Polymeric and Nanostructured Materials for Potential Biological Applications

J.K. Kallitsis,[a,b] G. Bokias[a]

[a]*Department of Chemistry, University of Patras, GR-26504 Patras, Greece*

[b]*ICE/HT FORTH, P.O. Box 1414, GR-26504 Patras, Greece*

B I O T A R G E T I N G – 1st Scientific Meeting

November 5, 2010

Overview

✓ Polymeric Materials with Biocidal Activity

- ***Polystyrene Beads containing Biocidal Species***
- ***Incorporation of Biocidal Oligomers into Polymeric Matrices***
- ***Dispersion of Biocidal Polymers into Matrices***
- ***Control of Orthopedic Biofilm Infections***

✓ Functional/Responsible Water-Soluble Polymers

- ***Temperature- or pH- induced Reversible Gelation***
- ***Stabilization of Core-Corona nanostructures in Water***
- ***Optically Responding Polymers***

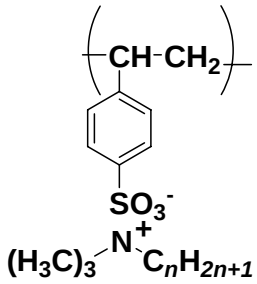
Polymeric Materials with Biocidal Activity

Incorporation of active oligomers into polymeric matrices

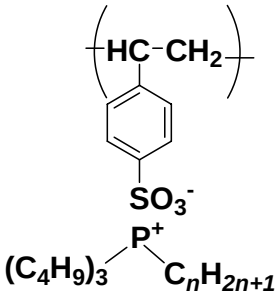
DISPERSION OF ACTIVE SPECIES INTO A POLYMERIC MATRIX

Polystyrene beads containing Triclosan trichlorohydroxydiphenylether or Phosphonium salts

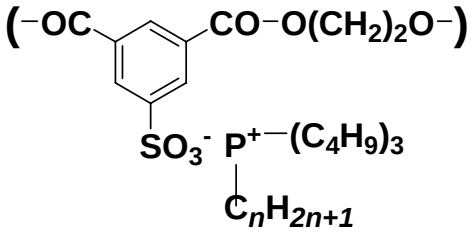
Dispersion of polymeric ammonium or phosphonium salts into polymeric matrixes



***n* = 12, 14, 16**



***n* = 8, 14, 16**

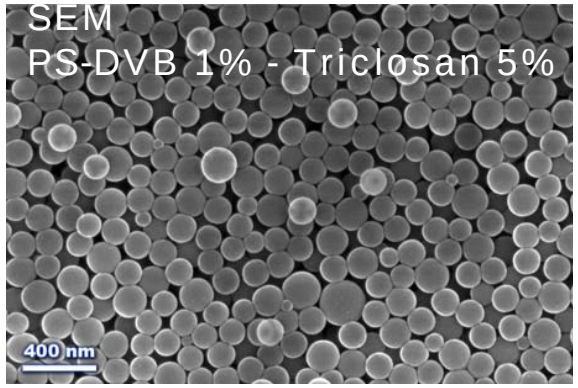


***n* = 14, 16**

"Controlled Release of Antimicrobial Substances from Polymeric Matrices" S. Ikonomopoulou, A. K. Andreopoulou, A. Soto, J. K. Kallitsis, G. A. Voyiatzis, *J. Controlled Release*, **2005**, *102*, 223.

C. Katsichtis, E. Tsartolia, A. Papadopoulos, S. Ikonomopoulou,K. Andreopoulou, A. Soto, J. Kallitsis, G. Voyiatzis. Appl. No. 04386006,3/6-5-2004 (European Patent)

Polystyrene Beads containing Biocidal Species



PS/DVB beads – Trichlosan

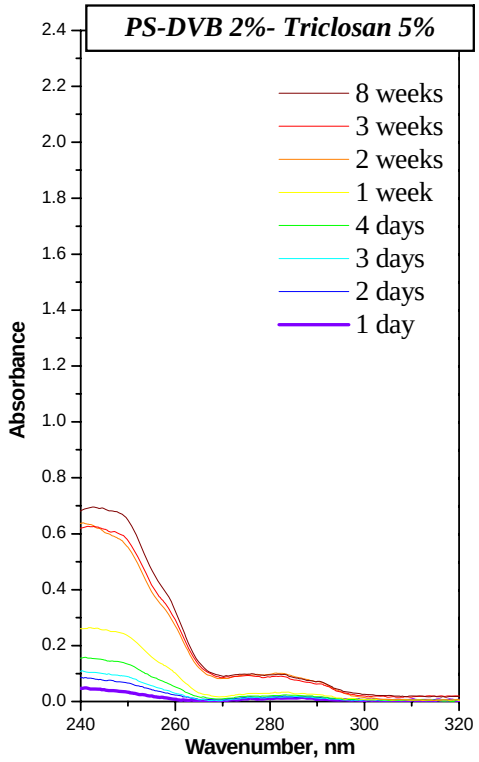
DVB: 2,5,10 %

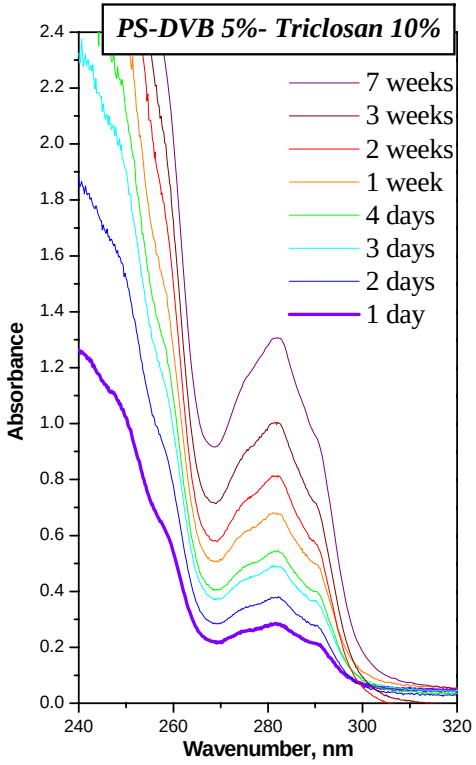
Trichlosan: 5,10,20,30 %

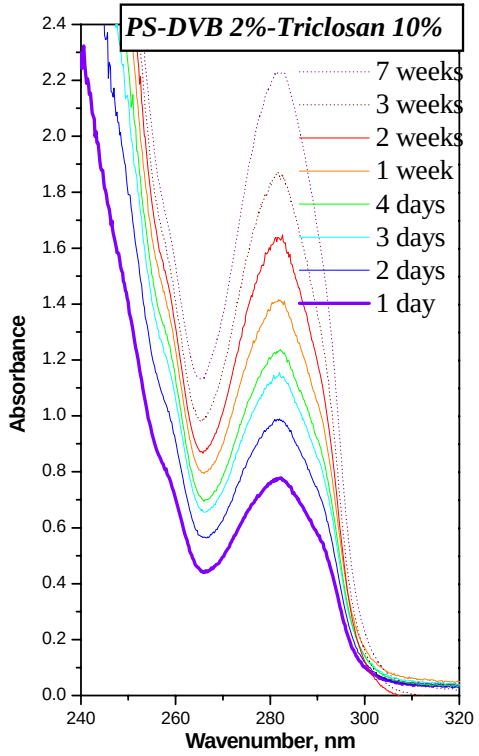
BLENDS

- HDPE: 0.5 - 3 %
- Nylon 6: 0.5 - 3 %

IMMERSED in EtOH 95%







Collaboration with Dr. G.Vogiatzis, S.Iconomopoulou, *FORTH/ICEHT Patras*

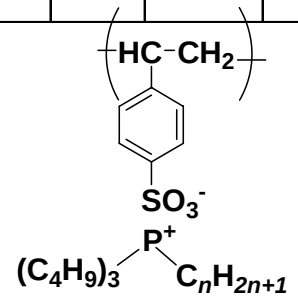
Incorporation of Active Oligomers into Polymeric Matrices

PERFORMED at **GAIGER** during the *SPAN: SPECIALITY ANTIMICROBIAL POLYMERIC MATERIALS*

Oligomer	PP + oligomer C14					PP + PSSPh C14					HDPE + oligomer C14				
Time (hour/days)	3 h	24h	7d	14d	28d	3 h	24h	7d	14 d	28d	3 h	24h	7d	14d	28d
EU-Ph Log Reduction	2 -	3 1	- 3	- -	NR NI	2 -	3 1	- 3	- -	NR NI	2 -	3 1	- 3	- -	NR NI
E coli		**2***	**1/2**	**3/ TMC**	**3**		**1**	**1**				**2***	**> 2 ***	**3/ TMC**	**> 3**
St aureus		**2**	**2/3**	**3***	**3**		**1**	**1/2**	**2***	**> 2**		**2***	**3***	**3***	**3**
Candida albicans			**> 1**	**2**	**3**			**1**		**1**			**1***	**3**	**> 3**
A niger			**> 1 ***	**2**	**2**								**1**	**2**	**3**

CONCLUSIONS ANTIMICROBIAL TESTS:

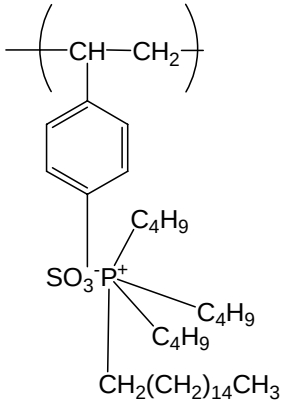
The polymer containing Phosphonium Groups (HDPE-C14) had a very good antibacterial and antifungal activity (log reduction >3) and showed strongest and long lasting biocide activity. PP- C14 polymer presented a good antibacterial activity as well. PSSPh C14- PP polymer presented a slight bactericidal activity against *Candida albicans* after 28 contact days and *Staphylococcus aureus* after 7-14 contac days.



***n* = 8, 14, 16**

Dispersion of Biocidal Polymers into Matrices

Antifouling Paints



45 Days after Immersion

Without **With**

Biocidal Polymer

6 Months after Immersion

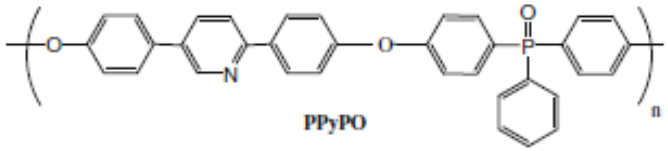
Without **With**

Biocidal Polymer

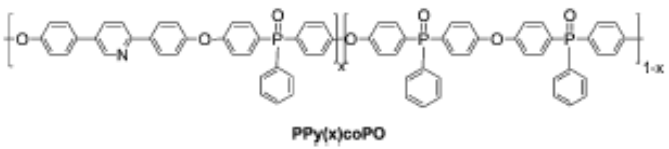
Collaboration with CHROTEX, S.A.

Control of Orthopedic Biofilm Infections

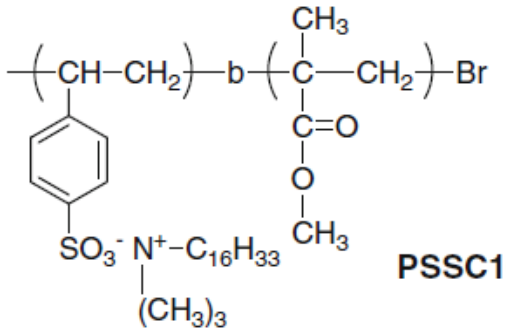
Nucleators for calcium phosphate (HAP)



Polymer 1



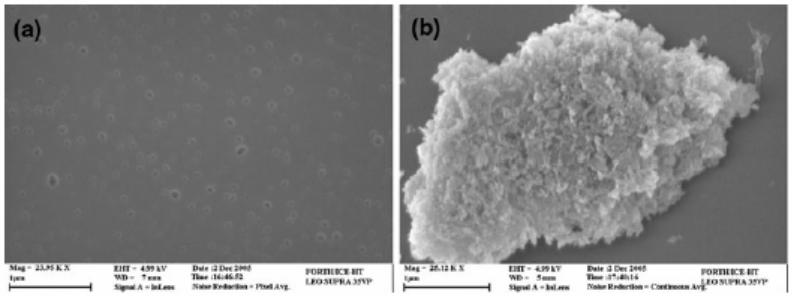
Polymer 2



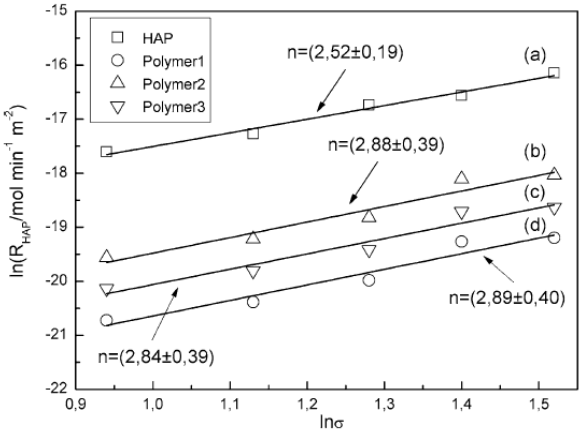
Polymer 3

Crystal growth of HAP

Polymer 1 Substrate



Rate of HAP precipitation



M. Tyllianakis, E. Dalas, M. Christofidou, J. K. Kallitsis, A. Chrissanthopoulos, P. G. Koutsoukos, C. Bartzavali, N. Gourdoupi, K. Papadimitriou, E. K. Oikonomou, S. N. Yannopoulos, D. Sevastos. *J Mater Sci: Mater Med*, **2010**, *21*, 2201

Control of Orthopedic Biofilm Infections

Presence of Microorganisms in biofilms

↓

Pathogenesis of orthopaedic infections

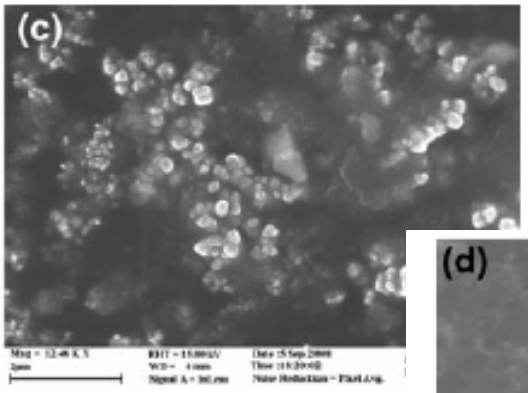
Antimicrobial Properties

a) Incorporation of TiO_2 nanocrystals in the polymer matrix after silver coverage
b) Use of Polymer 3 with Quartenary Ammonium Groups as biocide

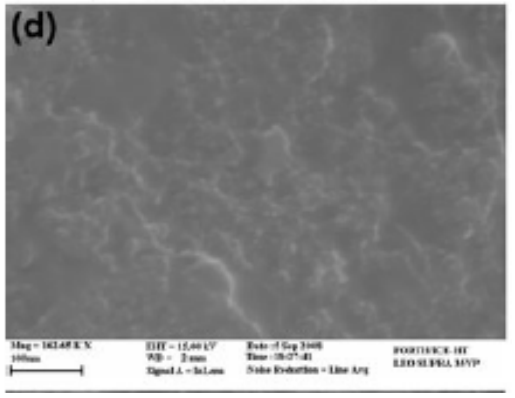
The antimicrobial activity of the composite material covered the cut parts (CP) of the "π plates"

Material	SAM	SEM	CAM	PAM	NC	
CP	>1000	>1000	60	>1000	(–)	
CP/polymer 2 + TiO_2 I/Ag	50	90	60	100	(–)	
CP	400	100000	10	400	(–)	
CP/polymer 2 + TiO_2 II/Ag	(–)	(–)	1	(–)	(–)	
CP	>1000	>1000	80	>1000	(–)	
CP/polymer 3 + TiO_2 II/Ag	(–)	(–)	(–)	(–)	(–)	+TiO_2 II

Staphylococcus epidermidis



Without

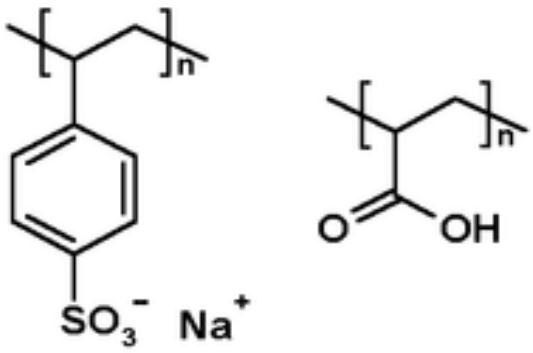


With Antimicrobial Species

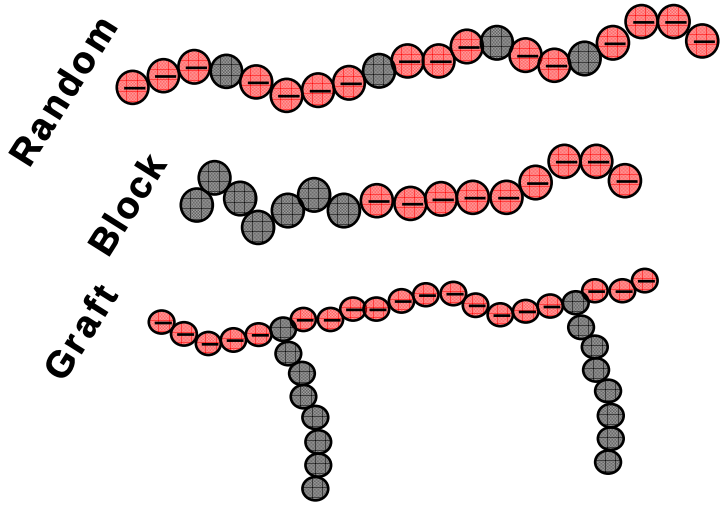
M. Tyllianakis, E. Dalas, M. Christofidou, J. K. Kallitsis, A. Chrissanthopoulos, P. G. Koutsoukos, C. Bartzavali, N. Gourdoupi, K. Papadimitriou, E. K. Oikonomou, S. N. Yannopoulos, D. Sevastos. *J Mater Sci: Mater Med*, **2010**, *21*, 2201

Functional / Responsible Water-Soluble Polymers

Typical Water-soluble Polymers



Design of Macromolecular Architecture



Functionality

- *Inherent Behavior*
- *Hydrogen-bonding*
- *Electrostatic interactions*
- *Hydrophobic interactions*
- *Coordination*

……

Sensitivity

- *Macromolecules*
- *Biomacromolecules*
- *Surfactants*
- *Metal ions*

……

Response

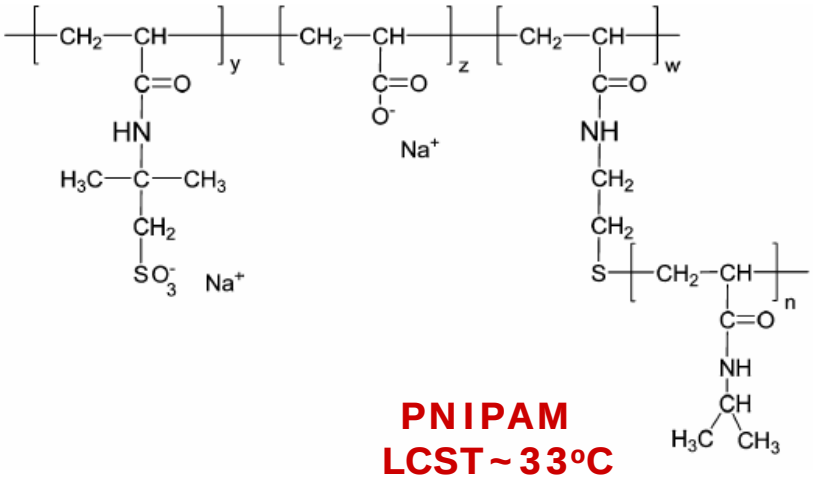
- *Phase separation*
- *(Self)-organization in core-corona nanostructures*
- *Reversible hydrogels*
- *Optical response*

……

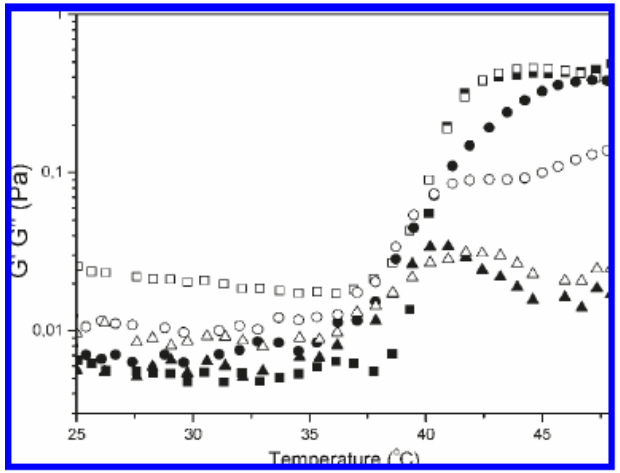
pH- or temperature-induced phenomena

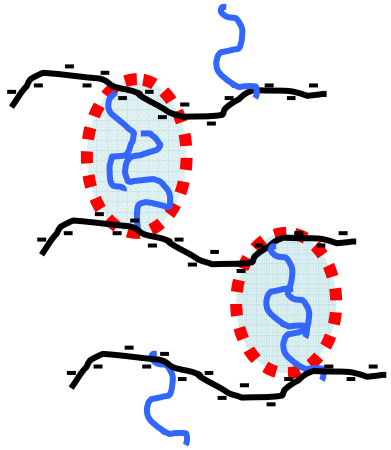
Reversible Gelation

Temperature-induced Hydrogel Formation



PNIPAM
LCST ~ 33°C



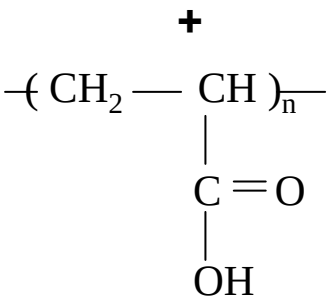


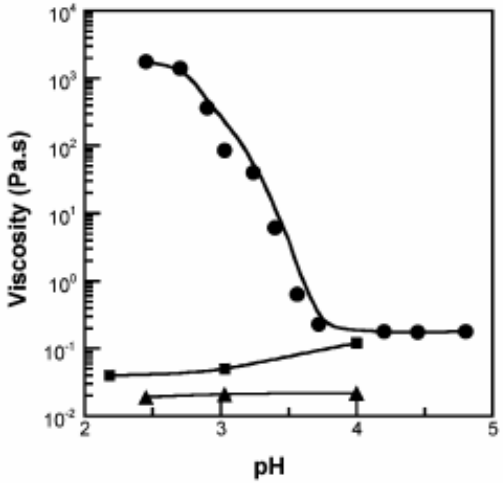
Z. Iatridi and G. Bokias. *Langmuir* 2009, *25*, 7695

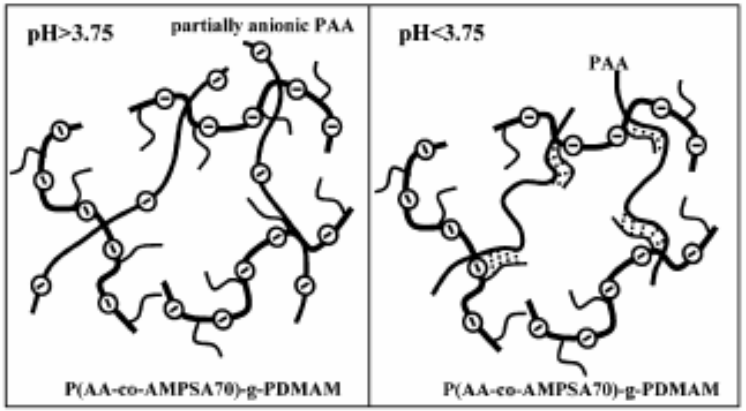
pH-induced Hydrogel Formation

Graft Copolymer

+







Hydrogen-bonding

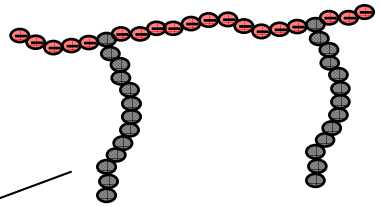
M. Sotiropoulou, G. Bokias and G. Staikos. *Macromolecules* **2003**, *36*, 1349

Core-Corona Nanostructures

Graft copolymers

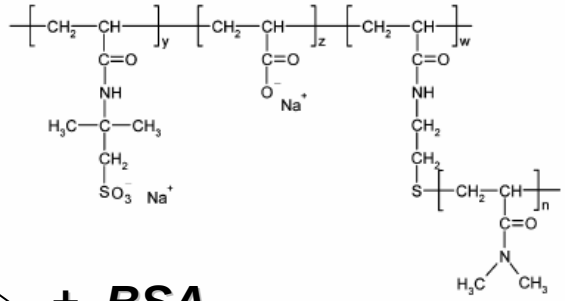
Sensing Abilities

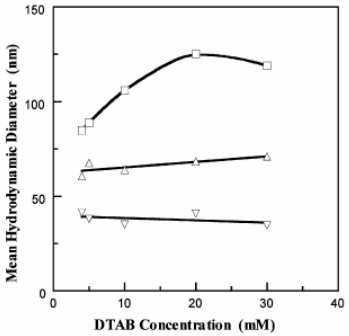
+

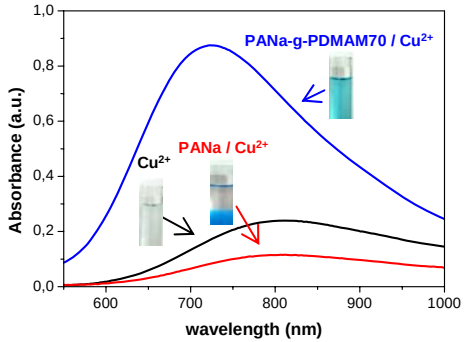


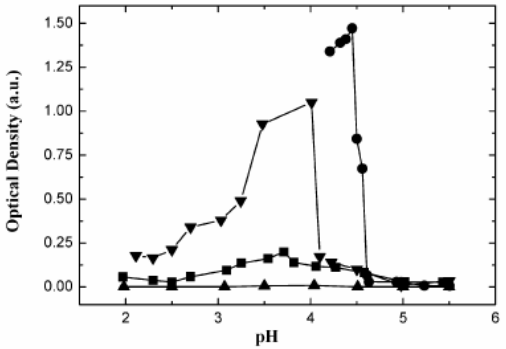
+ Cu^{2+}

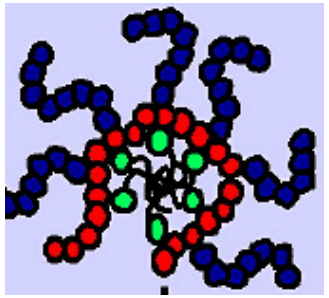
+ BSA

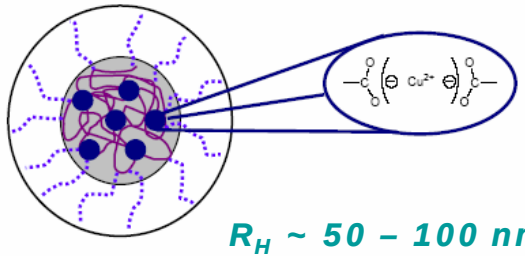












R_H ~ 50 – 100 nm

Stabilization in Water of Core-Corona Nanostructures

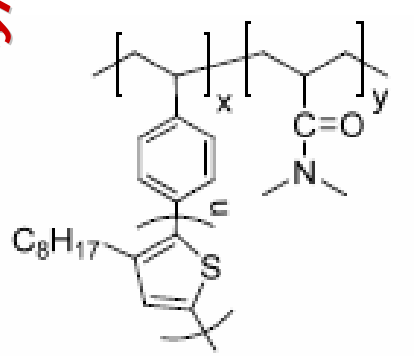
I. Balomenou and G. Bokias. *Langmuir* **2005**, *21*, 9038

Z. Iatridi and G. Bokias. *Macromol. Chem. Phys.* **2008**, *209*, 1029

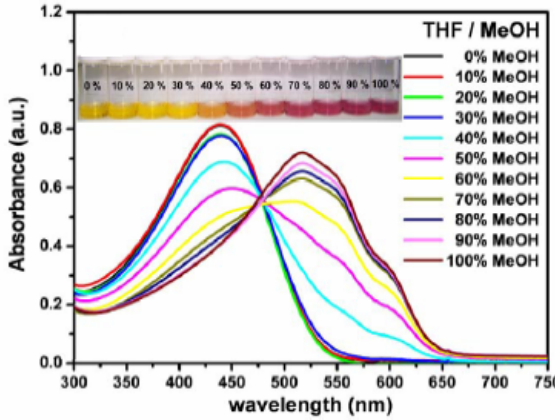
M. Sotiropoulou, G. Bokias and G. Staikos. *Biomacromolecules* **2005**, *6*, 1835

Optically responding Polymers

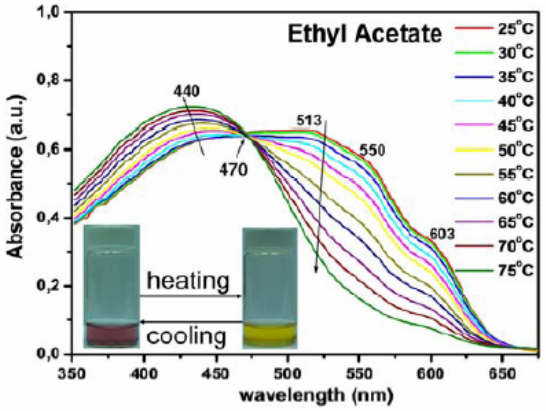
Thiophene-based Copolymers



Solvochromism

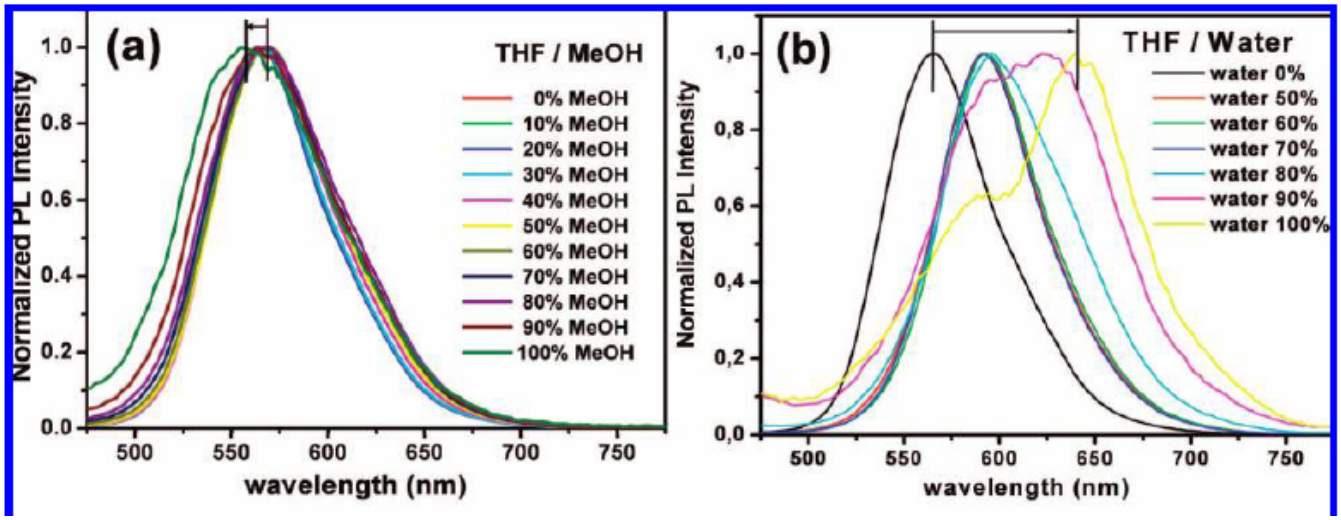


Thermochromism



Absorption Spectra

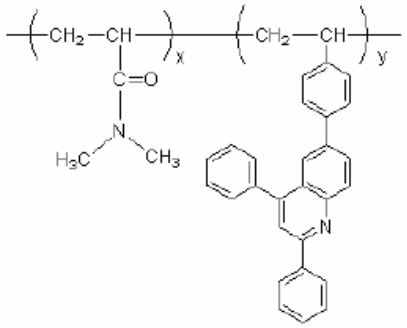
Photoluminescence

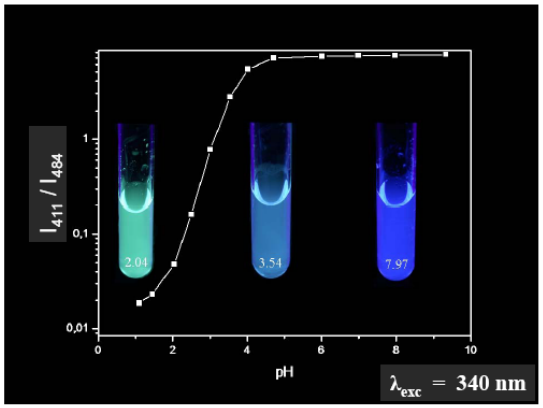


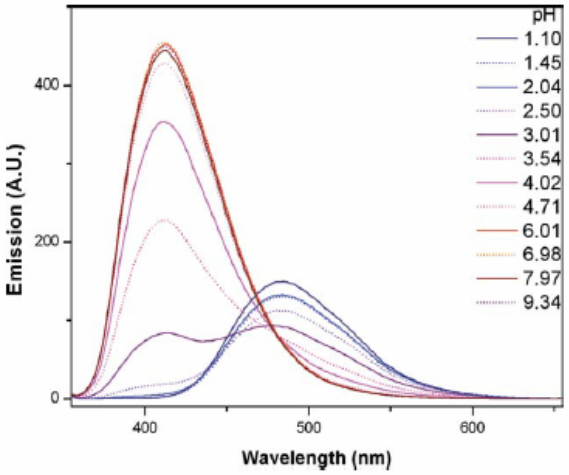
A.A. Stefopoulos, C.L. Chochos, G. Bokias and J.K. Kallitsis. *Langmuir* **2008**, *24*, 11103

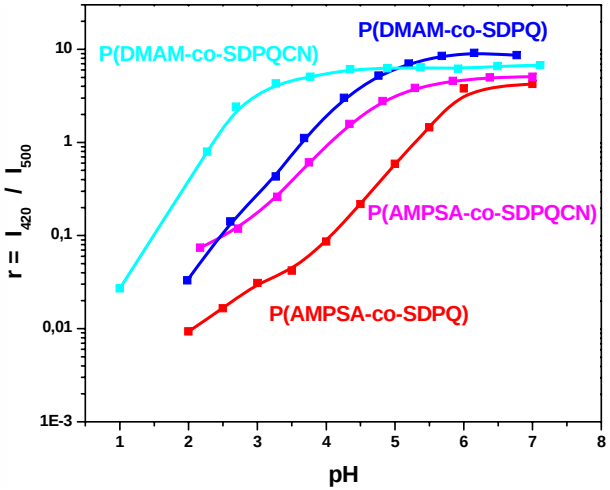
Optically responding Polymers

Quinoline-labeled Copolymers



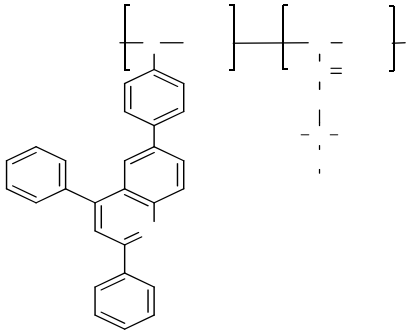




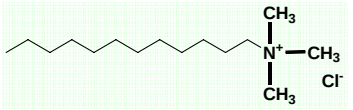


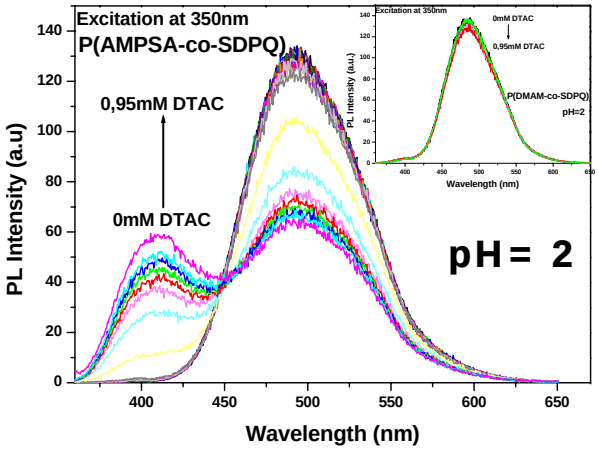
pH-controlled luminescence

Sensing properties



Titration with DTAC





A.Kalogianni, E. Pefkianakis, A. Stefopoulos, G. Bokias and J.K. Kallitsis. *J. Polym. Sci. Part B- Polym. Phys.* **2010**, *48*, 2078

Thank You for Your Attention