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7-P5. Poly(zwitterion)s for modification of bioactive agents

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Poly(zwitterion)s involved in biomedical applications are widely studied due to their hydrophilicity, biocompatibility, and superior resistance to nonspecific protein adsorption. They can be applied as PEG alternatives to modification of bioactive substances and delivery of biomacromolecules, such as nucleic acids and proteins. Therefore, the design of functionalised poly(zwitterion)s capable of conjugation to biomacromolecules or other active species under mild reaction conditions is a prerequisite for successful development of a delivery system.

This communication is reporting the preparation and characterisation of polysulphobetaines bearing end-functional groups able to react selectively with amines in aqueous media. They were used for modification of poly(ethyleneimine) and conjugation to human serum albumin as model bioactive molecules. The conjugation reactions were studied by NMR spectroscopy. The effect of poly(zwitterion) modification on the solubility and biological properties was evaluated.

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7-P6. Complexes of transition metals ions with block copolymers

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Complexes of block copolymers (BC) were prepared by interaction with transition metal salts such as $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in aqueous solution at room temperature. The metal complexes are formed by coordinatively bonding the polymer ligands with the metal ions through a reaction between the BC-containing donor atoms (in this case, N or O atoms) and the different metal ions. These complexes were characterised by elemental analysis, FTIR spectroscopy, and thermal analysis. Geometric optimisation of monomer fragments of transition metal ions complexes was carried out by the semi-empirical quantum method ZINDO/1 from HyperChem software package. The latter study of the complexes enabled us to suggest the probable stereo structures of the monomer fragments.

The catalytic epoxidation of cyclohexene in the presence of *tert*-butyl hydroperoxide as oxidant and toluene solvent was investigated in presence of the complexes. The reaction products were analysed by gas chromatography with flame ionisation detection. The catalytic activity of Mo(VI) complexes in the epoxidation reaction was generally higher than that of the V(IV), Cu(II), Co(II), and Fe(II) coordination compounds. Reaction by-products were 2-cyclohexene-1-ol and 2-cyclohexene-1-on.

7-P19. Novel water-soluble fluorescent nanomicelles as a tool for biomedical investigations

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Fluorescent probes for sensing and reporting of chemical species are currently of great interest due to the increasing need of fast and reliable detecting of chemical species in many areas of human activity. In recent years, most attention has been paid to development of fluorescent sensing systems for ions under physiological conditions. The biggest disadvantage of most organic probes is their hydrophobicity and work in organic solvents, which significantly restricts their practical applications. Fluorescent polymeric nanoassemblies have become a focus of intensive investigations during the past few decades due to combined advantages: improved biocompatibility, water dispersibility, stimuli-responsiveness, facile integration into optical detection devices, and ability of functionalisation. One approach to prepare such a structure consists of the use of amphiphilic diblock copolymers that can self-assemble in solution forming nanosized morphologies. In many cases, spherical micelles consisting of core formed by hydrophobic block and shell arising from the hydrophilic block can be obtained in an aqueous solution. Based on this consideration different organic fluorophores can be incorporated into the hydrophobic core of the micelles which can provide their water solubility. Herein, we report on the synthesis of novel water-soluble fluorescence micelles with embedded Dyad or PDI fluorescent probes. The prepared nanomicellar architectures show high cell-permeability and low cytotoxicity suggesting a high potential of the prepared micelles for future biomedical applications.

7-P20. Polyzwitterionic hydrogels for immobilisation of alkaline protease

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The interest towards zwitterionic polymers has grown significantly in recent years due to their exceptional biocompatibility. It is believed that the origin of their biocompatibility lies in their structural similarity with natural patterns, e.g. the betaine structure of the amino acids, the zwitterionic phospholipid head as a building block of cell membranes, etc.

This study deals with the synthesis and characterisation of zwitterionic polymers networks (PZI) and their application as hydrogel wound dressings. PZI could provide several advantages in this role as they swell more in salt solution, i.e. wound exudate, than in water (so-called antipolyelectrolyte effect). In order to functionalise the PZI hydrogels, alkaline protease was immobilised therein with the aim to impart cleaning ability of necrotic tissues, which is necessary for faster wound healing. The alkaline protease is already used as an agent in several products for wound healing (creams, ointments, etc.) that are available on the Bulgarian market.

To achieve this goal two types of monomers were used: (i) carboxybetaine methacrylate and (ii) sulphobetaine methacrylate. The resulting polymer networks were characterised in terms of their swelling ability and were then loaded with alkaline protease. The enzyme activity of the loaded protease in PZI materials was evaluated and related to PZI crosslinking density. Thus, the proteases immobilisation in PZI resulted in a new functional hydrogel wound dressing.

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7-P21. Water transport and behaviour in polysulphobetaine hydrogels

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Polysulphobetaines (PSBs) are a class of polymers containing a covalently bound positively charged quaternary ammonium group and a negatively charged sulpho group in each monomeric unit. These polymers provoke very low non-specific protein adsorption and thus possess very good haemo- and biocompatibility. The excellent performance of PSBs as biomaterials is explained by their ability to swell better in a low molecular weight salt (LMS) aqueous solution than in water (antipolyelectrolyte effect). This behaviour of PSBs is explained by cluster formation due to dipole-dipole interactions between PSB monomeric units. These clusters are stable in water but destroyed by LMS. Thus, the interactions in PSB-LMS aqueous solutions are interesting in view to understanding their properties and should reveal details about the PSB performance *in vivo* as the LMS aqueous solution resembles the body fluids.

The aim of the present study was to investigate the dynamic swelling and the structural mobility of PSBs networks in aqueous solutions as a function of LMS concentrations. LMS concentration increase resulted in enhanced PSB-water interactions when PSB hydrogels are swollen in LMS aqueous solutions as revealed by the dynamic swelling. DSC data confirmed this conclusion as the fraction of bound water in PSBs hydrogels increases with LME concentration. These results are in agreement with data obtained by HR MAS NMR spectroscopy.

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7-P22. Creep and deswelling peculiarities of the polyzwitterionic 'straight' and 'reverse' poly(dimethylmethacryloyl propanesulphonate)-poly(acrylamide) double networks

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Double network (DN) hydrogels with cross-linked poly(dimethylmethacryloyl propanesulphonate) as a high density single network (HDSN) and poly(acrylamide) as a low density single network (LDSN) were synthesised and the characteristics of their creep and deswelling curves (stationary levels and initial rates of displacement and deswelling) were determined. It was shown that the values of these characteristics depend on the monomer 1 to monomer 2 concentration ratios, monomer/cross-linking agent, duration of cross-linking polymerisation, and order of HDSN and LDSN formation. When the first SN is a polyzwitterionic (HDSN), the DN is called 'straight' DN, whereas in the opposite case the DN is called 'reverse'. It was established that by transition from 'straight' to 'reverse' DN, the network density decreases, the elasticity increases, and the weight fraction of the bound water rises. The results are explained by the formation of dipole-dipole clusters between the opposite oriented zwitterion groups in the side groups of the polyzwitterionic macromolecules.