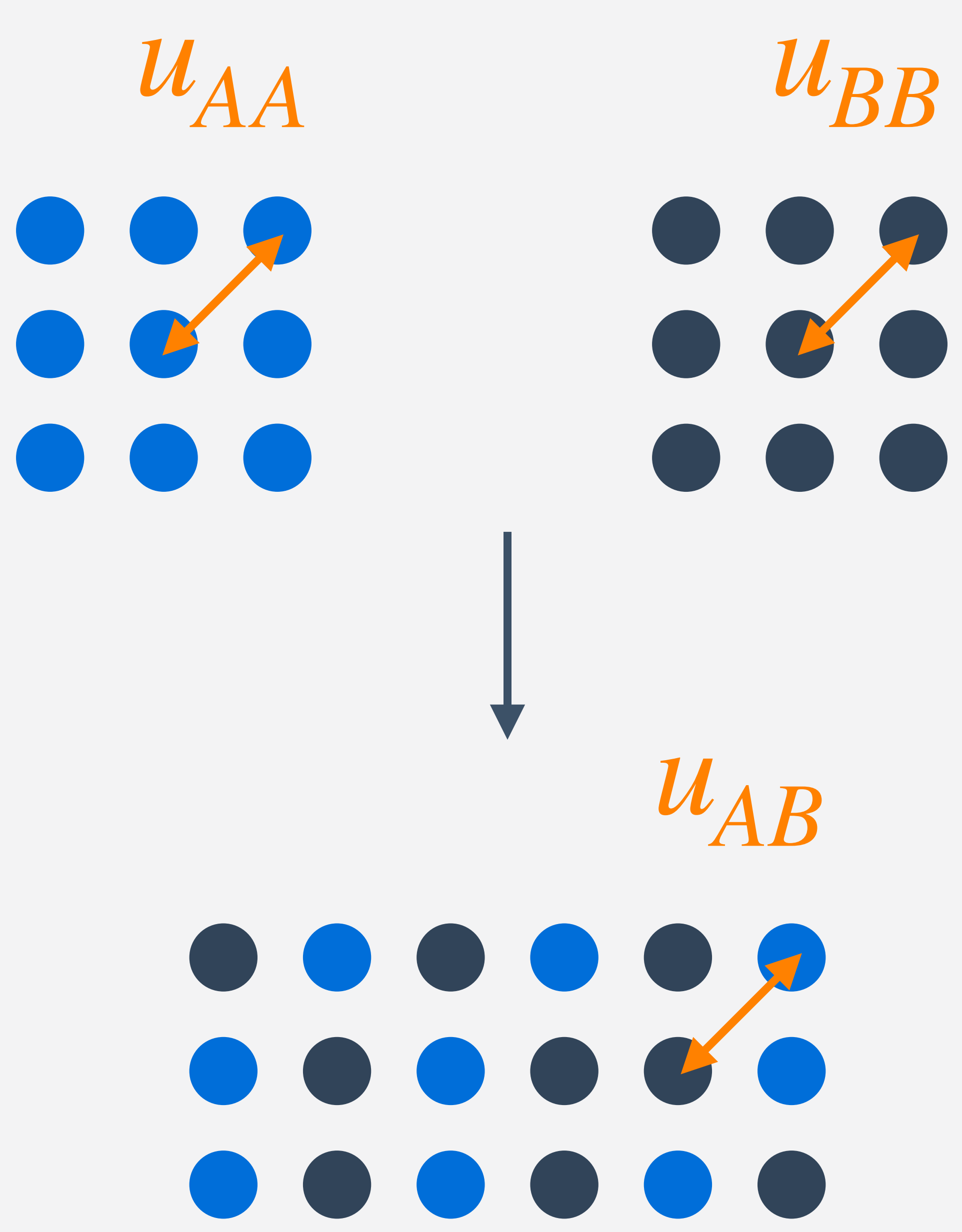
ideal polymer mixture (with $N_A = N_B = 10$)

ideal polymer solution (with $N_A = 10, \quad N_B = 1$)

ideal solution (with $N_A = N_B = 1$)

- ideal mixtures are homogenous as a result of an always positive mixing entropy

Mixing Enthalpy in Polymers



u_{AA}, u_{BB}, u_{AB}: pairwise interaction energies

average pairwise interaction energy:

$$U_A = u_{AA}\phi_A + u_{AB}\phi_B = u_{AA}\phi_A + u_{AB}(1-\phi_A)$$

total interaction energy of the mixture:

$$U = \frac{z}{2}\left(U_A n\phi_A + U_B n\phi_B\right)$$
$$= \frac{zn}{2}\left(u_{AA}\phi^2 + 2u_{AB}\phi(1-\phi) + u_{BB}(1-\phi)^2\right)$$

total interaction energy before mixing:

$$U_0 = \frac{zn}{2}\left(u_{AA}\phi + u_{BB}(1-\phi)\right)$$

the energy change on mixing per lattice site:

$$\Delta\overline{U}_{\text{mix}} = \frac{U-U_0}{n} = \frac{z}{2}\phi_A\phi_B(2u_{AB}-u_{AA}-u_{BB})$$

- **Flory interaction parameter, χ: describes the differences in the strength of pairwise interaction energies between species in a mixture**

$$\Delta\overline{U}_{\text{mix}} = \chi\phi_A\phi_B \mathrm{k}T \qquad \chi = \frac{z}{2}\frac{2u_{AB}-u_{AA}-u_{BB}}{kT} = \frac{\left(\sqrt{E_{coh}^{AA}}-\sqrt{E_{coh}^{BB}}\right)^2}{RT} = \frac{V_0(\delta_A-\delta_B)^2}{RT}$$

see **Lecture Notes** for details!

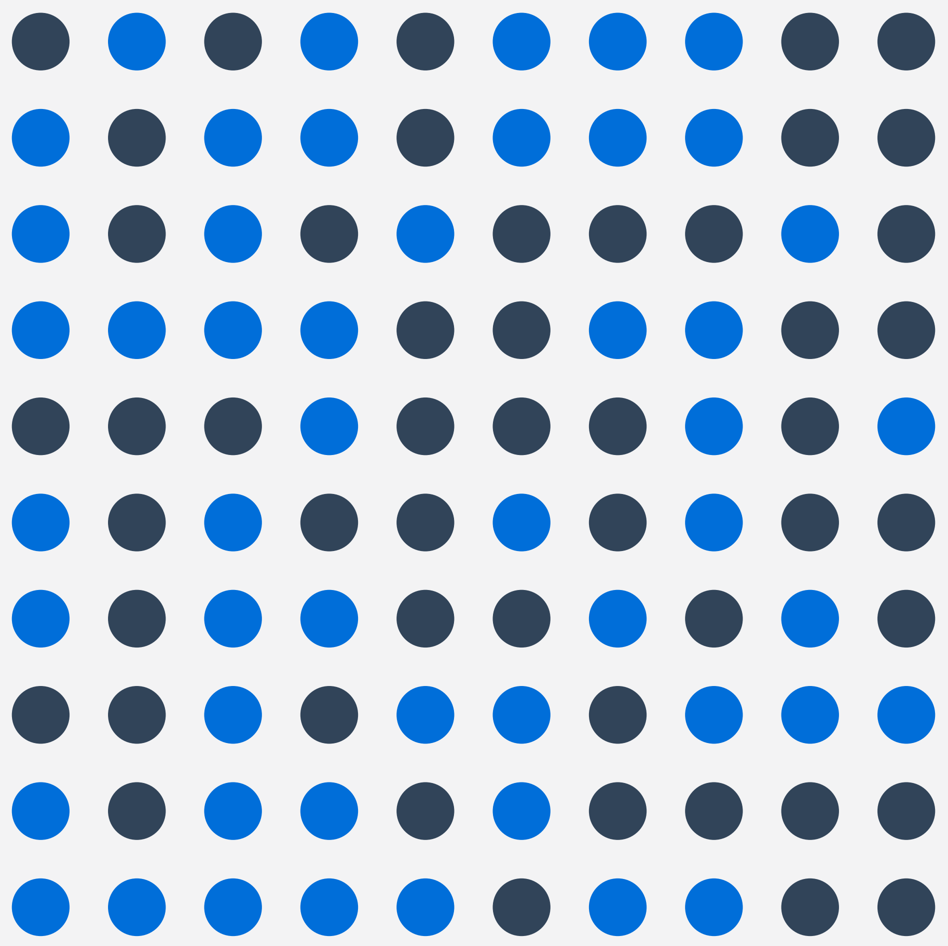
Free Energy of Mixing

- **Flory-Huggins equation:**

$$\boxed{\Delta\overline{G}_{\text{mix}} = \text{k}T\left(\frac{\phi_A}{N_A}\ \ln\phi_A + \frac{\phi_B}{N_B}\ \ln\phi_B + \chi\phi_A\phi_B\right)}$$

regular solution

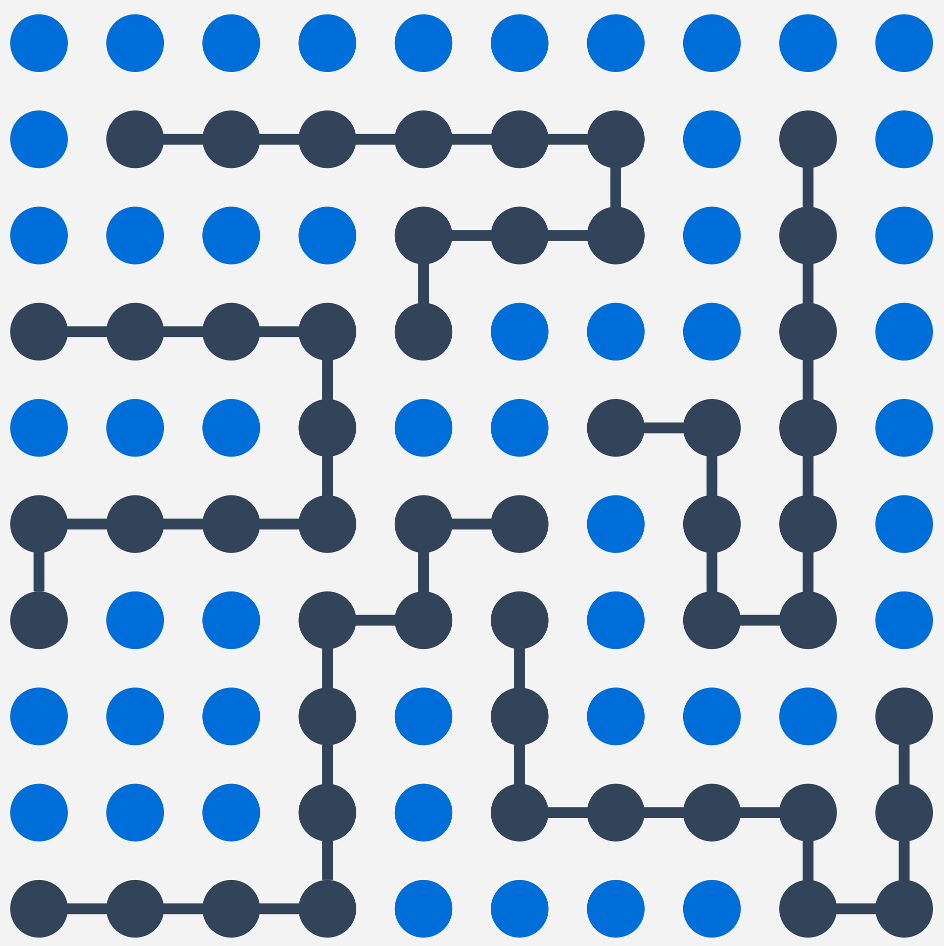
$(N_A = N_B = 1)$



$\Delta\overline{S}_{\text{mix}}/\text{k} = 0.69$

polymer solution

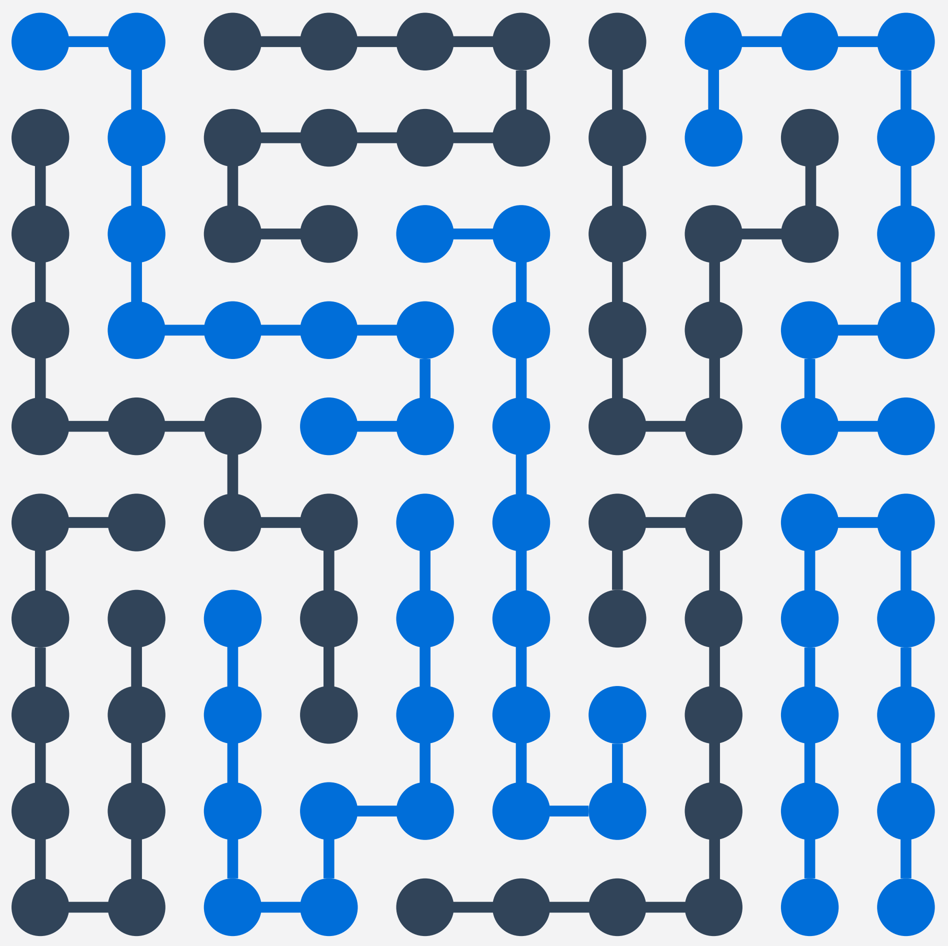
$(N_A = N \quad N_B = 1)$



$\Delta\overline{S}_{\text{mix}}/\text{k} = 0.38$

polymer blends

$(N_A \quad N_B)$



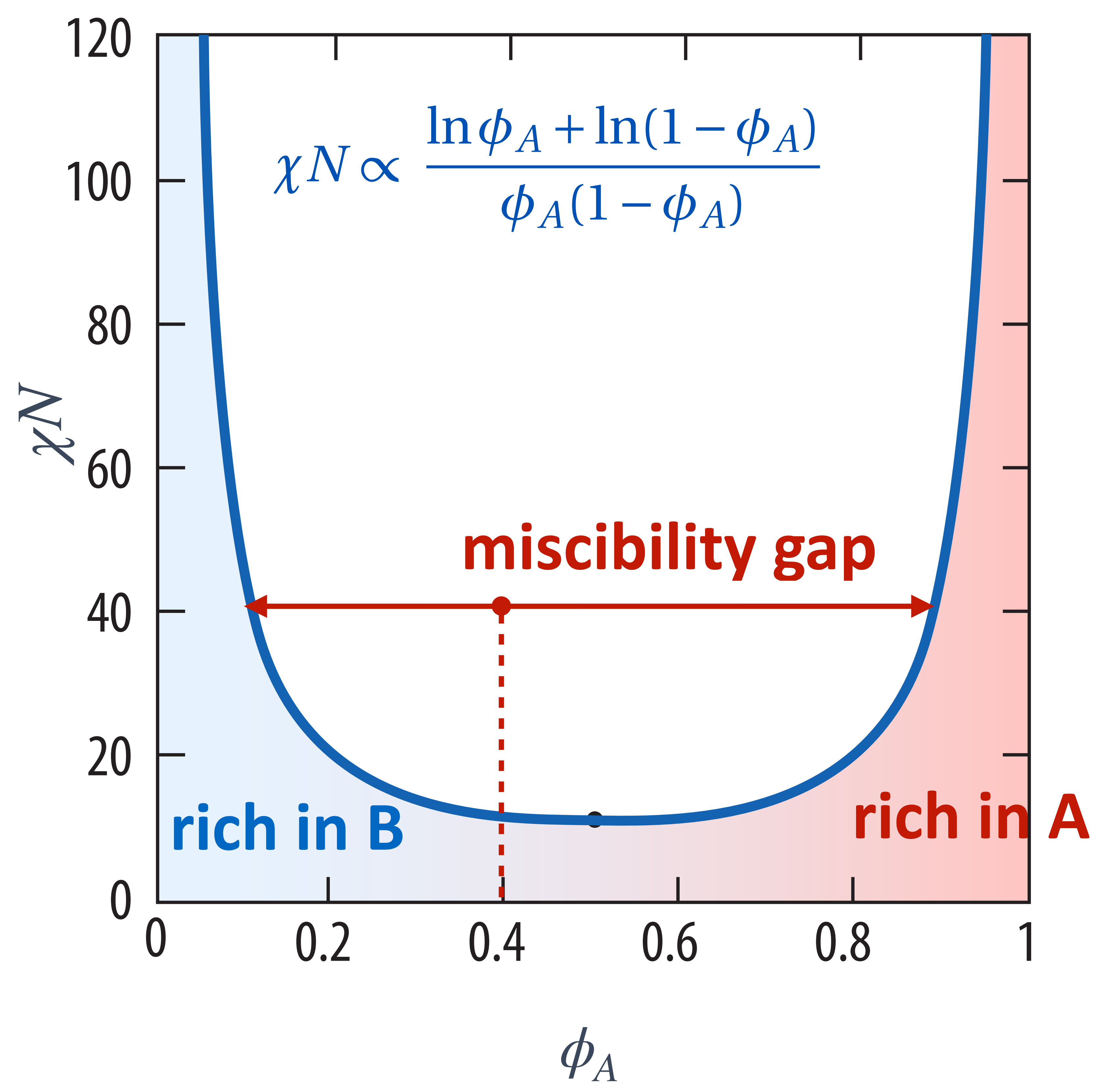
$\Delta\overline{S}_{\text{mix}}/\text{k} = 0.069$

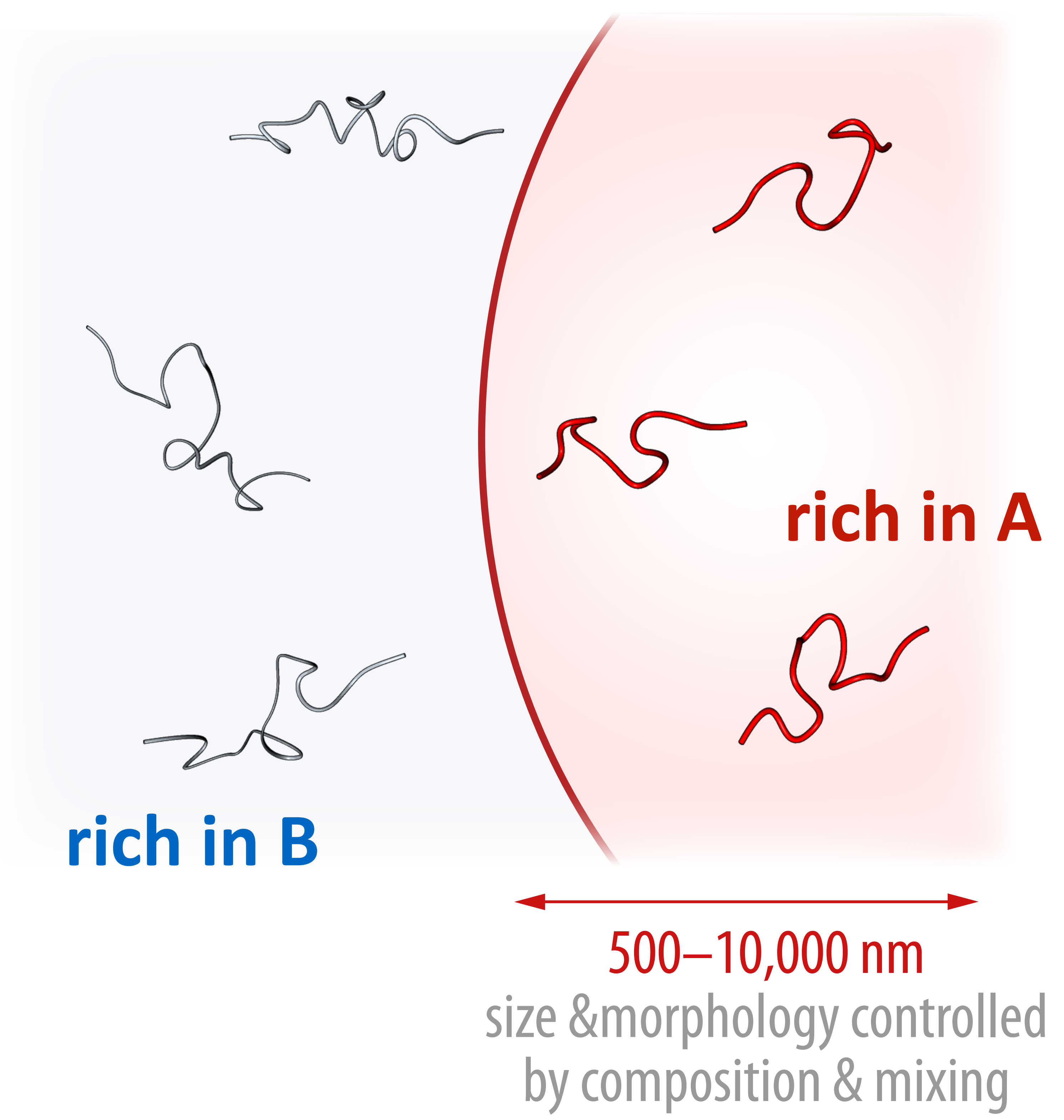
- entropic contribution becomes negligible for high molar masses (large N_A and N_B)
- since χ is positive (in case of no specific intermolecular interactions), a homogenous mixture of two polymers is thermodynamically unstable with respect to macroscopic phase segregation

Macroscopic Phase Segregation in Immiscible Polymer Blends

$$\phi_A \phi_B \chi + \frac{\phi_A \ln \phi_A}{N_A} + \frac{\phi_B \ln \phi_B}{N_B} = 0$$

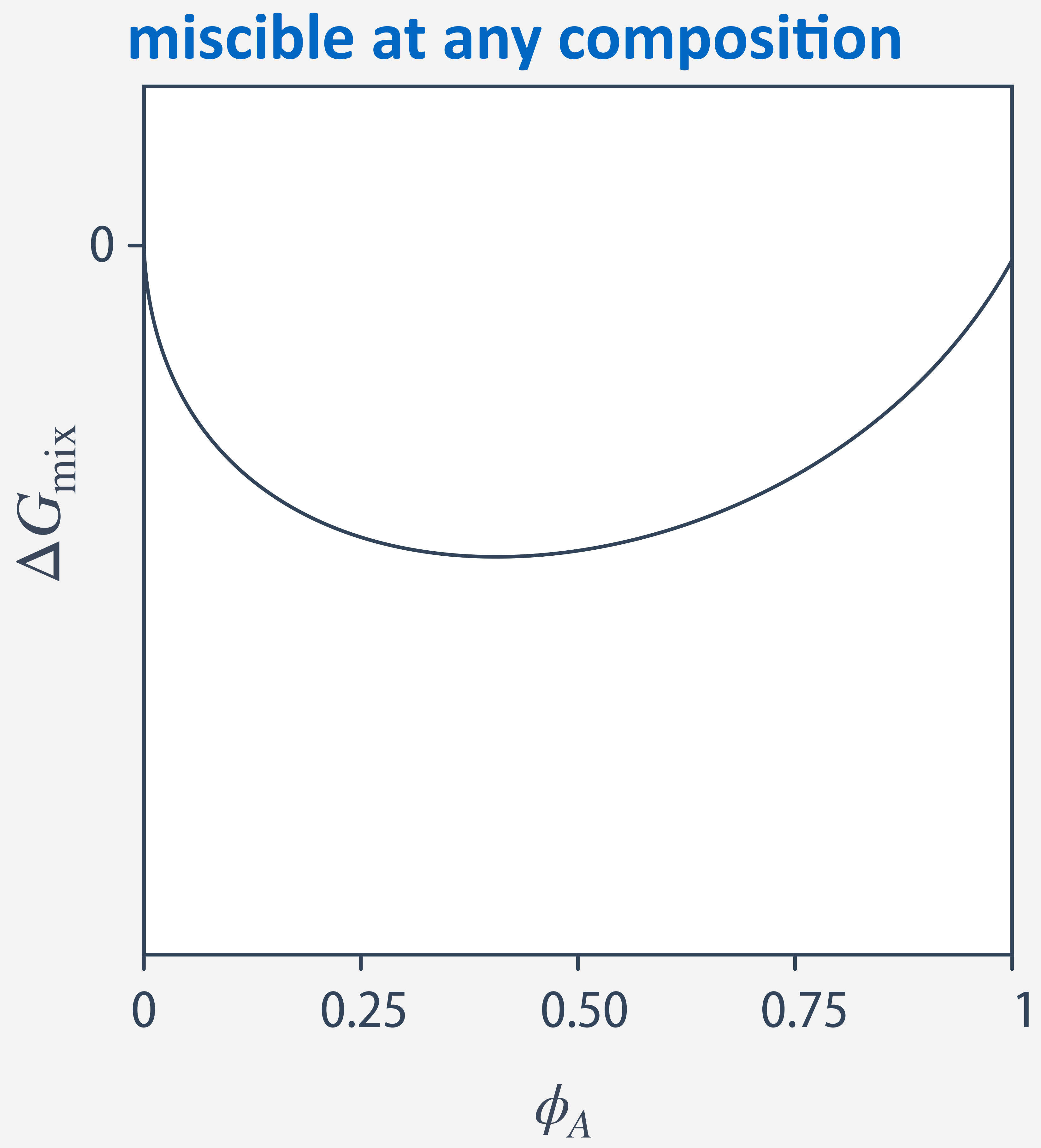
phase behavior of a symmetric blend:
$N_A = N_B = N$

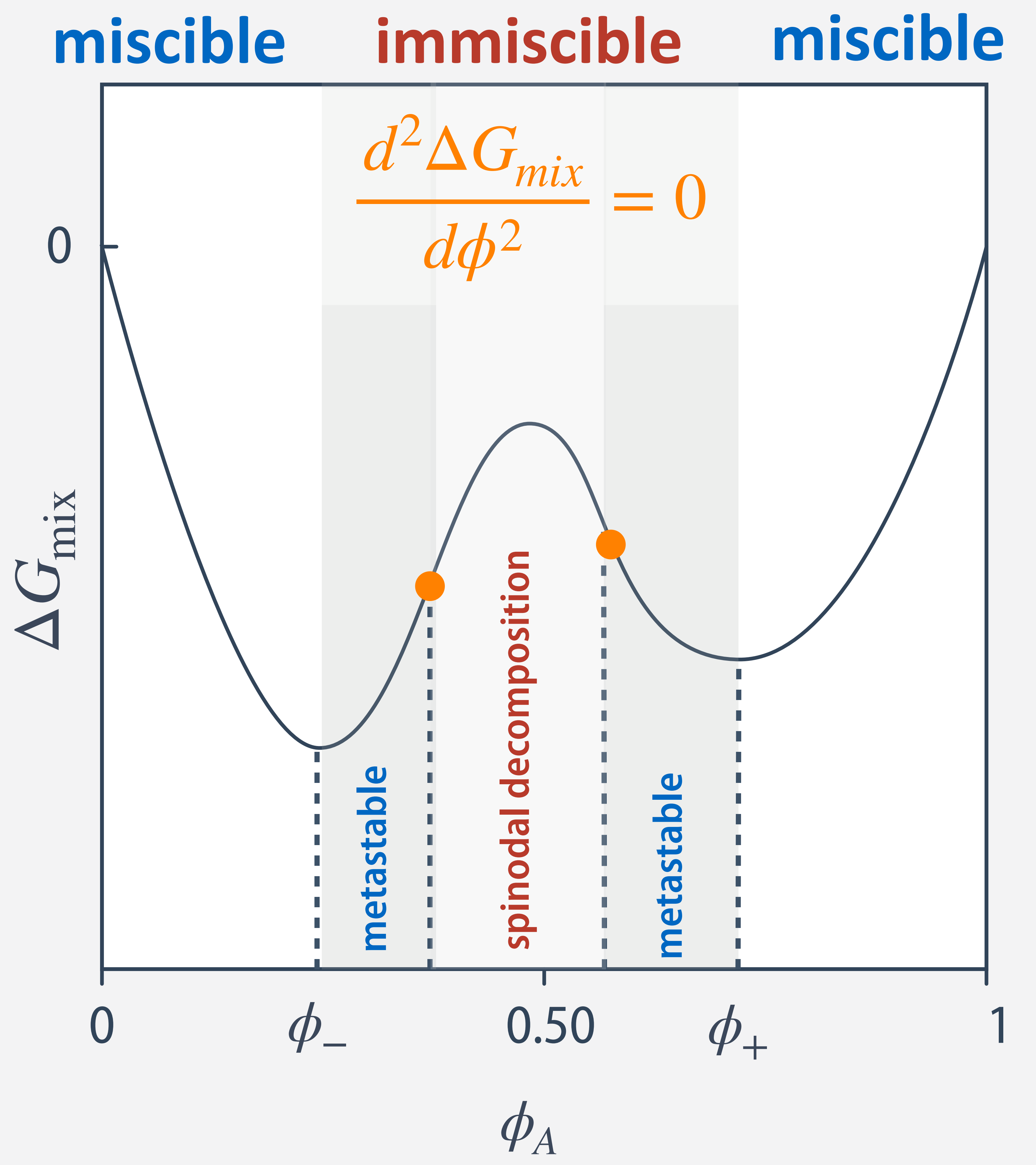




- **compositions corresponding to a state with two phases typically show macroscopically phase segregated domains, which often is not desired for mechanical properties.**

Phase Diagrams for Binary Mixtures





- **Lever rule:**

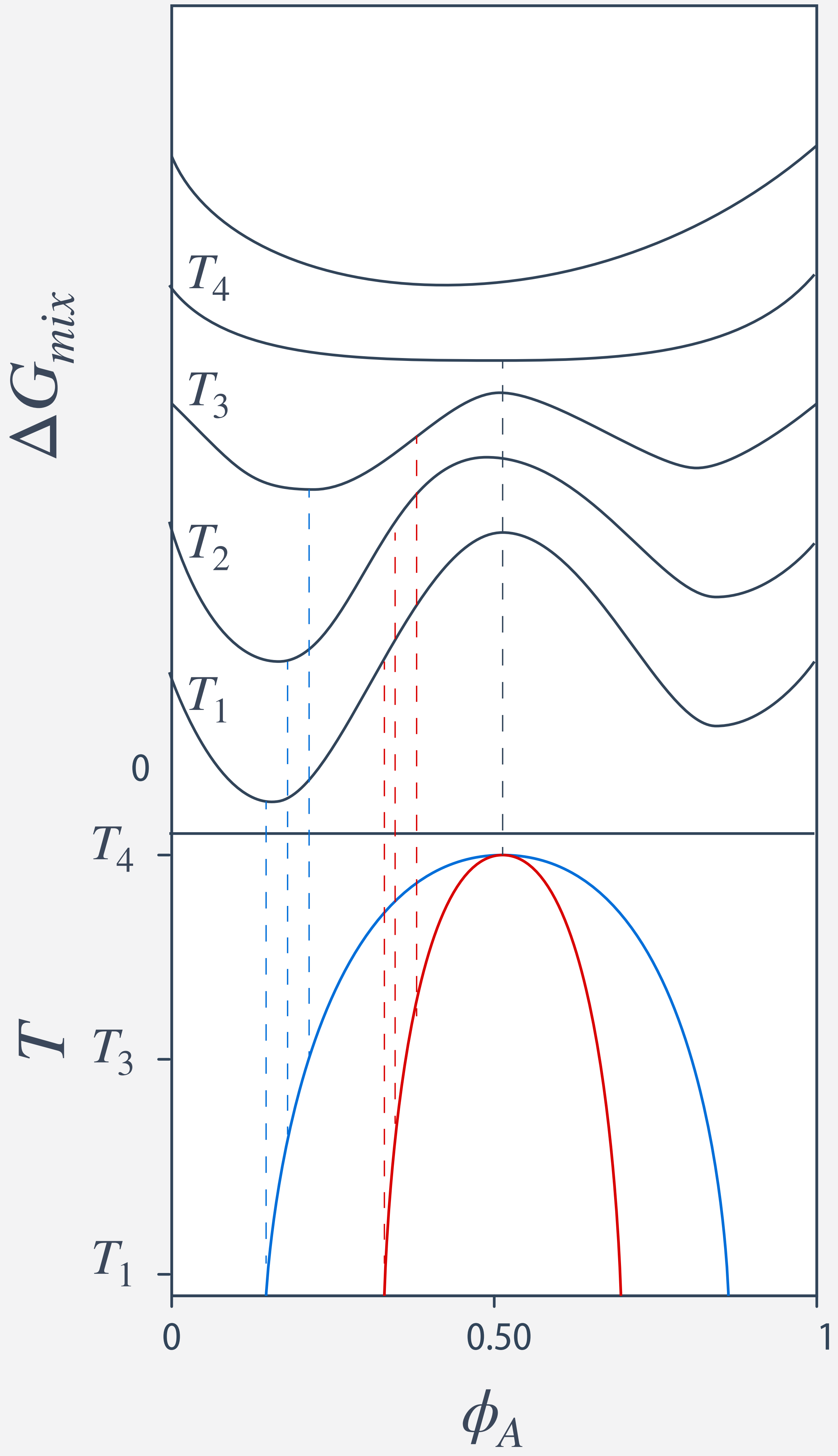
$$\phi = f_-\phi_- + f_+\phi_+ = f_-\phi_- + (1-f_-)\phi_+$$

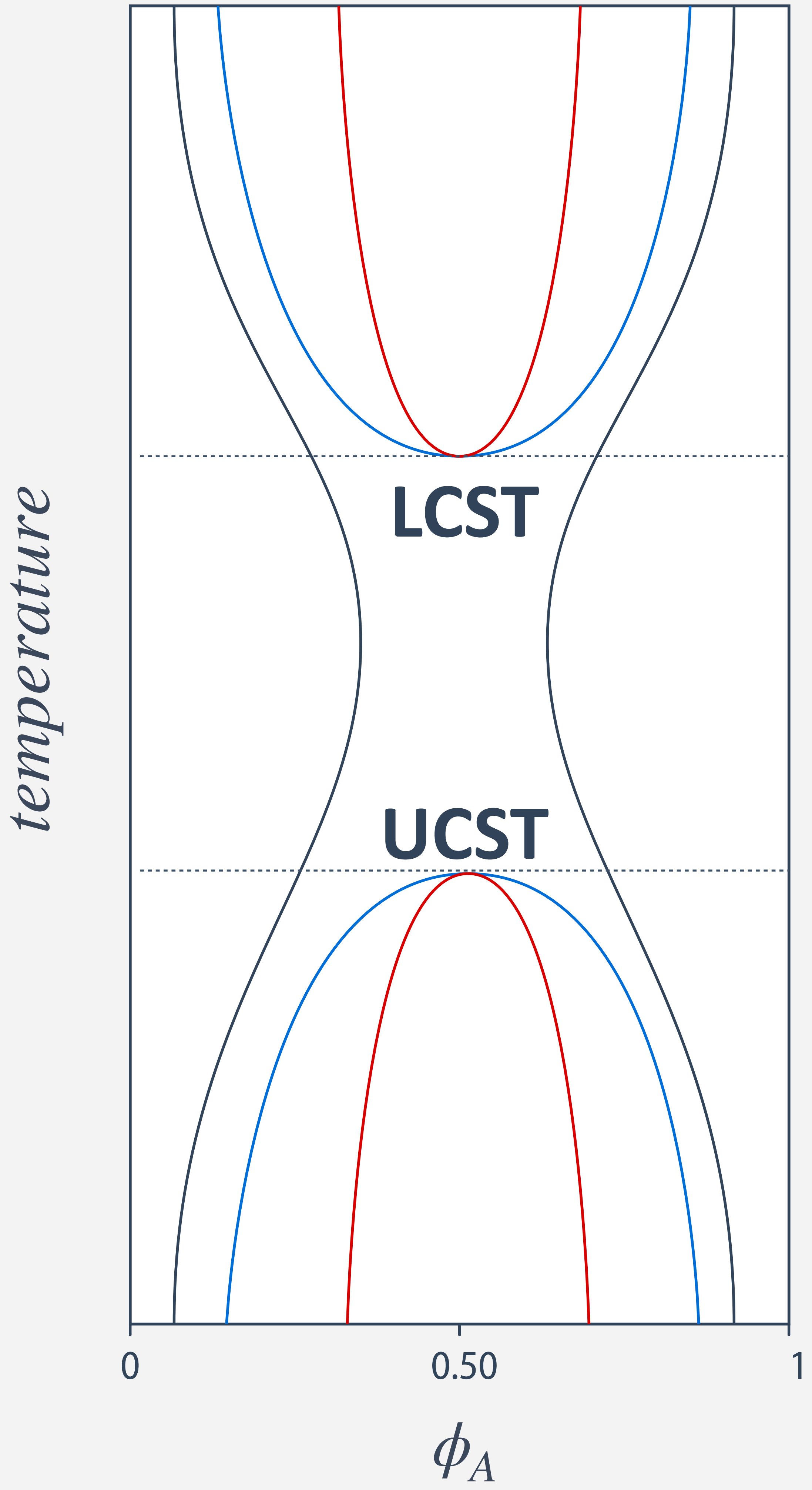
- **for certain combinations of χ, N_A, N_B two inflection points indicate the transition from binodal (nucleation-growth) to spinodal (instantaneous) decomposition**

Phase Diagrams for Binary Mixtures

Construction of Phase Diagrams

- construction of phase diagrams from the free energy curves versus χ at different T
- schematic representation of the binodal and spinodal curve for a binary mixture





lower critical solution temperature

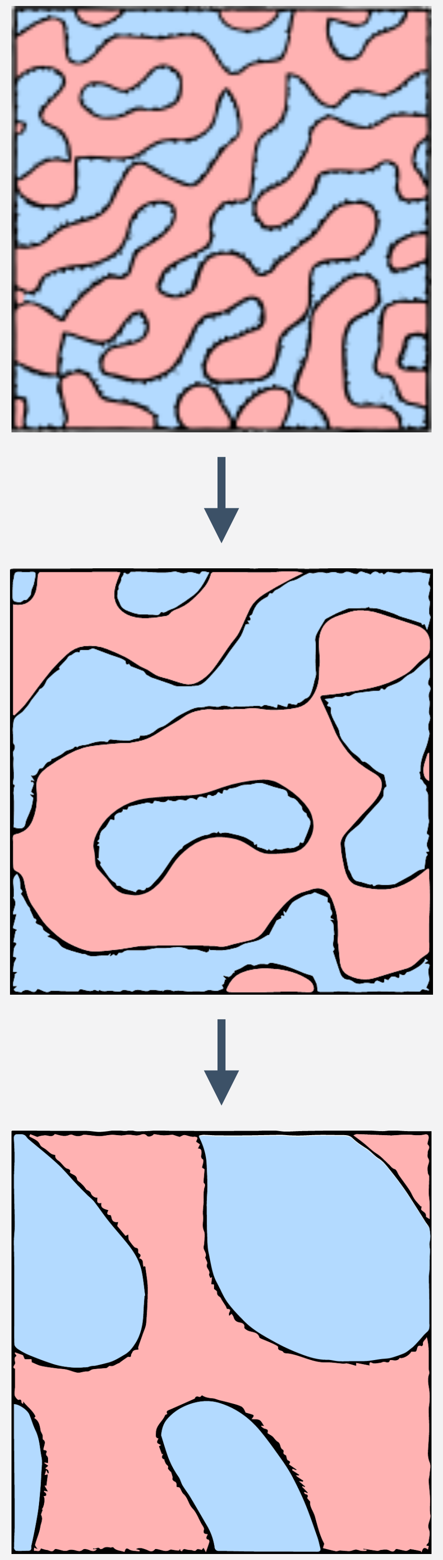
upper critical solution temperature

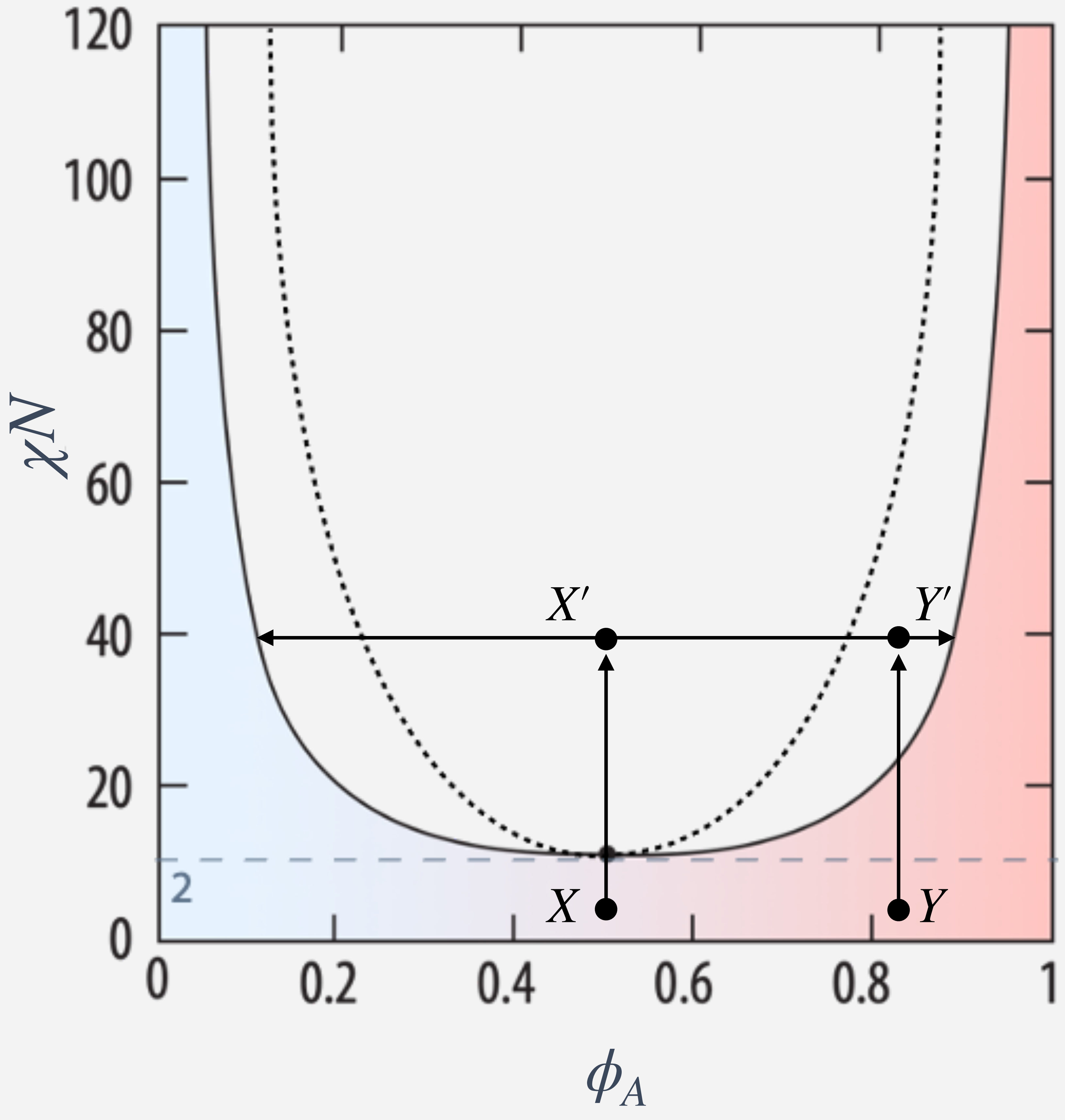
Spinodal Decomposition versus Nucleation & Growth

- small fluctuations in composition cause **immediate** phase separation in the spinodal regime
- nucleation in the metastable zone requires comparably large fluctuations and **requires time**

spinodal decomposition

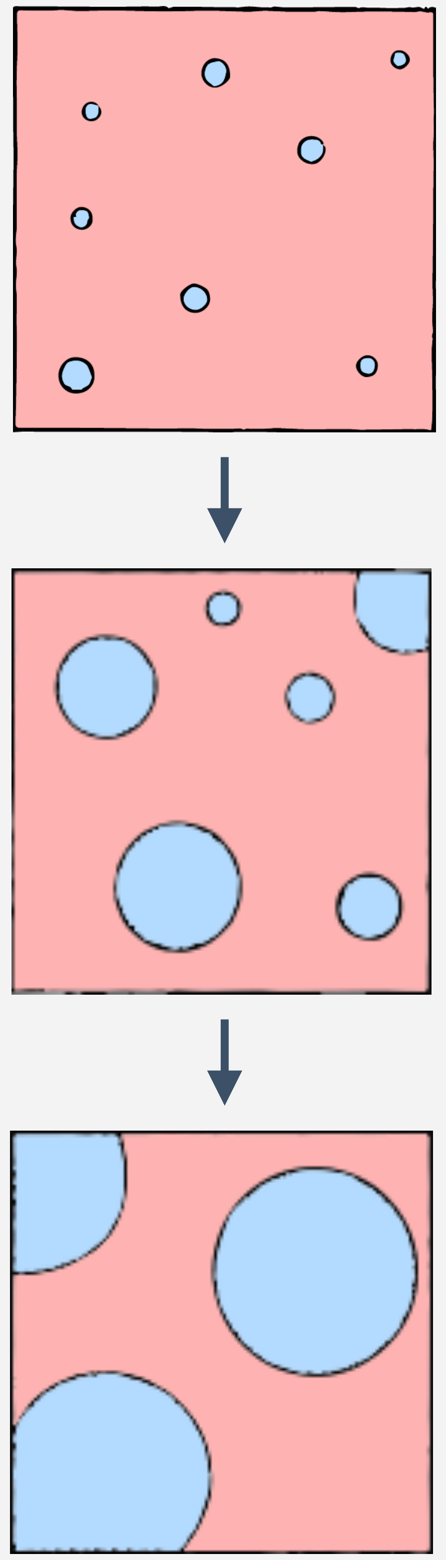
$X \rightarrow X'$





nucleation and growth

$Y \rightarrow Y'$



Effect of Flow on Mixing

- in general, immiscible polymers are exerted strong shear forces in an extruder

extrusion and injection molding

control parameters

viscosities η_1, η_2

viscosity ratio $\Lambda = \eta_1/\eta_2$

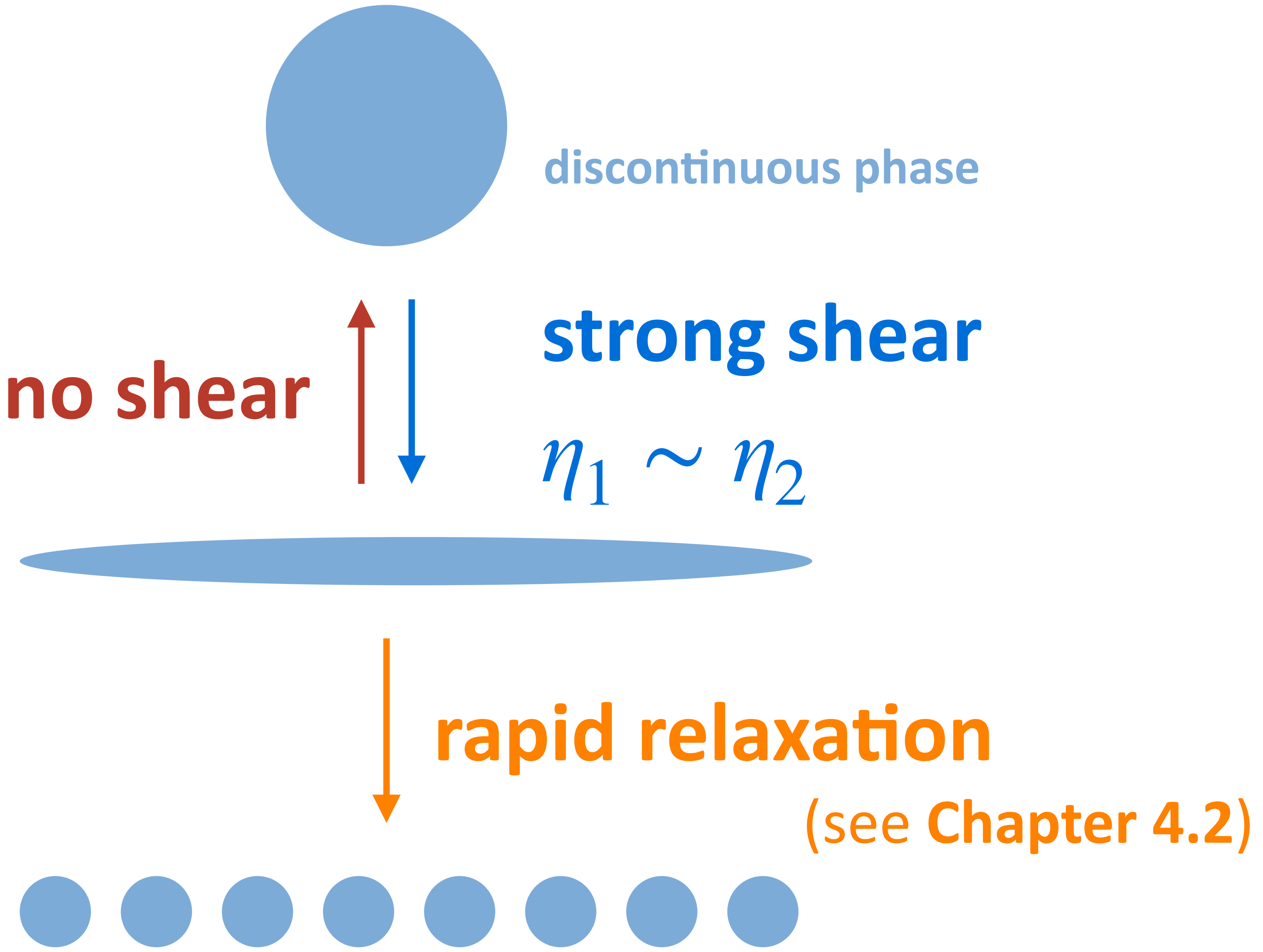
interfacial tension $\gamma_{1,2}$

capillarity index $\kappa = d\sigma/\gamma_{1,2}$

stress σ

initial domain size d

flow conditions

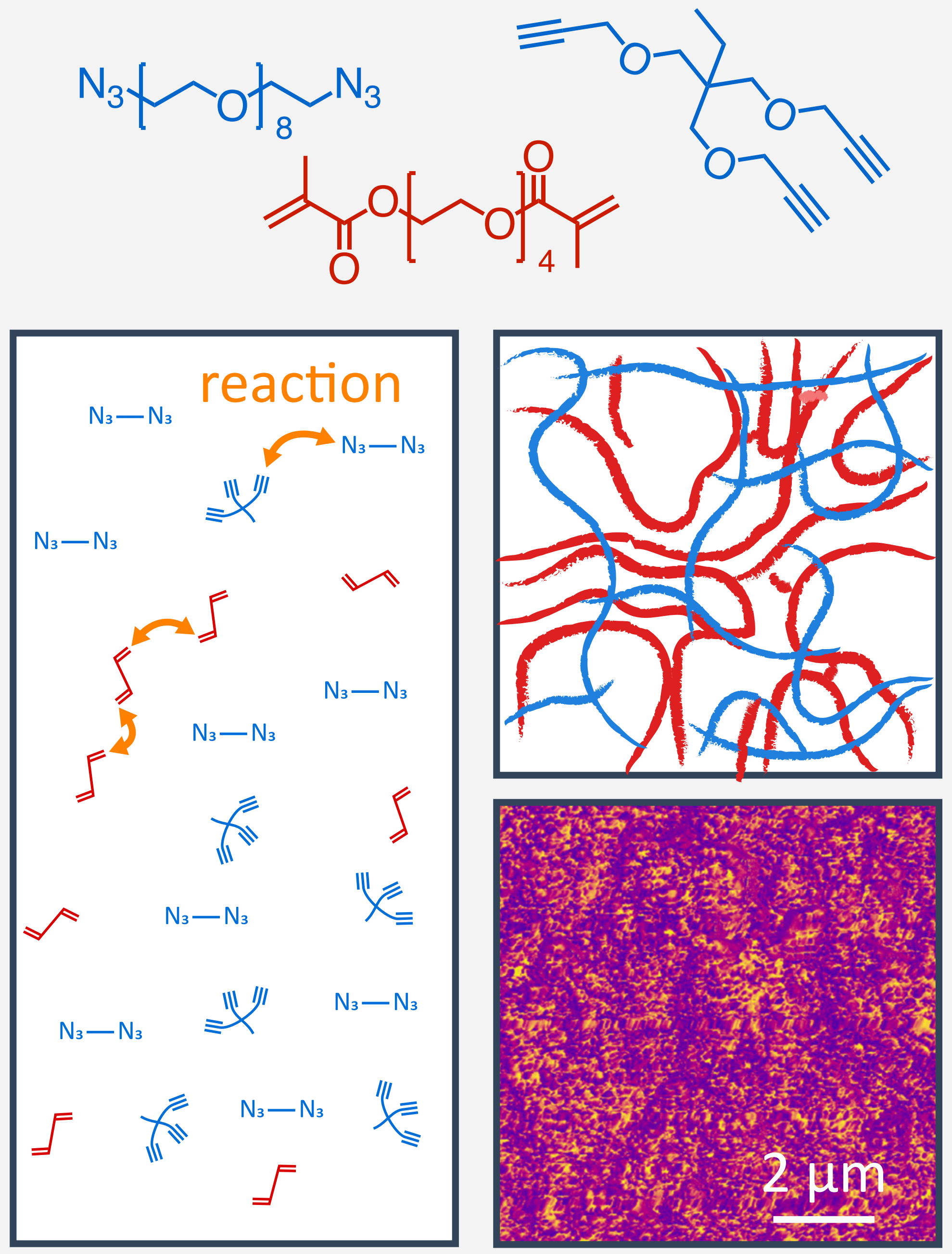


- for $\Lambda < 3.8,\ \kappa > 0.1$: general deformation of the domains of the minor phase
- for $\Lambda < 3.8,\ \kappa > 4$: fibrillar structures may transform into small spherical domains.

Other Ways of Producing Phase-Separated Mixtures

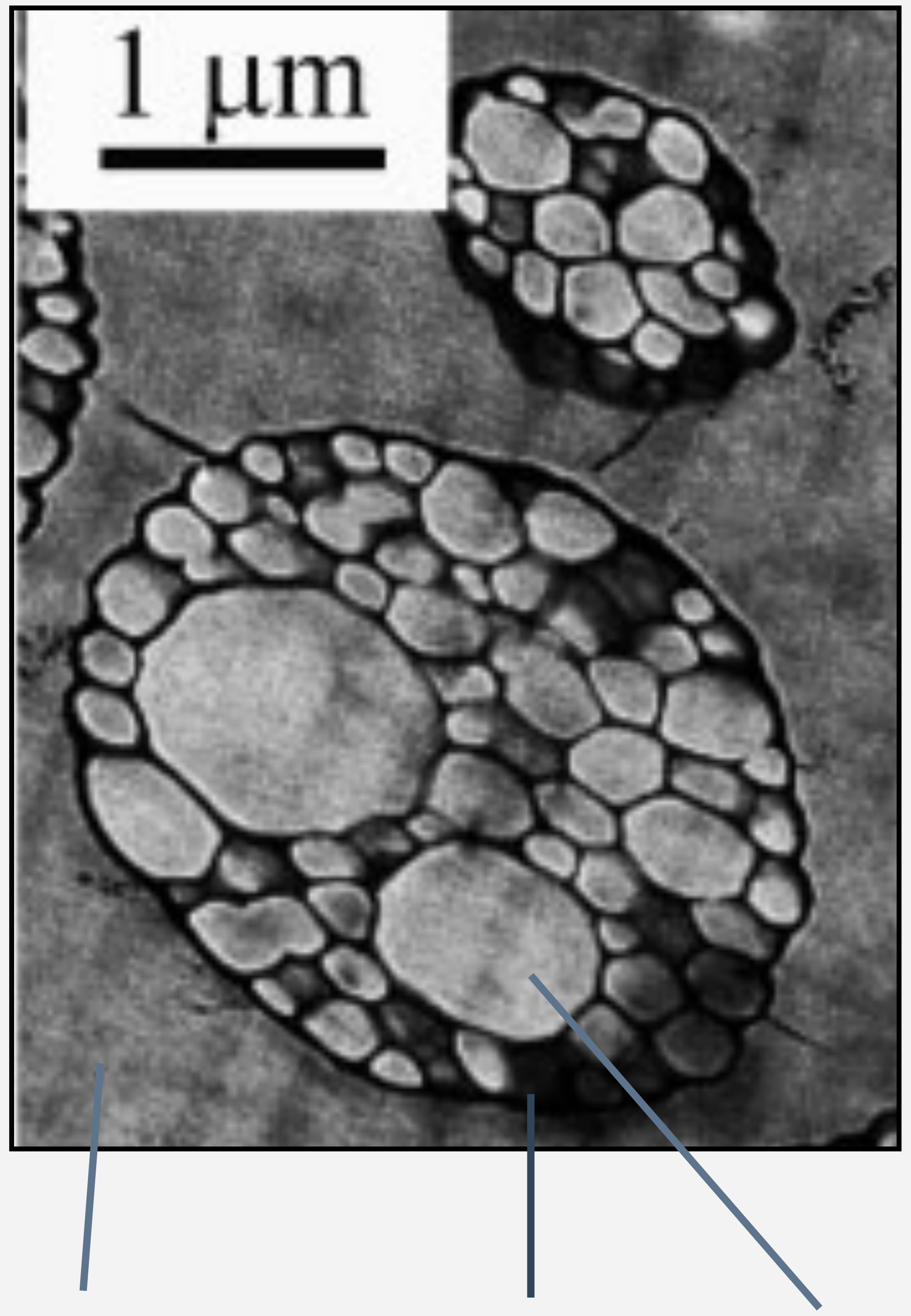
interpenetrating networks

highly cross-linked



emulsion polymerisation

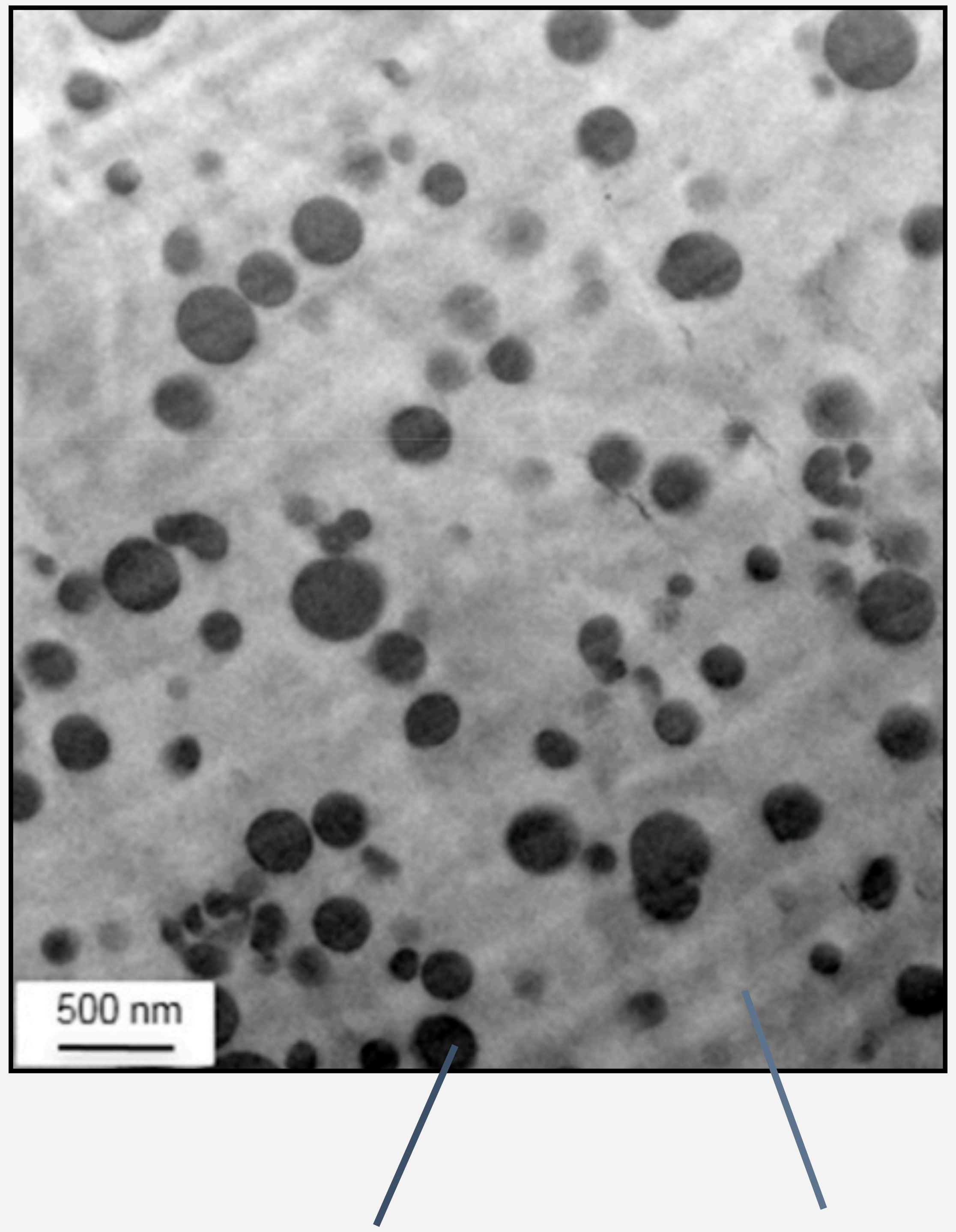
e.g. high impact polystyrene HIPS



PS PB PS

reactive blends

(in-situ synthesis of the different components)

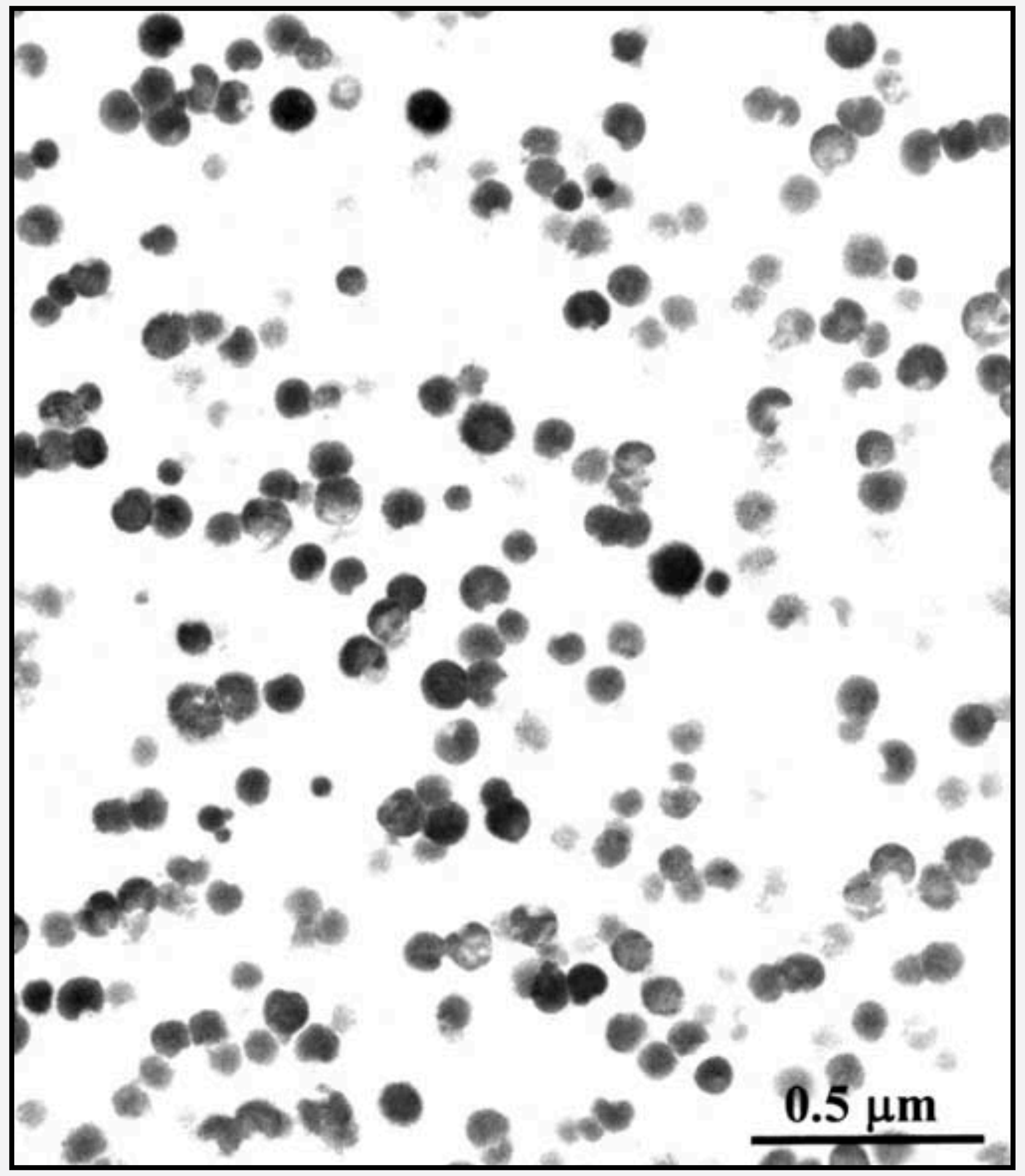


in-situ polymerised polyimide

iPP

preformed & cross-linked particles

(rubber-toughened PMMA)

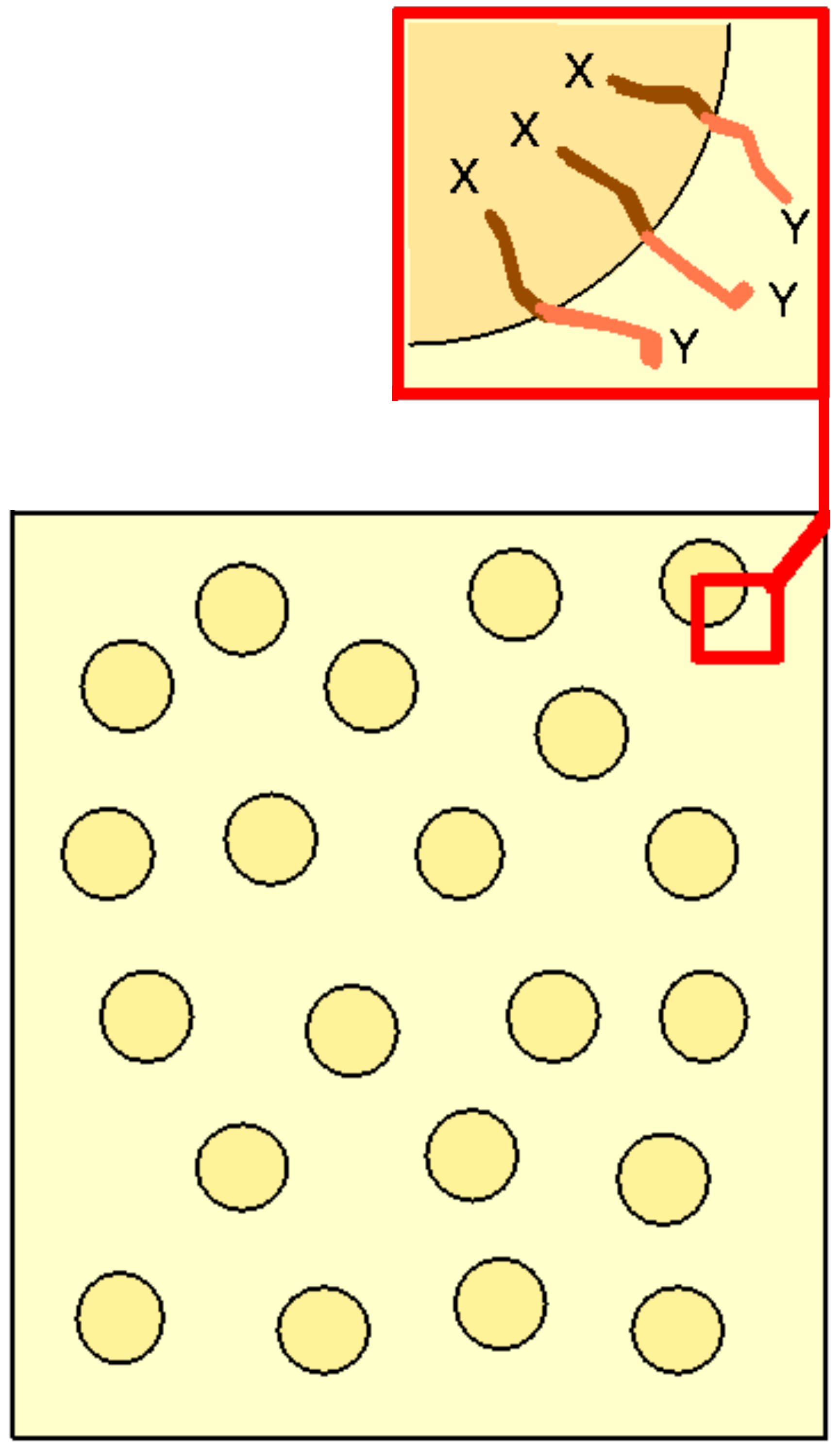


see Chapter 4.3

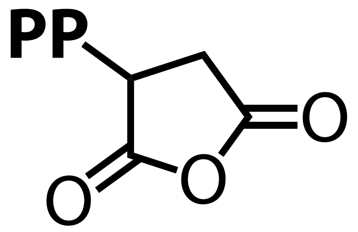
Compatibilization Strategies

- immiscible polymers are compatibilized to stabilize blend morphologies

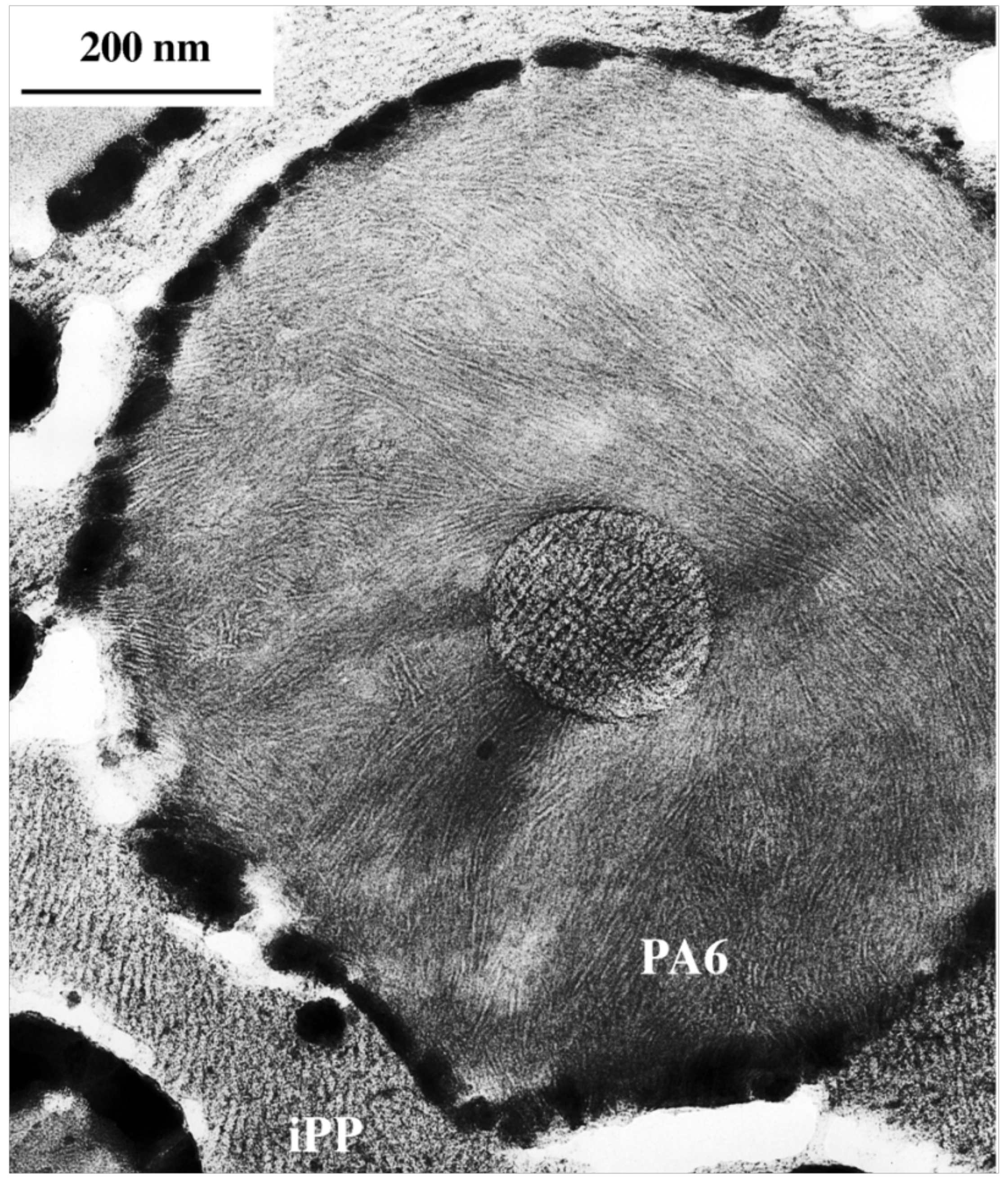
emulsification



in-situ compatibilization

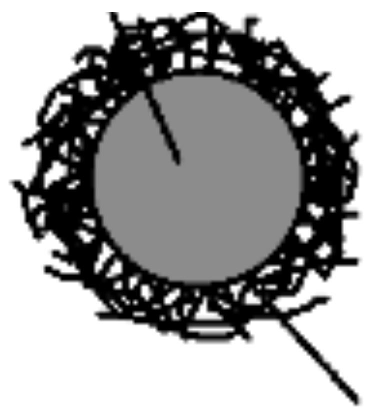


H_2N–**PA6**–NH_2



grafted particles

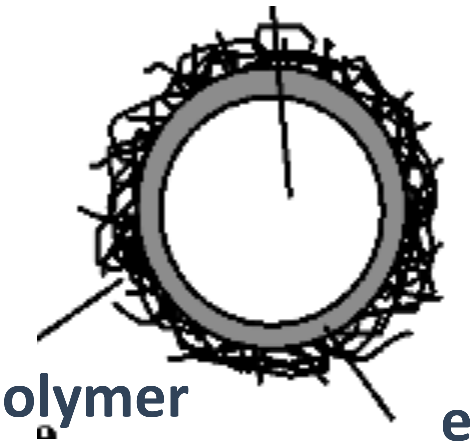
2 layers:



elastomeric core
(e.g. PB-co-styrene)

grafted polymer
(e.g. PMMA)

3 layers:



glassy core

grafted polymer
(e.g. PMMA)

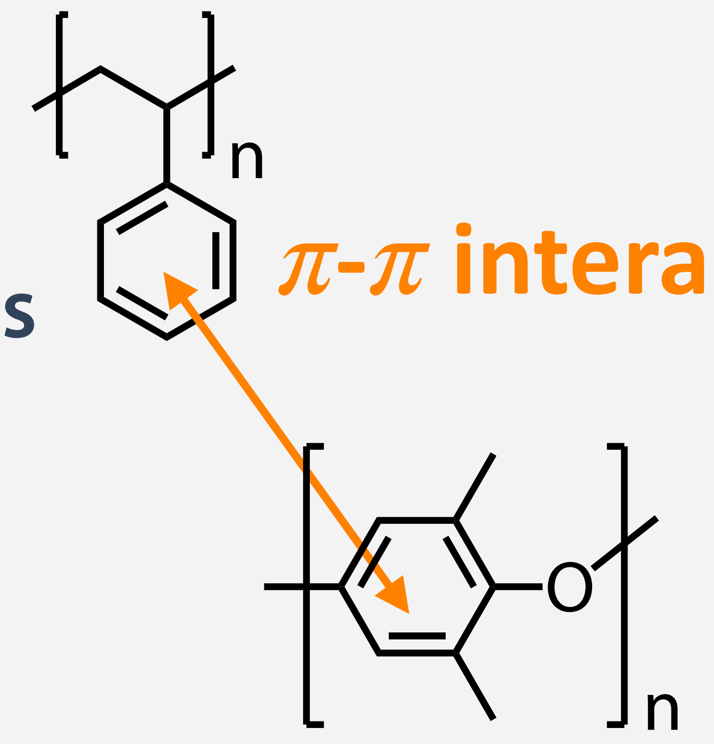
elastomeric shell
(e.g. PB-co-styrene)

- stabilization by improved interphase adhesion and/or lowered interfacial tension

Miscible Polymer Blends

- **Flory-Huggins theory is based on simplifications (ideal chains, constant volume, pure enthalpic origin of the interaction parameter, no specific intermolecular interactions)**
- though Flory-Huggins theory predicts general immiscibility of two polymers ($\Delta S \propto 1/N, \chi \propto 1/T$), more than 400 miscible systems are known:

PS/PPO

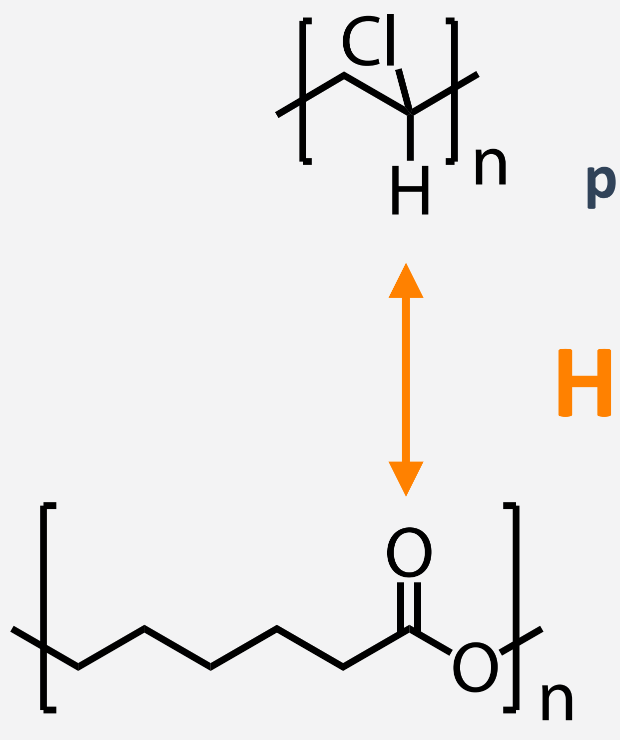


PS

π-π interactions

poly(phenylene oxide)

PVC/PCL



poly(vinylchloride)

H-bonding interactions

poly(ϵ-caprolactone)

- **miscibility can be favoured by π-π interactions, H-bonding, ionic interactions,…**

Applications of Miscible Polymer Blends

- **miscibility is particularly favoured, if the specific interaction are only encountered in the mixture**

PS + PPO

Noryl™

improved ductility

increased T_g

PVC + PEC (perchlorinated PE)

improved ductility

decreased T_g

- **modification of glass transitions without compromising transparency**
- **synergistic combination of advantageous properties of the respective homopolymers**

5.2

Block Copolymers

Two Types of Copolymers

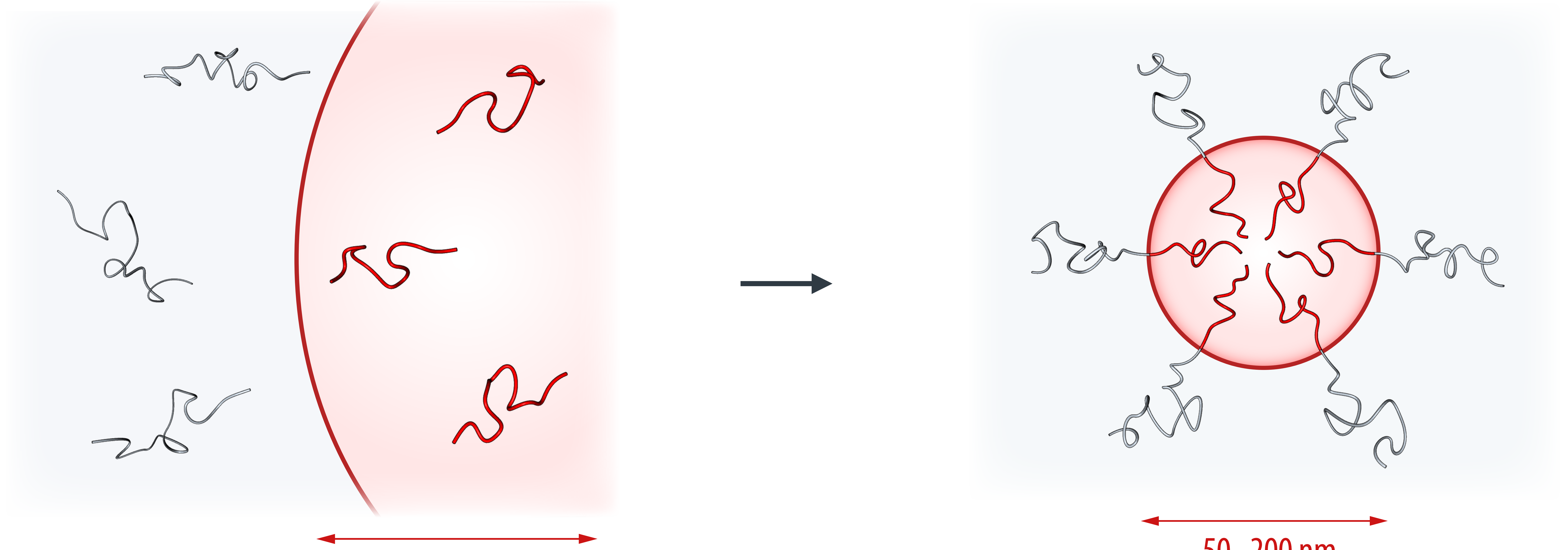
1. Random Copolymers

- T_g is roughly an average of the constitutional components; T_m is either low or not existent
- allows to combine incompatible monomers
- example 1: Poly(ethylene-*co*-propylene) (EPR): a rubber
- example 2: Poly(styrene-*co*-acrylonitrile) (PSAN): a glassy polymer, easier to process than PAN)

2. Block Copolymers

- typically two glass transition temperatures and at least one melting point
- allows to combine different properties (i.e. elastomer + glassy polymer) at reduced domain sizes (on the order of R_g) and stabilized interfaces
- total free energy depends on surface tension, entropic forces, and is a function of block length and stiffness as well as curvature of the interfaces, …
- for mono disperse blocks: well defined block length give rise to periodic structures with constant curvature at the interface (at least for diblock copolymers)

Polymer Blends versus Block Copolymers



polymer blends

500–10,000 nm
size &morphology controlled
by composition & mixing

coil–coil block copolymers

50–200 nm
size &morphology controlled
by block lengths

- **phase segregation occurs at smaller length scales and is controlled by block lengths**

Phase Diagrams

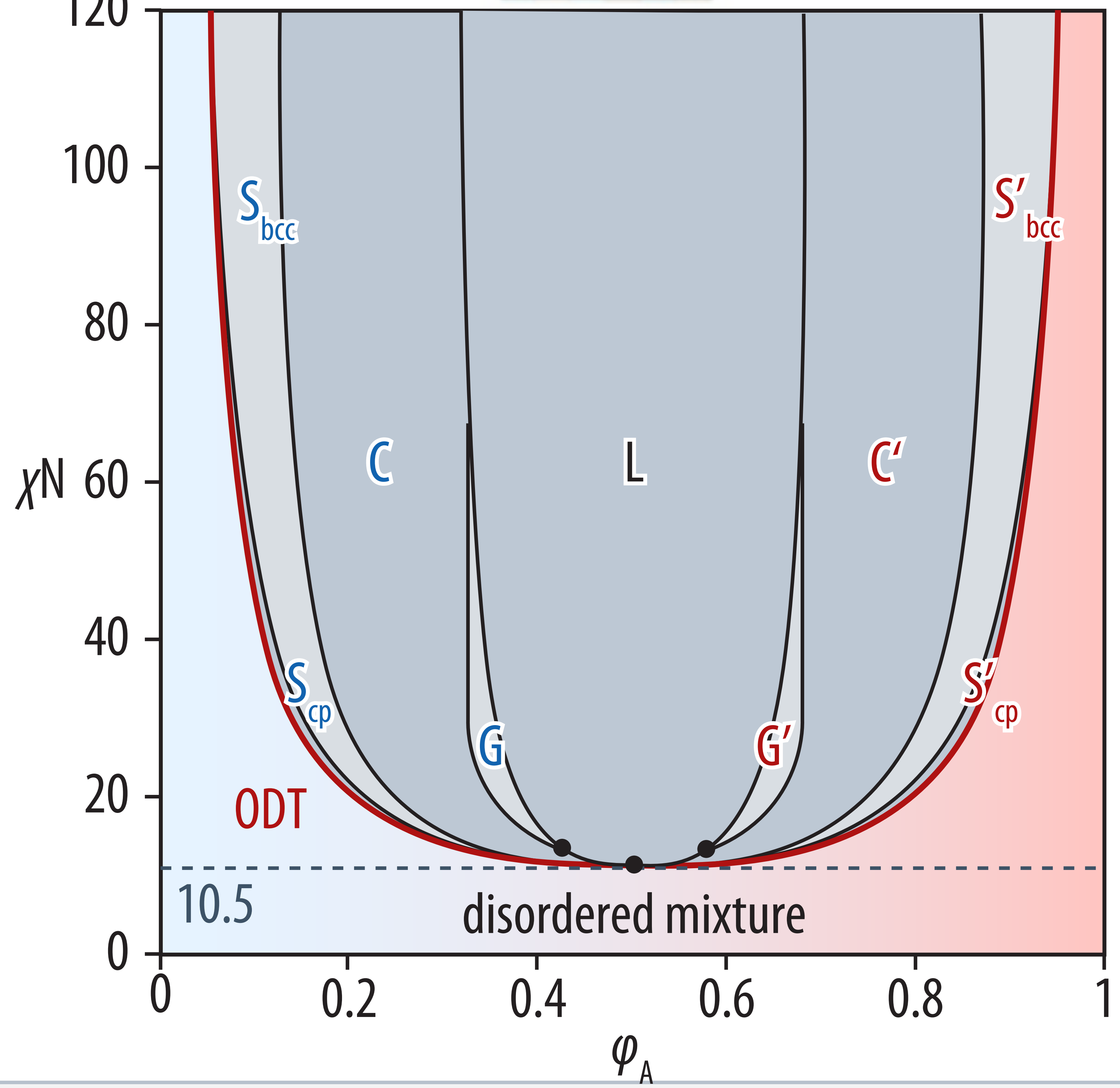
- very characteristic periodic morphologies for monodisperse blocks according to (i) the ratio of block lengths l_A/l_B and (ii) temperature

close-packed spheres (S_{cp})
body-centered spheres (S_{bcc})
body-centered cubic (bcc)
Q_{Im3m}

cylinders (C)
hexagonally (close) packed
cylinders (HPC, hex)

gyroid (G)
cubic bicontinuous (cbc)
Q_{Ia3d}

lamellar (L)



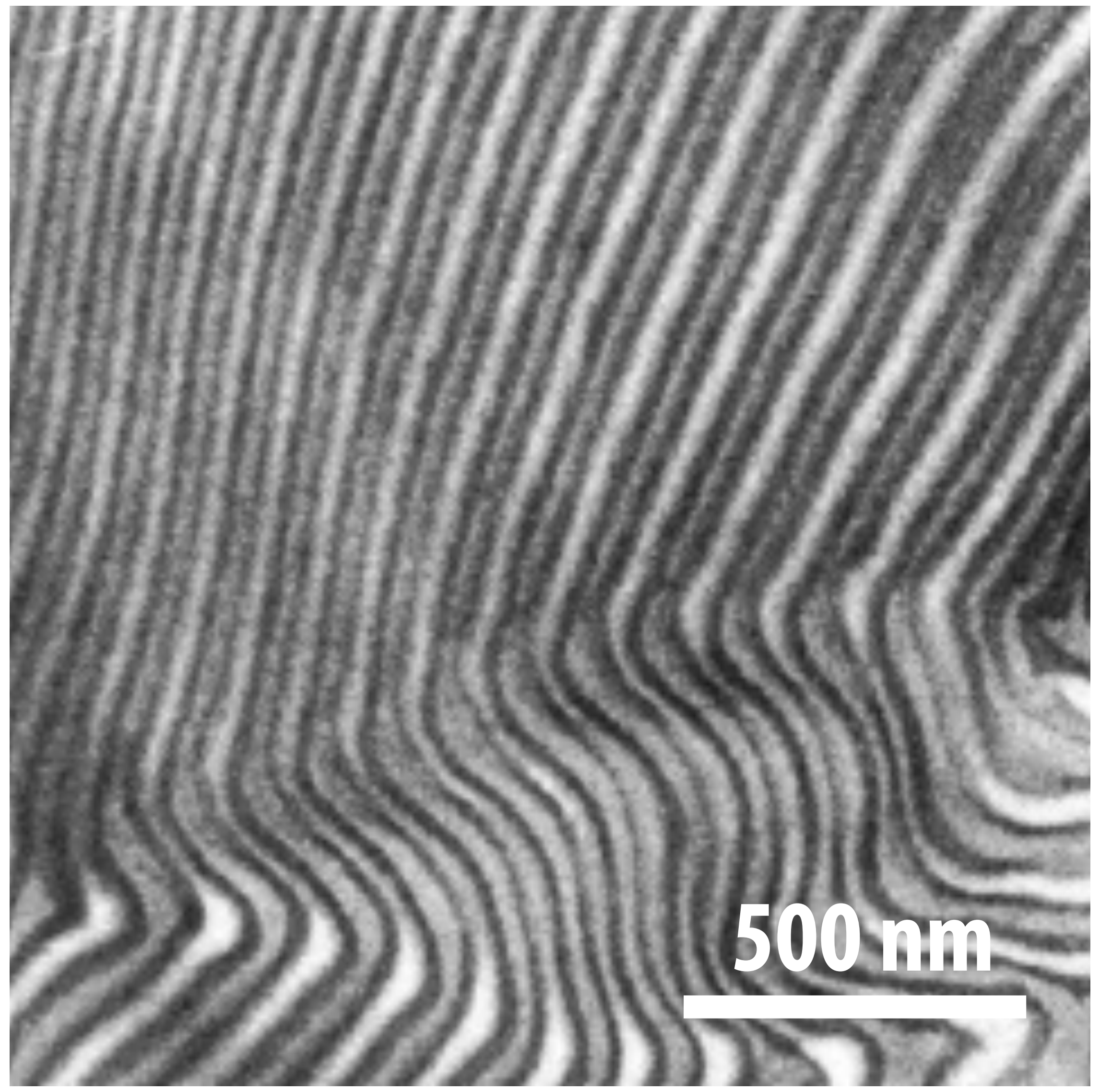
close-packed spheres (S'_{cp})
body-centered spheres (S'_{bcc})
body-centered cubic (bcc)
Q_{Im3m}

cylinders (C’)
hexagonally (close) packed
cylinders (HPC, hex)

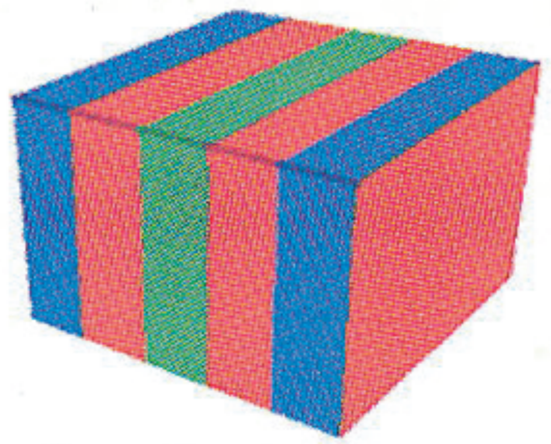
gyroid (G’)
cubic bicontinuous (cbc)
Q_{Ia3d}

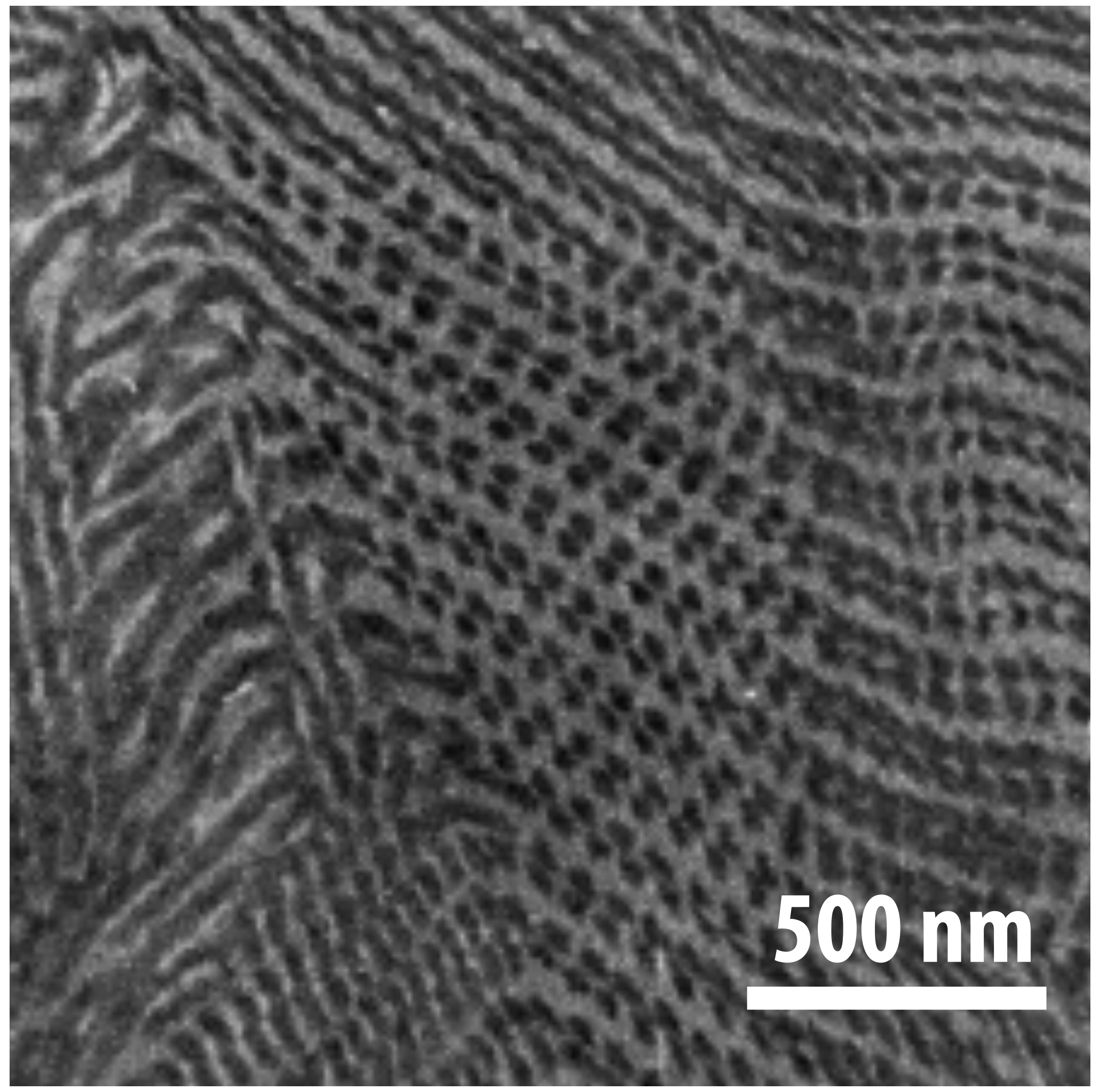
Triblock Copolymers

transmission electron microscopy (stained with OsO_4)

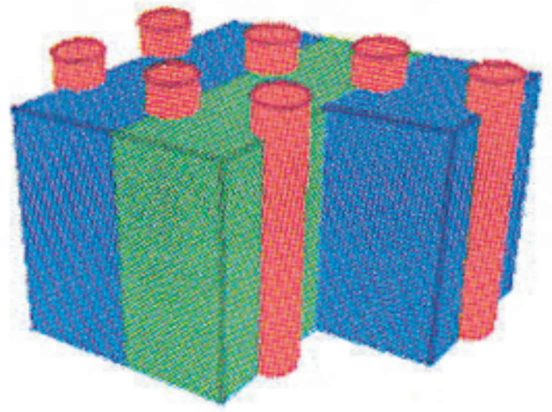


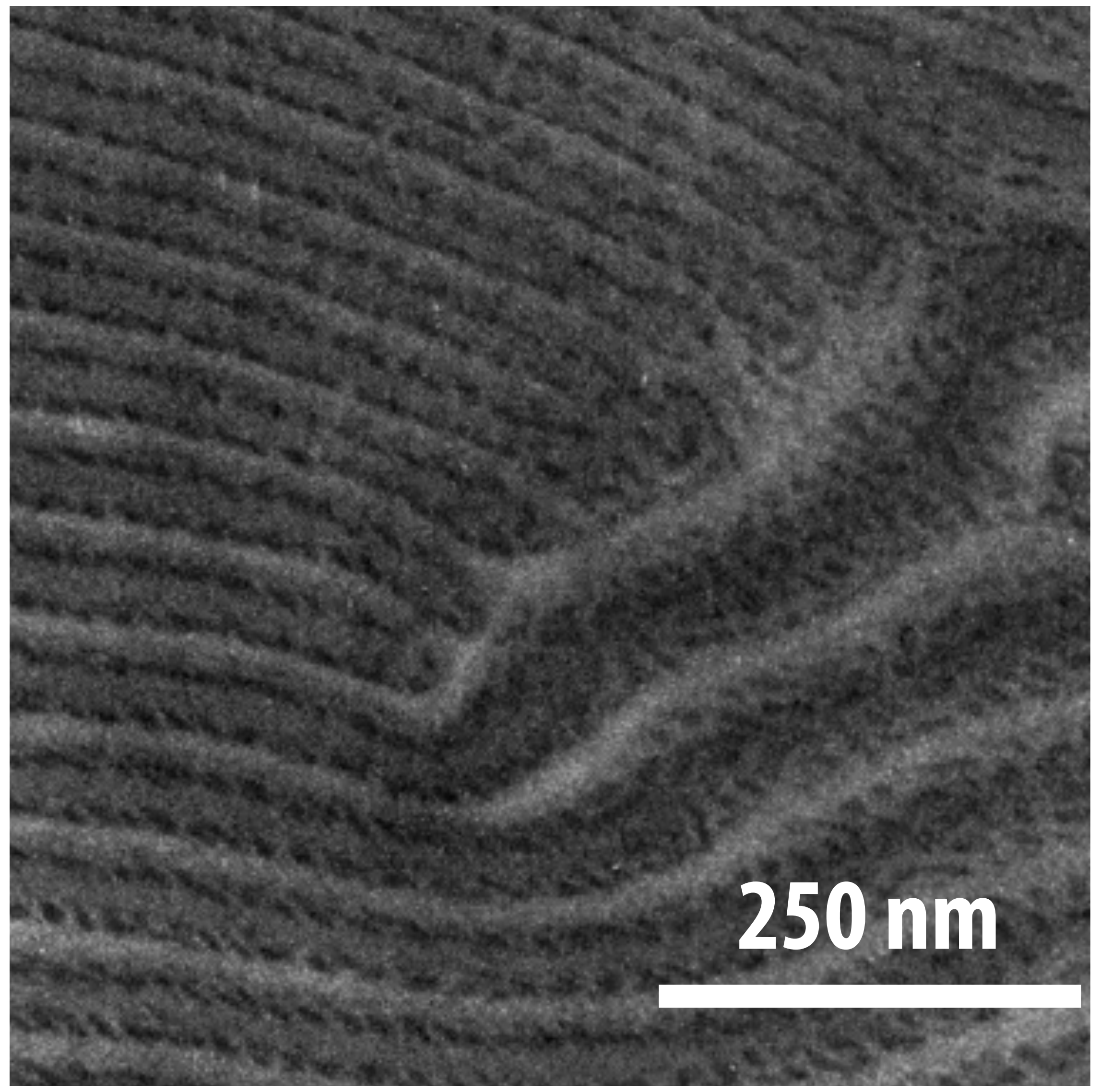
SBM 38
lamellae



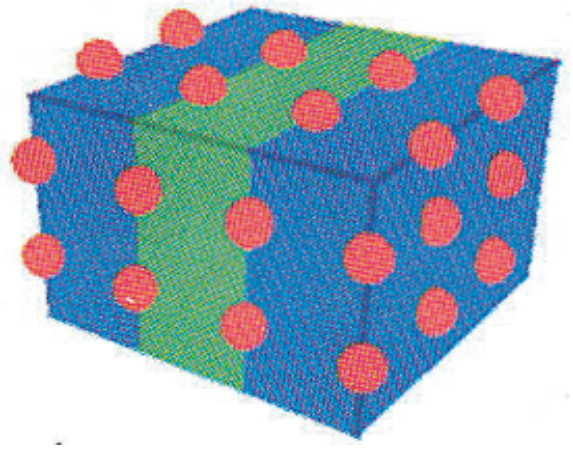


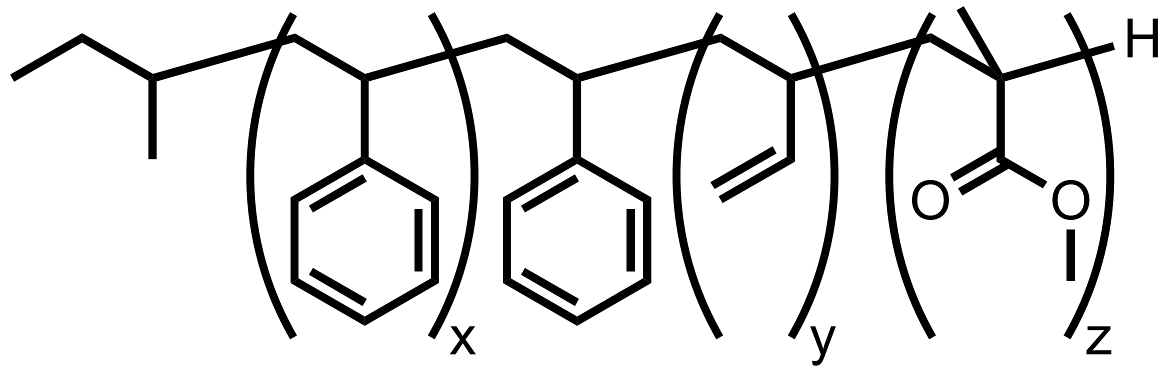
SBM 17
cylinders-at-lamellae





SBM 6
spheres-at-lamellae

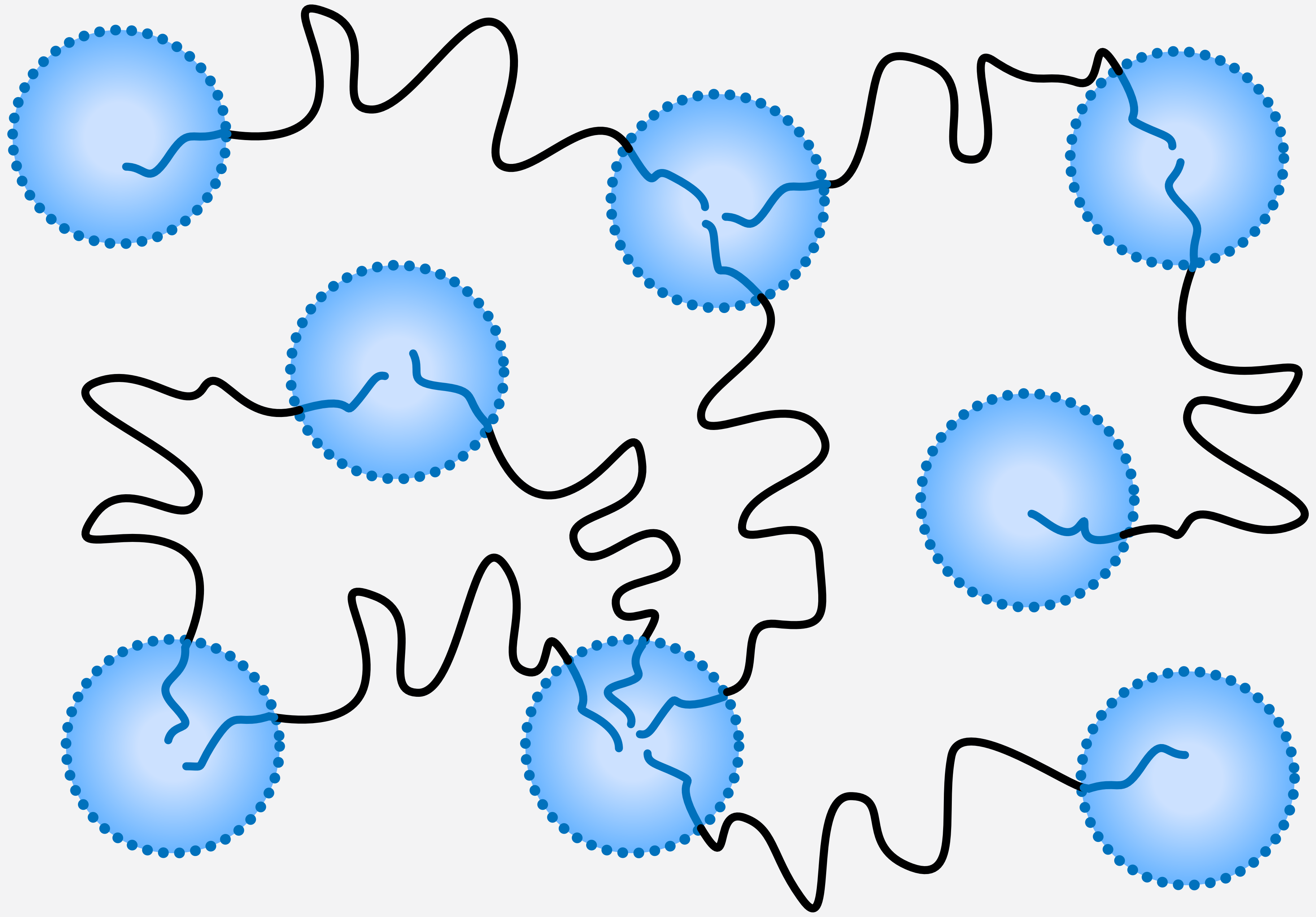




sequential anionic polymerization in THF
$M_n \approx 230.000$, symmetric PS and PMMA blocks
variation of PB block length (χ = 6, 17, 38%)

BAB Triblock Copolymers - Thermoplastic Elastomers

- hard segments serve as “physical” cross-links, all chains fixed into a network structure



soft segments
liquid (T_g < r.t.)

hard segments
glassy (T_g > r.t.) or
crystalline (T_m > r.t.)

BAB triblock copolymers

- below T_m or T_g of the hard segments, the result is a rubber (elastomer)
- above T_m or T_g of the hard segments, processable (extrusion, molding)
- thermoplastic elastomers are considered to be recyclable

Applications

1. **Thermoplastic Elastomers**
2. **Emulsifiers**
3. **Nanotechnology**
   - self-organised structures as precursors in the manufacturing of periodic arrangements of inorganic nanoparticles (quantum dots
4. **Compatibilization/Additive**
   - PS-*b*-PBD → PS-*b*-PE: compatibilization of PS/PE mixtures
   - PP + acrylic acid → improved adhesion with wood, CaCO3, cellulose (paper, cotton, …)
   - cellulose (paper, cotton,…) + fluorinated monomers: stain-resistant, hydrophobic, non-sticky materials.
   - cellulose (paper, cotton,…) + UV absorbing monomers: anti-UV textiles (T-shirts in New Zealand)
   - cellulose, polyesters + vinylphosphonates: flame retardant textiles
   - any non-harmful support + biocompatible monomers: biocompatible materials
   - etc., etc., etc.,…

Learning Outcome

- thermodynamics of binary polymer mixtures can be mapped within the framework of a lattice model. According to Flory-Huggins, polymer blends have very little mixing entropy, and mixing is determined by energetic factors. Most polymers are indeed immiscible with each other, but there are many exceptions to this rule of thumb because pairwise interaction energy differences are not always repulsive.

- by considering the temperature-dependence of the free energy of mixing, a phase diagram can be constructed to summarise the phase behavior of the mixture, showing regions of stability, instability, and metastability.

- block copolymers do not macroscopically phase separate but form domains on the scale of tens of nanometers. For monodisperse architectures, phase segregation (order-disorder transition) is accompanied by formation of well-defined periodic structures.