# Synthesis, Properties and Application of Amphiphilic Copolymers Based on Poly(fluoroalkylmethacrylate)s With Terminal Peroxide Group

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***Abstract* – *Polymers with terminal peroxide fragment were synrhesized via radical polymerization of fluoroalkyl methacrylates. Amphiphilic block-copolymers with hydrophilic block of different structure were synthesized by usage of obtained polymers with terminal peroxide group as macroinitiators. Kinethic peculiarities of polymerization were studied on both stages. The strucrure of polymers were confirmed by IR- and NMR-spectroscopy.***

Keywords – fluoroalkyle methacrylate, peroxide group, radical polymerization, controlled synthesis.

## I. Introduction

Polymeric materials are widely prevalence in all spheres of human life. However, the field of application of such materials is determined by their properties which in turn depend on the structure of macromolecule.

Control of polymeric structure can be done by regulation of the lengths of side- and main chains of macromolecule. The nature of polymeric fragments is also affects the polymeric properties. Thus, amphiphilicity of polymeric backbone possible to provide by combining fragments with different solubility in polar environment.

Unique properties of fluorine contained polymers led to the rapid growth of the number of their studies in different areas. Polymers with fluorine fragments are use as components of contact lenses [1], additives for surface modification [2] and semiconcuctors [3]. In additions, perfluorinated lengths in the structure of surfactant are most hydrophobic in comparison with their hydrocarbon counterparts [4]. This properties is interesting for increation of molecular amphiphilic character. Amphiphilic copolymers with fluorinated segments studied as carriers for nucleic acid delivery and marking and detection of biological objects [5-7].

In order to provide effective control of macromolecular structure and properties is important establishment of kinetic regularities of homo- and block-copolymers with controlled lengths and nature of side chains and blocks.

In this paper are presented research of synthesis of poly(fluoroalkyle methacrylate)s with terminal peroxide fragments and amphiphilic block/comb-like copolymers based on obtained polymers with peroxide group.

## II. Synthesis of F-contained polymers with terminal peroxide group

Comb-like fluorine-contained homopolymers with terminal peroxide fragments were synthesized by free radical polymerization of fluoromethacrylates in presence of peroxide contained chain transfer agent – monoperoxine (MP). General scheme of polymerization are shown in fig. 1.

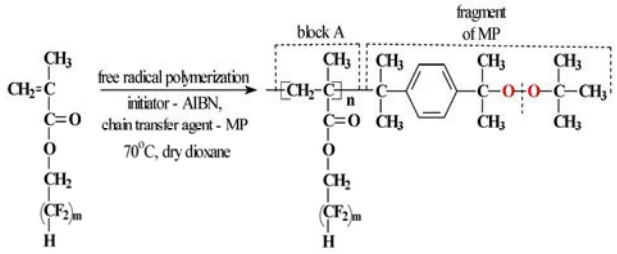


Fig. 1 General scheme of polymerization of poly(fluoroalkyl methacrylate)-MP

Kinetic peculiarities of polymerization were studied. Influence of polymerization parameters on the length of macromolecular backbone was established.

Structure of comb-like polymers confirmed by IR- and NMR-spectroscopy. The results of gas-liquid chromatography confirmed entrance of peroxide group to macromolecular structure.

Control of molecular-weight characteristics was carried out by addition of monoperoxine. Terminal peroxide group allows to use obtained polymers as macroinitiators on the next stage of synthesis.

## III. Synthesis and properties of amphiphilic copolymers based on prepared macroinitiators

Amphiphilic block-copolymers with fixed size of side chains and blocks were synthesized by free radical polymerization of hydrophilic monomers initiated by obtained poly(fluoroalkyl methacrylate)s. Block/comb-like copolymers obtained with different structure of hydrophobic (block A) and hydrophilic block (block B) (fig. 2). Thus, we changed the lengths of blocks and nature of hydrophilic blocks. Cumen and epoxide-contained derivative of cumen (KGE) were used for narrowing the molecular-weight distribution. The general scheme of synthesis of block/comb-like copolymers with amphiphilic character are shown on fig. 2.

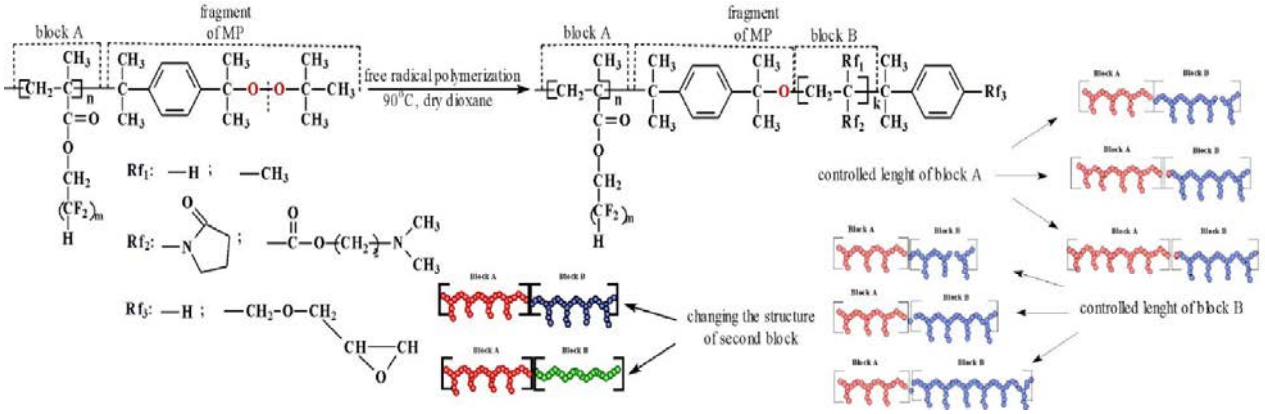


Fig. 2 General sqheme of synthesis of block/comb-like amphiphilic copolymers based on poly (fluoroalkyl methacrylate)-MP

Kinetic parameters of synthesis of hydrophilic block B were studied. The dependencies of molecular-weight characteristics from the length of block A, nature of the solvent, amount of chain transfer agent and macroinitiator were established.

Structure of amphiphilic copolymers was confirmed by IR- and NMR-spectroscopy and results of elemental analysis.

Including of hydrophilic part in the structure of macromolecule also confirmed by ability to dissolving of amphiphilic copolymers in water.

Colloidal-chemical properties of amphiphilic copolymers were studied. The avaibility of inflection point on obtained isotherms confirmed surface tentions properties of amphiphilic copolymers. The sizes of polymeric micellar structures were studied by results of dynamic light scattering (DLS). Influence of the length of blocks on CMC value and sizes of micellar structures were established.

## IV. Perspective of practical application of amphiphilic copolymers

The changing of nature of hydrophilic block or terminal group determine specifics of block-copolymers usage.

Thus, polymers with polyelectrolyte block B can form complexes with nucleic acids (called polyplexes). Such polymers are described at literature as nonviral vectors for nucleic acid/genes delivery. Well known [7], that fluoritated fragments in structure of nonviral vecrors prevent of interactions between delivery system and proteins. Furthermore, such components facilitate penetration of polyplex through cell membrane.

From the other way, terminal epoxy group was introduced for the purpose of binding polymeric macromolecule and biologically active components, for example oligonucleotides. Moreover, nonionic nature of block B are provide selective oligonucleotide binding with terminal group.

Proposed methods of synthesis block/comb-like copolymers are interesting for research, development and implementation of novel approaches to therapy for cancer and genetic diseases.

## Conclusion

In present work are described kinethic perculiarities of poly(fluoroalkyl methacrylate)s with terminal peroxide groupe and amphiphilic copolymers based on obtained macroinitiator. Colloidal-chemical properties of amphiphilic copolymers were studied. Perspective of practical usage of copolymers are shown.

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