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Photoactive graft amphiphilic polyelectrolyte: Facile synthesis, intramolecular aggregation and photosensitizing activity

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ABSTRACT

Simple and versatile two-step procedure for synthesis of graft amphiphilic polyelectrolytes has been developed. A photoactive copolymer of poly(vinylnaphthalene) grafted from poly(sodium 2-acrylamido-2-methyl-1-propanesulfonate) (PAMPS-*graft*-PVN) was obtained and characterized. By separating the processes of generation of grafting sites on the precursor main chain and subsequent nitroxide-mediated polymerization (NMP), the formation of the unwanted homopolymer could be avoided. Combination of charged polymer backbone with short hydrophobic side chains in PAMPS-*graft*-PVN leads to spontaneous intramolecular aggregation of the macromolecule in an aqueous solution with formation of hydrophobic domains consisting of highly packed naphthalene chromophores arranged in a "pearl-necklace" structure as shown using atomic force microscopy. The presence of fluorophores in the polymer structure is beneficial for the studies of such macromolecular system as it allows application of emission spectroscopy, which is very sensitive to structural arrangement of the fluorophores. The domains formed within the polymer chain in an aqueous solution were also characterized using fluorescent molecular probes. Studies on photophysical properties of PAMPS-*graft*-PVN indicated that the polymer can be an efficient photosensitizer in photoinduced electron transfer processes. The proposed here synthetic approach can be easily applied for syntheses of other graft copolymers that are otherwise difficult to be obtained.

1. Introduction

Amphiphilic copolymers are known to self-assemble into nanoscale superstructures in selective solvents [1–8]. Their structural organization, shape and morphology are determined not only by the intramolecular solvophilic/solvophobic balance but also by the polymer topology. In addition to commonly observed intermolecular aggregations of macromolecules also intramolecular aggregation is possible and it is particularly interesting [9–11].

Although linear block copolymers have been most commonly studied and shown to form different structures like micelles, polymersomes in solutions [12,13], the other amphiphilic copolymers of various architectures (multiblock, star-like, dendrimers, comb-like, etc.) have been also reported [14–17]. The presence of fluorophores in the macromolecules may be beneficial for determination of their conformation as fluorescence spectroscopy may be applied that is very sensitive to structural arrangement of these polymeric units [18]. Graft amphiphilic copolymers with solvophilic backbone and solvophobic side chains have been, with this respect, explored rather rarely [19,20]. It is believed that a graft amphiphilic copolymer have some difficulties to organize into the systems with different morphologies in a selective solvent and the formed structures are less precisely defined [21].

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Special class of amphiphilic copolymers, so-called antenna polyelectrolytes, has attracted considerable attention due to their wide range of possible practical applications resulting from their similarity to the natural systems [22–26]. The presence of charged groups in their macromolecules makes them soluble in water while the presence of chromophores makes them photoactive. The range of their photochemical sensitivity is very wide and it can be easily adjusted by incorporation of properly chosen chromophores into the macromolecule. Their functioning resembles that of natural antenna photosynthetic systems. They are able to collect the energy (absorb light), which then migrates between the chromophores attached to the polymer chain and can be transferred to the suitable energy traps at which the photophysical processes or photochemical reactions are induced. Usually the covalently bounded molecules or the molecular aggregates serve as the energy traps. However, the amphiphilic photoactive polyelectrolytes in aqueous solution offer one more possibility. Due to the unfavorable interactions between hydrophobic polymeric units (usually chromophores) and water molecules they are able to adopt the micellar conformation. This conformation limits the contact of hydrophobic units with water and results in formation the hydrophobic ‘pockets’ in which the poorly soluble organic compounds can be solubilized. High local concentration of chromophores within the hydrophobic nanodomains and their close contact with solubilized organic compounds increase the efficiency of energy migration/transfer and increase the probability of photochemical reactions.

We have studied amphiphilic photoactive polyelectrolytes, known also as antenna polyelectrolytes, which can function as photosensitisers in chemical reaction [27–30]. The systems described so far are mostly random or block copolymers. We have demonstrated that the nitroxide-mediated controlled radical polymerization (NMP) is an attractive method for synthesis of block amphiphilic copolymers [31,32]. In the current paper we report the synthesis of PAMPS-*graft*-PVN, graft amphiphilic polyelectrolyte with hydrophobic, poly(vinylnaphthalene) photoactive grafts. The graft copolymer was obtained in a two-step synthetic procedure which combines the free-radical “grafting from” technique and NMP offering the molecular control. By separating the processes of generation of grafting sites on PAMPS chain and nitroxide-mediated polymerization of vinylnaphthalene (VN), the formation of the PVN homopolymer was avoided. NMP has been also only recently used to synthesize various copolymers comprising polystyrene and polyether segments [33]. To the best of our knowledge, we present here the first example of synthesis of photoactive graft polyelectrolyte by “grafting from” NMP in which the hydrophobic grafts were created on the hydrophilic polyelectrolyte chain. The proposed here synthetic method is easy and versatile making possible the synthesis of variety well-defined graft and branched copolymers including polyelectrolytes.

Our interest in synthesis of graft photoactive polyelectrolytes is mostly related to the expected interesting physicochemical and photophysical/photochemical properties resulted from their superstructures formed in aqueous solutions. It is believed that unimolecular multimicellar structures can be formed by the graft amphiphilic copolymers in an aqueous solution. Also, the spatial organization of the chromophores within the grafts and their proximity should induce the formation of molecular aggregates in their ground electronic states. That should considerably effect the performance of these systems as photosensitizers and potential materials for optoelectronic devices as was shown before [34–40]. Such water-soluble unimolecular multimicellar structures can be also interesting as e.g., drug nanocarriers or nanoreactors.

2. Experimental

2.1. Materials

2-Vinylnaphthalene (VN, Aldrich, 95%) was purified by column chromatography using aluminum oxide as the stationary phase and cyclohexane as the eluent. Acryloylamino-2-methylpropane-1-sulfonic acid (AMPS, Aldrich, 99%), 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTEMPO, free radical, 98%, Aldrich), perylene (Pe, Aldrich, gold label, 99.9%), 10-camphorsulfonic acid (CSA, anhydrous 98%, Aldrich), iron(II) sulfate heptahydrate ($FeSO_4{\cdot}5H_2O$, >99.5%, Merck), hydrogen peroxide (30% solution, p.a., POCH Gliwice, Poland), HCl (30% solution, spectroscopic grade, POCH Gliwice), NaOH (p.a., POCH Gliwice), sodium hydrogen sulfite ($NaHSO_3$, Fluka, solution for synthesis, 38–40% in water), potassium persulfate ($K_2S_2O_8$, Aldrich, 99.99%), sodium carbonate (Na_2CO_3, POCH Gliwice, 99.9%), sodium chloride (NaCl, puriss, Lachner, Czech Republic), acetonitrile (HPLC grade, POCH Gliwice), sulfuric acid (96%, puriss, LachNer,), dimethylosulfoxide (DMSO, HPLC grade, POCH Gliwice), methanol (HPLC grade, POCH Gliwice), cyclohexane (p.a., POCH Gliwice), diethyl ether (p.a., POCH Gliwice), polyethylenimine (PEI, Aldrich) were used as received. Triethanoloamine (TEA, 98%, Aldrich) was distilled under vacuum. 4,4′-Bipyridinium-1,1′-bis(trimethylenesulfonate) (SPV) and [6-(N,N-dimethylamino)]-1-(4′-cyanophenyl)-3-phenyl-1H-pyrazolo[3,4-b] quinoline (PQ) were prepared according to the procedures described in the literature [41,42]. Deionized water was used to prepare all the solutions.

2.2. Polymer synthesis

Poly(sodium 2-acrylamido-2-methyl-1-propanesulfonate), PAMPS, was synthesized using nitroxide-mediated controlled radical polymerization. The monomer, 2-acrylamido-2-methyl-1-propanoic acid (AMPS, 0.07 mol), was first quantitatively neutralized using sodium carbonate and then mixed with redox initiator ($K_2S_2O_8$:$NaHSO_3$, 1:1 molar ratio, 1 mol%) and HTEMPO (1.5 mol%). The polymerization was carried out in DMSO: water (8:1, v/v, 50 mL) mixture, at 125 °C. The reaction was completed after 6.5 h and the resulting polymer was precipitated into diethyl ether and dried in a vacuum oven at 40 °C. The polymer was then dissolved in water, dialyzed for a week (Fisher, cellulose tubing, cutoff 12,000–14,000 g mol^{-1}) and freeze-dried.