



The
University
Of
Sheffield.

Polymer Processing: Application of X-rays & Neutrons

Anthony J. Ryan

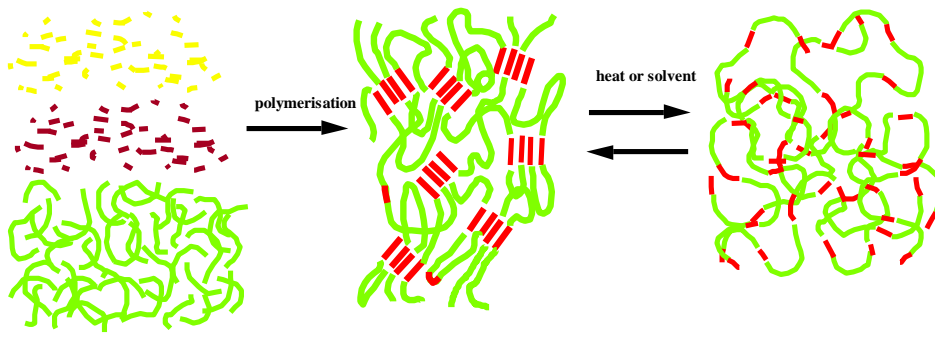
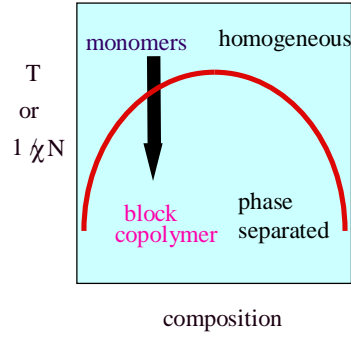
Outline

- Reaction induced phase separation in polyurethane
- PU foam is reactively processed from a dense liquid to a porous flexible solid

- PU thin films are coated from solution
- SAXS & SANS elucidate structure evolution

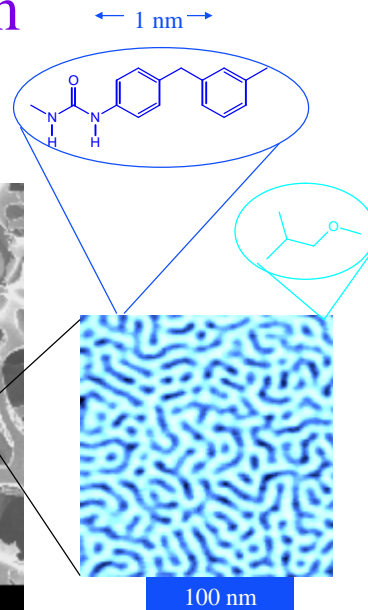
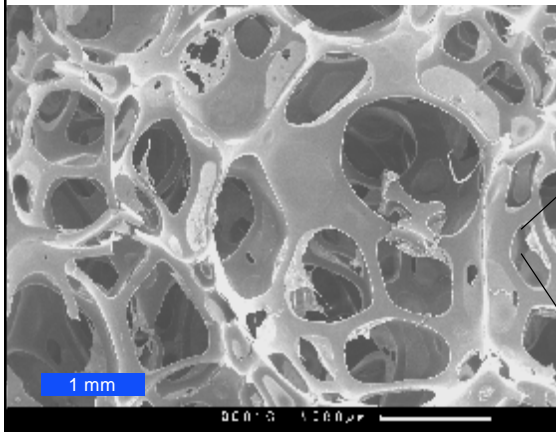
- High performance paint – PU-acrylic blend
- Core-shell structure by contrast variation

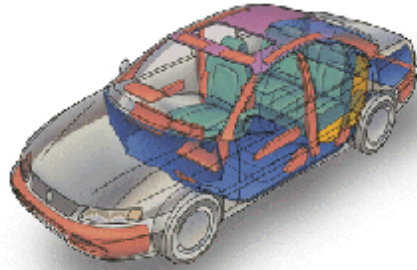
Phase separation in polyurethanes



Polyurethane Foam

SEM of high resilience foam



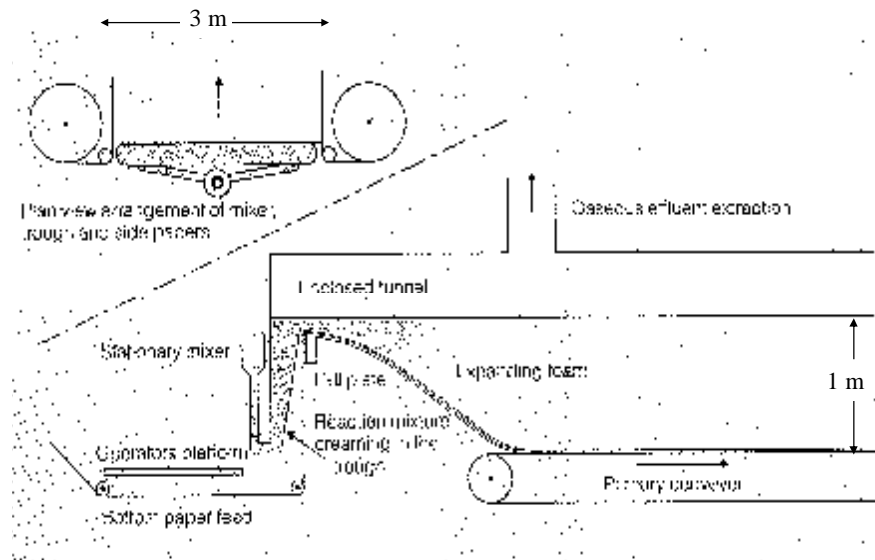


Polyurethane Foam Products

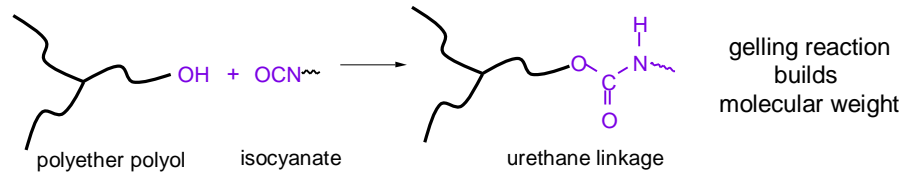
- Energy Absorbing Foam Components
- Structural Foam Components
- Seating Foam Components
- Mechanical Foam Components



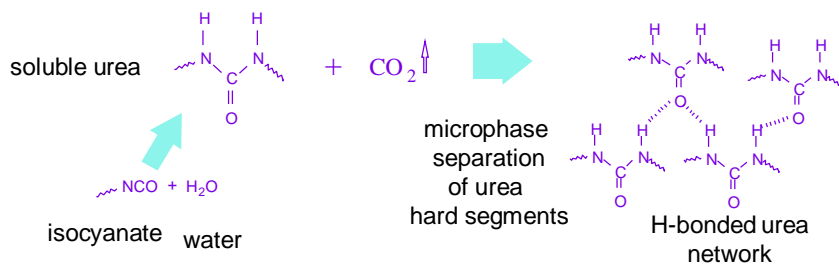
Polyurethane Foam Processing



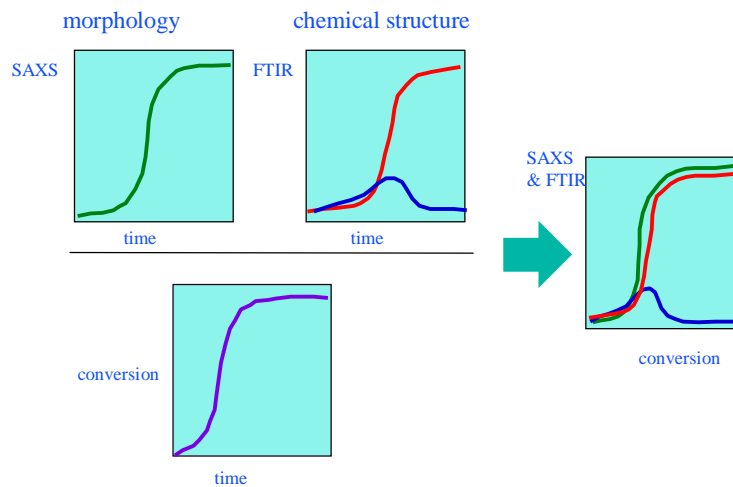
PU Foam Chemistry

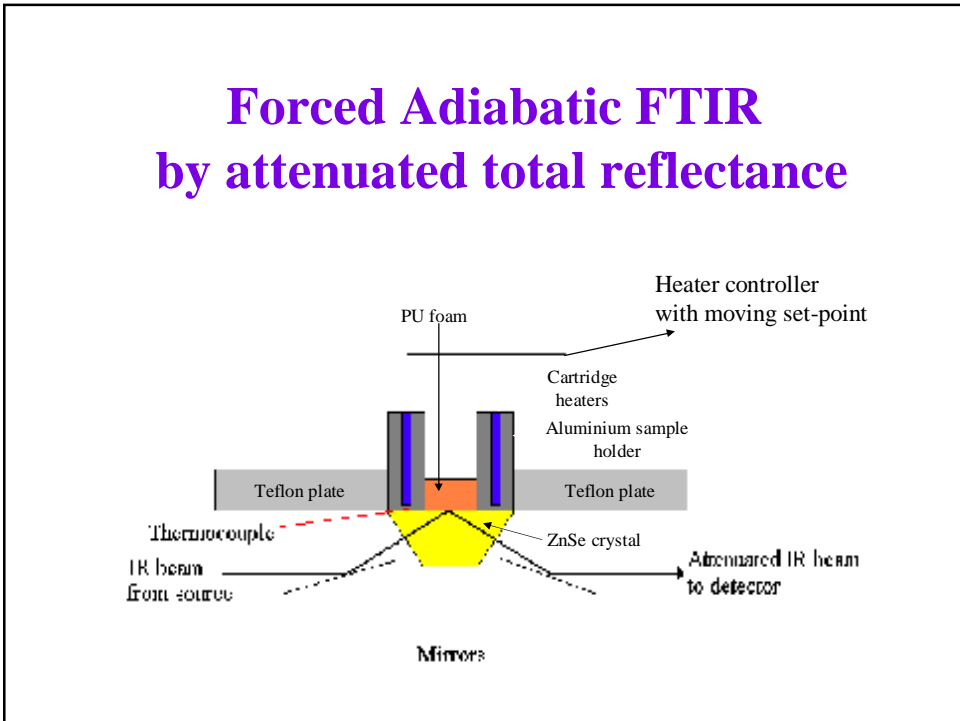
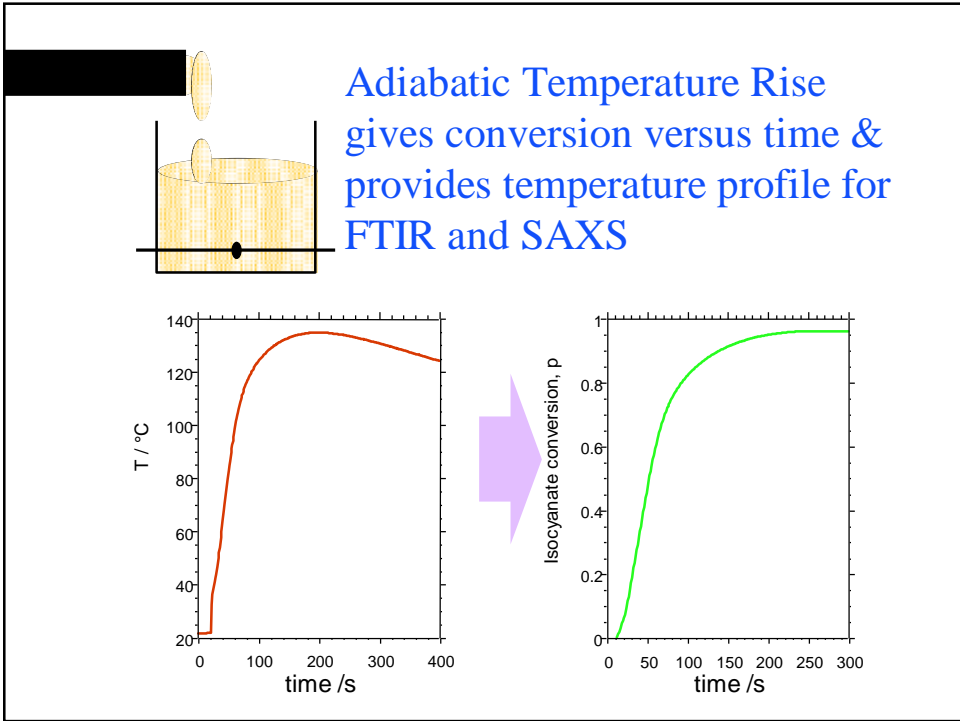


blowing reaction makes gas and hard segments

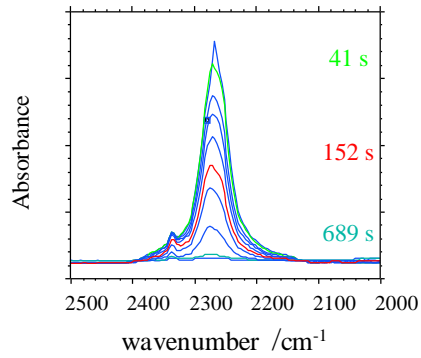


Time resolved experiments add value



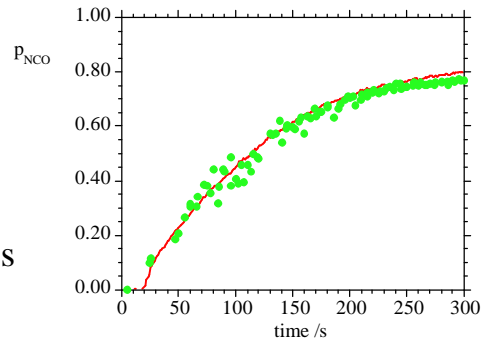


FTIR - reaction kinetics



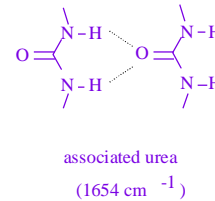
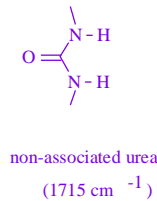
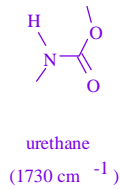
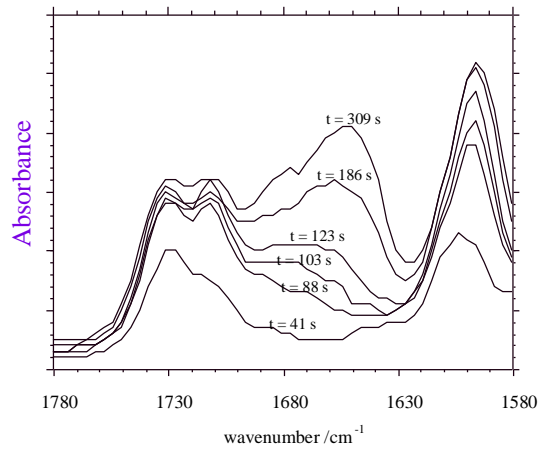
Comparison of kinetics
from **ATR** and **FTIR**

from the depletion in the
normalised isocyanate
absorbance



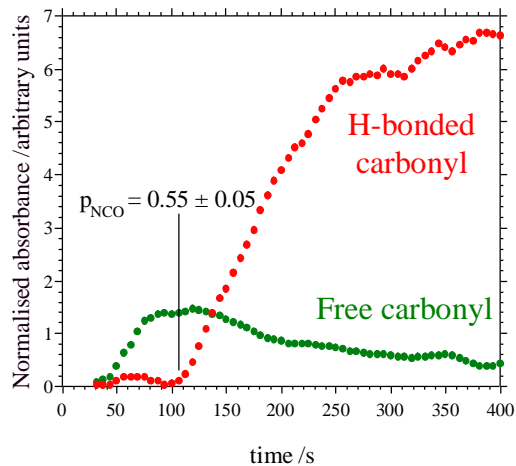
H-bonding from FTIR

"An FTIR Study of Reaction Kinetics and Structure
Development in Model Polyurethane Foam Systems", M.J.
Elwell, A. J. Ryan, H.J. Grünbauer, and H.C. Van Lieshout,
Polymer, 37, 1353, (1996).

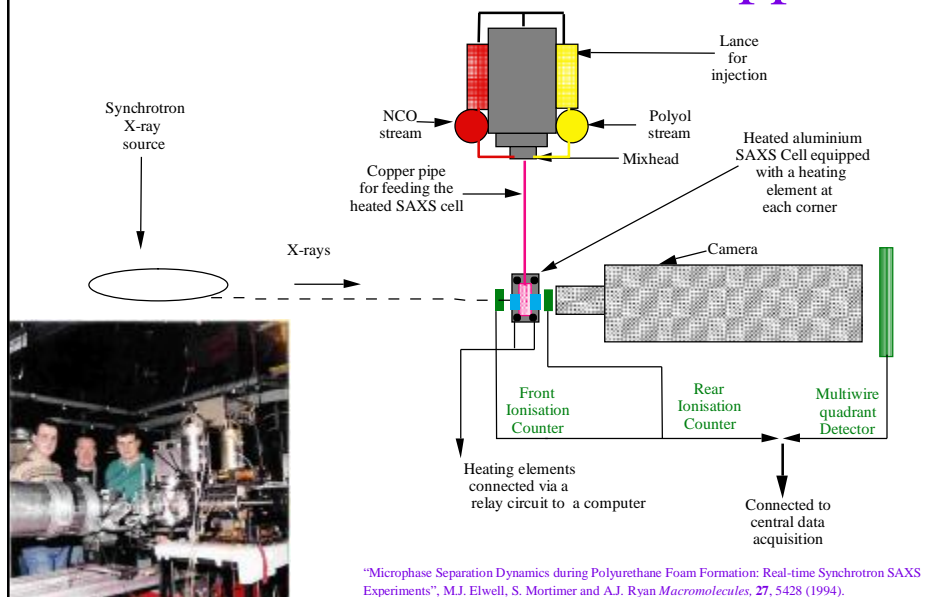


Evolution of H-bonds

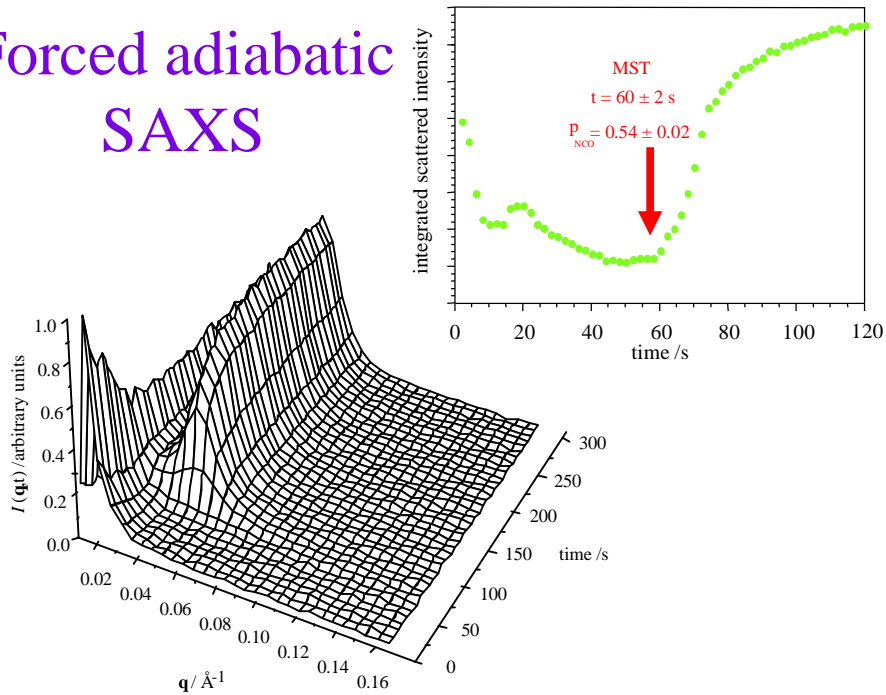
Average hard segment sequence length ~ 1.2 at onset of phase separation



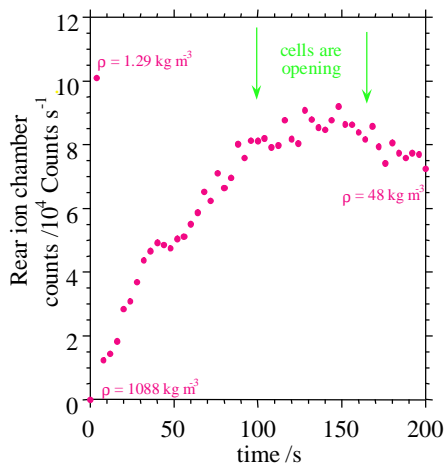
Forced adiabatic SAXS apparatus



Forced adiabatic SAXS



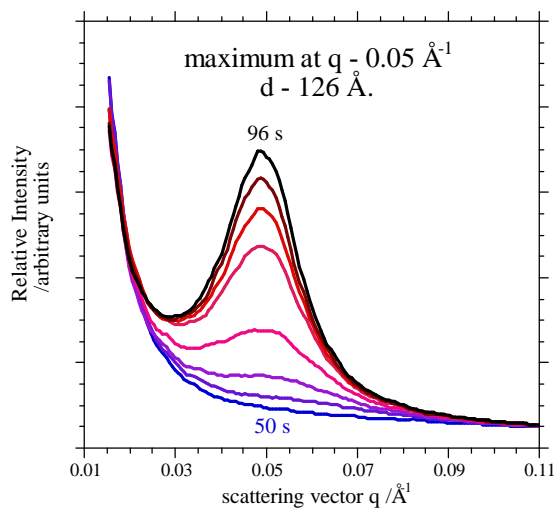
Cell opening time from density



ion chamber counts \approx
 $1/\log(\text{density})$

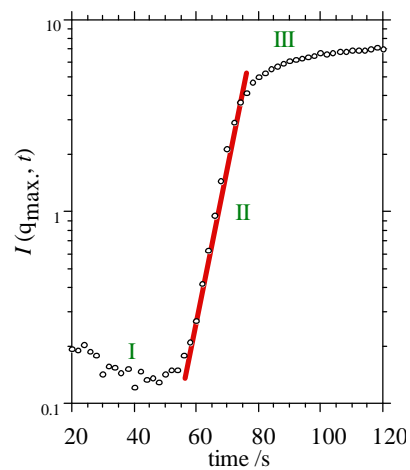
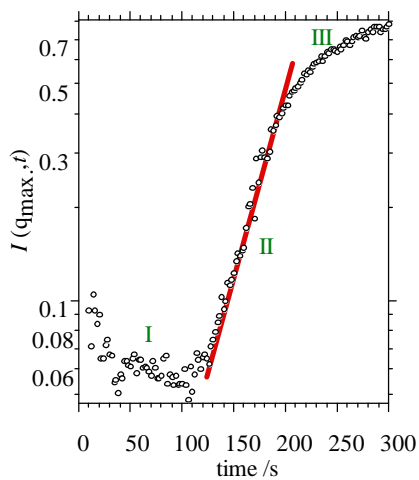
transmission $\approx e^{-\mu t}$

Peak that grows at fixed q^*

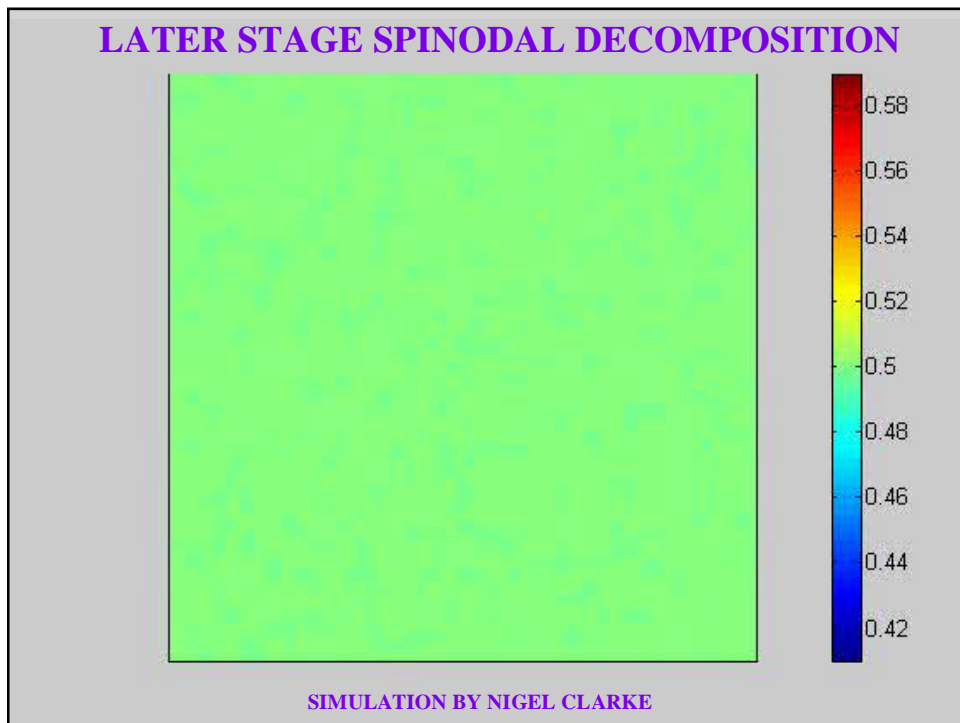
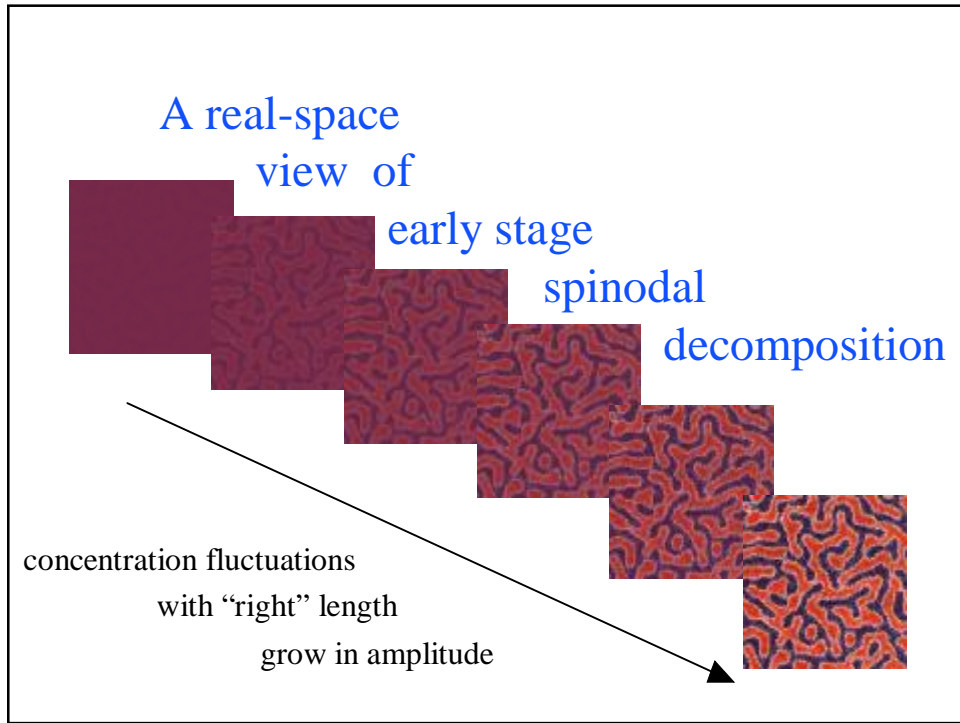


Is it spinodal decomposition?

Looks like spinodal decomposition!



I = Mw build **II = phase separation** **III = vitrification**



Smells like spinodal decomposition!

$I(q,t) = I(q,0) \exp [2R(q)t]$ Cahn Hilliard growth law

$$R(q) = -Mq^2 \left(\frac{\eta^2 G}{\eta r^2} + 2kq^2 \right)$$

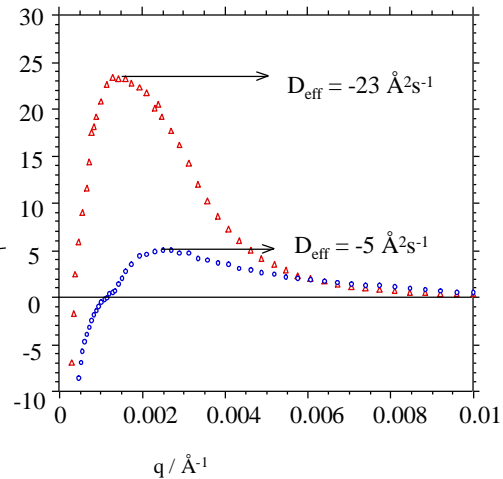
mobility

free energy
gradient

$$D_{eff} = -\frac{2R(q)}{q^2}$$

flux against the
concentration
gradient

$$\frac{R(q)/q^2}{\text{\AA}^2\text{s}^{-1}}$$

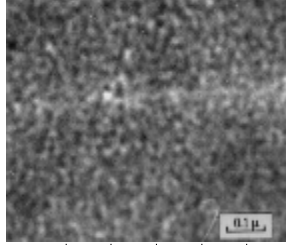


But what does it mean?

- n bicontinuous block copolymer morphology
- n HS continuous at low volume fractions
- n stiff polymer because of HS continuity
- n solidification by HS vitrification

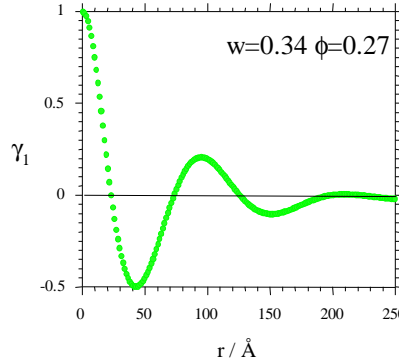
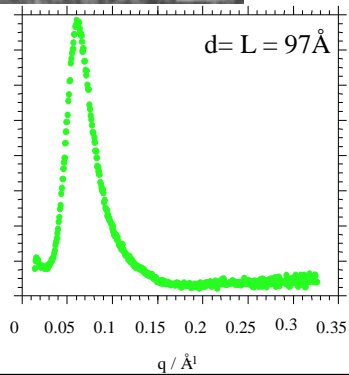
- n Ginzburg-Landau free energy functional implicit in data analysis

TEM, SAXS give $\sim 100 \text{ \AA}$ structure but correlation functions characterise lamellae



$$g(r) = \frac{\int I(q)q^2 \cos(qr)dr}{\int I(q)q^2 dq}$$

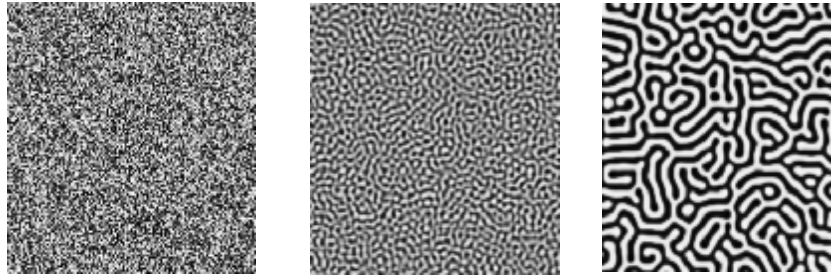
"Urea Hard Segment Morphology in Flexible Polyurethane Foam", R. Neff, A Adedeji, C.W. Macosko and A.J. Ryan, *J. Polym Sci. Polym. Phys. Ed.*, **36**, 573 (1998).



Spinodal kinetics imply Ginsburg-Landau free-energy functional

- $F = a_2\psi^2 + c_1(\nabla\psi)^2 + c_2(\nabla^2\psi)^2 + \dots$
- Cahn Hilliard only uses first two terms in the order parameter ψ
- Cell dynamics simulations also use the first two terms in the order parameter ψ
- Teubner-Strey micro-emulsion structure factor uses the first three terms
- $I(q) = 1/ a_2 + c_1q^2 + c_2q^4$ to model SAXS

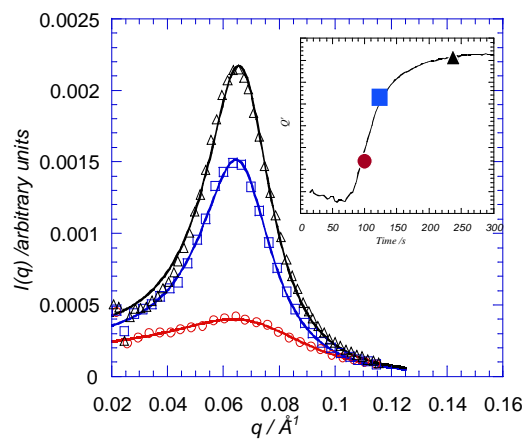
Simulation of PU structure using cell dynamics based on the time-dependent Ginsburg-Landau



time \longrightarrow

"Structure development in multi-block copolymerisation: comparison of experiments with cell dynamics simulations."
I.W. Hamley, J.L. Stanford, A.N. Wilkinson, M.J. Elwell, A.J. Ryan, *Polymer* 41, 2569 (2000).

Teubner-Strey Bicontinuous Microemulsion Model



$$I(q) = 1 / a_2 + c_1 q^2 + c_2 q^4$$

Average domain size

$$d = ((a_2/c_2)^2/2 + (c_1/4c_2))^{-1/2}$$

Short range order

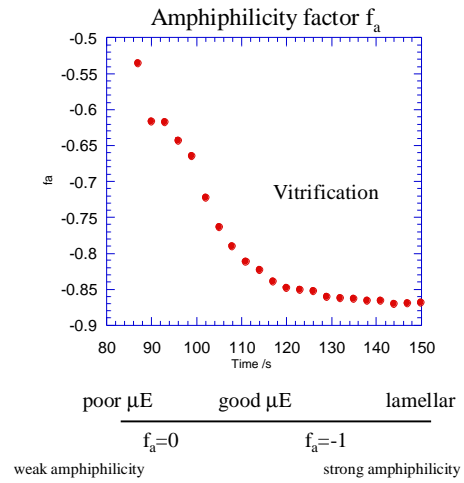
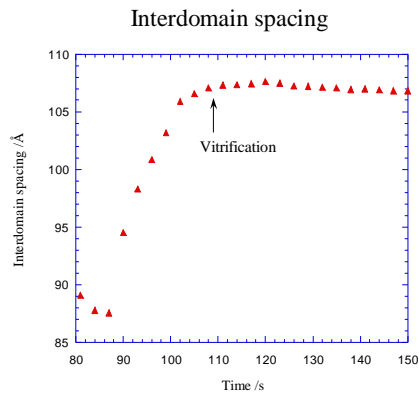
$$\xi = 2\pi((a_2/c_2)^{1/2}/2 - (c_1/4c_2))^{-1/2}$$

Amphiphilicity

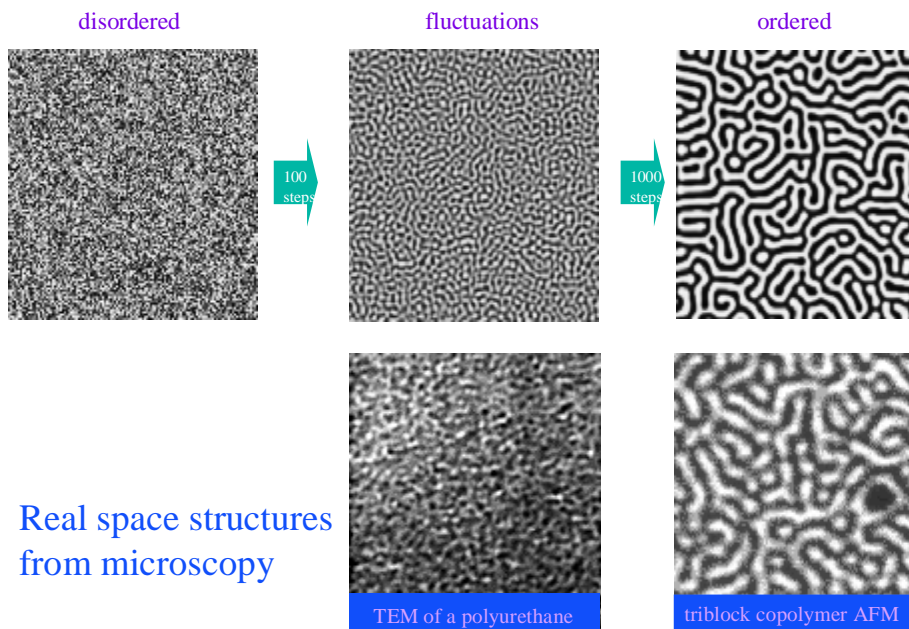
$$f_a = c_1/(4a_2c_2)^{1/2}$$

"Phase Separation in Flexible Polyurethane Foam."
Li, Wu, Ryan, Anthony J.; Meier, Ingrid K.
Macromolecules 35, 5034-5042 (2002).

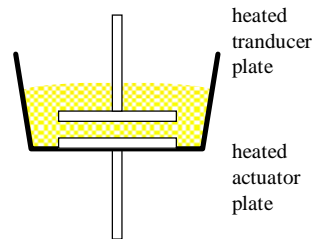
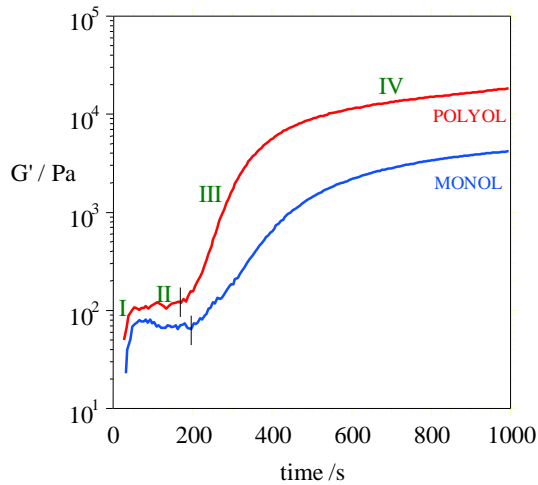
Teubner-Strey Model: structure information



Modelling block copolymer structuring using cell dynamics



Development of modulus by forced adiabatic rheology



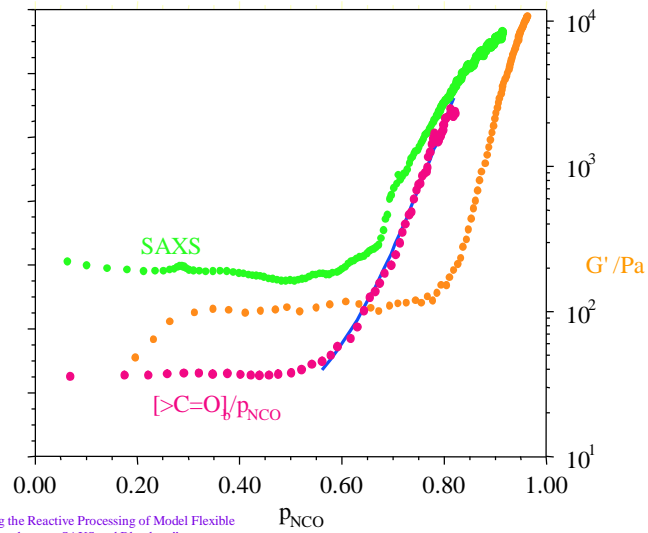
I = Mw build

II = phase separation

III = vitrification

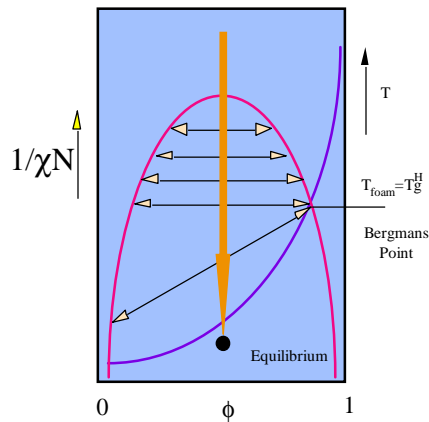
IV = consolidation

Added value from time resolution



"*In-situ* Studies of Structure Development during the Reactive Processing of Model Flexible Polyurethane Foam using FTIR Spectroscopy, Synchrotron SAXS and Rheology",
M.J. Elwell, A. J. Ryan, H.J. Grünbauer, and H.C. Van Lieshout,
Macromolecules, 29, 2960 (1996).

FOLLOWING POLYURETHANE FOAM THROUGH THE PHASE DIAGRAM DURING PROCESSING



start of reaction $p=0$

density reduction

microphase separation $p=0.55$

cell opening $p \approx 0.6$

constant density

modulus growth $p = 0.7$

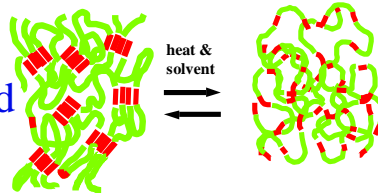
$p = 0.9$

Na vijf weken heb je een comfortabele stoel!

Funding : Dow Chemicals, Shell Chemicals, Air Products, Johnson & Johnson
 Researchers : Mike Elwell, Wu Li, John Stanford & Paul Cookson

A more interesting polyurethane

- n Premade polymer
- n Dissolved in solvent (THF)
- n Coated on former
- n Solvent evaporated
- n Washed to remove last traces of solvent!
- n Dried in rotating oven
- n Problems in processing and on storage

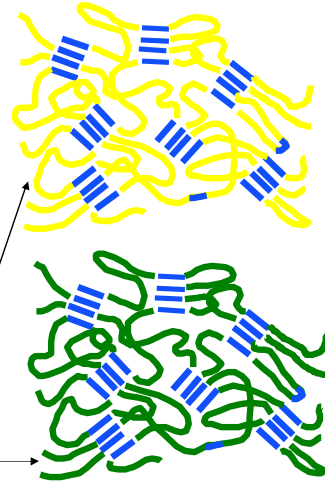
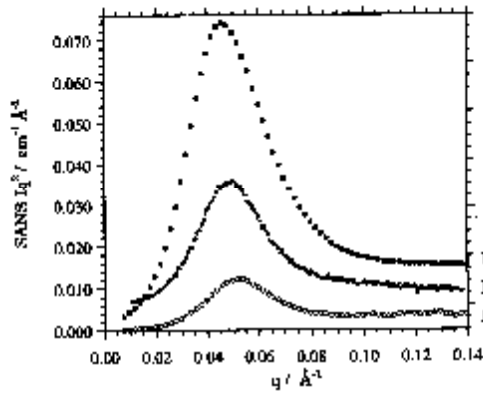


Why did we do SANS?

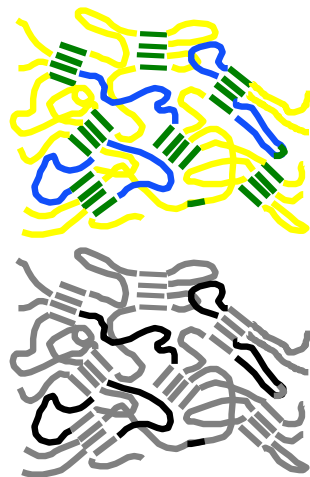
SAXS & SANS on labelled PU

D and H soft segments give contrast with different magnitude & opposite sign

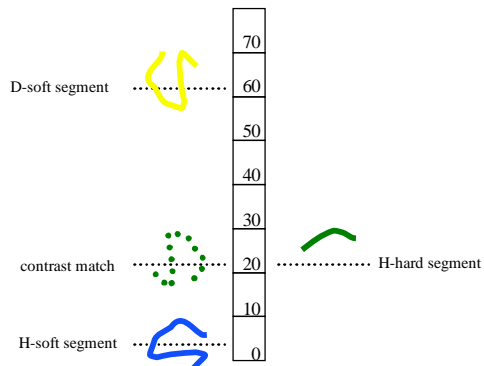
$$\int I(q)q^2 = f(1-f)\langle h^2 \rangle$$



Molecular Dimensions of PU by zero-sum contrast SANS

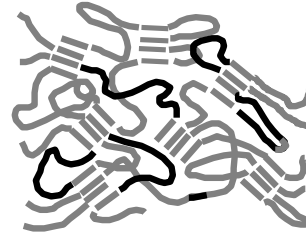
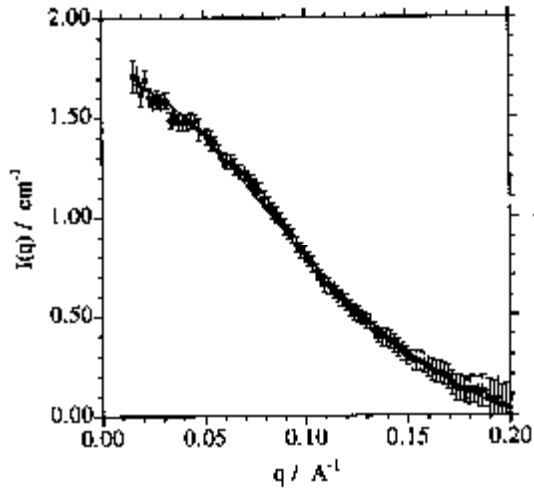


Scattering length density / cm⁻²



"Temperature Dependence of Chain Conformations in a Model Block Copolyurethane" S. Naylor, N.J. Terrill, G-E. Yu, S. Tanodekaew, W. Bras, S. M. King, C. Booth and A.J. Ryan, *Polym. Int.*, 44 371 (1997).

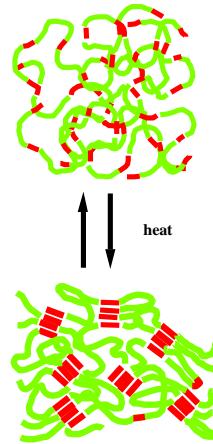
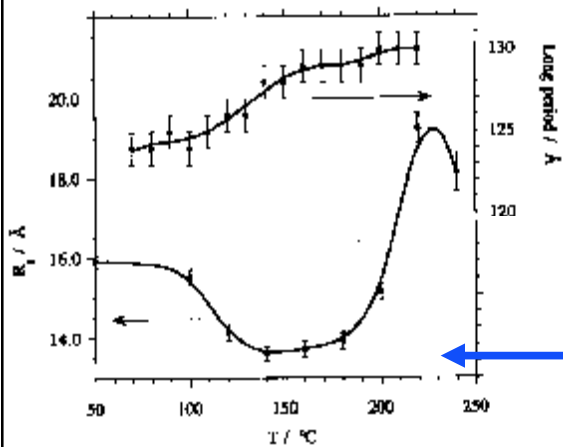
Rg of soft segments from SANS



The Debye equation for a Gaussian Coil

$$P_B(q) \approx I(q) = K \frac{2(e^{-q^2 R_g^2} + q^2 R_g^2 - 1)}{(q^2 R_g^2)^2}$$

Molecular Dimensions, Rg versus T



R_g of unperturbed soft segment coils

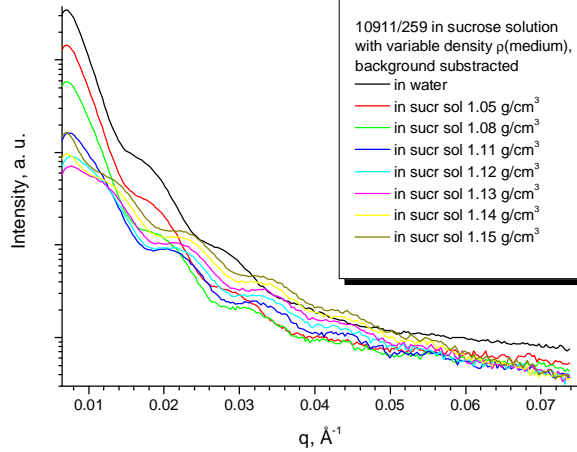
Nanostructured paint



A dispersion of
~ 50 nm particles
of PU ionomer in
acrylic monomer

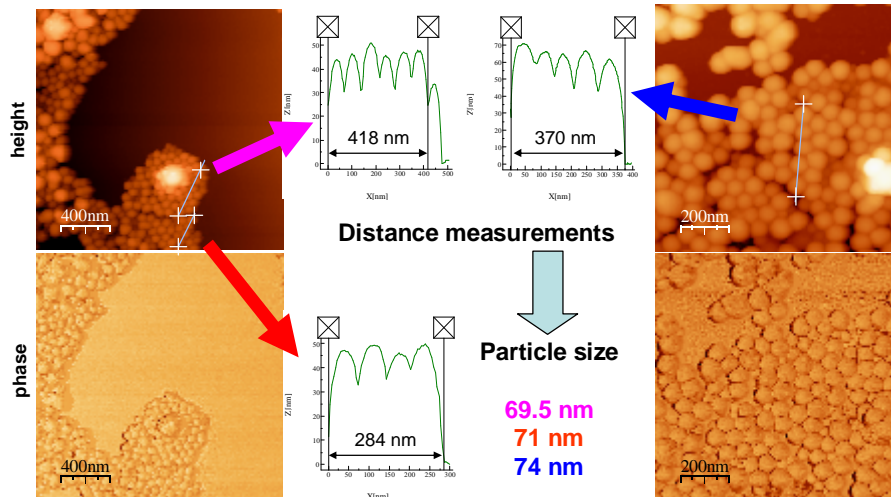


polymerisation of
acrylic leads to phase
separation inside the
particles



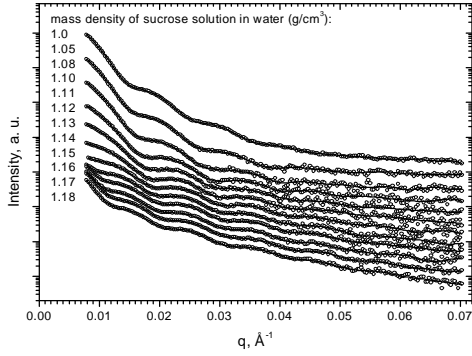
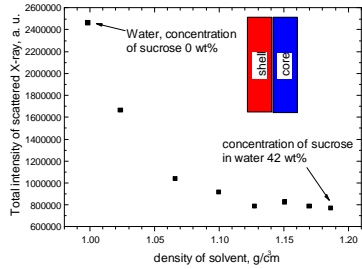
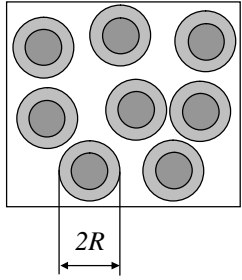
AFM of latex particles

Non-filtered water solution of the latex (0.5 wt.%) spin coated on silicon substrate at 1000 rpm



Contrast variation in SAXS

"The application of distance distribution functions to structural analysis of core-shell particles."
 Mykhaylyk, O. O.; Ryan, A. J.; Tzokova, N.; Williams, N., *Journal of Applied Crystallography* 2007, 40, 506-511.

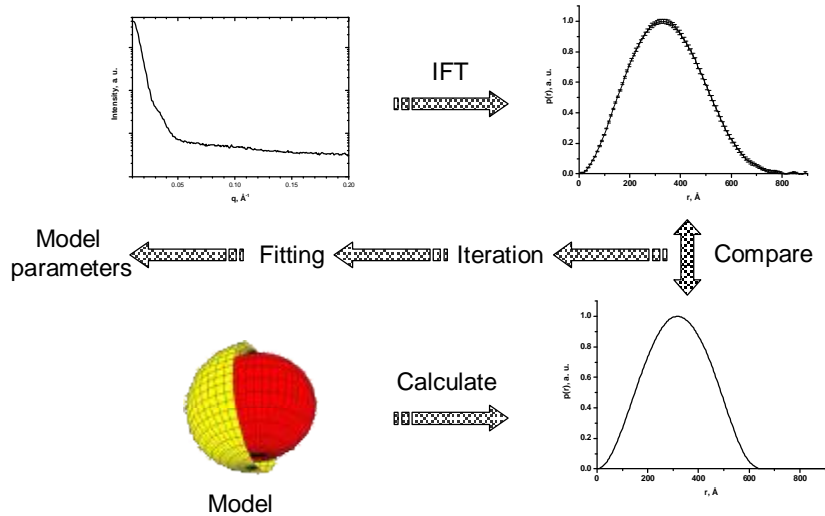


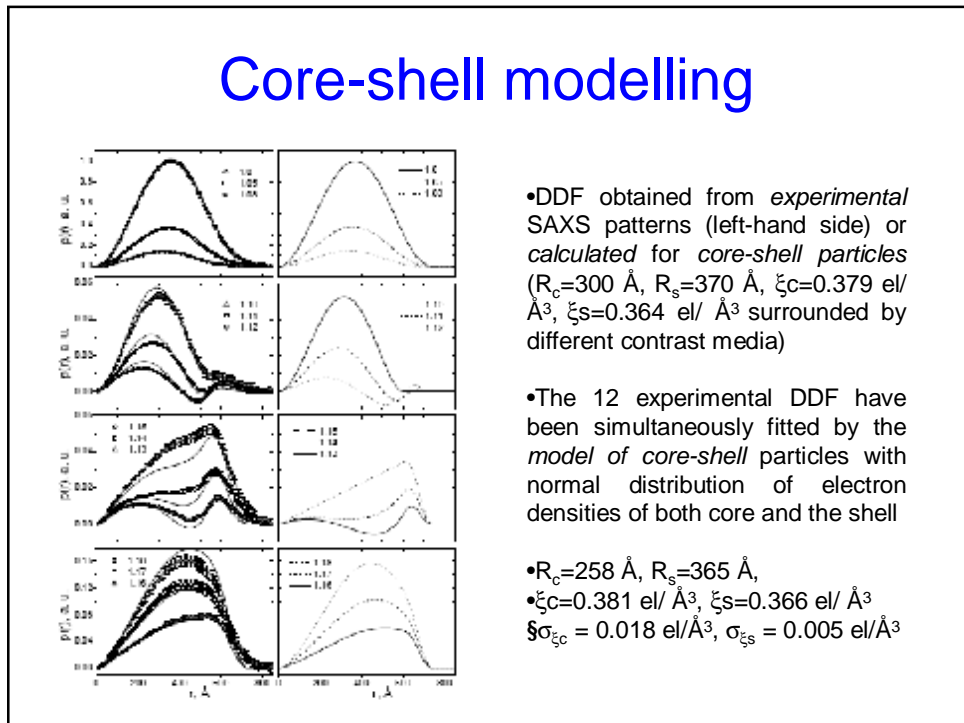
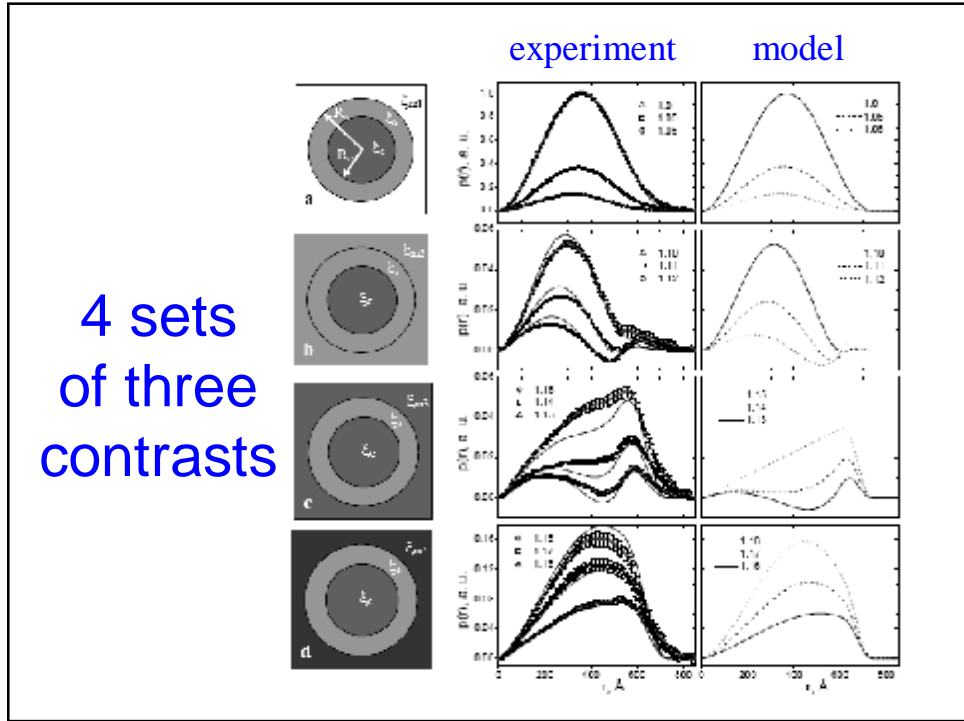
•SAXS patterns of diluted suspensions of particles comprising 35% PU in water sucrose solution

Volume fraction of the polymer in the solutions 0.083

The method chosen for modelling

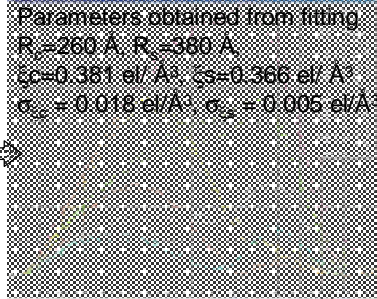
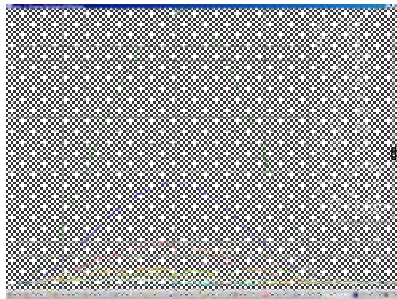
"The application of distance distribution functions to structural analysis of core-shell particles."
 Mykhaylyk, O. O.; Ryan, A. J.; Tzokova, N.; Williams, N., *Journal of Applied Crystallography* 2007, 40, 506-511.





Core-shell modelling

"The application of distance distribution functions to structural analysis of core-shell particles."
 Mykhaylyk, O. O.; Ryan, A. J.; Tzokova, N.; Williams, N., *Journal of Applied Crystallography* 2007, 40, 506-511.



Parameters obtained from fitting
 $R_c=260 \text{ \AA}$; $R_s=380 \text{ \AA}$
 $\rho_c=0.381 \text{ e/\AA}^3$; $\rho_s=0.366 \text{ e/\AA}^3$
 $\sigma_c = 0.018 \text{ e/\AA}^3$; $\sigma_s = 0.005 \text{ e/\AA}^3$

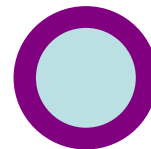
$$p(r) = \int P(r_c) \int P(r_s) \int_0^\infty I(q) q r \sin(qr) dq dr_c dr_s$$

- ∅ Double integration over probability distribution functions of electron densities of the core part $P(\xi_c)$ and the shell part $P(\xi_s)$ of the particles
- ∅ The result of integration is an analytical expression, used for fitting all twelve DDF calculated from experimental SAXS pattern

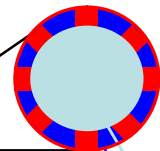
- ∅ The model reproduce most of the features observed in the DDF calculated from experimental SAXS data
- ∅ The parameters are consistent with the results obtained from TEM $R_s=370 \text{ \AA}$, AFM $R_s=360 \text{ \AA}$

But the shell has its own internal structure

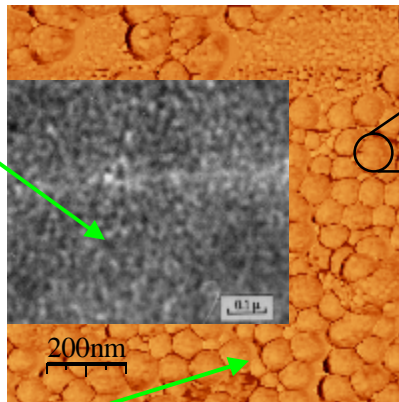
NOT



BUT



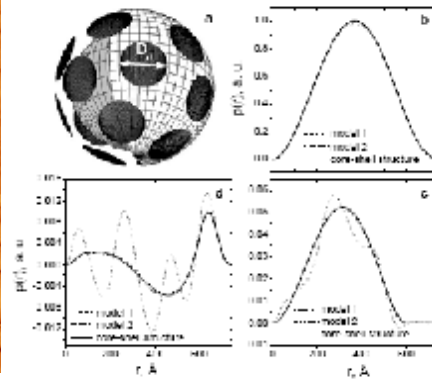
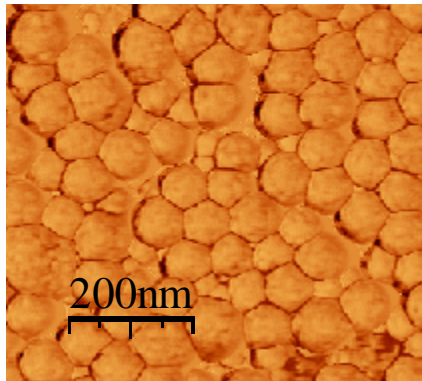
A TEM image of a phase separated polyurethane



An AFM phase image of a dried film of latex

PU hard block
 PU soft block
 core polyacrylate

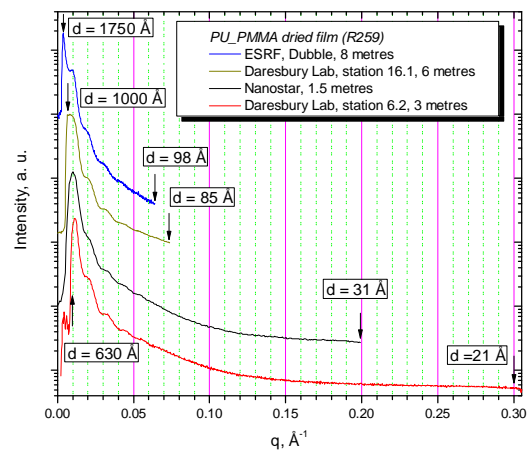
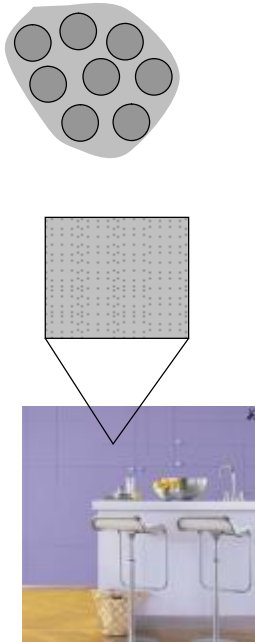
Trying to model the shell structure



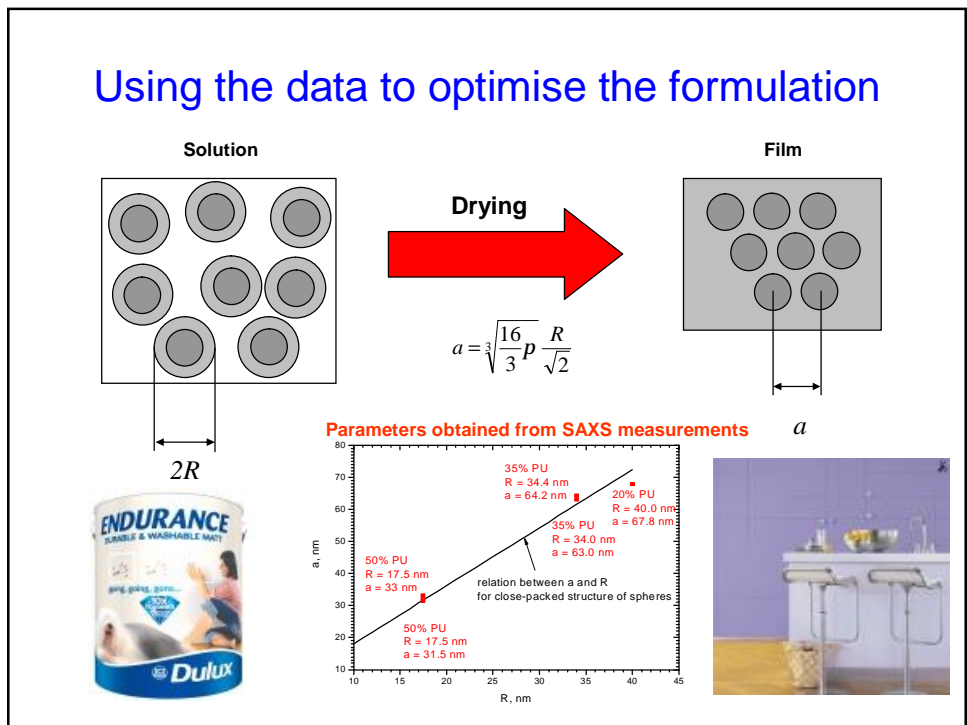
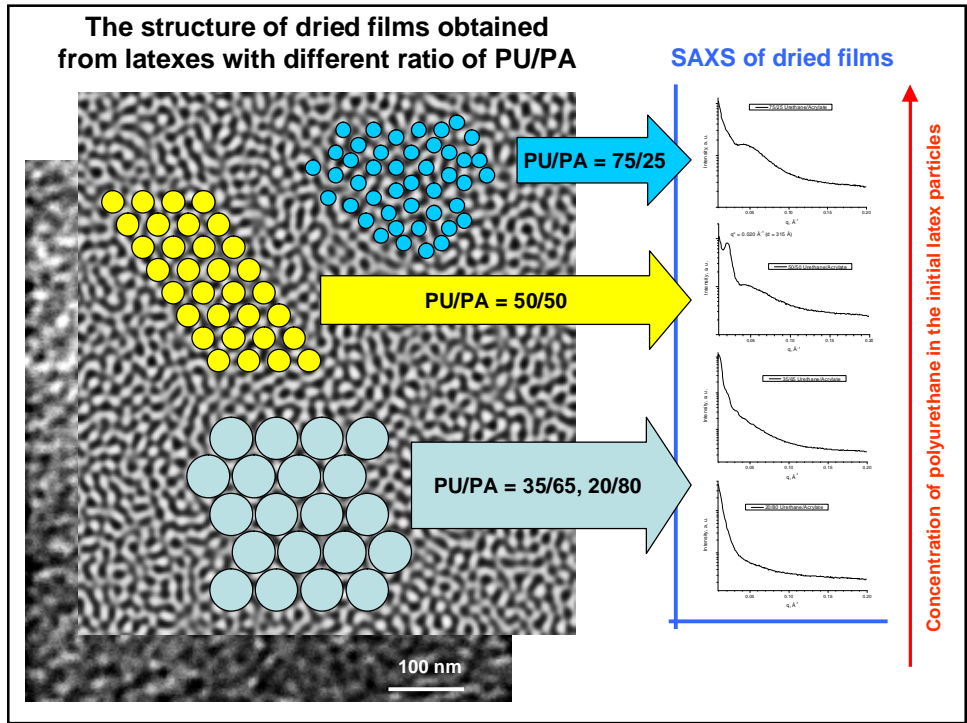
Best fits from a model that has density variations in both core and shell

"The application of distance distribution functions to structural analysis of core-shell particles,"
Mykhaylyk, O. O.; Ryan, A. J.; Tzokova, N.; Williams, N., *Journal of Applied Crystallography* 2007, 40, 506-511.

SAXS patterns of a dried film on different SAXS cameras



(recorded using different camera length)



Summary

- Scattering can give valuable insight into materials processing
- Scattering should be used in combination with other techniques
- The models used should be fit for purpose

Can improve processes

Reduce environmental impact

Increase profits!