

ΠΑΝΕΠΙΣΤΗΜΙΟ ΚΡΗΤΗΣ  
ΤΜΗΜΑ ΕΠΙΣΤΗΜΗΣ ΚΑΙ ΤΕΧΝΟΛΟΓΙΑΣ ΥΛΙΚΩΝ

ΠΑΡΟΥΣΙΑΣΗ ΜΕΤΑΠΤΥΧΙΑΚΟΥ ΔΙΠΛΩΜΑΤΟΣ ΕΙΔΙΚΕΥΣΗΣ

**Τίτλος:**

**« pH-responsive microgels: polyelectrolyte, homopolymer  
and polyampholyte mix and core-shell particles»**

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**Τετάρτη, 05/11/2008,**

**ώρα 11:00 - 13:00**

**Αίθουσα Σεμιναρίων 3<sup>ου</sup> ορόφου,  
Κτίριο Φυσικού, Πανεπιστήμιο Κρήτης**

**Abstract**

The aim of this study is the synthesis and characterization of pH-responsive microgel particles. We have synthesized pH-responsive homopolymer microgel particles based on 2-(diethylamino)ethyl methacrylate (DEA) or methacrylic acid (MAA) using emulsion polymerization. Ethylene glycol dimethacrylate (EGDMA) was used as the cross-linker. Steric stabilization of the microgel particles was achieved using poly(ethylene glycol methacrylate) ( $M_n=2000$  gr/mole) as the stabilizer. PMAA-based microgel particles were prepared using *tert*-butyl methacrylate (*t*-BuMA) as the protected form of MAA. Next, the P(*t*-BuMA)-based microgels were hydrolyzed to convert the *t*-BuMA segments into MAA units via acid hydrolysis. The above microgels exhibit reversible swelling properties in water by adjusting the solution pH or the degree of ionization of the monomer units. Thus, the PDEA-based microgel particles, swell at low pH upon ionization of the DEA units due to the hydrophilicity of the protonated amine groups, while an increase of the solution pH leads to the deprotonation of the DEA moieties and the formation of

hydrophobic latex particles. The PMAA-based microgel particles swell at high pH due to the ionization of the carboxylic acid units, while at low pH values the acidic moieties become neutral and the particles shrink. The effective equilibrium constants  $pK_a$ 's of the PDEA and PMAA microgel particles were calculated from potentiometric titration curves of the microgel dispersions. The pH-responsive character of the microgel particles and its effect on the particle size of the microgels was examined by dynamic light scattering (DLS) as a function of the degree of ionization of the monomer units. The effect of the cross-link density on the degree of swelling of the PDEA microgels was also investigated. Scanning and Transmission Electron Microscopy studies verified the spherical shape and the uniform size distribution of the particles.

In the second part of our study mixed polyampholyte microgel particles comprising both DEA and MAA units randomly distributed within the particle have been prepared. Potentiometric titrations were used to determine the ionization range of the microgels. The size of the mixed microgels particles as a function of the degree of ionization of the monomer units was studied by DLS. The microgels swell at both high and low pH when the particle net charge is negative or positive, respectively, while collapsed microgel particles were found at the isoelectric point at zero net charge when the hydrophobic interactions dominate.

Finally, we have synthesized microgel particles with a core-shell topology comprising either a PDEA core and a PMAA shell or a PMAA core and a PDEA shell. Potentiometric titration curves revealed the independent ionization range of the core and the shell of the particles, in contrast to the mixed polyampholyte microgel particles discussed above which exhibit a common ionization region for the basic and acidic monomer units. The swelling properties of the microgel particles as a function of the solution pH were examined by DLS. The core and the shell of the particles were found to swell at a different pH range resulting in microgel particles in which the overall size, the net charge, the softness and the hydrophylicity of the core and the shell can be tuned independantly. SEM showed spherical particles of a narrow size distribution, while TEM verified their core-shell topology by selectively staining the core or the shell of the microgels.

These core-shell microgels carrying different responsive functionalities in the core and the shell of the particle are very attractive materials for use in numerous applications such as targeted drug-delivery, chemical separations, etc.

Ο Πρόεδρος του Τμήματος

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