Organizing Immiscible Polymers with Balanced Diblock Copolymer Surfactants

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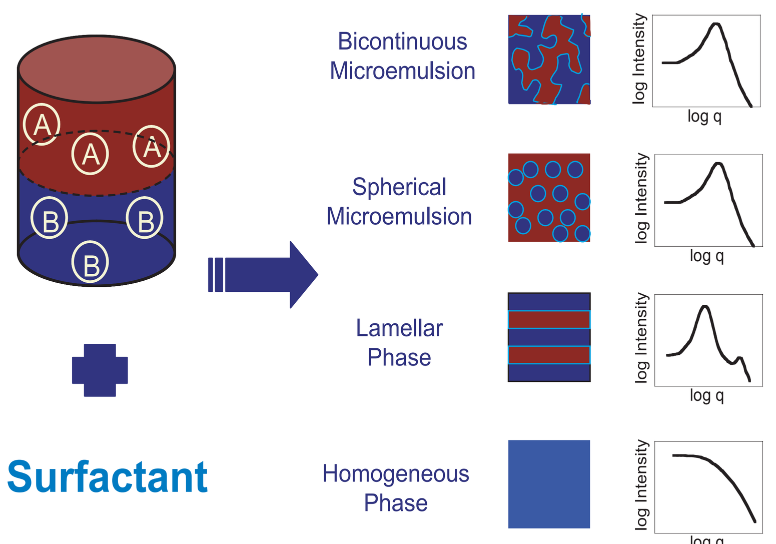
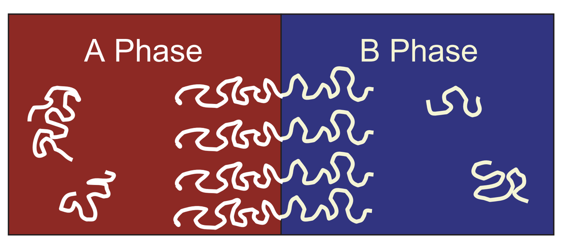
Motivation

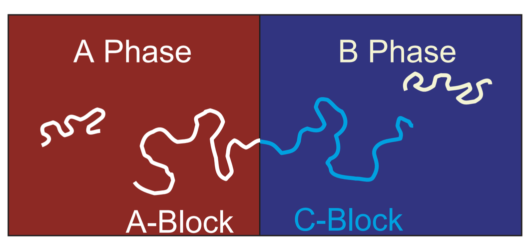


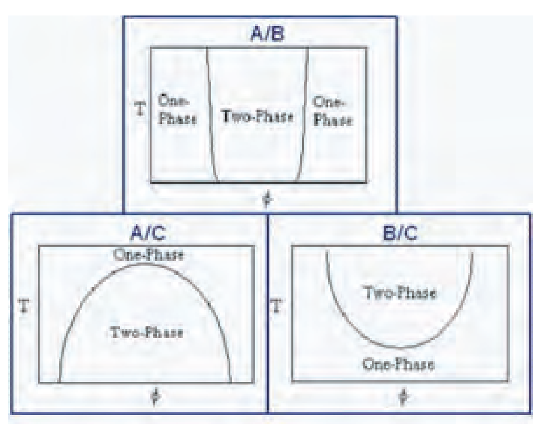
Traditional Approach: A-B Diblock Copolymer to Organize A and B Homopolymers



~10% diblock copolymer is required to organize two homopolymers with N_h / N_{A-B} = 0.2 (predicted by Broseta and Fredrickson, J. Chem. Phys: 93, 2927.)

Our Design: A-C Surfactants Analogous to Oil / Water / Non-Ionic Surfactant System

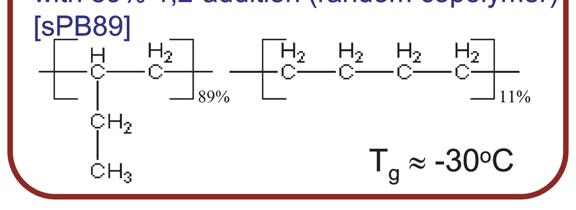




Experimental Design

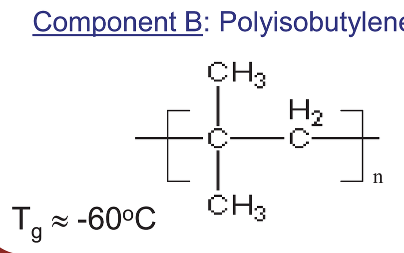
A/B/A-C Polymer Blend Components

Component A: Saturated polybutadiene with 89% 1,2-addition (random copolymer) [sPB89]



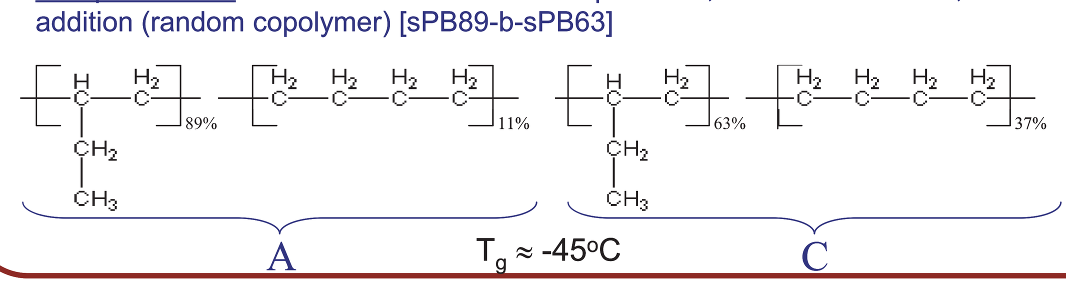
$T_g \approx$ -30°C

Component B: Polyisobutylene [PIB]

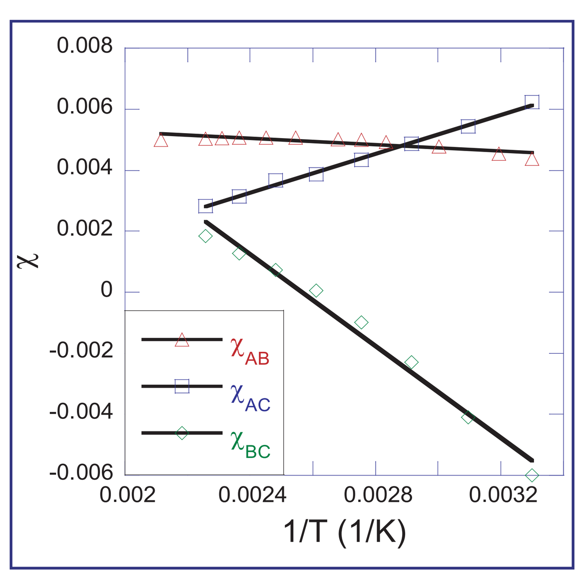


$T_g \approx$ -60°C

Component A-C: Block A is the same as component A, block C has 63% 1,2-addition (random copolymer) [sPB89-b-sPB63]



$T_g \approx$ -45°C

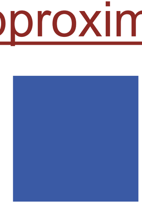


$N_A = 464$, $N_B = 437$
$\chi_{AB} N_{ave} = 2.3$
N_{A-C} = 1507-1266

Mean Field Theory Calculations

Random Phase Approximation

Homogeneous Phase



$$I(q) = \boldsymbol{B}^T \underline{\underline{S}}(q)\boldsymbol{B}$$

$$\underline{\underline{S}}(q)^{-1} = \underline{\underline{S}}_o(q)^{-1} + \underline{\underline{V}}(q)$$

Contrast: $B_j = \dfrac{b_j - b_{Bh}}{v}$ $(j = Ah, Ab, Cb)$

Structure factor in the absence of interactions:

$$S^o_{AbCb}(q) = S^o_{CbAb}(q) = (N_{Ab}\phi_{Ab}N_{Cb}\phi_{Cb})^{1/2} vF_{Ab}(q)F_{Cb}(q)$$

$$S^o_{jj}(q) = N_j\phi_j vP_j(q) \qquad S^o_{AbAh}(q) = S^o_{CbAh}(q) = S^o_{AhAb}(q) = S^o_{AhCb}(q) = 0$$

Include the effect of interactions:

$$V_{jj}(q) = \frac{1}{v}\left(\frac{1}{N_{Bh}\phi_{Bh}P_{Bh}(q)} - 2\chi_{jBh}\right)$$

$$V_{jk}(q) = \frac{1}{v}\left(\frac{1}{N_{Bh}\phi_{Bh}P_{Bh}(q)} - \chi_{jBh} - \chi_{kBh} + \chi_{jk}\right)$$

$$P_j(q) = \frac{2}{x_{j^2}}(\exp(-x_j) + x_j - 1) \qquad F_j(q) = \frac{1-\exp(-x_m)}{x_m} \qquad x_j = q^2 N_j l_j^{\,2}/6$$

Self-Consistent Field Theory

Periodic Phases

Random walk in a field: $\dfrac{\partial p_A}{\partial s} = \dfrac{b^2}{6}\nabla^2 p_A - w_A p_A$

Field: $w_m(z) = \xi(z) + E_m(z)$ $\qquad E_m(z) = \sum_n \chi_{mn}\phi_n(z)$

Enforce incompressibility: $\xi(z) = \Delta w(z) - \sum_i \dfrac{\phi_i(z)}{N_i} - \sum_{m,n}\chi_{mn}\phi_m(z)\phi_n(z)$

$\Delta w(z) = \varsigma\left(\sum_i \phi_i(z) - 1\right)$ $\quad \varsigma$ is chosen to be a sufficiently large value to ensure that the blend is essentially incompressible.

Partition function of part of chain from 0 to s:

$$\frac{\partial q_i(z,s)}{\partial s} = \sum_m \sigma_{i,m}(s)\left[\frac{\tilde{l}_m^{\,2}}{6}\frac{d^2}{dz^2}q_i(z,s) - w_m q_i(z,s)\right]$$

Partition function of entire chain: $Q_i(z,s) = q_i(z,s)q_i^*(z,s)$

$$\phi_{i,m}(z) = C_i\int_{s=0}^{N_i} ds\,\sigma_{i,m}(s)Q_i(z,s) \qquad C_i = \frac{\phi_i M}{\int_0^{N_i}\int_0^{M} ds\,dz\,Q_i(z,s)} \qquad \phi_m(z) = \sum_i \phi_{i,m}(z)$$

Initially guess $\phi_m(z)$, and calculate the fields. New $\phi_m(z)$ and fields are calculated. Continue until convergence.

$$\frac{f^{ext}v}{kT} = -\frac{\ln Q}{V} = -\sum_i \frac{\phi_i}{N_i}\left(\ln Q_i - \ln Q_i^{ref}\right) \qquad Q_i = \frac{V}{N_i M}\int_0^M dz\int_0^{N_i} ds\,Q_i(z,s)$$

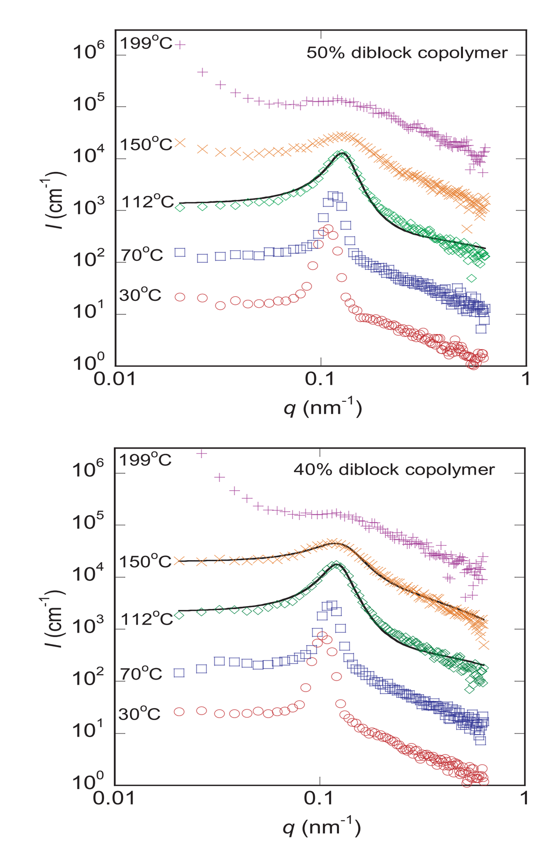
$$\ln Q_i^{ref} = \ln(\phi_i V) + N_i\sum_m \frac{\phi_{i,m}}{\phi_i}w_{i,m}^{ref}$$

$$\frac{fv}{kT} = \frac{f^{ext}v}{kT} + \left[\frac{1}{M}\int_0^M dz\left(\sum_{m,n}\chi_{mn}\phi_m(z)\phi_n(z)\right) - \sum_i \frac{1}{\phi_i^2}\sum_{m,n}\chi_{mn}\phi_{i,m}\phi_{i,n}\right] - \left[\frac{1}{M}\int_0^M dz\sum_m \phi_m(z)w_m(z) - \sum_{i,m}\phi_{i,m}w_{i,m}^{ref}\right]$$

$$= \sum_i \frac{\phi_i}{N_i}\left(\ln\left(\frac{\phi_i V}{Q_i}\right) + 1 - \frac{N_i}{\phi_i^2}\sum_{m,n}\chi_{mn}\phi_{i,m}\phi_{i,n}\right) - \frac{1}{M}\int_0^M dz\,\Delta w(z)$$

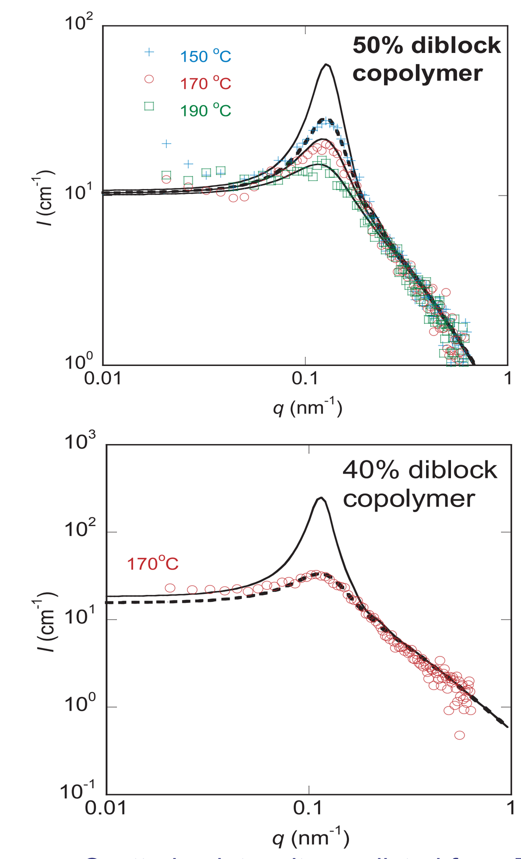
Results

SANS data obtained from multicomponent blends



Lamellar phase → Microemulsion → Macrophase Separation

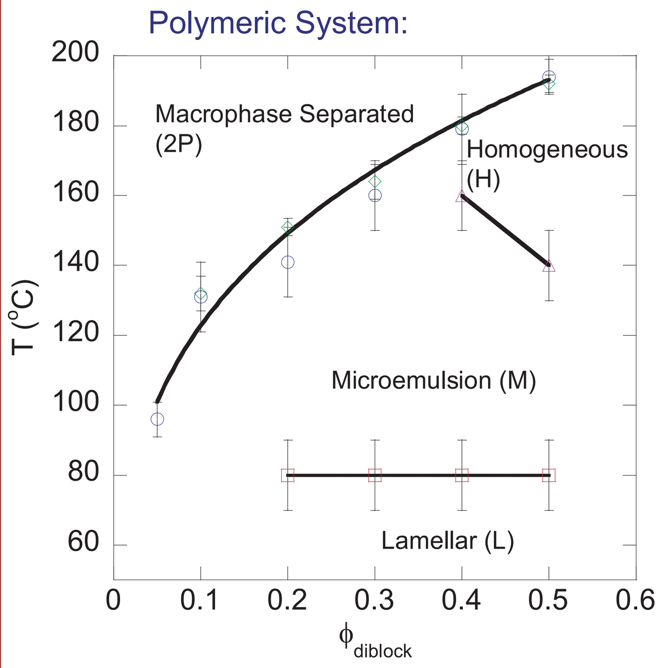
Comparing RPA calculations with SANS data



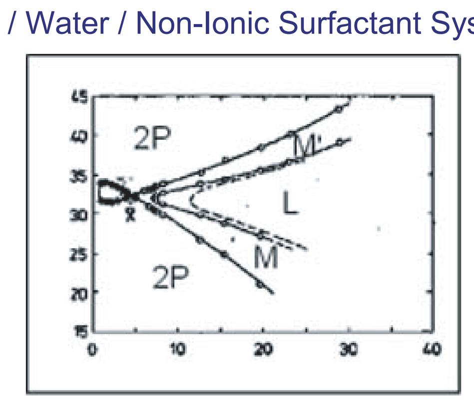
Scattering intensity predicted from RPA with no adjustable parameters (solid lines). Dotted lines indicate fitting one χ parameter.

Results

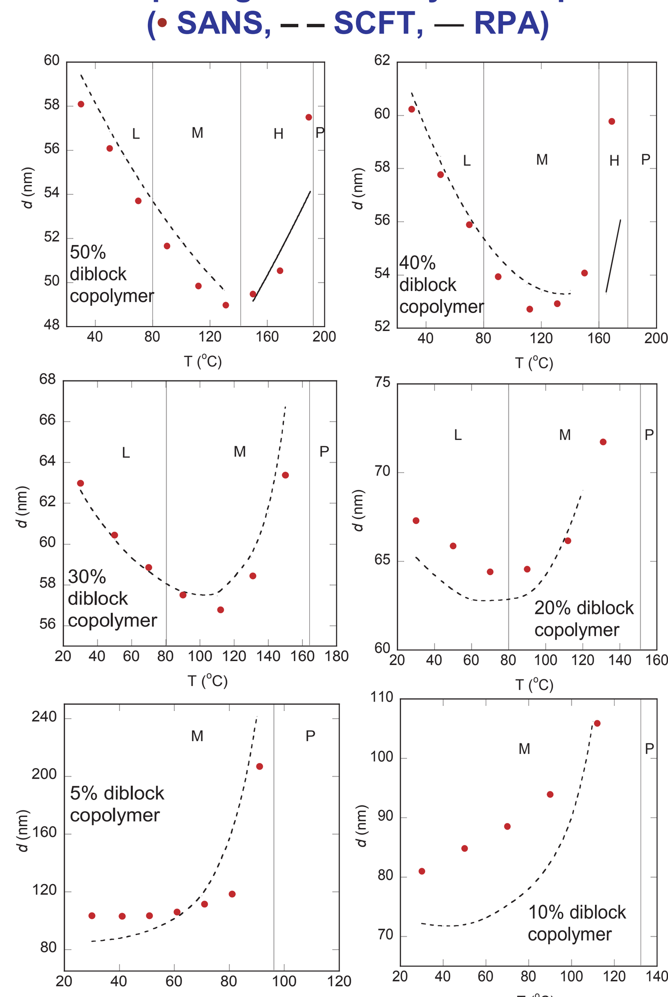
Polymeric System:



Oil / Water / Non-Ionic Surfactant System:

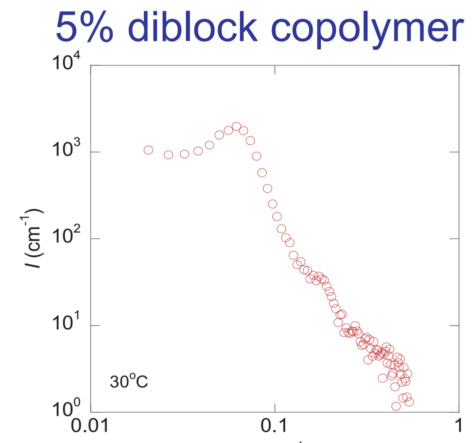


Domain Spacing from Theory and Experiment (• SANS, – – SCFT, — RPA)

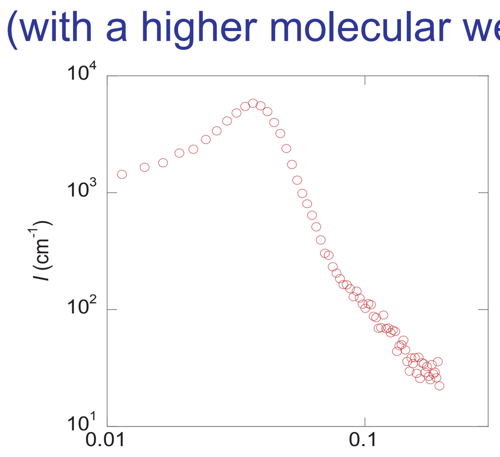


Minimizing the Diblock Copolymer Concentration

5% diblock copolymer



Only 2% diblock copolymer!
(with a higher molecular weight)



Conclusions

- Polymeric A-C surfactants were designed for the organization of immiscible A and B homopolymers.
- SCFT and RPA were used to predict the phase behavior and domain spacing in the A/B/A-C blends.
- Theoretical predictions for the domain spacing were often within 5% of the experimental values.
- Immiscible A and B homopolymers were organized with only 2 and 5% of the diblock copolymer in the blend.