

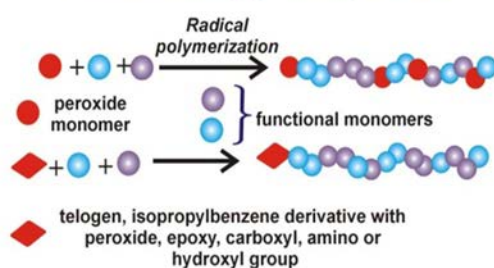
MOLECULAR ASSEMBLAGE OF BLOCK/COMB-LIKE POLYAMPHIPHILS AND SELF-ASSEMBLIES IN LIQUIDS AND ON SURFACES

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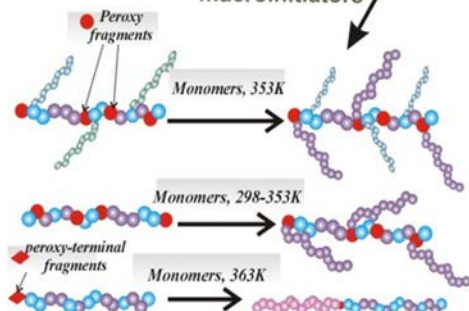
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Developed synthesis and properties of functional polyamphiphils (PA) and self-assemblies (SA), micelles, nanoparticles (NPs), and nanobrushes (NBs) of desired size and functionality is discussed. Combined radical and non-radical methods of the synthesis of primary oligomer-precursors containing terminal or side reactive groups and their using for LEGO-like assemblage of PA of block and/or comb-like structures were studied. Proposed approaches are based on polymerization of functional monomers including unsaturated peroxides in the presence of functional chain transfer agents. That provides controlling oligomer-precursor chain length and entering reactive side and terminal groups.

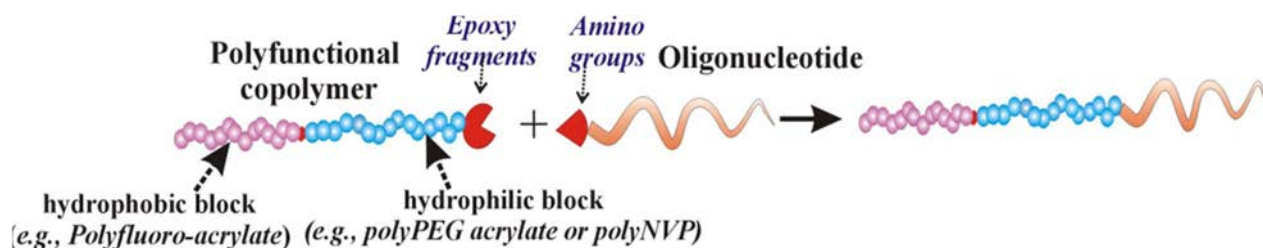
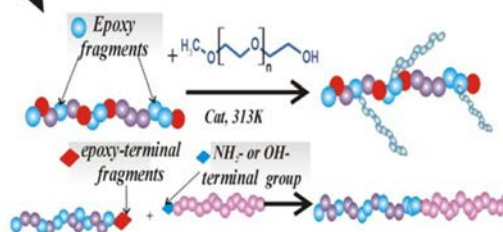
1. Obtaining primary units



2. Radical polymerization with macroinitiators



3. Poly condensation of the macromers



General scheme of molecular assemblage of functional polyamphiphils

The oligomer-precursors were used for construction of PA via:

- Polymerization providing formation of comb-like or block-copolymers using oligomer-precursors with side or terminal peroxide groups as macroinitiators, respectively;
- Polymerization providing formation of block-copolymers using oligomer-precursors with terminal hydroxyls (PEGs, polyoxazolines, fluorine alkyl alcohols, saccharides, rhamnolipids) as RedOx macroinitiators with Ce⁴⁺ salt;
- attachment of the blocks of distinct branching degree and functionality using oligomer-precursors with epoxide, amino, hydroxyl terminal groups via non-radical coupling reactions.

The general scheme of the molecular assemblage of the polyamphiphils is presented on the Figure.

Kinetic peculiarities of every polymerization step were studied. Novel copolymers were soluble in solvents of different polarity in wide pH range. Novel oligomer-precursors and PA of variable architectures, controlled lengths of blocks and side branches were studied using GPC, spectroscopy, and colloidal-chemical techniques. PA form SA of different degree of self-organization, size and morphology in liquids of various polarities as well as on surfaces of polymeric and inorganic nanoparticles and flat plate surfaces of various natures. These self-assemblies are specific containers for solubilization of water-insoluble substances and nanoreactors for nucleation and functionalization of magnetic, luminescent and scintillation NPs and NBs on the surfaces. TEM, DLS, SAXS, RAMAN and luminescent spectroscopy were used for study of SA, NPs and NBs.

The developed functional nanostructures were successfully tested as vehicles for drug and nucleic acid delivery and as physically detectable cell labels and scintillators for registration of X-ray and neutron irradiation.