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BIOINSPIRED ADHESION COPOLYMERS CARRYING CATECHOL GROUPS: SYNTHESIS AND PROPERTIES

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It is well established [1] that excellent adherence properties of blue mussels to rocks in wet conditions are predetermined by catechol-containing amino acid, 3,4-dihydroxyphenylalanine. Many catechol group containing polymeric materials were synthesized which were designed to be used as adhesives, anticorrosion polymer coatings, and surface modifiers [2]. Between these polymeric materials, there are only very few examples of the brush copolymers carrying catechol groups [3]. The main task of the present work was to synthesize and study brush copolymers containing PEO side chains and carrying units with catechol groups providing excellent adhesion in aqueous media and lubricating properties to the modified surfaces.

Polymerization of catechol group containing monomers is a challenge since catechol groups act as weak inhibitors of radical reactions, and are readily oxidized to quinones. In order to avoid undesirable reactions, we used two approaches – protection of the catechol group present in a monomer or introduction of moieties with catechol group by modification of random copolymers.

Random brush copolymers were synthesized by RAFT copolymerization of poly(ethylene oxide) methyl ether methacrylate M_n 950 (PEOMEMA) with acetonide protected dopamine methacrylamide (A-DOPMA) (the first approach), or PEOMEMA with DMAEMA (the second approach). Copolymerization kinetics and the copolymers were studied by size exclusion chromatography with tripple detection (RI, LS, and DP) and ^{1}H-NMR spectroscopy. Degree of polymerization of the copolymers was close to 100, and the dispersity index Đ less than 1.2.

The acetonide protecting groups of A-DOPMA units in the copolymers were removed using trifluoroacetic acid. DMAEMA units in the copolymers by the second approach were quaternized with 2-chloro-3,4-dihydroxyacetophenone (QDMAEMA). The copolymers of PEOMEMA and DOPMA are catechol groups containing brush copolymers without charge, and the copolymers of PEOMEMA and QDMAEMA are cationic catechol groups containing brush copolymers.

Resistance to oxidation of the catechol copolymers was studied by UV-Vis spectroscopy, and nanoscale wear resistance of the adsorbed layers by AFM-based methodology. The copolymers with protected catechol groups were resistant to UV irradiation, while those with deprotected catechol groups were susceptible to oxidation. The most unstable were cationic catechol groups containing copolymers. The copolymers with catechol groups formed a more wear resistant polymer layer on silica compared to cationic brush copolymers. The combination of cationic and catechol anchoring groups, as in the mussel adhesive proteins, provided the most wear resistant polymer layers.

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