

SECTION XII. CHEMISTRY, CHEMICAL ENGINEERING AND BIOENGINEERING

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NEW POLYMERIC AMPHIPHILES OF COMPLICATED ARCHITECTURE: FROM THE SYNTHESIS OF PRIMARY OLIGOMER ELEMENTS TO THEIR ASSEMBLY INTO POLYMERIC SURFACTANTS WITH A BLOCK AND COMB-LIKE STRUCTURE

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The routes of tailored synthesis and properties of novel polymeric surfactants and derived supramolecular structures, micelles, intermolecular complexes and nanoparticles, of desired size, morphology and functionality are developed. Combined radical and non-radical methods of the synthesis of primary building blocks containing end or side reactive groups and their using for controlled assemblage of polymeric surfactants of block- and/or branched architectures were developed.

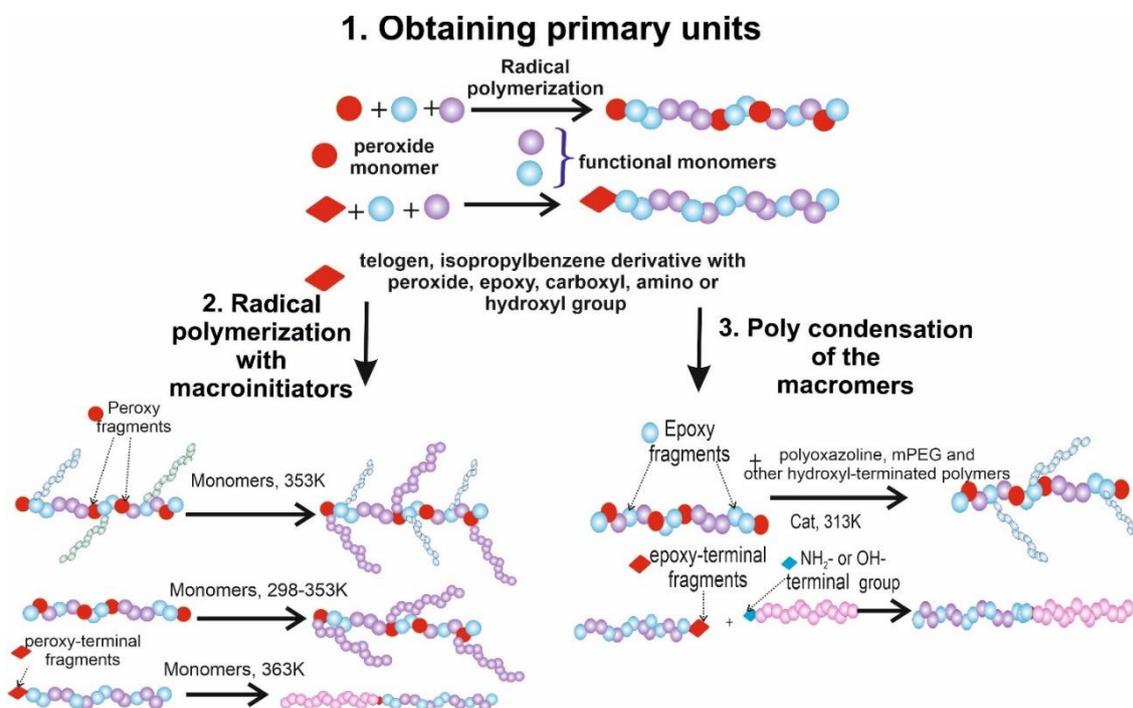


Fig. 1. General scheme for the production of functional polymeric amphiphils

Such building blocks were used for “LEGO” like construction of polymeric surfactants via (Fig.1):

- polymerization initiated by primary building blocks with side or end peroxide groups as macroinitiators in the presence of functional chain transfer agents providing;
- polymerization initiated by primary building blocks with end hydroxyls as macroinitiators in RedOx systems with Ce⁴⁺ salt in the presence of functional chain transfer agents;
- use of the primary building blocks containing epoxide, amino, hydroxyl side or end groups of synthetic or natural origin for the assemblage of branched, block and block/branched polymeric surfactants of controlled functionality and structural characteristics.

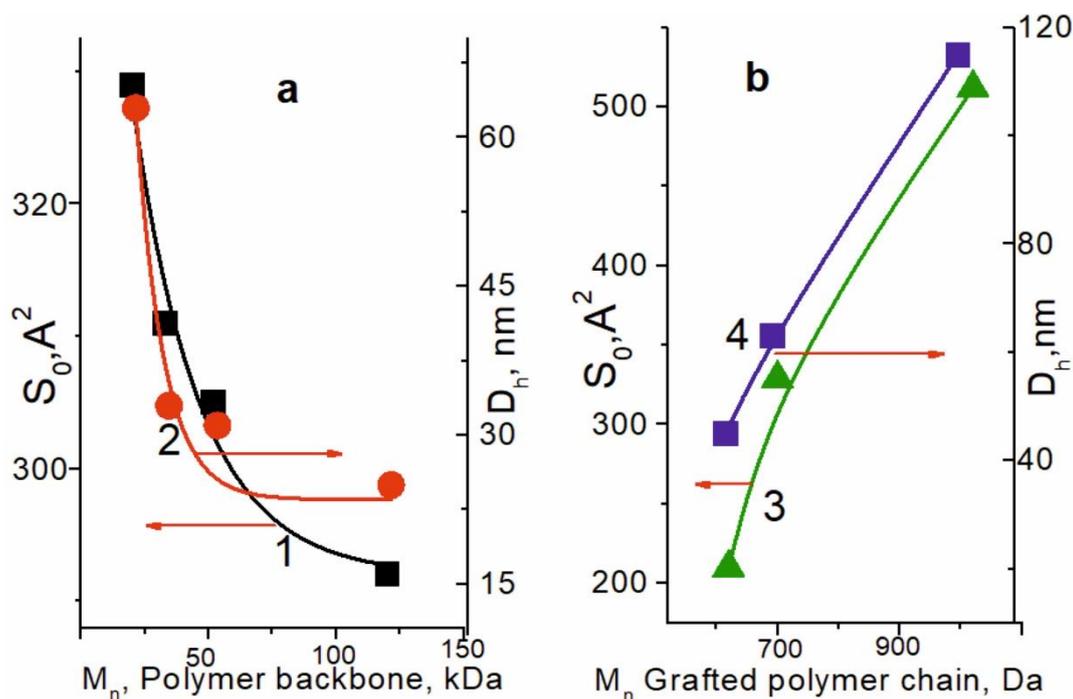


Fig. 2. **Dependence of the average minimum area per molecule ($S_0, \text{Å}^2$) of the PEG-containing copolymer (1,3) and the hydrodynamic diameter of micelles (D_h) (2,4) on the length of the backbone chain and side PEG chains: a - the backbone chain of poly(VEP-co-GMA) and side chains mPEG ($M_n=750\text{Da}$); b - the backbone chain of poly(VEP-co-GMA) (25:75%; $M_n=6000\text{g/mol}$) and side chains of mPEG molecular weight (500 Da, 700 Da and 1000 Da).**

The colloid-chemical properties of novel polymeric amphiphiles can be easily controlled by combining different functional monomers during polymerization, altering the length of the backbone, and altering the type and molecular weight of the grafted chains. Figure 2 shows how the colloid-chemical characteristics and sizes of micelles that form macromolecules of a branched PEG-containing polymer change. The backbone chain is a copolymer of glycidyl methacrylate (GMA) and peroxide monomer VEP; grafted chain - PEG monomethyl ether.

Conclusions. Functional non-ionic, polyelectrolyte, including polyampholytes, polymeric surfactants form supramolecular structures of different degree of self-organization, size, charge and morphology. These are specific containers for solubilization of water-insoluble substances and polymeric carriers for the delivery of nucleic acids, as well as nanoreactors for nucleation and functionalization of magnetic, radiopaque and luminescent nanoparticles. The created functional nanostructures can be used as physically observable cell labels as well as biocompatible delivery systems for drugs and nucleic acids in vitro and in vivo.