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Micro/nanospheres from polysilsequioxane containing UVB-absorbing group

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1. Introduction

Polysilsequioxane is one of the well-known organic-inorganic hybrid materials which have been used for designs of new materials [1]. Many polysilsequioxane were synthesized via basic or acid catalysis mechanism [2]. The synthesis of polysilsequioxane spherical particles using aminopropyltriethoxysilane (APTES) as a self-catalysis was reported by R.M. Ottenbrite et al [3]. Y.B. Kim synthesized UV filter based on polysilsequioxane by attaching UV-absorbing chromophores onto the starting silane monomers [4]. However, the obtained UV-absorbing particles possess non-uniform and large size. This paper demonstrates the synthesis of small uniform UV-absorptive particles based on poly[propyl-4-methoxycinnamamide silsesquioxane].

2. General Instructions

Synthesis of triethoxysilylpropyl-4-methoxycinnamamide (TES4C) hybrid monomers

Triethoxysilylpropyl-4-methoxycinnamamide (TES4C) monomer was synthesized using a condensation reaction between 4-methoxycinnamoylchloride and 3-aminopropyl triethoxysilane (APTES) (Scheme 1). First, the 4-methoxy cinnamoylchloride was prepared by reacting 4-methoxy cinnamic acid (14.25 g, 0.08 mol for self-catalyst process and 17.81 g, 0.1 mol for acid/basic-catalyst processes) with excess thionyl chloride in 200 mL of dry toluene. The mixture was refluxed for 6 h under N_2 atmosphere. Then, the solvent and excess thionyl chloride were removed by rotary evaporation under reduced pressure. Finally, toluene addition (5 mL) and evaporation were performed to remove the last traces of thionyl chloride. 4-Methoxy cinnamoylchloride was dissolved in 250 mL of dry toluene. Then, 3-aminopropyltriethoxysilane (APTES) (22.13 g, 0.1 mol) and triethylamine (TEA) (10.11 g, 0.1 mol) were added. The mixture was refluxed for 3 h under N_2 atmosphere. The solvent and TEA were removed by rotary evaporation under reduced pressure. The obtained oil product was dried under vacuum to constant weight.

Preparation of poly[propyl-4-methoxycinnamamidesil-sesquioxane] (PTES4C) micro/nanospheres

The formations of micro/nanoparticles from TES4C monomer at room temperature using ethanol/water as a solvent through self-catalyst, acid-catalyst and basic-catalyst were compared.

Table 1 shows size of the poly[propyl-4-methoxy cinnamamidesilsesquioxane] (PTE4C) spherical particles obtained from various catalysis processes, e.g. self-catalyst, 0.1% HCl, 3% NH_4OH and 5% NH_4OH (Fig. 1).

The study demonstrates the amount of ethanol used during the self-catalysis polymerization affects the particles size (Fig. 2) while concentration of monomer affected synthesis yields. Polymerization at higher monomer concentration gave lower yield due to the formation of sticky gummy masses, Fig. 3(a). Polymerization in basic condition gave not only lower yields but also particles with less water disperability, Fig. 3(b).

Table I Particle characteristics of the synthesized poly[propyl-4-methoxycinnamamidesilsesquioxane] (PTE4C).

Catalysis	Concentration (g/mL) [a]	% Ethanol (v/v)	Particle characteristics
			Average diameter (nm) [b]
Self-catalyst	0.02	10	~300
	0.02	20	558 ± 9
	0.02	30	1354 ± 44
	0.04	20	552 ± 17
	0.06	20	566 ± 7
0.1%HCl	0.02	20	797 ± 10
3%NH_4OH	0.02	20	~600
5%NH_4OH	0.02	20	~800

[a] Concentration of monomer during polymerization
[b] Hydrodynamic diameters (nm) (Average size ± SD)

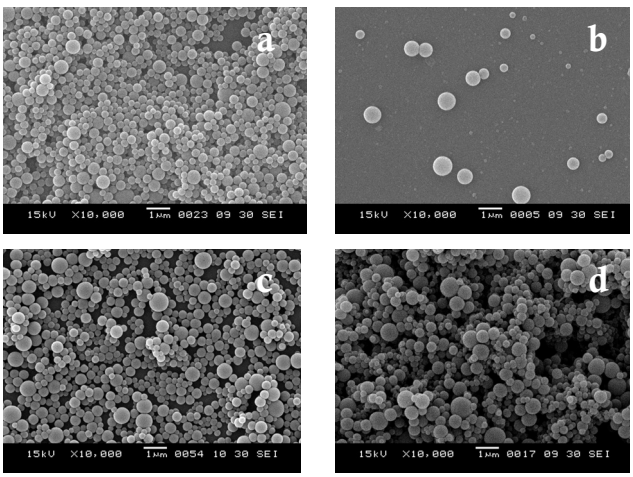
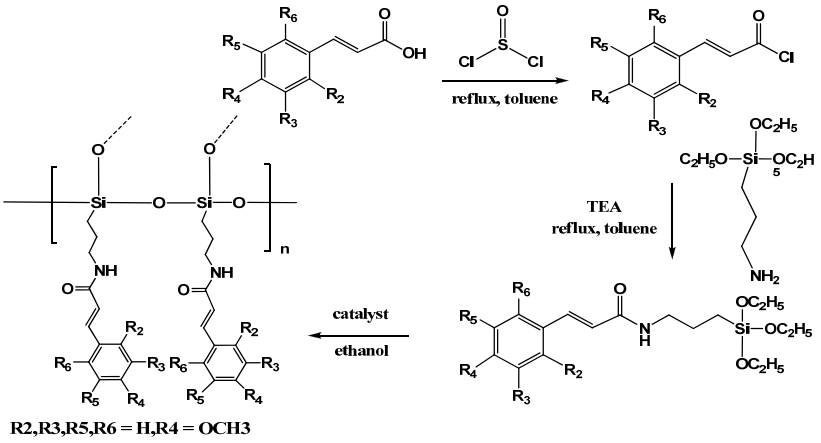


Fig.1 Morphology of particles prepared at 0.02 g/mL monomer concentration under self-catalyst (a), 0.1% HCl (v/v) (b), 3% NH_4OH (v/v) (c) and 5% NH_4OH (v/v) (d).



Scheme 1. Synthesis of poly[propyl-4-methoxycinnamamidesilsesquioxane] (PTES4C) micro/nanospheres of the obtained 4-methoxycinnamic acid and 3-aminopropyltriethoxysilane (APTES).

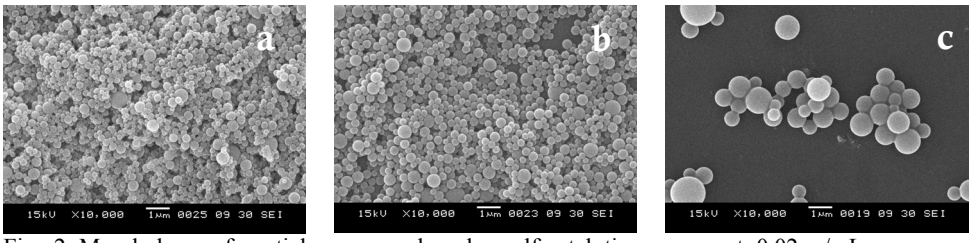


Fig. 2 Morphology of particles prepared under self-catalytic process at 0.02 g/mL monomer concentration with the ethanol percentages of 10% (v/v) (a), 20% (v/v) (b) and 30% (v/v) (c).

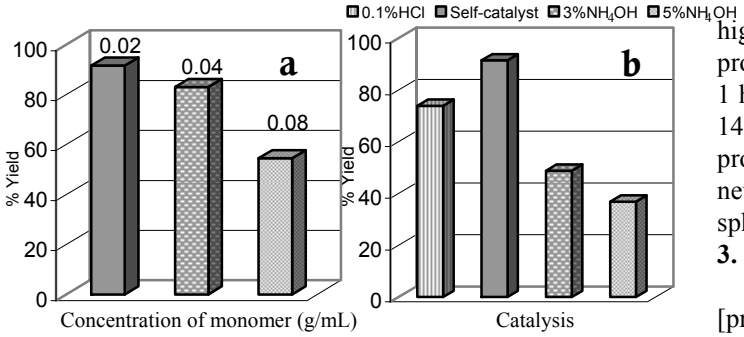


Fig. 3 Synthesis yield (%) of particles prepared at various concentration by self-catalysis processes (a), synthesis yield (%) of particles prepared at 0.02 g/mL monomer concentration under various catalysis processes (b).

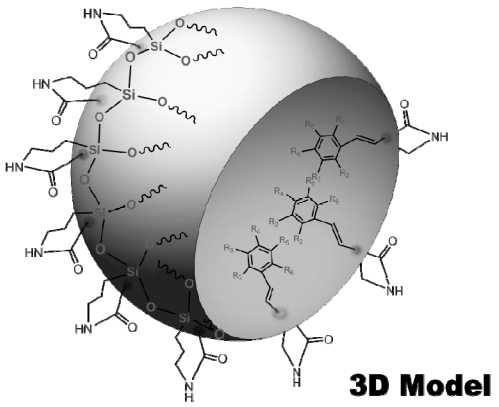


Fig. 4 The 3D model of spherical particles from poly[propyl-4-methoxycinnamamidesilsesquioxane] (PTE4C).

Self catalysis process gave more uniform spheres and higher yield comparing to acid and basic catalysis processes. Although basic-catalysis process required only 1 h comparing to 24 h for self-catalysis and the other hand 14 days for acid-catalysis processes, the self-catalysis process was the most convenient since neither washing nor neutralization were needed. Fig. 4 illustrates 3D model of spherical particles.

3. Conclusions

UV-absorptive hybrid nanospheres based on poly [propyl-4-methoxycinnamamidesilsesquioxane] (PTE4C) could be best prepared under self-catalytic condition. Size and yield of the particles could be controlled through the amount of ethanol and concentration of the monomer used during polymerization process.

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Appendix

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