FRACTIONATION OF POLYACRYLAMIDE IN LAMELLAR MESOPHASES

Yahya Agzenai, Isabel E. Pacios, Carmen S. Renamayor

Dept. CC. y TT. Fisicoquímicas, Facultad de Ciencias
Universidad Nacional de Educación a Distancia (UNED), Madrid, Spain

csanchez@ccia.uned.es

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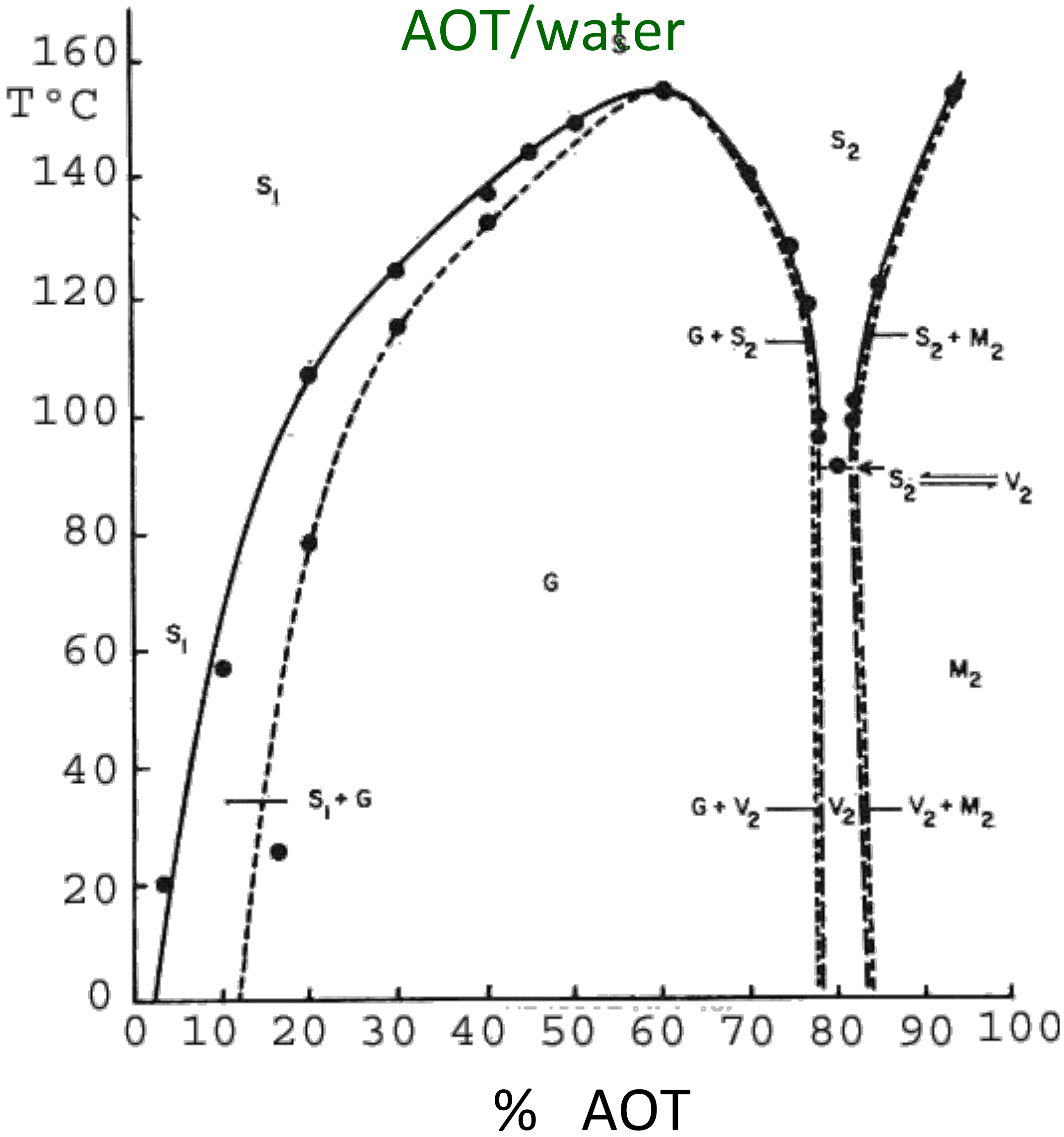
MODELICO-CM / PROJECT: P-2009/ESP-1691

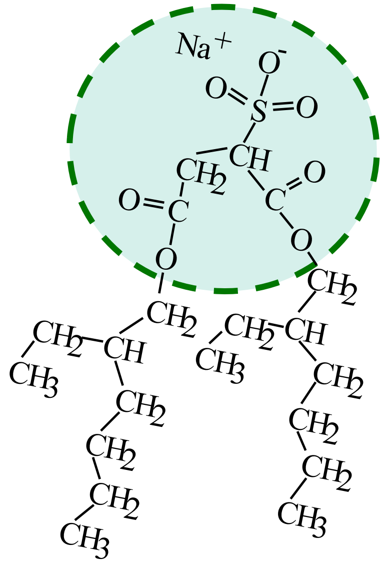
1.- The aim of this work

- To confine polyacrylamide (PA) in a lamellar liquid crystal formed by the anionic surfactant Aerosol OT (AOT) and water.

- To analyse how the concentration and the polymer dimensions affect the stability of the mesophase, in order to establish the conditions for polymer confinement.

2.- The surfactant: Sodium bis(2-ethylhexyl)sulfosuccinate



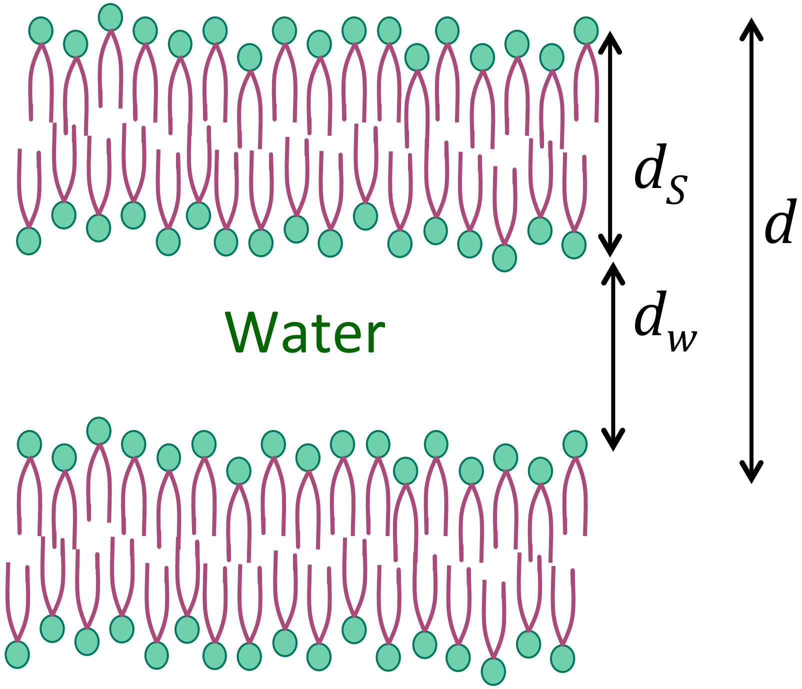


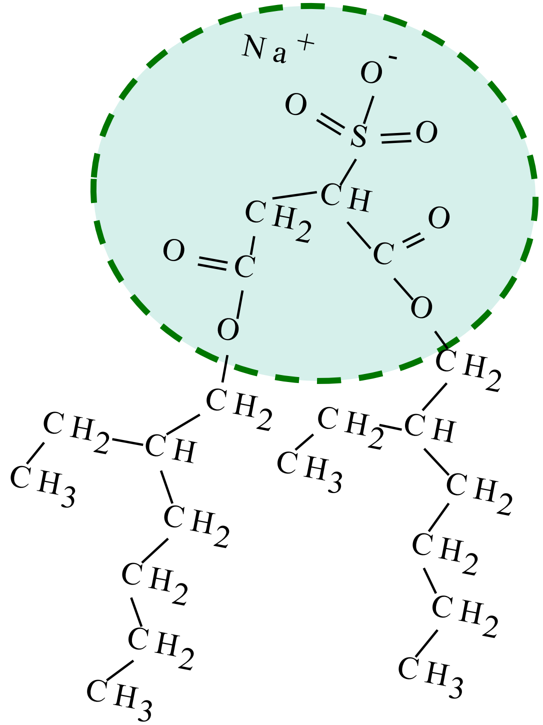
Symbol	Mesophase
S	Micellar
G	Lamellar
V	Cubic
M	Hexagonal

1=normal; 2=reverse

J. Rogers , P.A. Winsor, J. Collloid and Interface Sci., **30**, 247 (1969)

3.- Lamellar Mesophase:

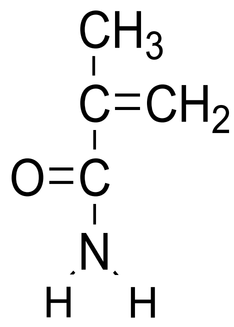




$$d = d_S + d_w$$

Dilution Law $$\frac{1}{d} = \frac{1}{d_S}\phi_S$$

4.- The Polymer



Characterization

- Molecular weight distribution (SEC)
- Intrinsic viscosity
- R_h (Diffusion NMR)

Sample	[η] (dL/g)	M_v	M_w	*r*	R_h (nm)
PA1	0.039	500	563	3.6	1.3
PA2	0.09	8.7×10^3	4.5×10^3	7	3.1
PA3	6.06	1.7×10^6	5.7×10^6	1.2	64.8

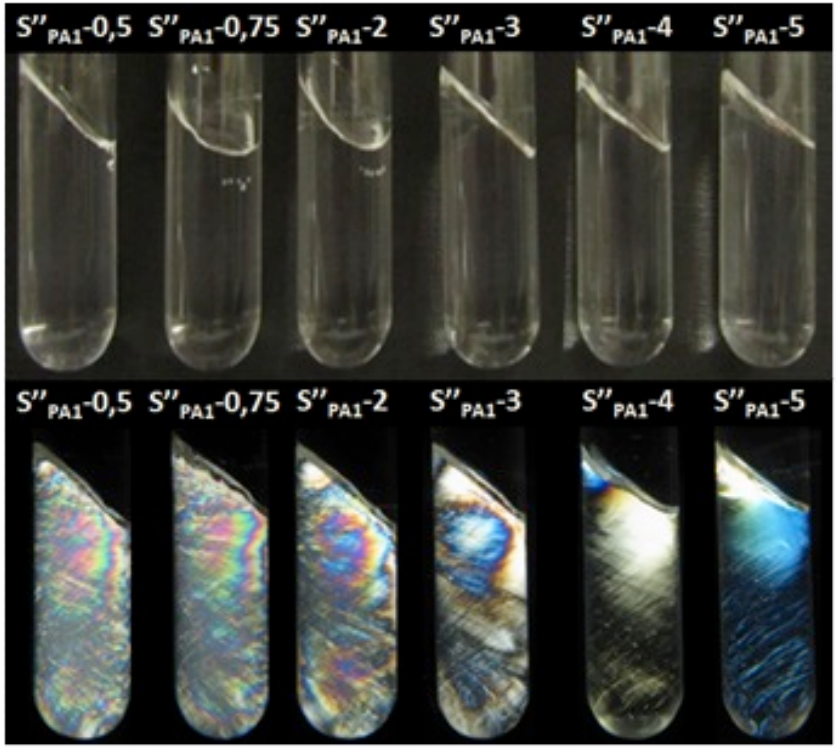
5.- Sample Preparation and Characterization

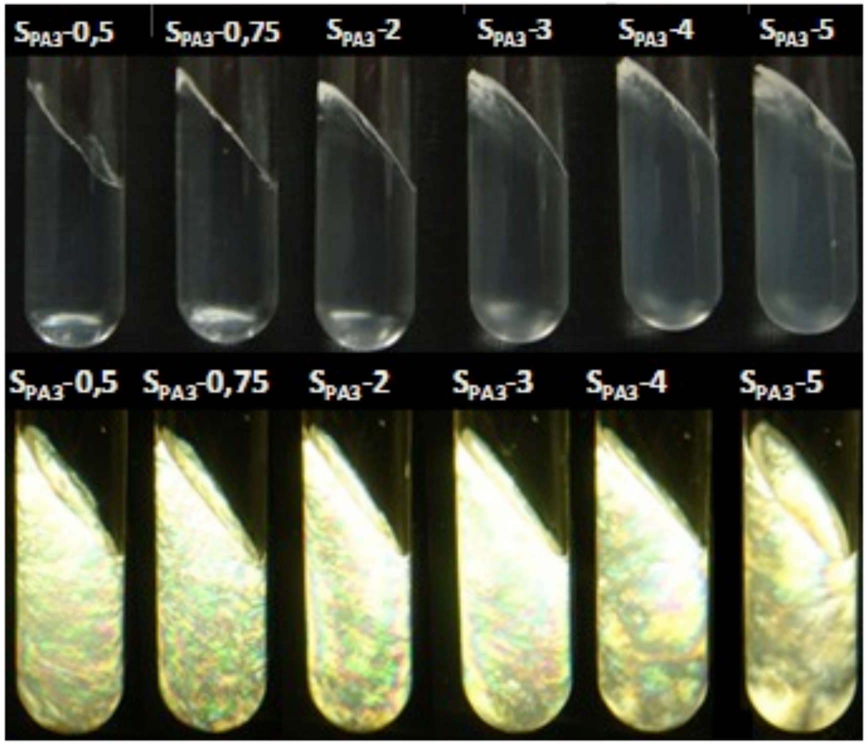
PA_S-#	Poly(acrylamide) wt %= 1.25	AOT wt %= 20 – 45
S_{PA}-#	Poly(acrylamide) wt %= 0.5 – 5	AOT wt %= 25
S'_{PA}-#	Poly(acrylamide) wt %= 0.5 – 5	AOT wt %= 30
S''_{PA}-#	Poly(acrylamide) wt %= 0.5 – 5	AOT wt %= 35

Characterization

- Optical Microscopy
- ^2H NMR
- SAXS: Synchrotron ESRF

6.- Results





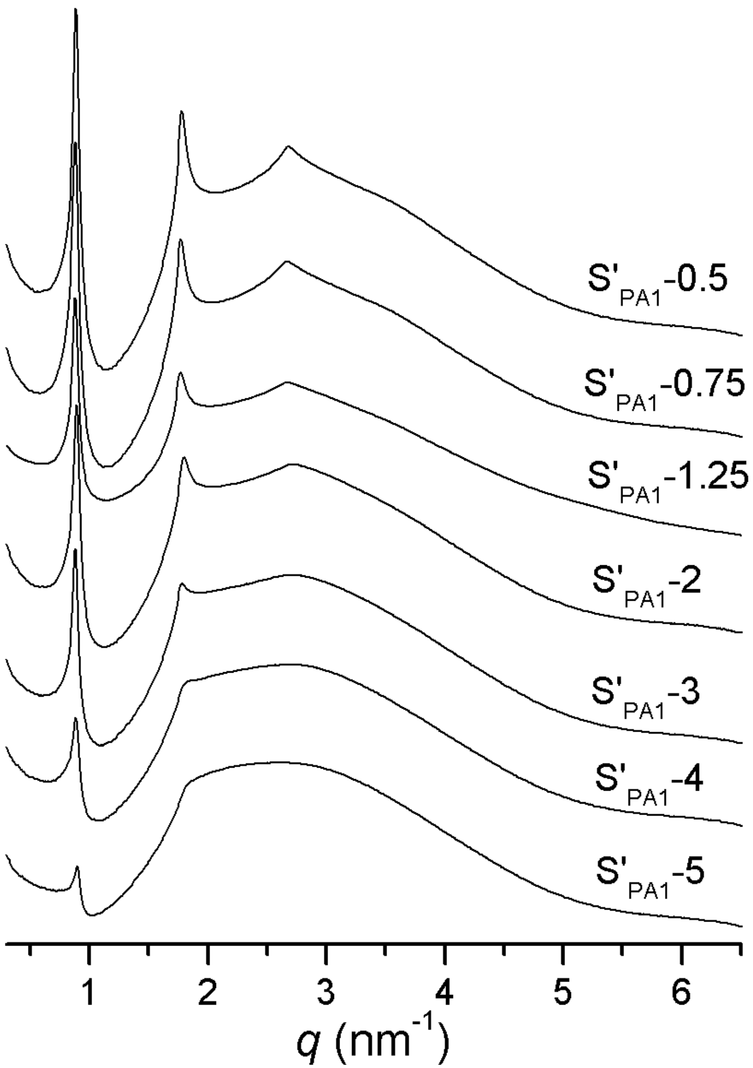
S''_{PA1}-#

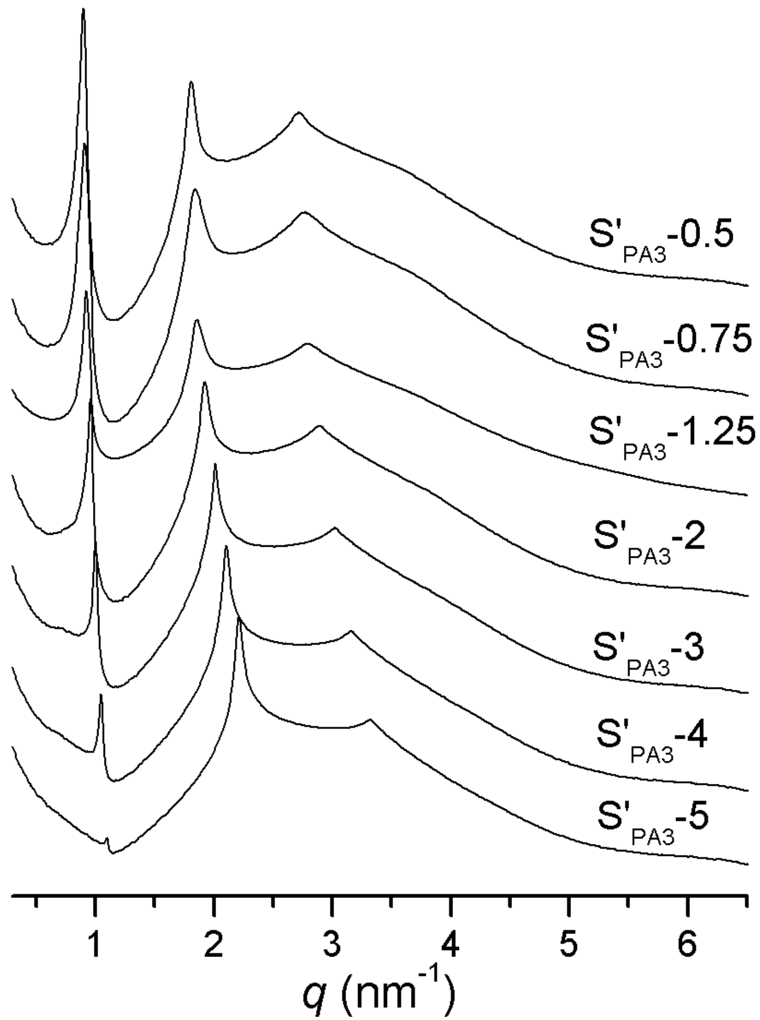
AOT: 35 %; PA1: 0.5 – 5 %

S_{PA3}-#

AOT: 25 %; PA3: 0.5 – 5 %

7.- Results



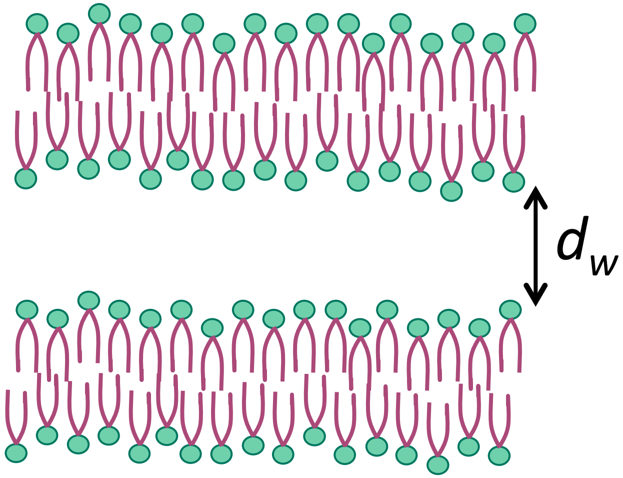


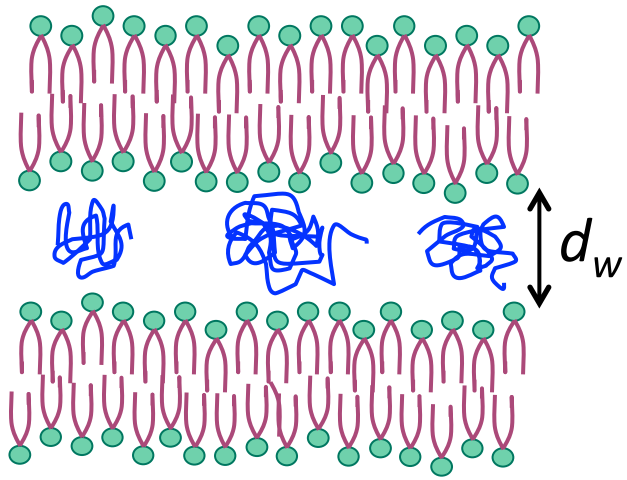
S'_{PA1}-#
AOT: 30 %; PA1: 0.5 – 5 %

S'_{PA3}-#
AOT: 30 %; PA3: 0.5 – 5 %

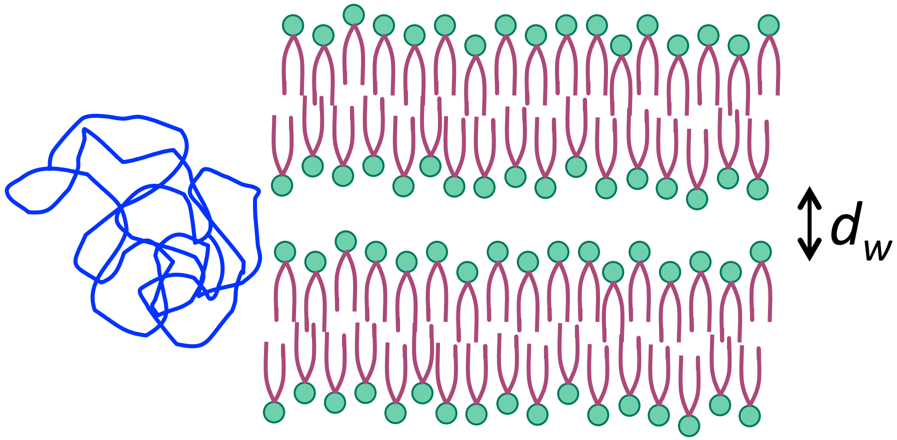
8.- Confinement/Segregation

Polymer Size/water layer thickness

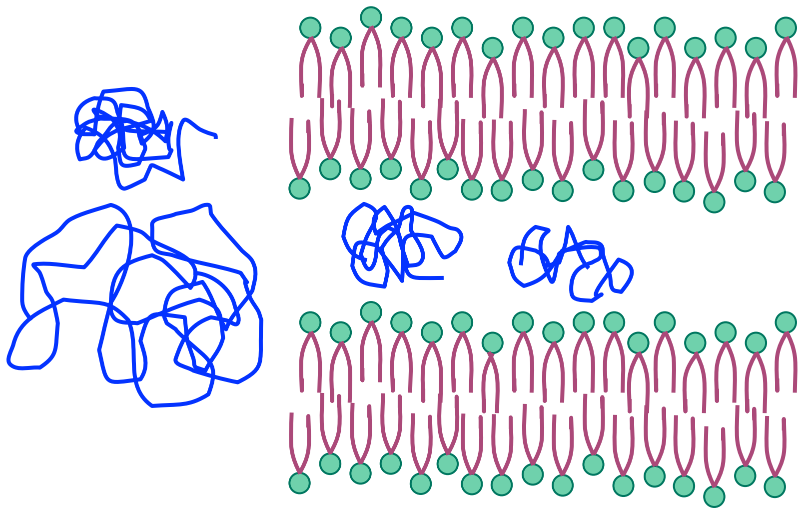




Total Confinement



Total Segregation



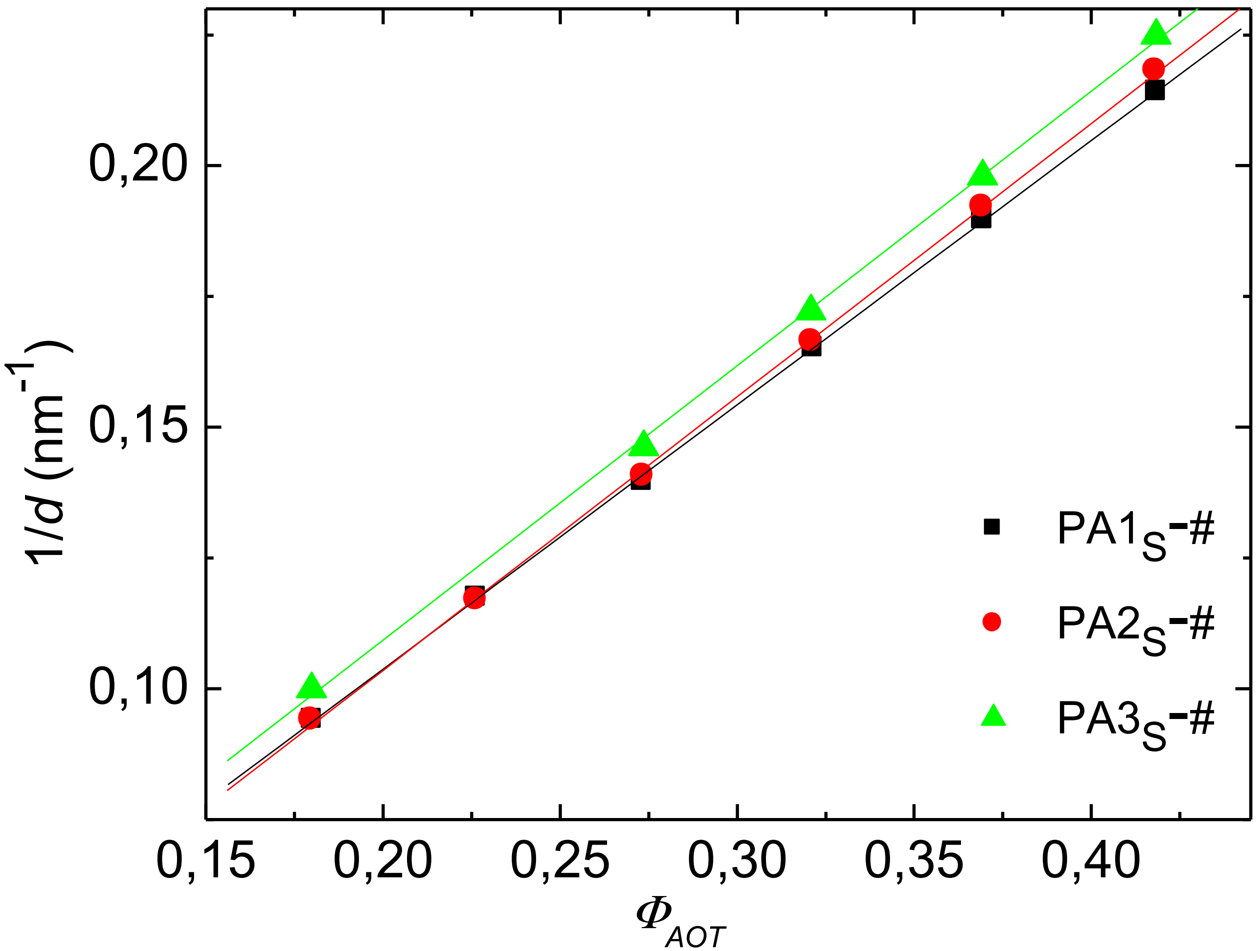
Partially confined/excluded

9.- SAXS Results

I.E. Pacios, C.S. Renamayor, A. Horta, B. Lindman, K. Thuresson, Macromolecules (2002) 35, 7553

$$\frac{1}{d} = \frac{1}{d_{AOT}} \phi_{AOT} \quad \Longrightarrow \quad \frac{1}{d} = \frac{1}{d_{AOT}} \left(\phi_{AOT} + K\phi_{PA} \right)$$

$$\frac{1}{d} = \underbrace{\frac{K\phi_{PA}}{d_{AOT}}} + \frac{1}{d_{AOT}} \phi_{AOT}$$



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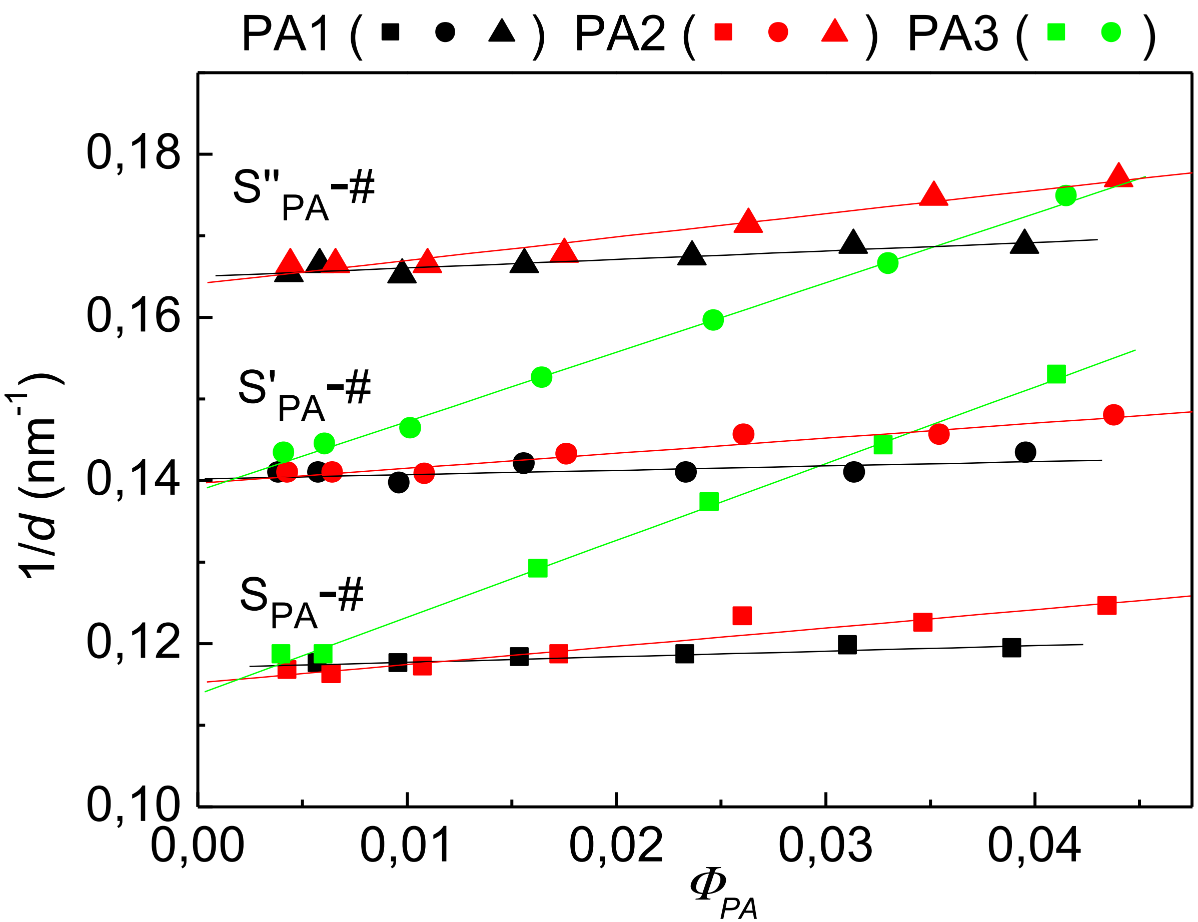


$$\frac{1}{d} = \frac{\phi_{AOT}}{d_{AOT}} + \overbrace{\frac{K}{d_{AOT}}}\phi_{PA}$$

10.- Fraction of polymer excluded from the lamellae (1)

I.E. Pacios, C.S. Renamayor, A. Horta, K. Thuresson, B. Lindman, Macromolecules (2005) 38,1949-1957

$$K = K_\infty f \quad \Longrightarrow \quad \frac{1}{d} = \frac{1}{d_{AOT}}\left(\Phi_{AOT} + K_\infty f \Phi_{PA}\right)$$

f: fraction of polymer excluded from the lamellae

K∞: limiting partition constant for total segregation

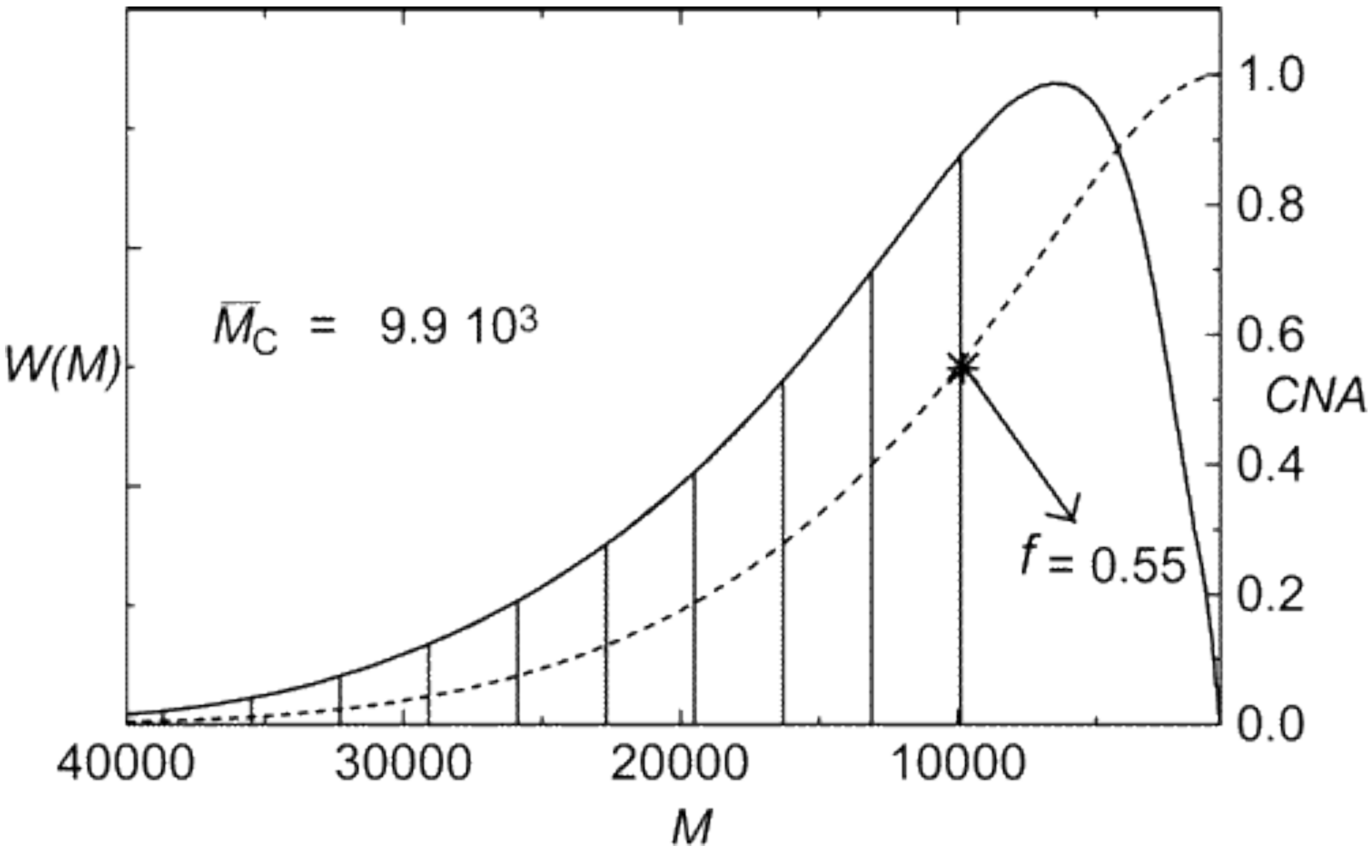
Serie	$K_\infty f$	f	d_{AOT} **(nm)**
S_{PA1}-#	0.10±0.06	0.06±0.04	1.96±0,02
S'_{PA1}-#	0.13±0.03	0.07±0.02	1.94±0,02
S''_{PA1}-#	0.20±0.04	0.11±0.03	1.95±0,01
S_{PA2}-#	0.36±0.04	0.20±0.04	1.96±0,01
S'_{PA2}-#	0.44±0.06	0.25±0.05	1.97±0,02
S''_{PA2}-#	0.56±0.05	0.31±0.05	1.96±0,01
S_{PA3}-#	1.87±0.07	1.1±0.1	1.99±0,03
S'_{PA3}-#	1.68±0.02	0.95±0.08	1.98±0,01

$K_\infty = 1.78$

11.- Fraction of polymer excluded from the lamellae (2)

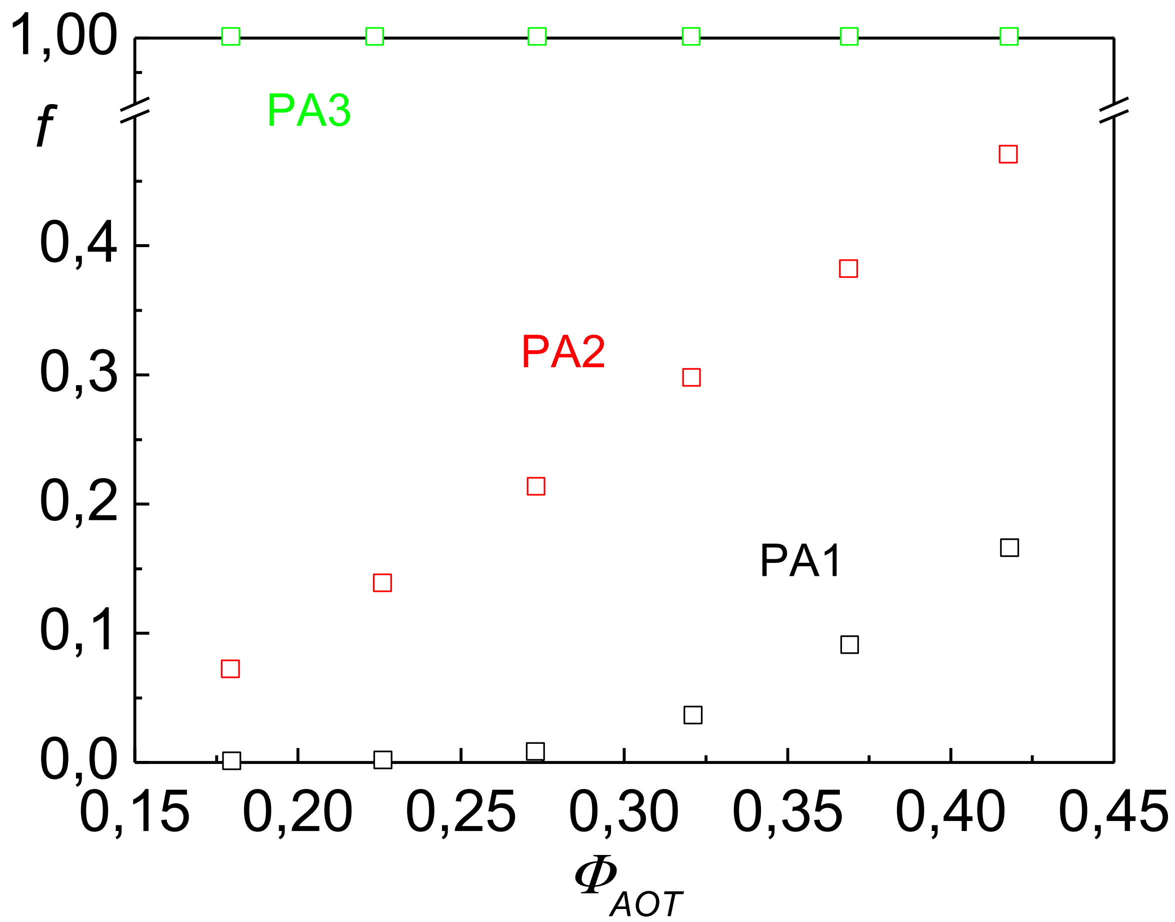
SAXS → $d_w = d - d_{AOT}$ → V_h → M_c

SEC → $f = \int_{M_C}^{\infty} W(M)\, dM$



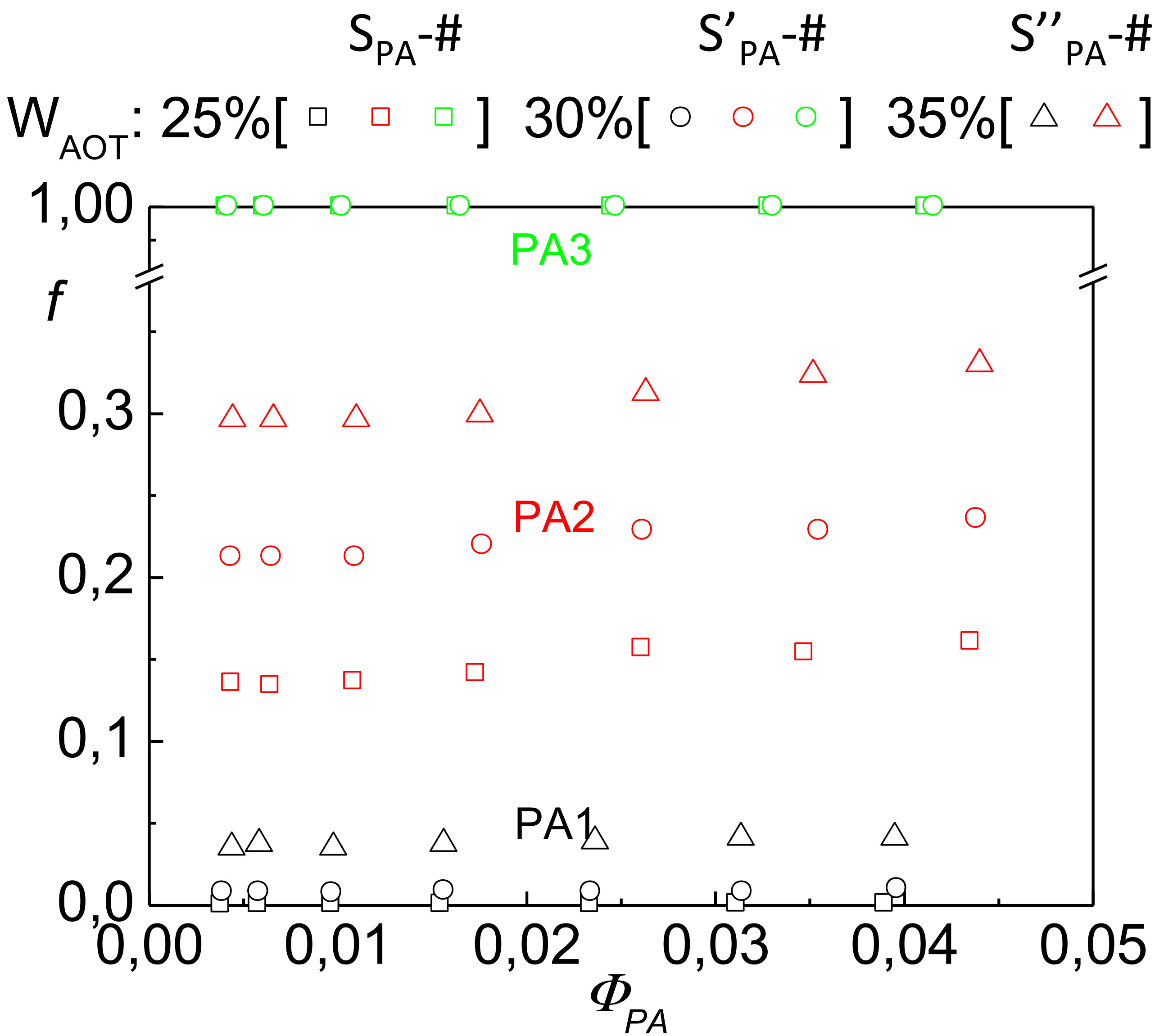
I.E. Pacios, C.S. Renamayor, A. Horta, B. Lindman, K. Thuresson , J. Phys. Chem. B (2005) 109, 23896-23904

12.- Fraction of polymer excluded from the lamellae (2)



PA_S-#: AOT=20-45 wt %; PA= 1.25 wt%

13.- Fraction of polymer excluded from the lamellae (2)



CONCLUSIONS

- The lamellar phase acts as a grating, fractionating the molecular weight distribution.
- Only the fraction of polymer having coil dimensions smaller than the thickness of water layers are dissolved in the mesophase.
- SAXS and SEC results can be combined to determine the fraction of polymer excluded from the lamellae.
- There is a cooperative effect of the polymer in its own exclusion, since the polymer deswells the lamellar structure, and thus contributes to shorten the lamellar distance, which then excludes more polymer.

ACKNOWLEDGEMENTS

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