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Modification of Triblock-Copolymers by Mannich Rection

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The amphiphilic block copolymers attract considerable attention as polymer drug delivery systems. Among them the asymmetric micelle forming triblock-copolymers (TBC) of polyacrylamide (PAA) and polyetylenoxide (PEO) have been studied quiet well. It was established that structure of these copolymers consists of hydrophilic and hydrophobic fragments due to which, they can bind colloid particles, organic substances and different ions in water solutions. For the successful implementation of mentioned TBC for a safe transport of toxic drugs they have to contain ligands or vectors (saccharides, peptides, proteins or antibodies) letting substances to reach definite cells of the organism.

In order to introduce the necessary vectors into TBC, corona forming PAA blocks have to contain active groups. In this aspect the methods of functionalization of TBC is particularly important. Reactions of polymer analogous modification are well known, comparatively simple and reliable method of functional groups transformation.

In the present work the reaction of polymer analogous transformation of TBC PAA-*b*-PEO-*b*-PAA by aminomethylation of PAA blocks in the presence of dimethylamine and formaldehyde (Mannich reaction) is studied.

The conditions and reagents were selected to obtain comparatively small degree of PAA links modification (~10%). Reaction was carried out at 20 °C and 50 °C, pH=12 and molar ratio TBC: formaldehyde: dimethylamine =1: 0,2 : 0,2. Two samples of asymmetric TBC with different length of PEO blocks (Mv_{PEO}=6-35 kDa) were synthesized by the radical block copolymerization of AA to PEO and used in the reaction. Sample splitting were realized via 20, 60, 120, 180 and 240 min. Kinetic investigations of Mannich reaction for TBC in comparison with initial PAA were performed by the potentiometric titration.

It was established that aminomethylation reaction accompanied by hydrolyses one. Significant influence of the temperature on the both processes was observed. Thus, at room temperature the aminomethylation process has primary importance while the higher temperature (50 °C) promote hydrolyses reaction. Hereby, the temperature variation makes it possible to obtain new polyampholytes with the setting number of tertiary amine groups and carboxylic groups. Such polyampholytes can be used as genetic material carrier systems (for example, nucleic acids) in living organism. The effect of rate increasing of TBC aminomethylation as against PAA was determined and discussed.