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The role of functional monomers on producing nanostructured lattices obtained by surfactant-free emulsion polymerization – A Novel Approach

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Nanostructured lattices were prepared in a single step emulsion polymerization reaction in the absence of surfactants by exploring the so called “pickering” stabilization mechanism. The synthesis protocol and the properties of the obtained particles were evaluated and discussed simultaneously considering processing and formulation aspects with special emphasis to the chemical properties of the functional monomers selected on the present study. Colloidal silica was used to ensure the physical stability required to produce nanoparticles as a result of the emulsion polymerization route. Three different monomers including methyl methacrylate (MMA), styrene (Sty) and vinyl acetate (VAC) were used to structure the particles of interest. Four different functional polymers including acrylic acid (AA), styrene sulfonate (StySO₃), hydroxyethyl methacrylate (HEMA) and dimethylamino ethyl methacrylate (DMAEMA) were evaluated. The formulation and experimental conditions are described in **Table 1**. The obtained lattices were comparatively characterized regarding to surface tension, particle size distribution, morphological aspects, viscosity, zeta potential and colloidal stability and the obtained results are presented in **Table 2**. The one-step pickering emulsion polymerization proved to be an effective approach to prepare lattices of industrial interest without the use of surfactants. The obtained particles presented average mean diameters ranging from 155 to 345 nm with relatively low polydispersity indices (0.39 – 2.02). The most promising behavior was experimentally verified once selecting the styrene sulfonate (StySO₃) as the functional monomer. The hydroxyethyl methacrylate (HEMA) also proved to be an interesting alternative although its limitation related to high surface tension applications. The high resolution images registered with the HRSEM-FEG technique explicit morphological aspects that effectively contribute to elucidate the “pickering” stabilization mechanism and the resultant core-shell structure derived thereof (**Figures 1 and 2**).

Keywords: latex, emulsion polymerization, nanoparticle, silica, MMA.

Table 1: Formulation and Experimental Conditions used to Polymerization Reactions.

Reactions	MMA	Sty	VAc	AA	HEMA	StySO ₃ Na	DMAEMA	Silica	Temperature
Mass (g)									(°C)
R0	20	-	-	-	-	-	-	2.5	70
R1	20	-	-	0.2	-	-	-	2.6	70
R2	20	-	-	0.6	-	-	-	2.5	70
R3	20	-	-	-	0.6	-	-	2.6	70
R4	20	-	-	-	0.3	-	-	2.6	70
R5	50	-	-	0.2	-	-	-	1.6	85
R6	20	-	-	-	-	0.2	-	2.6	85
R7	20	-	-	-	-	-	0.2	2.6	70
R8	-	20	-	-	0.2	-	-	2.5	85
R9	-	20	-	0.2	-	-	-	2.5	70
R10	-	-	10	-	-	0.1	-	1.5	75
R11*	-	-	20	-	-	-	0.3	2.6	75

* Potassium bicarbonate mass added= 0.2g

Table 2: Physical and Chemical Results of the Nanoparticles Dispersions obtained by Polymerization Reactions.

Reactions	SC (%)	ZP	ST	Visc (cP)	pH	PS			
						D ₁₀	D ₅₀	D ₉₀	PI
R0	-	-	-	-	-	6,236	37,410	82,000	2.02
R1	18.1	-59.3	56.4	6.5	3.99	276	344	437	0.47
R2	17.6	-66.4	49.1	-	3.05	237	295	378	0.48
R3	19.9	-43.9	64.8	-	5.94	3,784	6,608	10,910	1.08
R4	17.7	-33.3	55.6	6.2	5.24	190	240	302	0.47
R5	49.6	-64.4	-	-	2.17	446	3,366	5,396	1.47
R6	19.0	-65.2	-	5.5	3.25	124	155	194	0.45
R8	20.9	-65.2	-	-	2.30	285	345	419	0.39
R9	16.3	-52.9	59.0	5.5	2.67	239	290	351	0.39
R11	13.1	-55.7	-	-	4.47	325	2,026	3,326	1.48

SC (%) = Solids content; ZP (mV) = Zeta Potential; ST (mN/m) = Surface tension; Visc(cP) = Viscosity; PS (nm) = Particle Size; D₁₀ = 10th percentile; D₅₀ = volume median diameter; D₉₀ = 90th percentile; PI = Polydispersity Index = (D₉₀ - D₁₀)/D₅₀

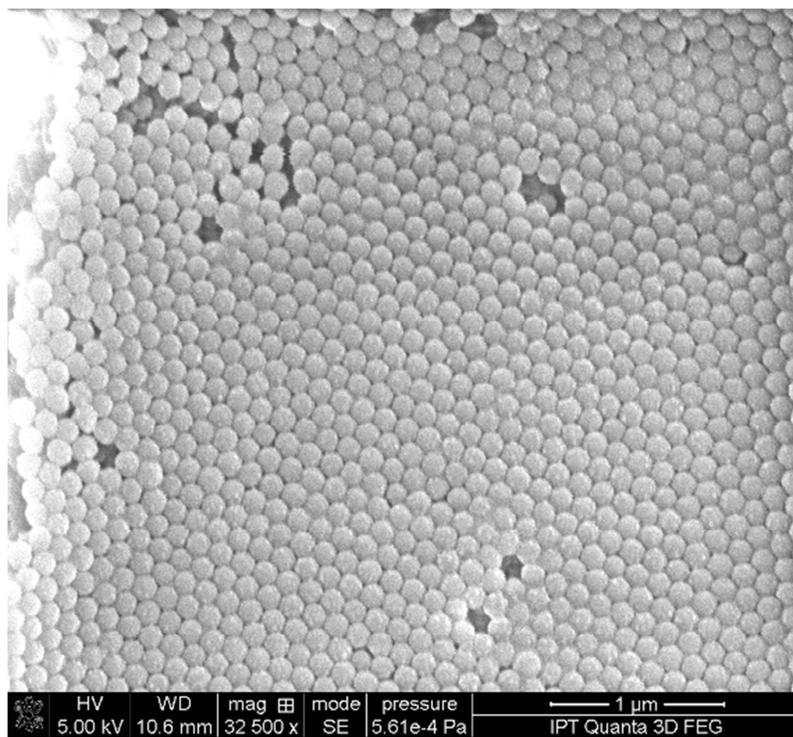


Figure 1: SEM-FEG image of nanoparticles obtained using the StySO3 as functional monomer (sample R08) demonstrating the homogeneity and low polydispersity of nanostructures.

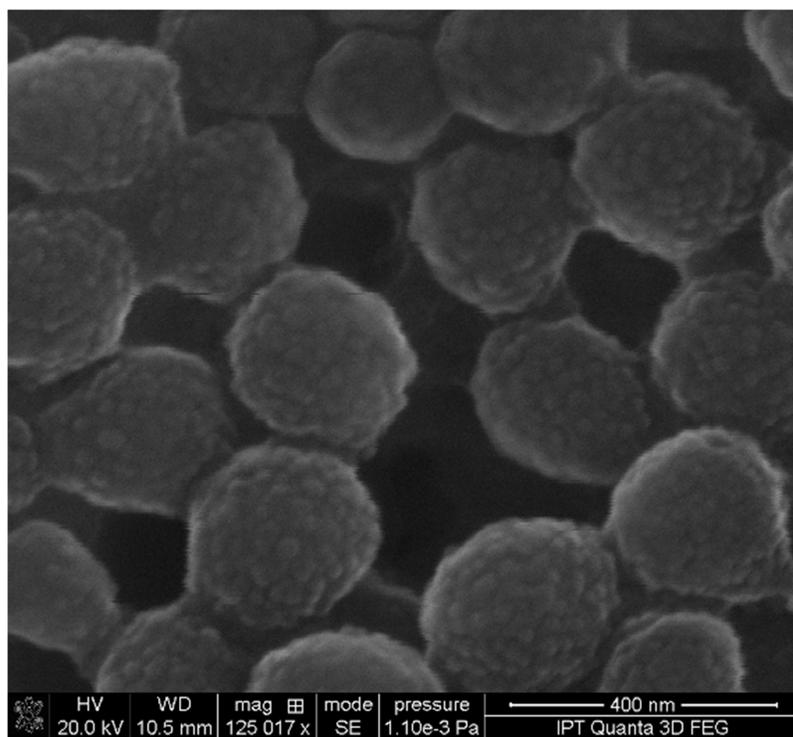


Figure 2: SEM-FEG image of nanoparticles performed using AA (sample R01) evidencing the mechanism of stabilization and the presence of colloidal nanoparticles on the surface of the latex.