



Stabilized in Organic Media Hybrid Materials Based on Complexes of Well-Defined Functional Block Copolymers with Palladium Acetate.



Maria Demetriou and Theodora Krasia-Christoforou

Department of Mechanical and Manufacturing Engineering, University of Cyprus,

P.O. Box 20537, Nicosia 1678, Cyprus

E-mail: demmaria@hotmail.com; krasia@ucy.ac.cy; Internet: http://www.ucy.ac.cy/

INTRODUCTION AND MOTIVATION

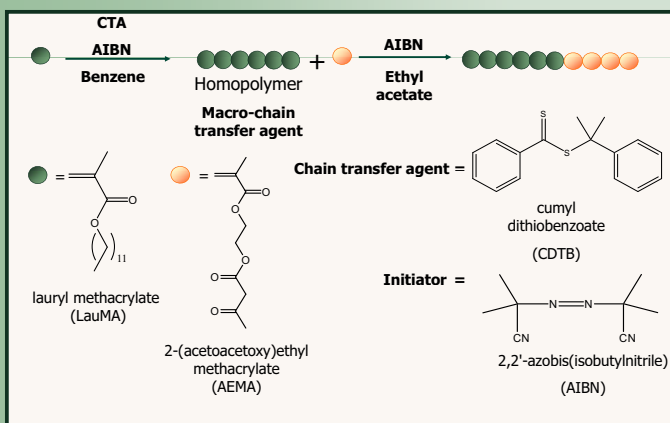
Over the past three decades macromolecular science seems to be strongly oriented towards the field of organic-inorganic hybrid materials. The combination of polymers with metal compounds can lead to the formation of nanometer-scale structured materials with unique properties. The unique size-dependent properties and high surface-to-volume ratios of metal nanoparticles (MNP) leads to an increased interest in many scientific fields such as chemistry, physics and nanotechnology [1]. Palladium (Pd) nanoparticles attract great interest due to their catalytic [2] and hydrogen storage properties [3]. A very selective method applied for the preparation of stabilized in solution palladium nanoparticles involves the use of amphiphilic block copolymer micelles formed in selective solvents for metal colloid nanoparticle preparation.

Herein we report the preparation of stabilized in organic media hybrid micelles generated *via* complex formation between Pd(CH₃COO)₂ and well-defined diblock copolymers consisting of lauryl methacrylate (LauMA), a high alkyl-chain monomer, and 2-(acetoacetoxy)ethyl methacrylate (AEMA) a monomer possessing a metal-binding functionality. RAFT controlled radical polymerization was employed for the preparation of the block copolymers which were characterized in terms of molecular weights and compositions by size exclusion chromatography and proton nuclear magnetic resonance spectroscopy respectively. The pLauMA-*b*-PAEMA micelles served as an ideal nano-environment for the complexation and solubilization of Pd(CH₃COO)₂, which is otherwise insoluble in *n*-hexane. This was accomplished by simply mixing a micellar solution of pLauMA-*b*-pAEMA in *n*-hexane with the transition metal salt at room temperature in the presence of triethylamine. The formation of polymer-metal complexes was demonstrated by UV-Vis spectroscopy. Dynamic light scattering (DLS) was employed for determining the size of the resulting organic-inorganic hybrid micelles. Subsequently, the Pd(II) ions were reduced into Pd(0) via the addition of hydrazine monohydrate which served as the reducing agent. Upon reduction, highly stable, transparent, brown-colored solutions were obtained. The Pd(0)-containing micellar solutions were characterized by UV-Vis spectroscopy. Furthermore, DLS and AFM were employed to obtain information on the size and morphology of the hybrid systems. The decomposition temperature of pLauMA-*b*-pAEMA and Pd(0) loaded pLauMA-*b*-pAEMA block copolymers was determined employing thermal gravimetric analysis (TGA).

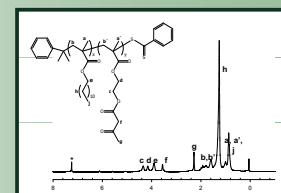
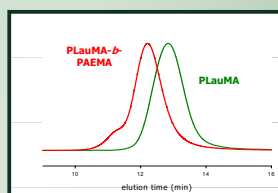
References: [1] "Nanoparticles – Building blocks for nanotechnology", V. Rotello (Editor), Springer, (2004). [2] "Palladium metal catalysts in Heck C-C coupling reactions" A. Biffis, M. Zecca, M. Basato, Journal of Molecular catalysis A: Chemical **173**, 249 (2001). [3] "Hydrogen evolution and entry in palladium at high-current density" Seanson, P. C., Acta Metallurgica et Materialia, **39**, 2519 (1991).

SYNTHESIS AND CHARACTERIZATION OF PLauMA-*b*-PAEMA COPOLYMERS

Polymer Synthesis performed via Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization



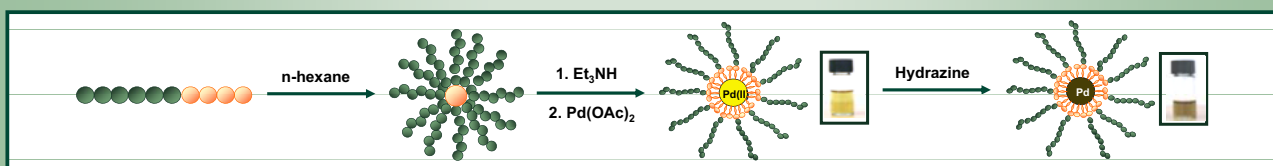
Molecular Weight Characterization of the PLauMA homopolymers and the PLauMA-PAEMA block copolymers.



Experimental structure ^a	Conversion (%)	Theor. MW g mol ⁻¹ ^b	SEC results ^c	AEMA (% content by ¹ H NMR)
			M _n PDI	
LauMA ₇₅	89.5	18670	19100 1.19	0
LauMA ₁₂₀	90.0	31830	30700 1.08	0
LauMA ₇₅ - <i>b</i> -AEMA ₅₁	80	27664	35400 1.23	41
LauMA ₇₅ - <i>b</i> -AEMA ₅₆	81	24301	30700 1.13	38
LauMA ₁₂₀ - <i>b</i> -AEMA ₆₇	68	40940	45100 1.16	36
LauMA ₁₂₀ - <i>b</i> -AEMA ₃₄	85	38027	39400 1.16	22

^a determined by SEC and ¹H NMR; ^b (mol monomer)/(mol RAFT agent) × (polymerization yield); ^c SEC calibrated with PMMA standards; M_n = number average molecular weight; PDI = polydispersity index; LauMA = lauryl methacrylate; AEMA = 2-(acetoacetoxy)ethyl methacrylate.

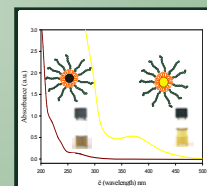
MICELLIZATION BEHAVIOR OF PLauMA-*b*-PAEMA COPOLYMERS AND PREPARATION OF HYBRID MICELLES



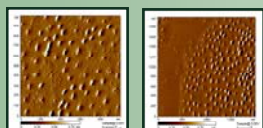
Dynamic Light Scattering

Exper. structure	R _h contour-length (nm)	R _h exper. (nm) polymer	R _h exper. (nm) polymer + Pd(II)	R _h exper. (nm) polymer + Pd ⁰
LauMA ₇₅ -AEMA ₅₁	39	32	55	23
LauMA ₇₅ -AEMA ₅₆	37	37	44	35
LauMA ₁₂₀ -AEMA ₆₇	58	58	54	36
LauMA ₁₂₀ -AEMA ₃₄	47	47	39	Not Determined

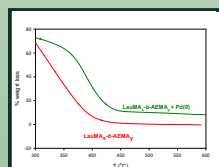
UV-Vis spectrum of Pd(II) and Pd(0) loaded PLauMA-*b*-PAEMA micelles



AFM Images of LauMA₁₂₀-*b*-AEMA₆₇ micelles loaded with Pd(0)



Thermal Gravimetric Analysis (TGA)



CONCLUSIONS

- Well-defined PLauMA-PAEMA diblock copolymers were successfully synthesized *via* RAFT polymerization.
- PLauMA-*b*-PAEMA block copolymers formed micelles in *n*-hexane characterized by hydrodynamic radii in the range of 30-50 nm.
- Successful complexation and solubilization of Pd(II) in *n*-hexane, in the presence of PLauMA-*b*-PAEMA.
- Preparation of polymer stabilized palladium nanoparticles in organic media.
- The thermal stability was improved in the presence of the Pd(0) nanoparticles within the PLauMA-*b*-PAEMA polymer matrix.

ACKNOWLEDGEMENTS

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