OLIGOPEROXIDE BASED SYNTHESIS OF NOVEL FUNCTIONAL POLYMERIC AND HYBRID NANOCOMPOSITES OF BIOMEDICAL APPLICATION

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Main experimental approaches based on tailored synthesis of oligoperoxide surface-active substances (SAS) and derived metal complexes (OMC) with transition or rare earth metal cations and their application for obtaining polymeric and hybrid nanoscale carriers possessing targeted functionality and biocompatibility are presented. Molecular design of novel linear, block and comb-like oligoperoxide surfactants and derived coordinating complexes of transitional and rare earth metal cations is convenient tool for the synthesis of luminescent, X-ray detectable, super paramagnetic, colored and other functional nanocomposites with controlled size distribution, and reactivity.

For the synthesis of reactive functional nanocomposites various approaches were developed and studied, namely:

1. Water and hydrocarbon dispersion polymerization including miniemulsion and emulsifier free polymerizations initiated by OMC;

2. Water dispersion co-polymerization with novel surface-active including fluorine- or galactose -, or mannose containing monomers;

3. Homogeneous nucleation of functional hybrid mineral - polymeric nanoparticles (Au, Ag, Pd, $LaPO_4$…Eu^{3+}, Fe_3O_4, Ni, Fe_2O_3 etc.) from the salt solutions in the presence of SAS or OMC including magnetic and luminescent ones;

4. Seeded polymerization initiated from the surface of functional polymeric and hybrid nanoparticles and colloids previously modified by SAS or OMC;

5. Tailored OMC based synthesis and study of comb-like and highly branched functional surface-active oligoperoxides with alternate hydrophilic and hydrophobic branches forming micelle-like nanostructures in the media of various polarities;

6. Tailored synthesis and study of surface – active functional oligoperoxides of telechelic or block structures forming micelle-like nanostructures in the media of various polarities;

7. Tailored synthesis and study of functional oligoelectrolyte based nanogels with controlled porous size and functionality capable to adsorb and release poor soluble in water drugs, form polyplexes with DNA or to be filled with gold (magnetite) nanoparticles.

The methods developed provide combining the stage of formation of polymeric, metal and metal-oxide nanoparticles with the stage of their surface irreversible modification by functional surface-active oligoperoxides capable of binding physiologically active substances. Novel functional nanoparticles are studied by chemical, colloidal-chemical, and rheological methods, X-ray diffraction technique, luminescent spectroscopy, transmission and scanning electronic microscopy. The availability of reactive ditertiary peroxide fragments appearing on the particle surface as a result of oligoperoxide sorption causes their reliable protection, hydrophilicity and ability to radical grafting functional polymer chains. Functional nanoparticles developed can be recommended for study of phagocytosis, as pathological cell markers, antimicrobial remedies and for targeted drug and DNA delivery. Some of them are untoxic and biodegradable substances and successfully studied as cell recognizing carriers for targeted anticancer drug delivery and for DNA transfection.

The study was performed owing to financial support of STCU foundation, Projects 4140 and 4359.