



FTIR-ATR REAL-TIME MONITORING OF THE ADSORPTION OF PS-*b*-PEO COPOLYMERS ON Ge, FROM MICELLAR SOLUTIONS

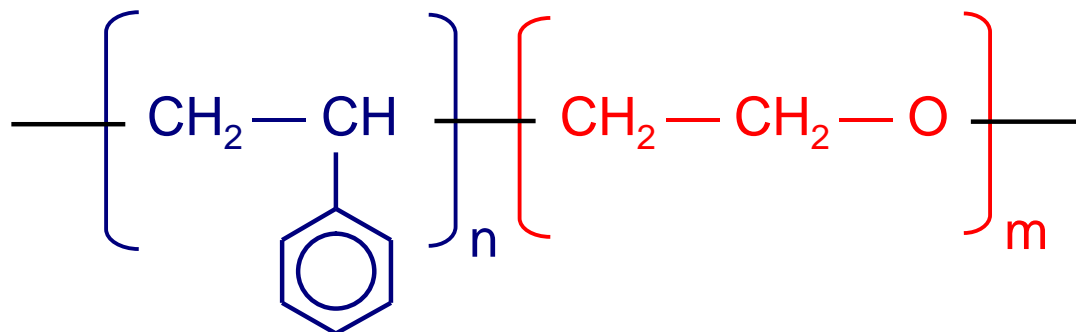
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6th HELLENIC CONFERENCE IN POLYMERS



Poly(styrene-b-ethylene oxide) Copolymer

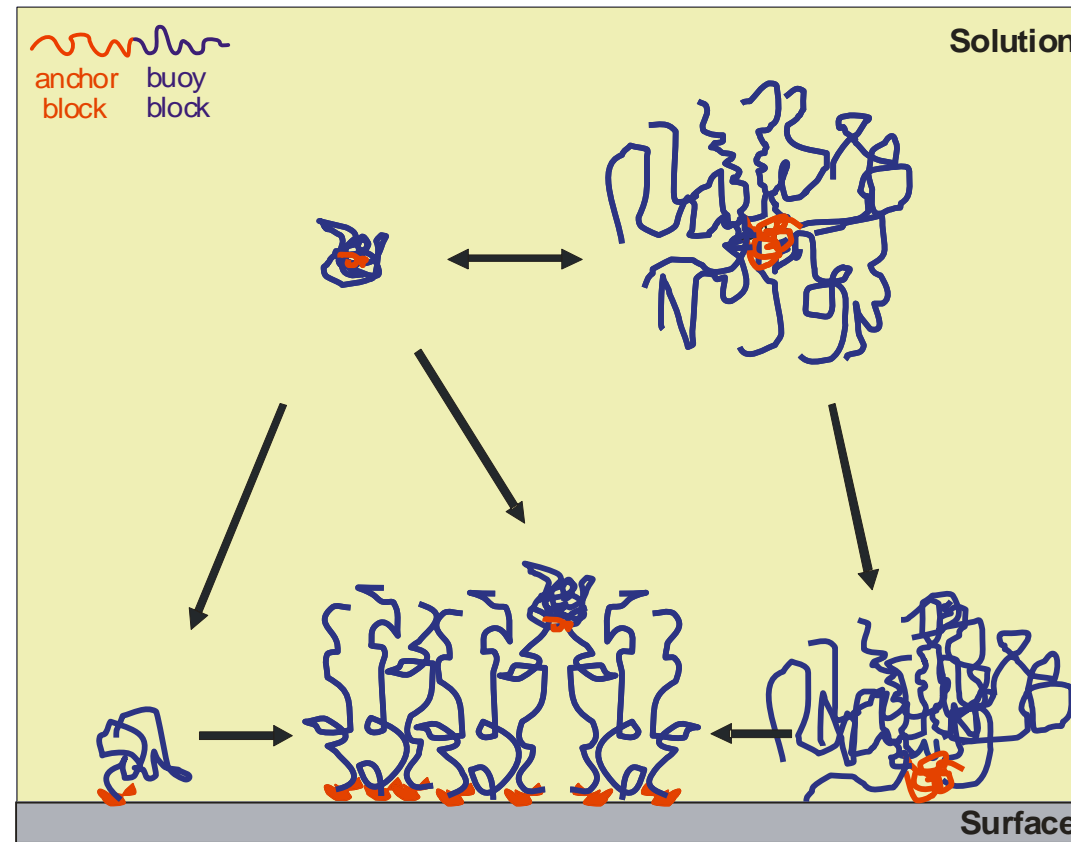


forms reverse micelles in decalin (selective solvent for PS)

all solutions studied were well-above the critical micelle concentration (cmc)

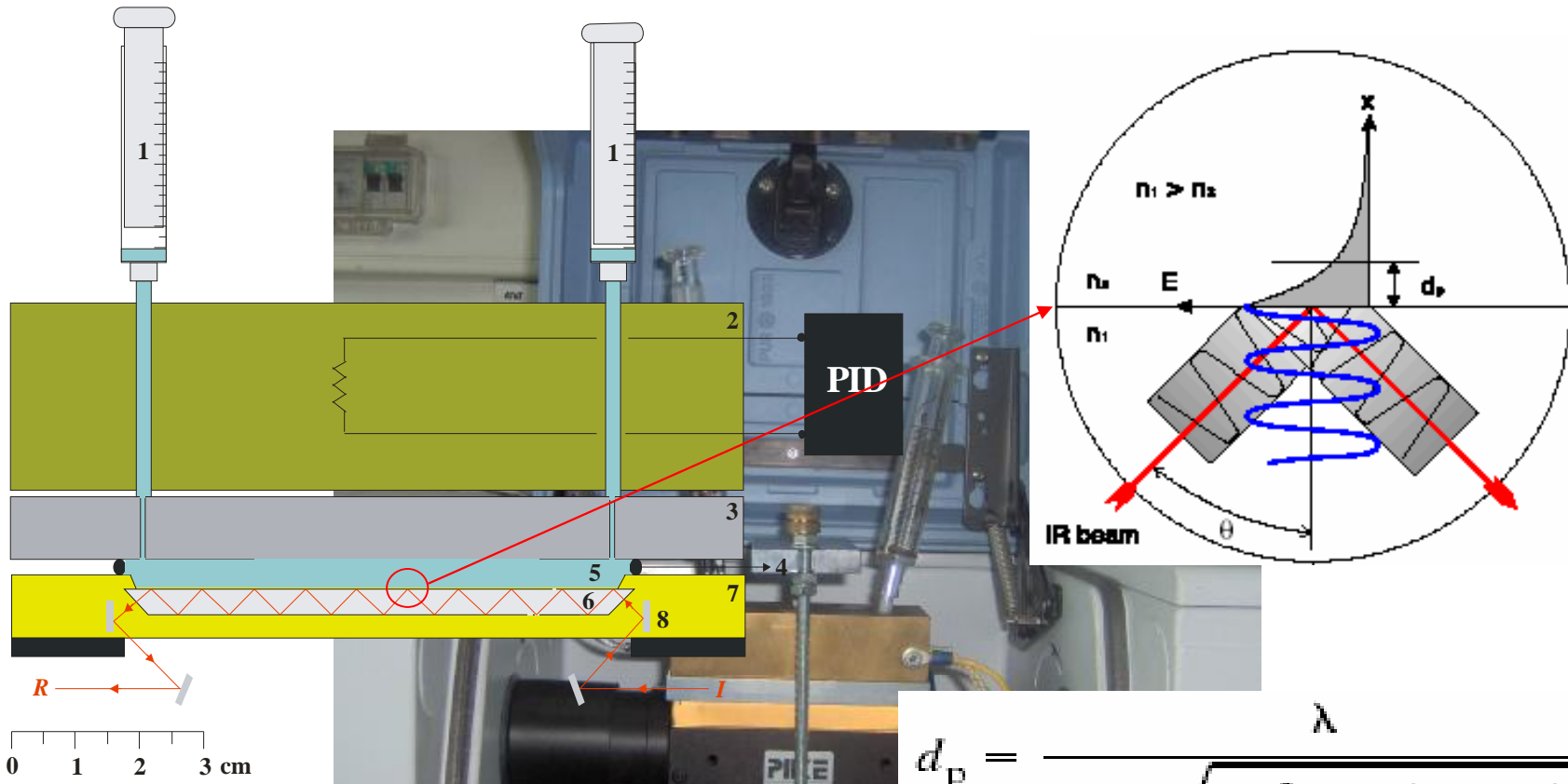
(our study also included one $\text{PS}_{93}\text{-b-PEO}_{237}$ copolymer and one $\text{PI}_{211}\text{-b-PEO}_{192}$ copolymer)

Adsorption Mechanisms of Amphiphilic Diblock Copolymers from Micellar Solutions



- ∅ Indirect: micelles release free chains which may subsequently adsorb (Johner-Joanny 1990)
- ∅ Direct: adsorption of micelles

Attenuated Total Reflectance Spectroscopy



$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2\theta - (n_2/n_1)^2}}$$

ATR Cell

- 1: Syringes, 2: Heating Block
- 3: Lid, 4: O-ring
- 5: Solution, 6: Ge Prism
- 7: Base, 8: Mirrors

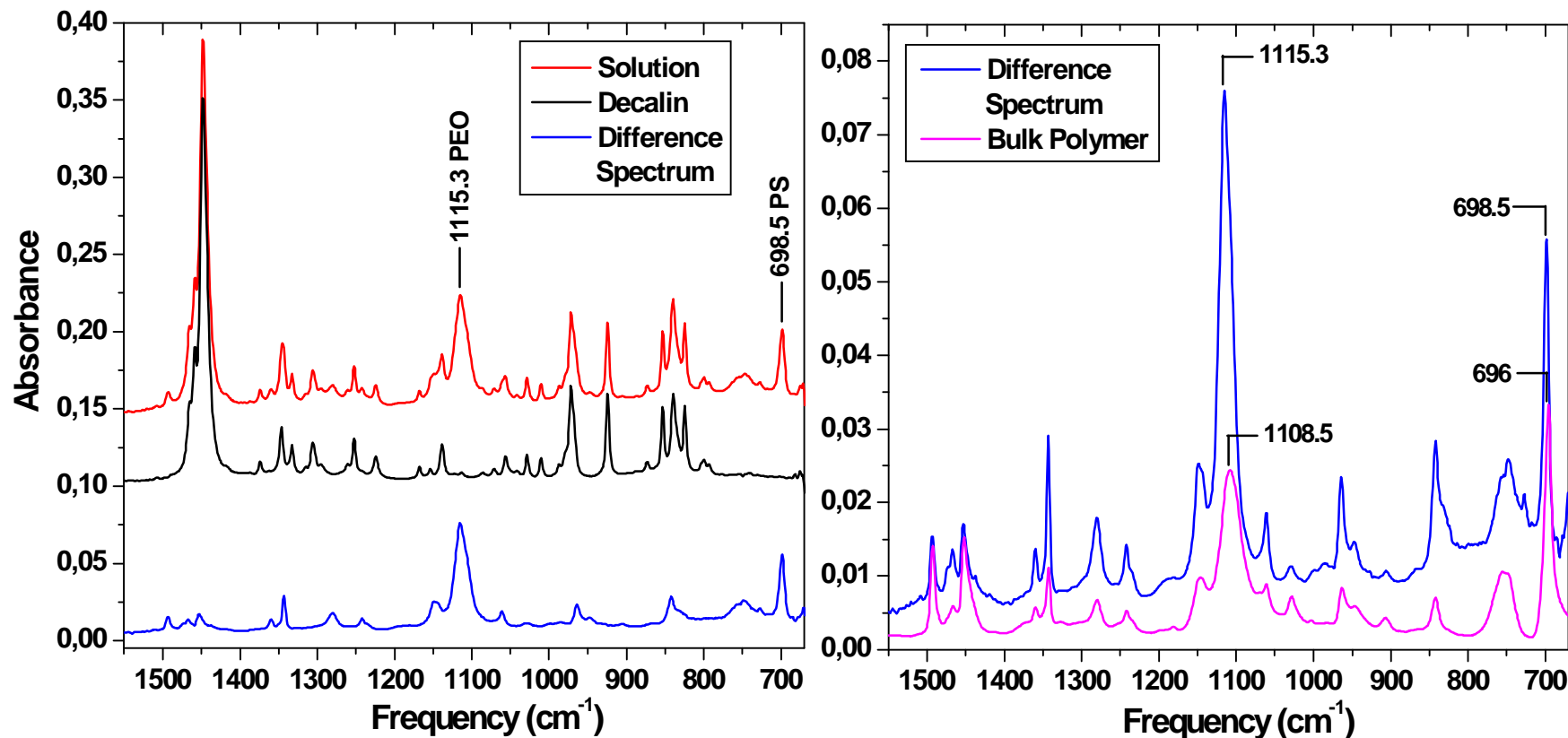
for $\lambda=10 \mu\text{m}$, $n_1=4$ (Ge), $n_2=1.5$, $\theta=45^\circ$

$d_p=0.66 \mu\text{m}$

The Adsorbed Layer by ATR Spectroscopy



$C=5 \times 10^{-3}$ g/ml at 30°C 2 hours after measure onset

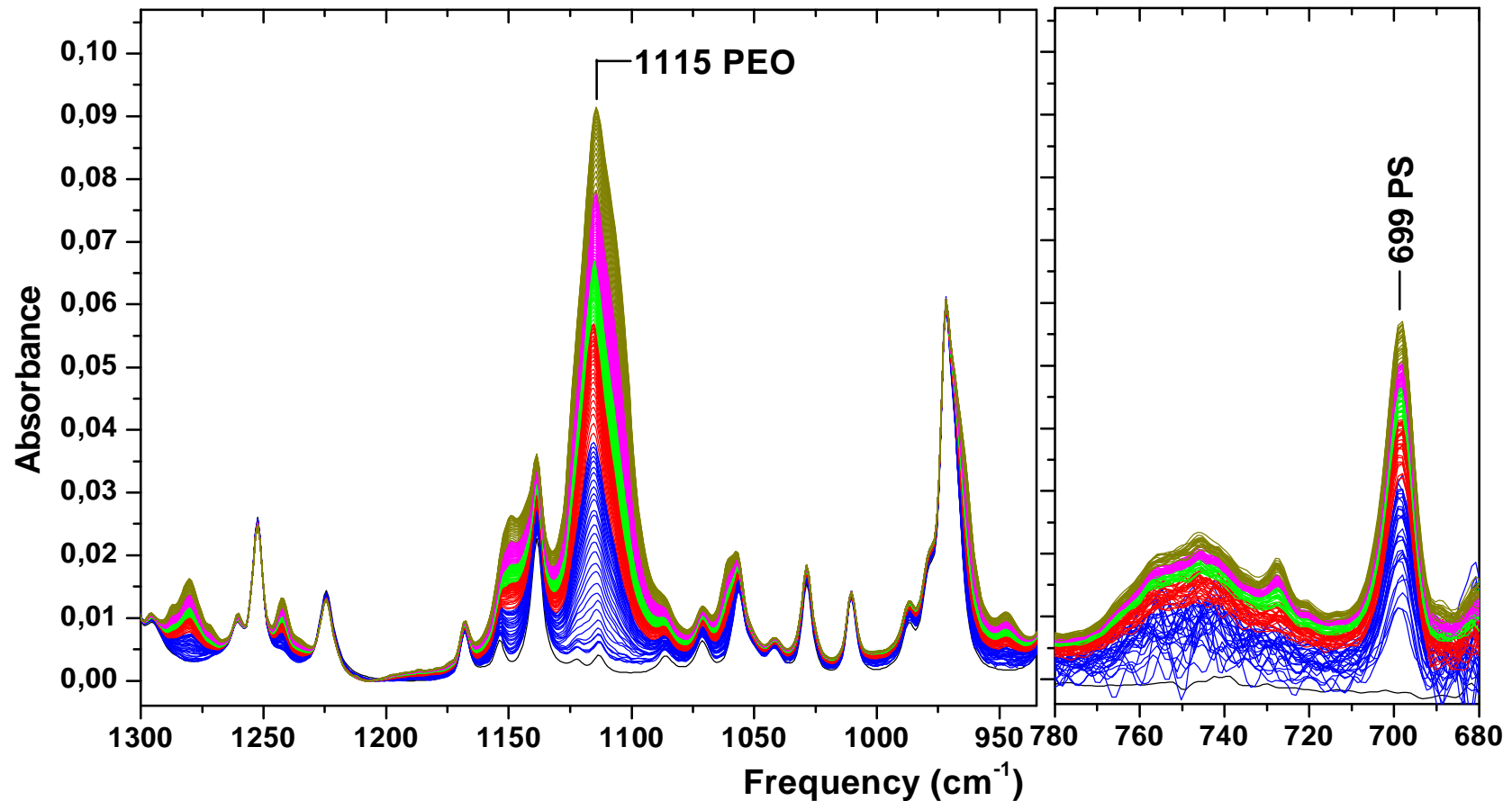


Diagnostic bands: PEO at 1115 cm⁻¹ (C-O-C stretching)
PS at 699 cm⁻¹ (C-H o. o. p. bending)



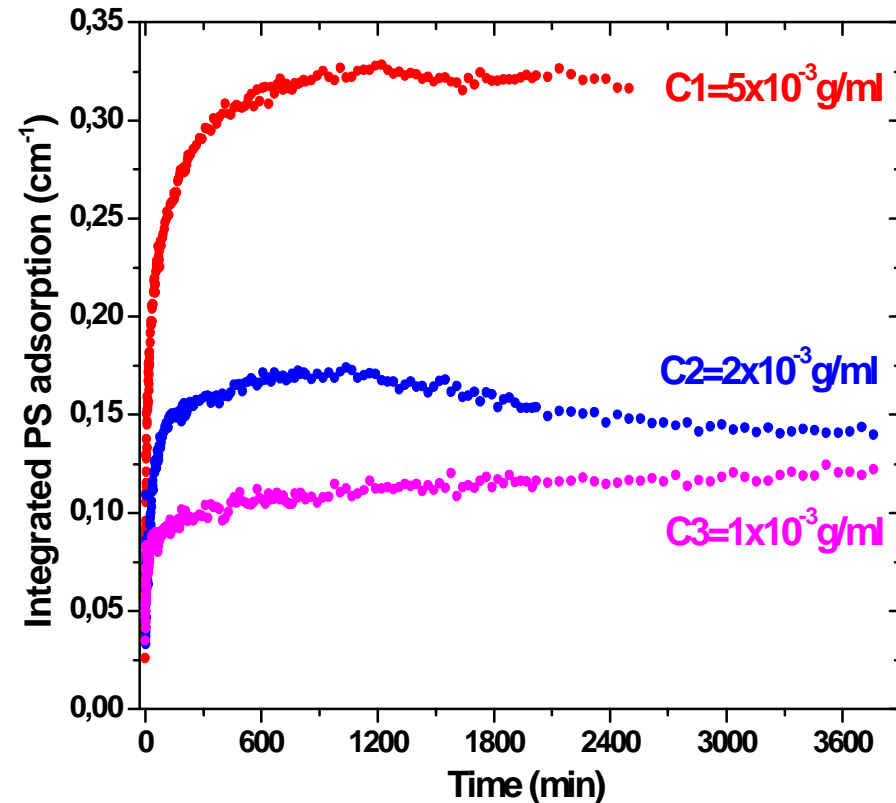
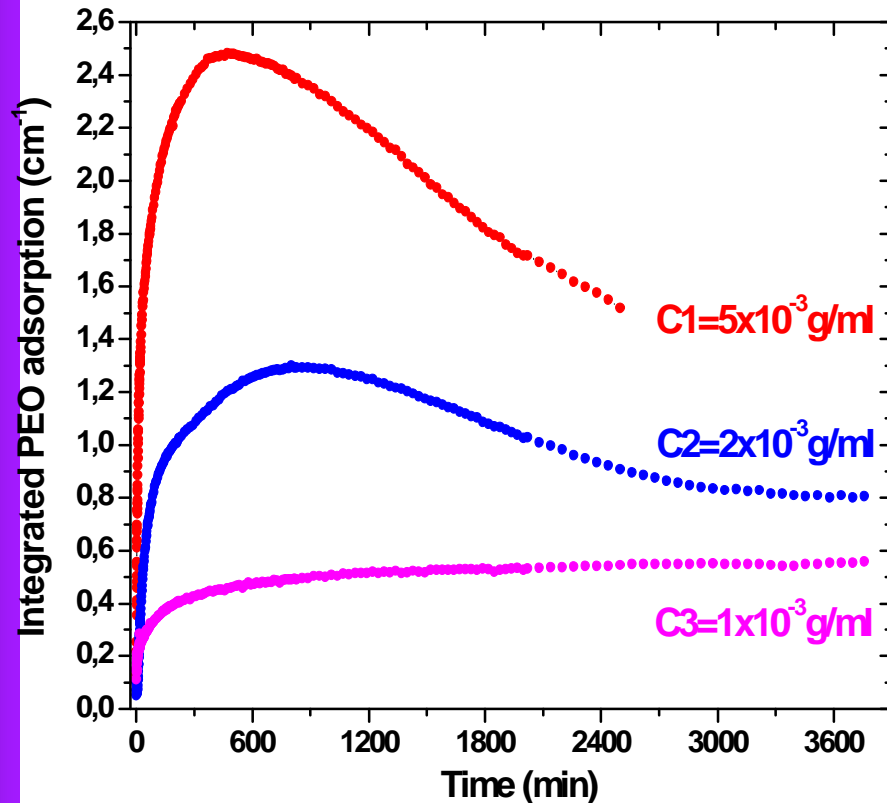
Adsorption Monitoring

$C_1 = 5 \times 10^{-3} \text{ g/ml}$ at 30°C
during the first 8 hours of measurement



Two independent ways for monitoring the adsorption by integrating the PEO and PS bands.

Adsorption Kinetics at 30°C



The PEO (and to a lesser extent the PS) kinetics of the higher concentrations exhibit non monotonic behavior (“overshooting”).

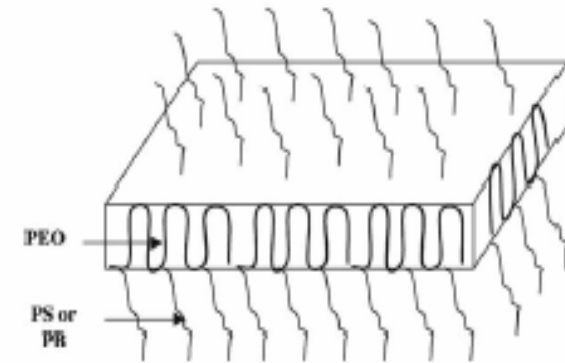
Dynamic Light Scattering Measurements



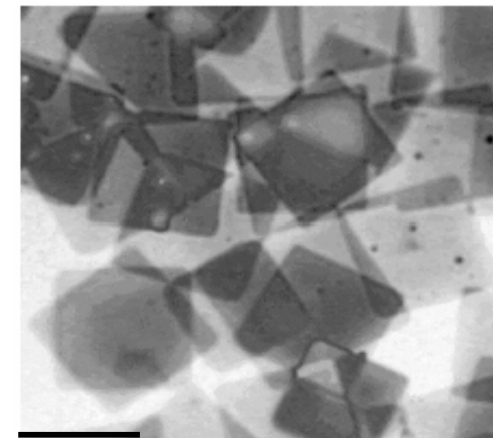
C (g/ml)	I ₉₀ (kcts/s)	D _h (nm)	μ ₂ /Γ ²
30°C			
1x10 ⁻⁴	131	67, 850	1
2x10 ⁻⁴	145	76, 1400	1
5x10 ⁻⁴	460	100, 1900	1
55°C			
1x10 ⁻⁴	9.2	33.5	0.18
2x10 ⁻⁴	24.3	36	0.03
5x10 ⁻⁴	76.4	37.4	0.05

At 30°C: Two aggregate populations, one of small, spherical, star-like micelles and another of much larger lamellar microcrystals, known as “platelets”

At 55°C: One aggregate population of small, spherical, well-defined micelles



Self-assembly of PS-PEO or PB-PEO diblock copolymers in organic solvents (Riess 2003)

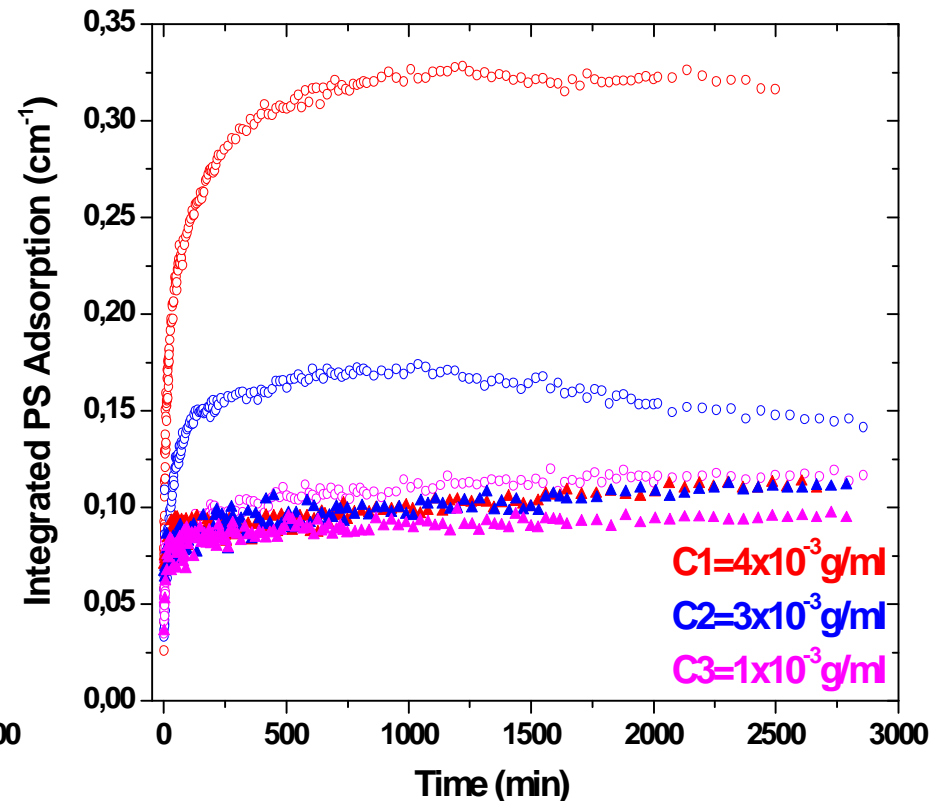
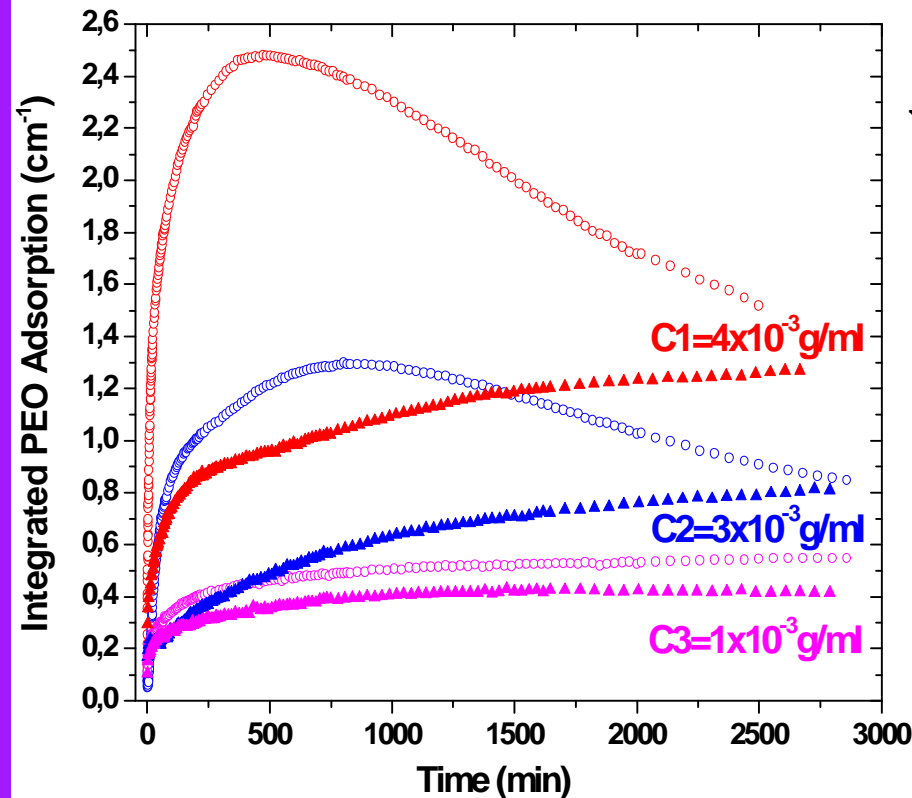


10 μm

Optical micrograph of PS-PEO platelets (Reiter 1998)

Adsorption Kinetics at 55°C

open symbols: adsorption kinetics at 30°C

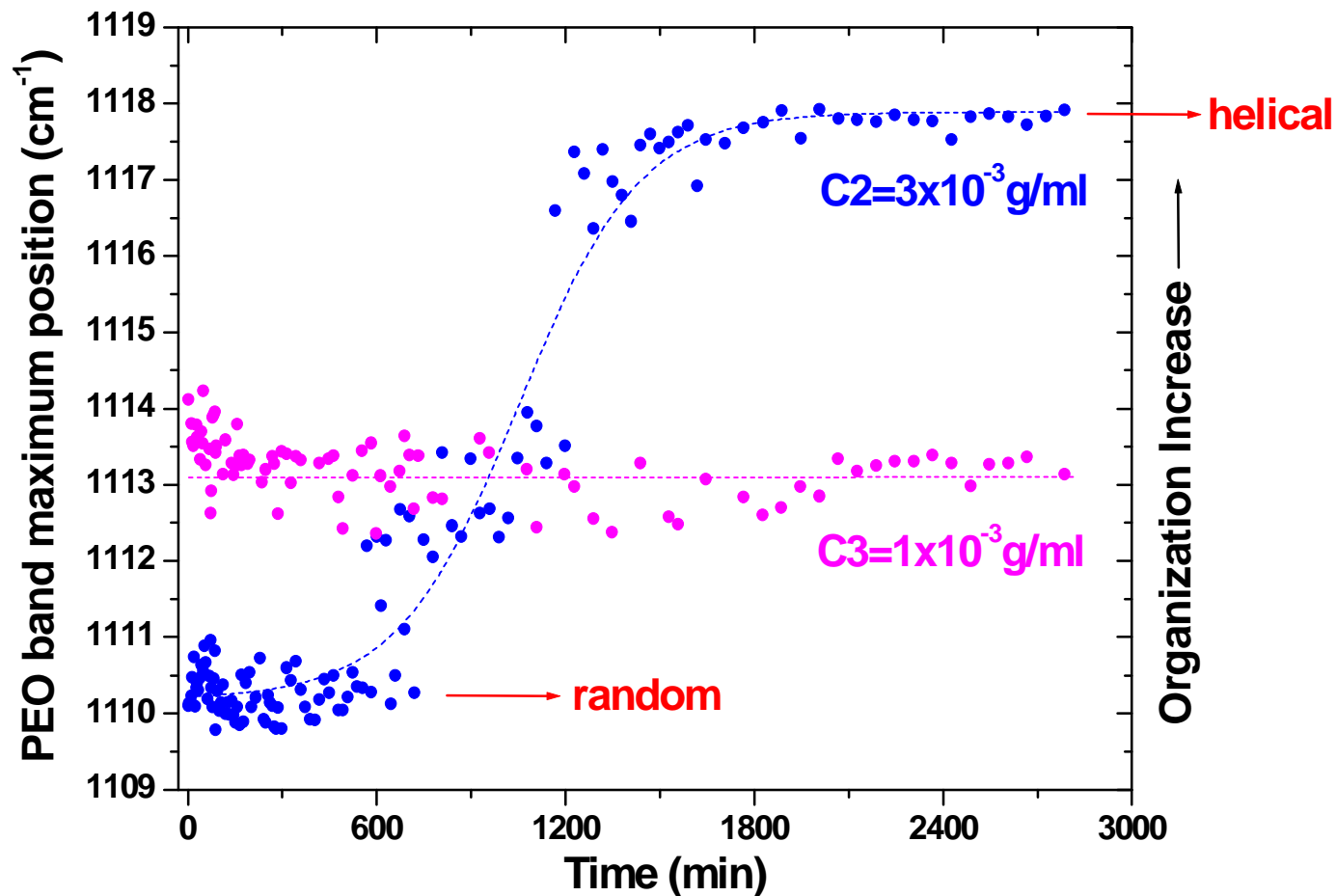


Both PEO and PS kinetics exhibit more regular behavior, with evidence of more than one underlying processes at higher concentrations.

The PS kinetics result in almost the same final plateau value, which indicates that the amount of the adsorbed copolymer is nearly independent of concentration.



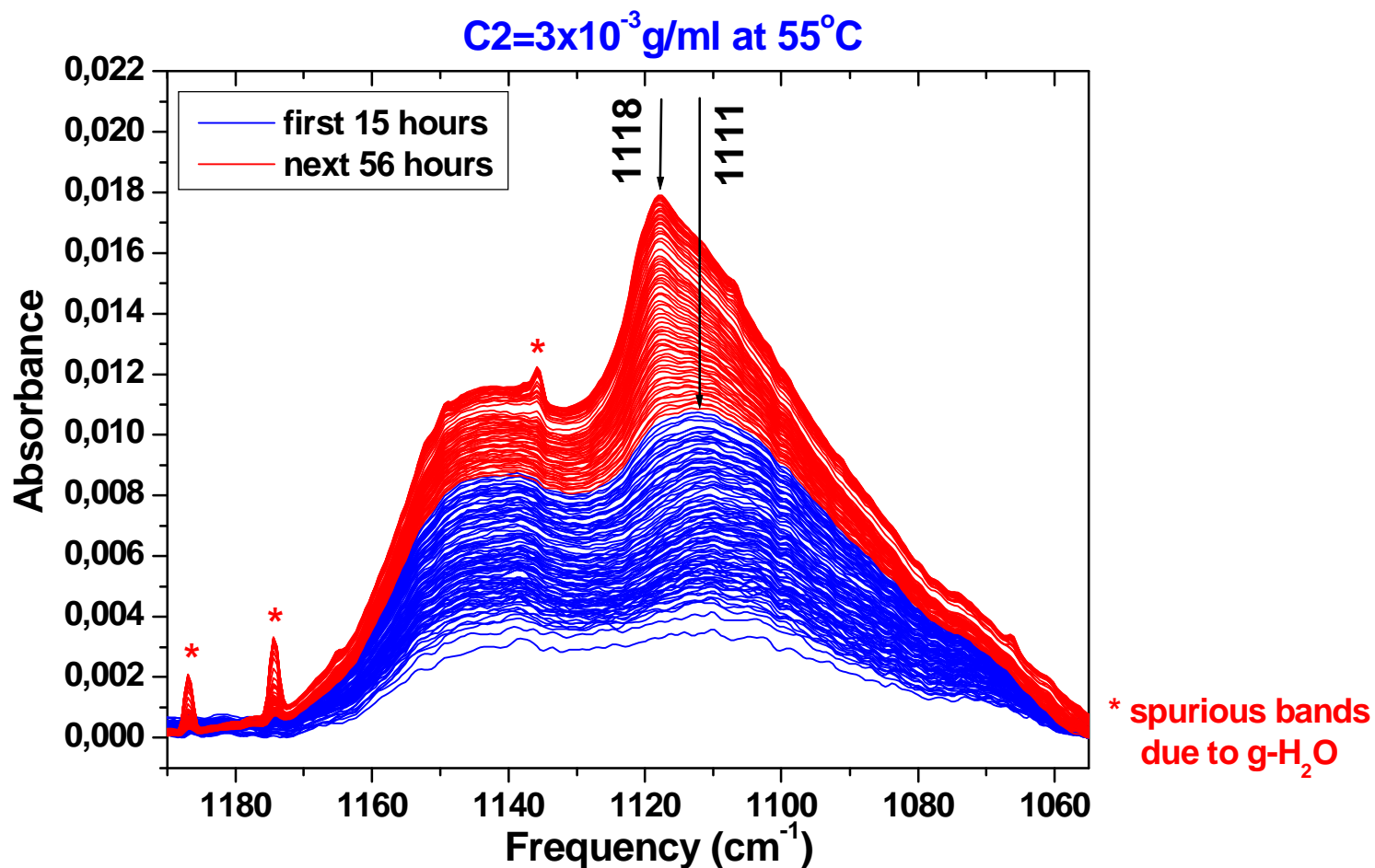
PEO Conformational Changes at 55°C



Regular behavior, although at higher concentrations the final band maximum position indicates high PEO organization near the solution-Ge interface.

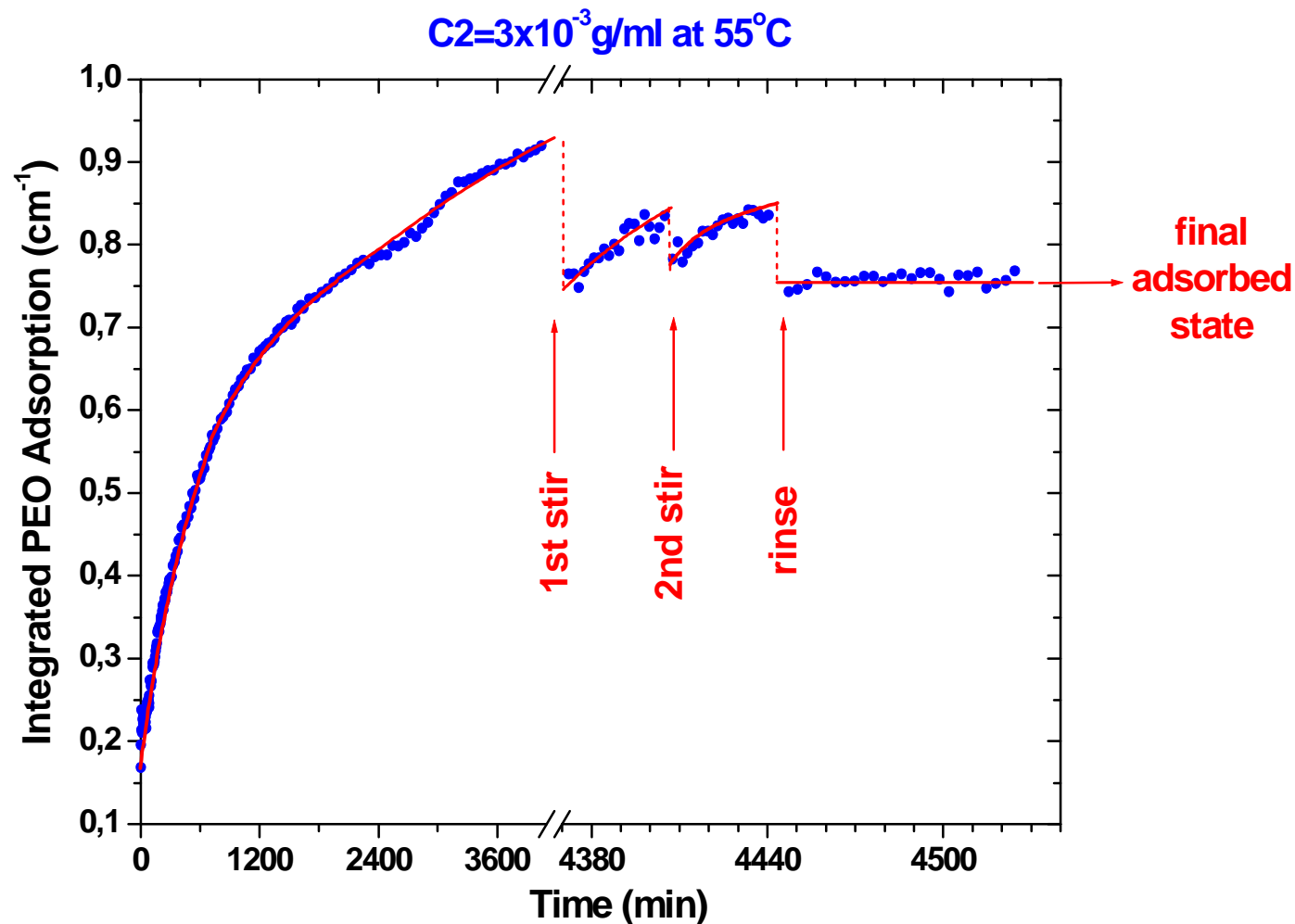


PEO Conformational Changes at 55°C ATR Spectra



PEO band conformation changes gradually to a more organized PEO conformation after the first 15 hours of measurement.

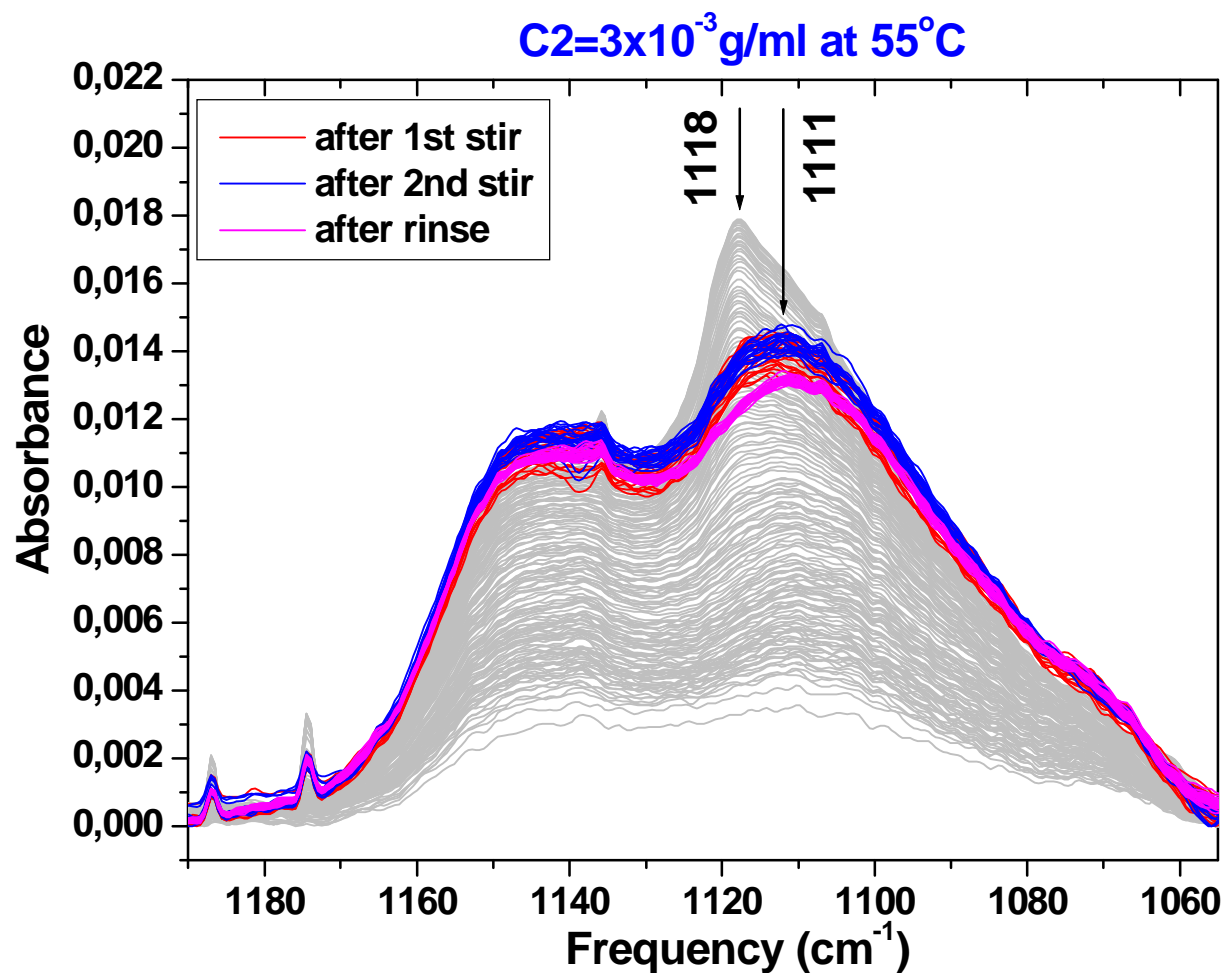
Stirring-Rinsing Procedure



Formation of a loosely attached layer, above the adsorbed layer, characterized by well-ordered helical PEO conformations.



Stirring-Rinsing Procedure ATR Spectra



After stirring-rinsing procedure PEO main peak conformation changes back to the original conformation characteristic of amorphous PEO.

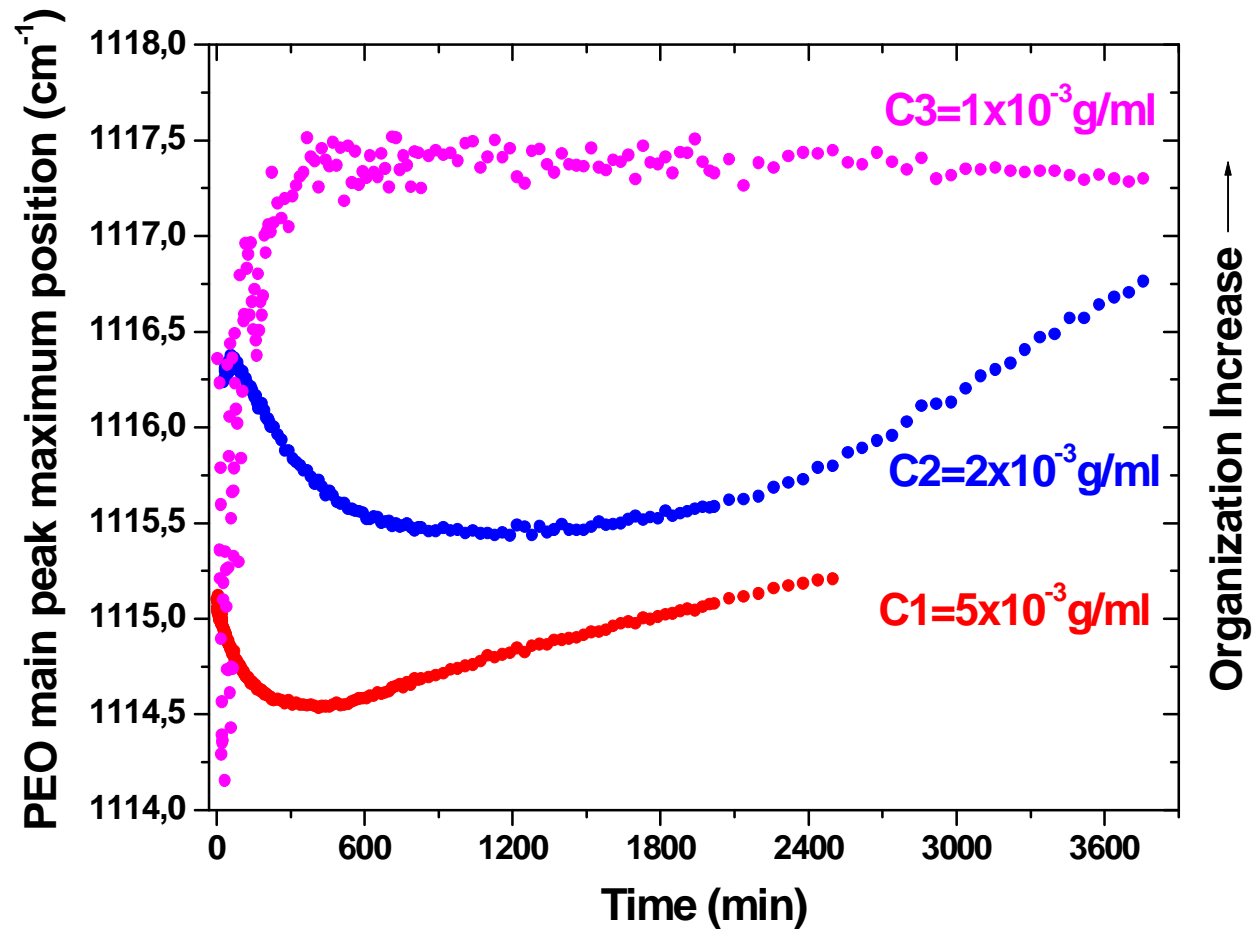


Conclusions

- ∅ FTIR-ATR Spectroscopy is suitable for monitoring the adsorption of PS-b-PEO copolymer above the cmc at the decalin-Ge interface
- ∅ More than one diagnostic bands to monitor independently both kinetic and conformational aspects
- ∅ At 30°C: non monotonic behavior, probably due to changes in micellar morphology
- ∅ At 55°C: more regular behavior, amorphous adsorbed layer and formation of a loosely attached layer, above the adsorbed, characterized by well-ordered helical PEO conformations

Thank you for your attention

PEO Conformational Changes at 30°C



Non monotonic behavior at higher concentrations, probably due to changes in micellar morphology.