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# Driving Innovation in Polyolefin Research with Modeling and Simulation Methods




3DEXPERIENCE®

Nick Reynolds
Dassault Systemes BIOVIA,
February 27th, 2017

2017 SPE INTERNATIONAL
POLYOLEFINS CONFERENCE
February 26 - March 1 | Houston, Texas

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- 108 nationalities
- One global R&D / 57 labs
- Game changing 3DEXPERIENCE solutions



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## 13,500 partners

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## Long-term driven

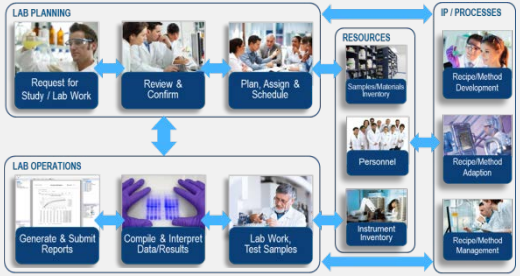
- Majority shareholder control
- Revenue: $2.8 Bn*
- Operating margin: 29.8%*

** Non-IFRS*

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# BIOVIA Solution Portfolio

## Unified Lab Management



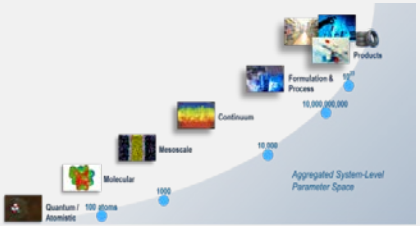

## Process Production Operations



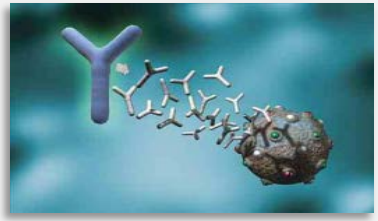
## Quality and Regulatory



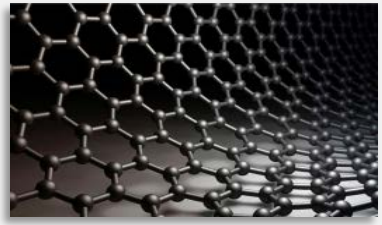

## Collaborative Science




Predictive Models



Novel Therapeutics



Engineered Materials



Chemicals & Formulations

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# BIOVIA Mission

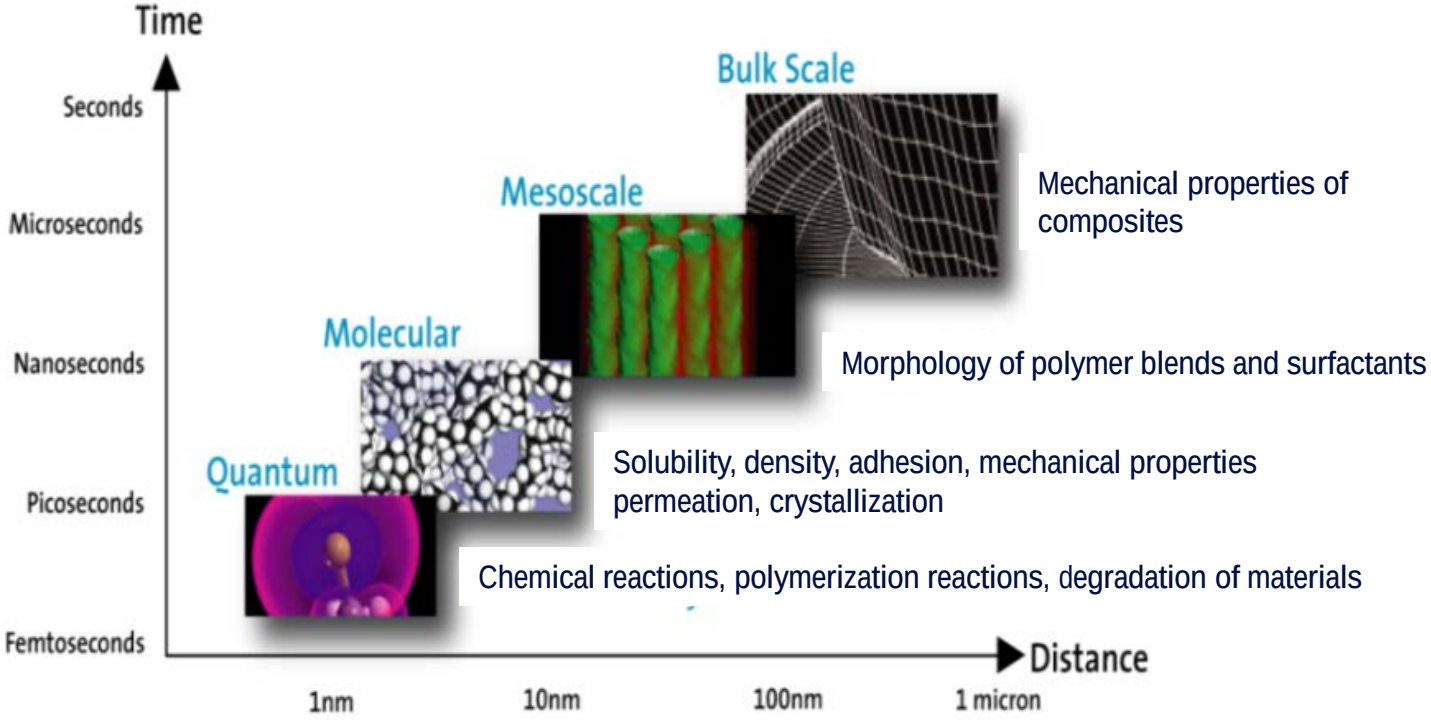


## BIOVIA | Virtual BioSphere and Materials

BIOVIA provides a **scientific** collaborative environment for advanced biological, chemical and materials experiences. The sophisticated enterprise system of modeling, simulation, laboratory and quality management enables **innovation** for science-based industries.

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# What is Materials Simulation?




Mechanical properties of composites

Morphology of polymer blends and surfactants

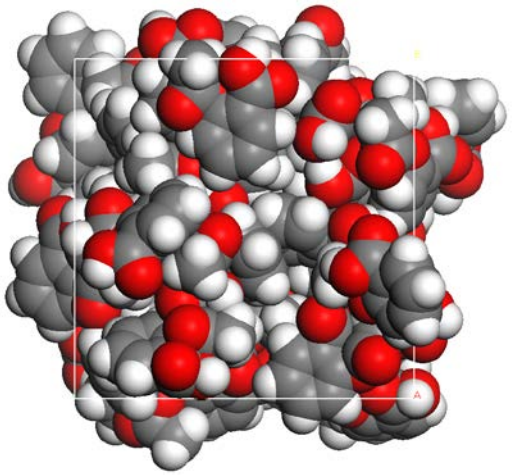
Solubility, density, adhesion, mechanical properties permeation, crystallization

Chemical reactions, polymerization reactions, degradation of materials

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# Predicting Properties of the Amorphous State

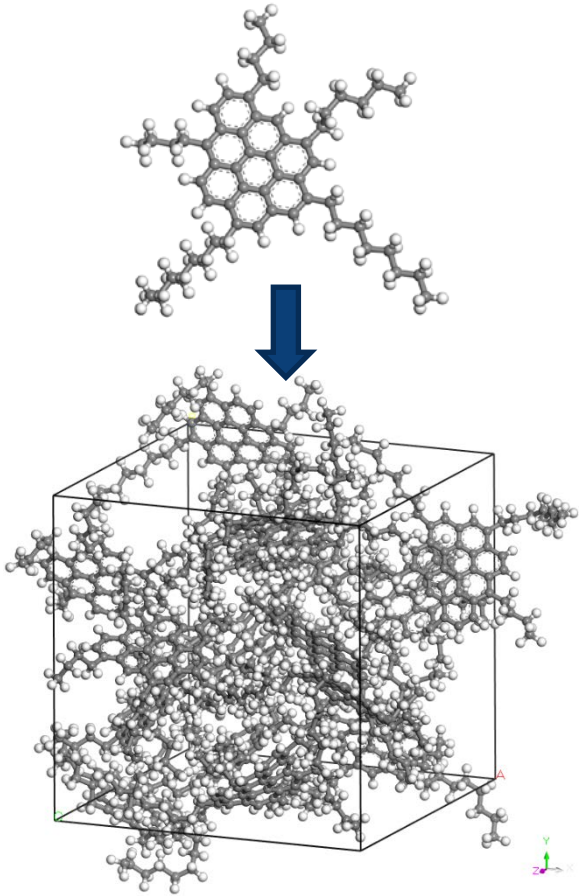
- Properties one can calculate:
  - Miscibility of small molecule in a polymer matrix
  - Solubility parameter and free energy of solvation
  - Diffusion rate of molecules in polymers
  - Glass transition temperature
  - Mechanical properties
  - Chemical instability



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# Prediction of the Solubility Parameter

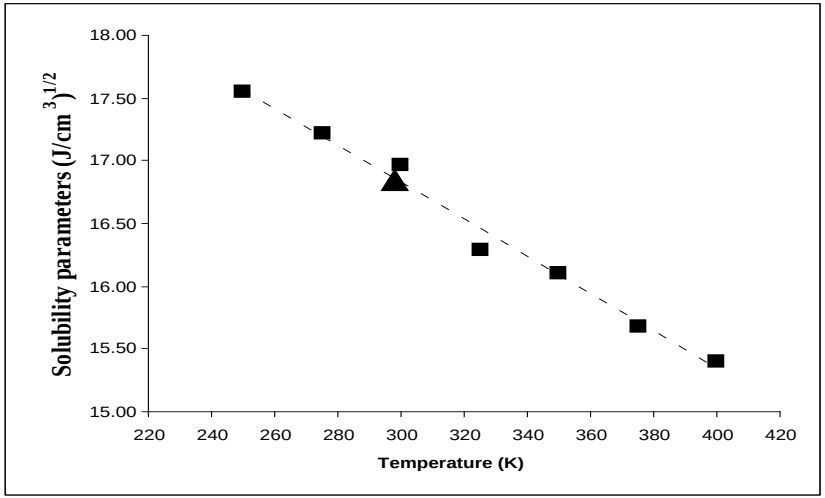
- Applied to *determine miscibility*: materials with similar solubility parameter values are more likely to blend
- The solubility parameter is defined as the square root of the cohesive energy density
- $\delta = \sqrt{\frac{E_{coh}}{V}}$
- The cohesive energy is defined as
- $E_{coh} = E_{tot}^{condensed} - \sum_i^N E_i^{mol}$



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# Prediction of Solubility Parameter

Cis-Polybutadiene solubility parameter variation with Temperature. Filled squares, simulation[1]; triangles, experiment.[2]




$$\delta = \sqrt{\frac{E_{coh}}{V}}$$

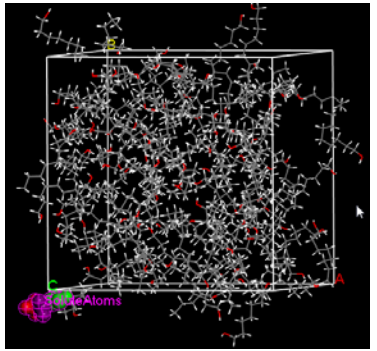
1. *M. Meunier, J. Chem. Phys.* 123 (2005).

2. S. Pauly, in *Polymers Handbook*, 3rd ed., edited by J. Brandrup and E. H.Immergut Wiley, New York, 1989.

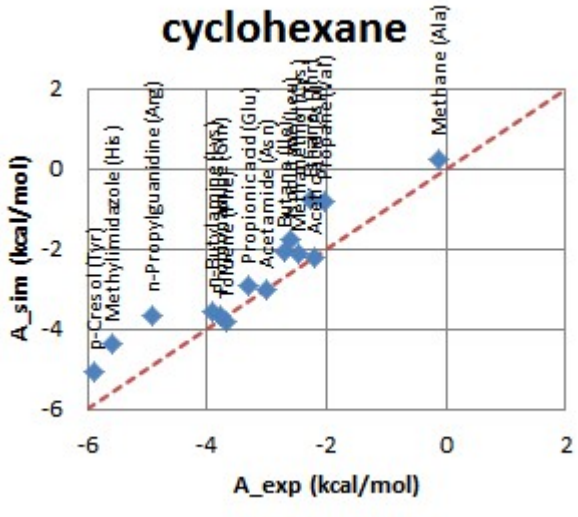
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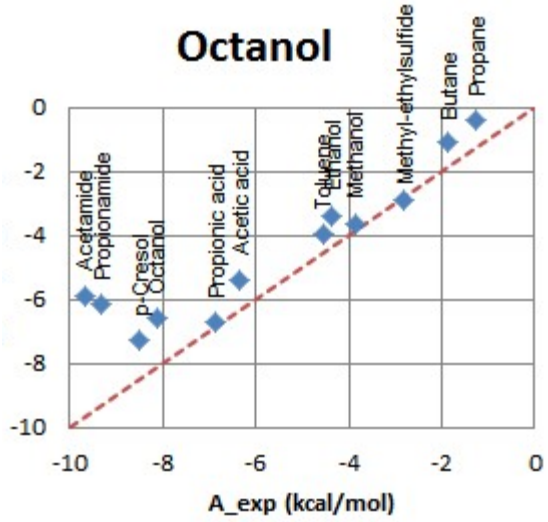
# Prediction of the Free Energy of Solvation

- Small molecules in solvents



Predicted




Experimental

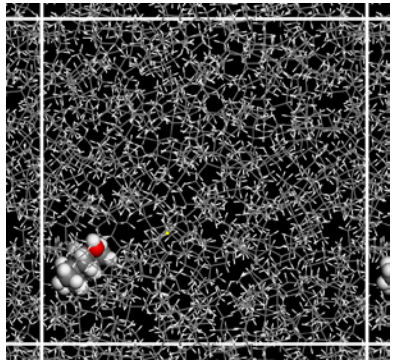
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# Prediction of the Free Energy of Solvation

- Small molecule solubility in polymers

Menthol is predicted to have a more negative solvation free energy in polyethylene, than in polypropylene, and this agrees with the observation of greater menthol solubility in polyethylene.[1]

| System | Experimental Solubility (g/cc*bar)[2] | Predicted Solvation Free Energy (kcal/mol) |
|---|---|---|
| Menthol in PE | 62 | -11.6 |
| Menthol in PP | 24 | -9.1 |



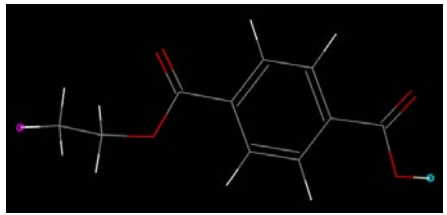
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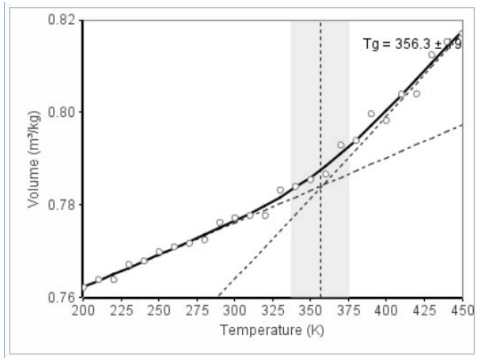
1. Franz, R. (1993), Permeation of volatile organic compounds across polymer films—Part I: Development of a sensitive test method suitable for high-barrier packaging films at very low permeant vapour pressures. Packag. Technol. Sci., 6: 91–102. doi: 10.1002/pts.2770060207

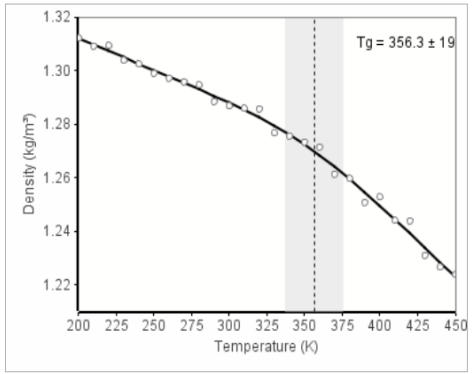
# Prediction of Glass Transition Temperature (Tg)

Follow change in volume (and density) with temperature to evaluate the Tg and Thermal Expansion Coefficient

- Simulations on PET (polyethylene terephthalate) give a Tg of 356K, which agrees well with the experimental value of 348K





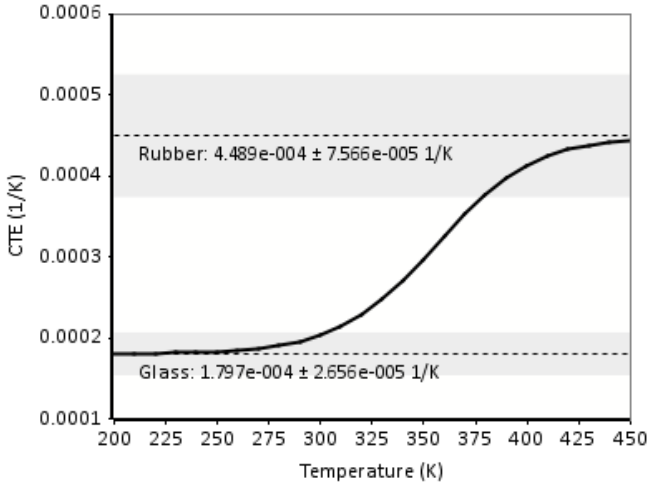




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# Prediction of Glass Transition Temperature (Tg)

Follow change in volume (and density) with temperature to evaluate the Tg and Thermal Expansion Coefficient

- Simulations on PET give a thermal expansion coefficient in the glassy state of 1.797E-04 /K, which agrees very well with the experimental value of 1.788E-04 /K.

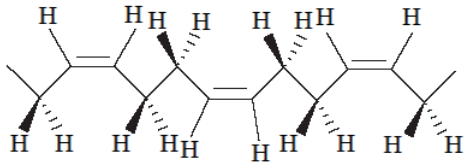


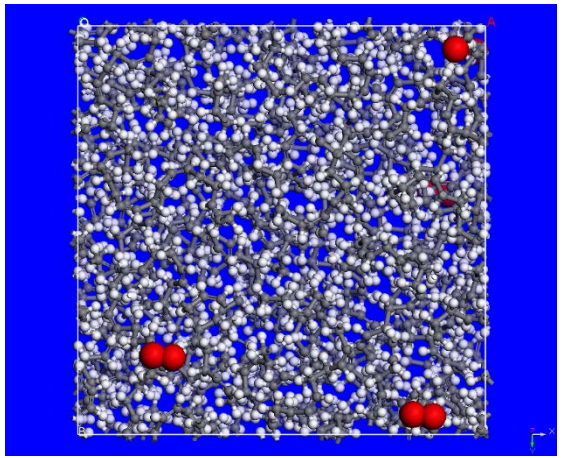

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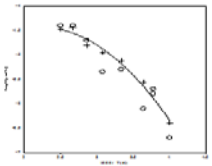
# Prediction of Gas Diffusion in Amorphous Cis-1,4-Polybutadiene

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- Introduction
  - Molecular Dynamics simulations were employed to compute the diffusion coefficients of small gas molecules (Ar, $O_2$, $N_2$, $CO_2$, $CH_4$) in amorphous cis-1,4-polybutadiene (cis-PBD) in the temperature range 250-400 K.
  - The diffusion mechanism is examined at the different temperatures of study.







** M. Meunier, J. Chem. Phys.* 123 (2005)

# Estimated and Experimental Diffusion Coefficient for Ar, $O_2$, $N_2$, $CO_2$ and $CH_4$ in amorphous cis-PBD.[a]

| | *Ar* | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ |
|---|---|---|---|---|---|
| (1) Exp. (298 K) | 4.06 | 1.5 | 1.1 | 1.05 | - |
| (2) Calc. (this work, 300K) | 7.03 | 9.5 | 8.8 | 5.3 | 7.5 |
| (3) Calc. [ref. 47] | - | - | - | - | 2.25 |

[a] Units of Diffusion Coefficients, D ($10^{-6}$ $cm^2/s$).

Exp. $\underline{Ar} > O_2 \geq N_2 > CO_2$

Calc. $O_2 \geq N_2 > \underline{Ar} > CO_2$

Except for Argon, trend is correct!

Overestimation of D due to short-chain model

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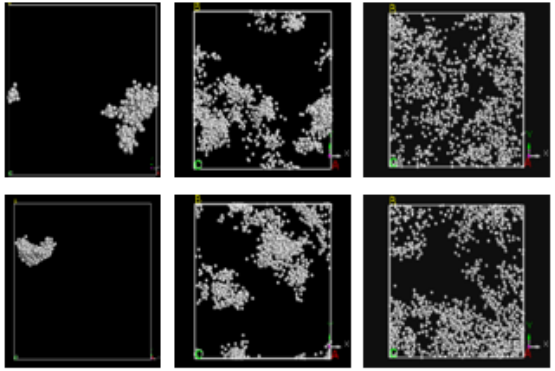
# Gas Diffusion Mechanism

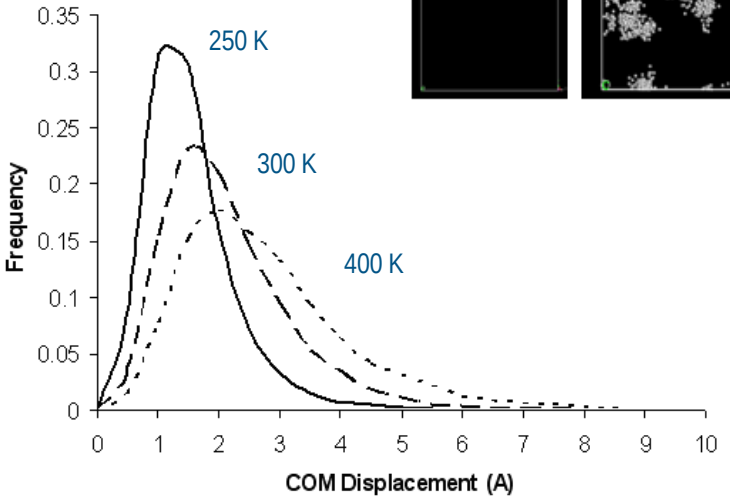
*The decrease of the activation energy with the temperature is attributed to a gradual change in the diffusion mechanism of the gas molecule as temperature varies:*

❖At low temperature:
•the polymer chains quasi-immobile, channels opening are rare.
•density is higher (number and volume of micro -voids is minimal)
--> number of jumps of gas molecule is small.

❖As temperature increases the average jump distances increases too.

This shows that the methane molecules follow a hopping mechanism at low temperature and behave more like a liquid as temperature increases.



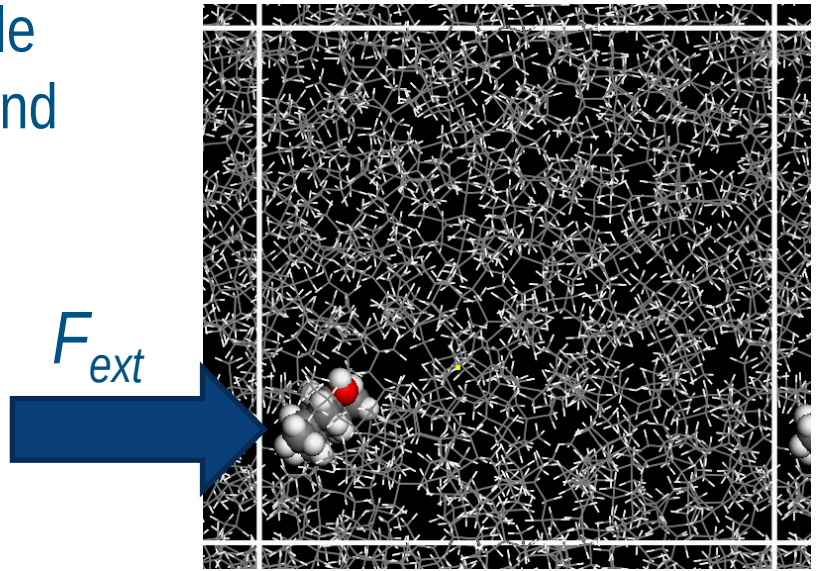



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# Predict Diffusion of Larger Molecules

- Plot displacement of molecule centroid against time, $v_{drift}$, and calculate diffusivity, D.

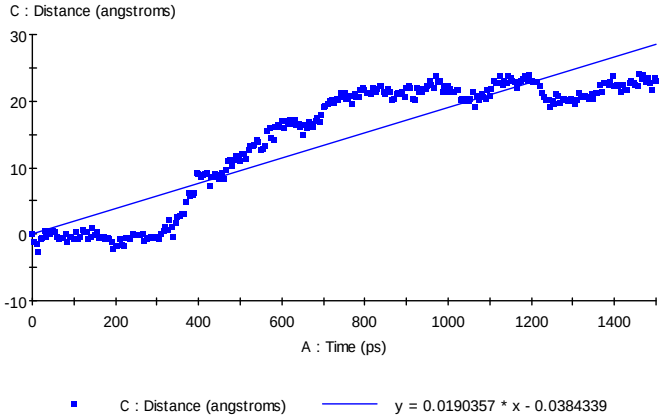
$$D = \frac{k_B T v_{drift}}{F_{ext}}$$




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# Prediction of Flavor Diffusion in Polymer Packaging

- Plot displacement of molecule centroid against time (drift velocity), $v_{drift}$ and calculate diffusivity, D.




$$D = \frac{k_B T v_{drift}}{F_{ext}}$$

Diffusion ($10^{-6}$ $cm^2/s$)

| Molecule | Polyethylene | Polypropylene |
|---|---|---|
| Menthol | 2.254 | 0.250 |

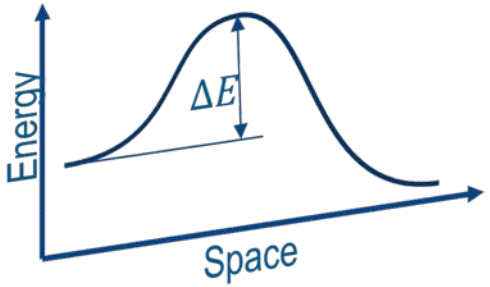

Franz, R. (1993), Permeation of volatile organic compounds across polymer films—Part I: Development of a sensitive test method suitable for high-barrier packaging films at very low permeant vapour pressures. Packag. Technol. Sci., 6: 91–102. doi: 10.1002/pts.2770060207

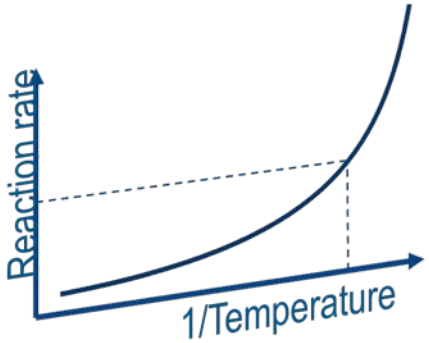


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# Prediction of Chemical Reactions: Reaction Engineering and Catalyst Development

- Business Problem
  - How does a polymerization catalyst operate?
  - What factors control the products formed?
  - How can you control these factors
- From modelling
  - Determine $\Delta H_{REACT}$ and $E_{ACT}$
  - Understand reaction mechanism
  - Determine transition state and reaction rate




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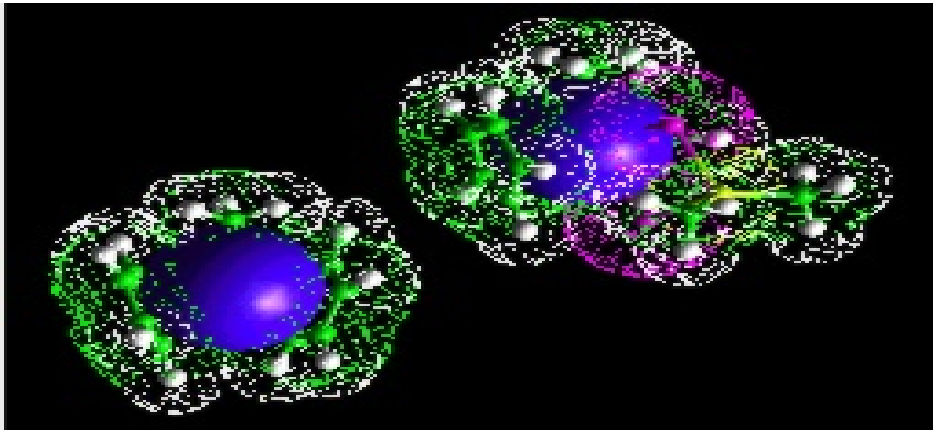
# Olefin Polymerization via Metallocene Catalysis

Problem:

- Catalytic efficiency of metallocenes depends upon choice of metal, ligand, concentration of co-catalyst
- 2 forms of catalyst exist: cationic & bimetallic
- Reaction mechanism is poorly understood
- How to produce optimal catalyst?

Solution:

- Study both cationic vs. bimetallic forms with theory and experiment



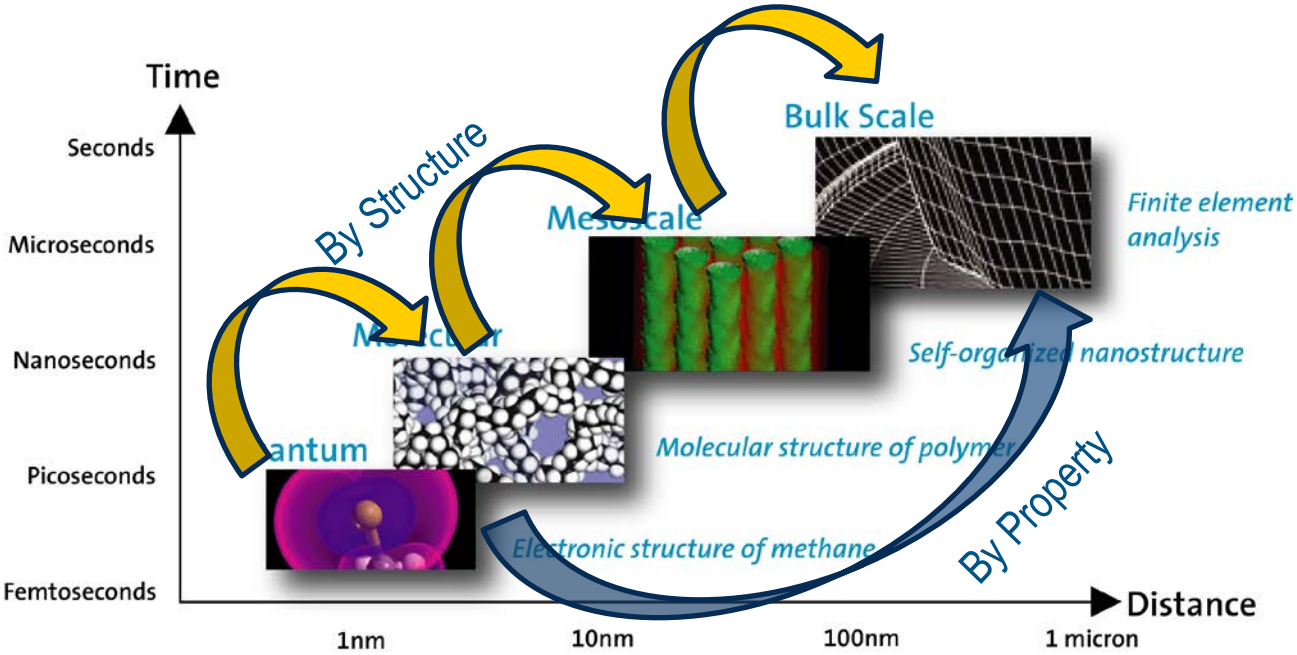
Fusco, R. & Longo, L, *Macromol. Theory Simul.*, 3, 895 (1994)

"The multidisciplinary effort discussed here allowed our molecular modeling group … to contribute substantially to the deposit of patents…"
Drs. Longo, Fusco, & Accomazzi, EniChem

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# Multiscale Modelling of Materials

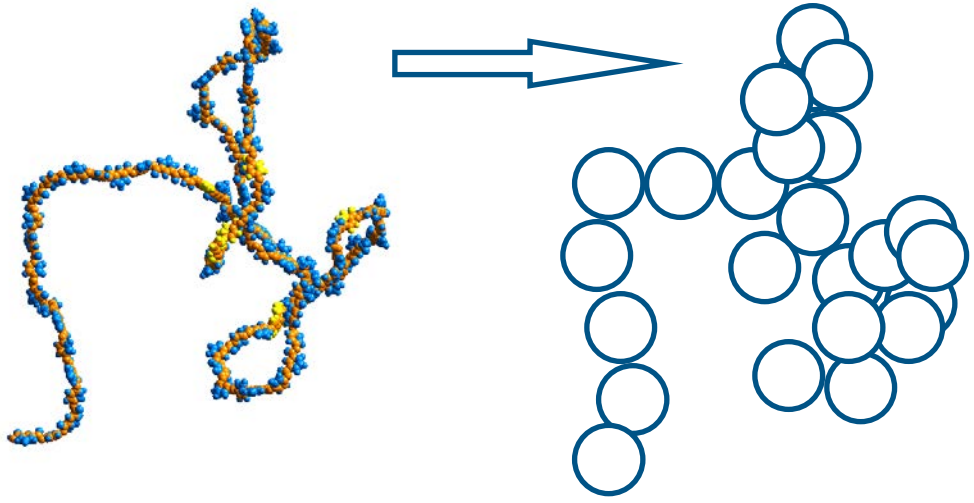
- Connection by Property
- Connection by Structure




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# Mesoscale Modeling - Course Grain Approach: Prediction of Polymer and Surfactant Morphology

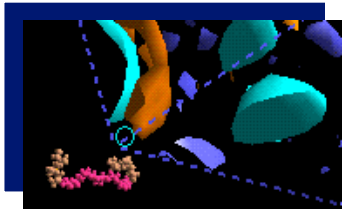
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Atomistic Scale Model

Mesoscale Model

# Compatibilization of Polymer Blends



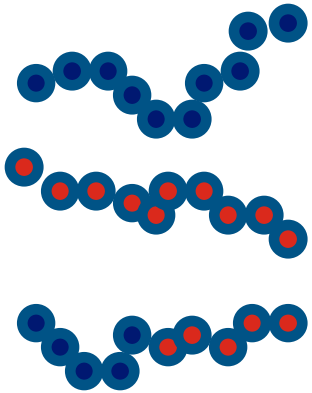
**Background:** Many polymeric materials are in fact blends. The objective is to design a material which will retain the best properties of its constituents; frequently this means using blends which may demix to some extent.

**Task**: to design a blend **compatibilizer** which does the job most efficiently.

**Problem**: Tools are needed which can rapidly search the large space of compatibilizer molecular structures -- yet at the same time *quantify* the resulting changes in blend morphology and material properties.

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# Polymer Blend Compatibilization



Polystyrene, 45%

Polybutadiene, 45%

S-B, 10%

Mesoscale parameters determined by atomistic modeling

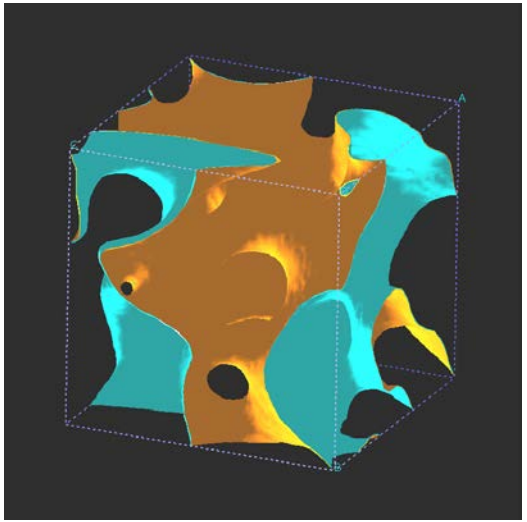
$MW_{A-B} = MW_A = MW_B = 80{,}000$

Sakurai, Kawada, Hashimoto and Fetters, *Macromolecules* 26, 5796 (1993) for a study of diblock phases only

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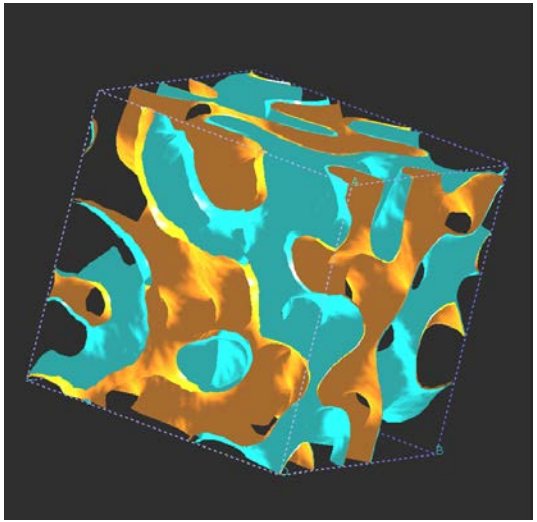
# Morphology Prediction: Ternary PS/PBD/S-BD Blend System

Without compatibilizer



With compatibilizer

- solubilizes homopolymer
- lowers surface tension

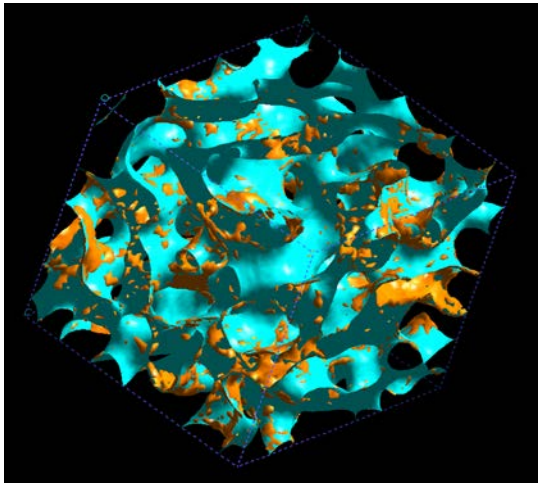


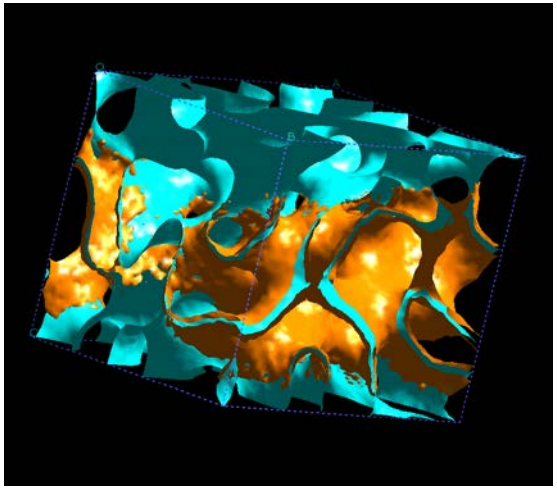
D. Nicolaides, Molecular Simulations, 2001.

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# Morphology Prediction: PS – PBD Blends

Below we present a confirmation of the existence of the so-called ‘middle phase.’ This causes a weakening of the performance of the compatibilizer, though there is still a surface excess.

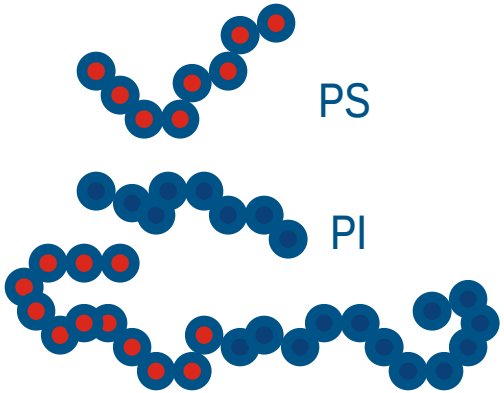




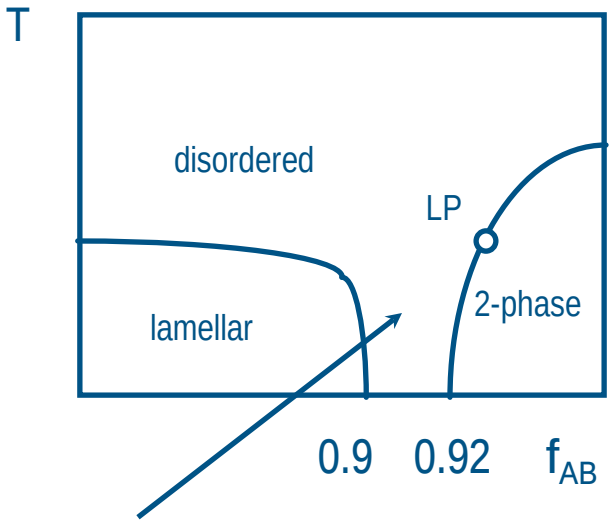
D. Broseta and G.H. Fredrickson, *J. Chem. Phys*. 93, 2927 (1990)

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# Polymer Blend Morphology Prediction




$MW_{A-B} = 5\ MW_A = 5\ MW_B$

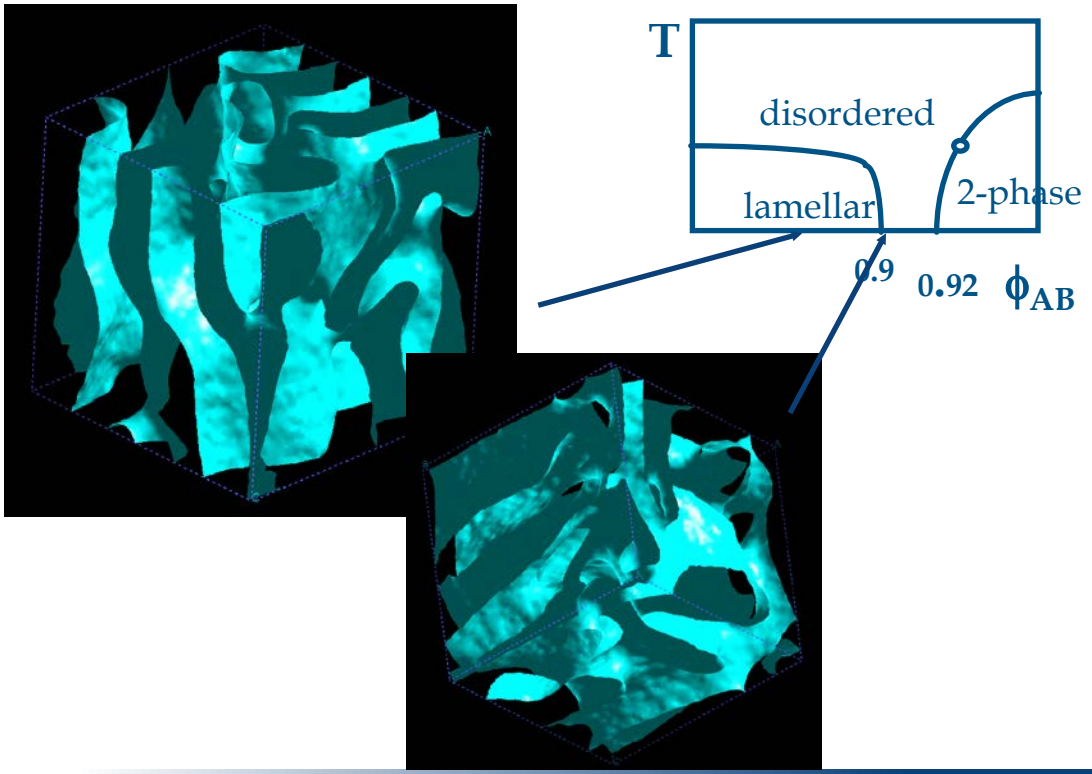



polymeric bicontinuous microemulsion phase!

F.S. Bates et. al. *Phys. Rev Lett*. 79, 849 (1997)

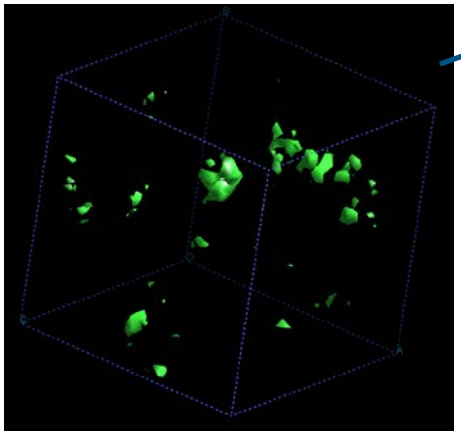
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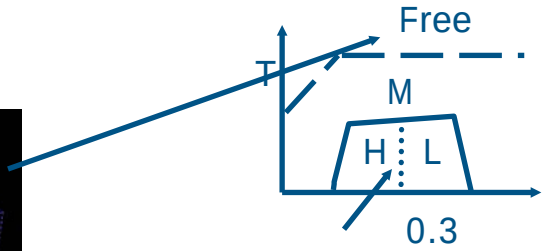
# Polymer Blend Morphology Prediction



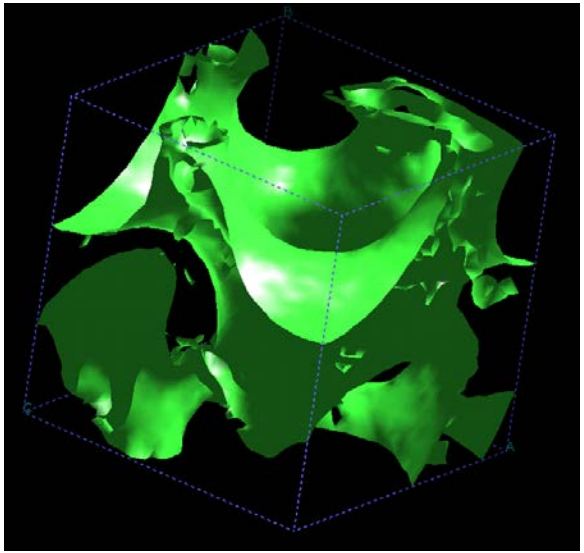

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# Mesoscale simulation matches experimental phase diagram






M-micellar
H – hexagonal
L - lamellar



The 400 K results show no mesoscale ordering (homogeneous), and the 300 K results show a structure that is nearly hexagonal.

I.W. Hamley et.al., Macromolecules 1998 31, 1188-1196

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# Rapid Polymer property prediction with Quantitative Structure Property Relationships (QSPR)

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## Correlations developed by Jozef Bicerano (Dow Chemicals)

- Correlations have been developed to estimate properties for any amorphous, atactic, homopolymer or random copolymer containing C, H, O, N, Si, S, Br, Cl, F
- Mechanical, thermal, transport, and optical properties predicted
- The only input required are optimized models of the polymer repeat units – topological descriptors are calculated

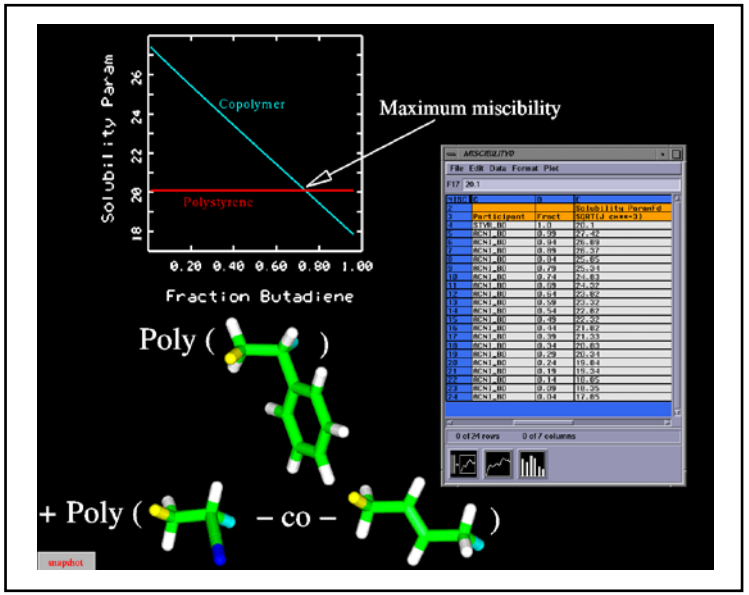
# Polymer Property Prediction: Maximizing Miscibility by Varying Copolymer Composition

The less miscible a polymer blend is, the more difficult it is to control and stabilize its morphology and properties.

Miscibility of a homopolymer/copolymer blend can be enhanced by controlling the copolymer composition.

For a blend of polystyrene with a copolymer of acrylonitrile and butadiene, Synthia (a quantitative structure-property relationship program) was used to calculate solubility parameters as a function of copolymer composition.

Miscibility is maximized at about 75% butadiene content.




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# Summary

- Simulation at different levels allows one to predict properties of polymers and a range of materials.
- Prediction of thermal, solvation, and mechanical properties, and blend morphology is possible, and allows one to make decisions on materials selection
- Application of simulation provides direct insights into structure– property relationships and help to *guide experimentation*.

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