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Novel Photosensitizers Based on Polysaccharides – Dextran Modified with Anthracene

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Summary: Series of novel water-soluble photosensitizers based on dextran was synthesized and studied. Dextran was modified by covalent attachment of anthracene chromophores. Photophysical and photochemical properties of the photosensitizers in aqueous solutions were determined. Their applicability for sensitization of oxidation of polynuclear aromatics and degradation of pesticides was demonstrated. Removal of photosensitizers from the environment after their usage was discussed.

Keywords: dextran; energy transfer; photosensitizers; polyaromatics; polysaccharides

Introduction

The main challenges which have to be addressed by the chemistry of XXI century are related to the problems with resources, environment, and energy. More specifically, one should deal with the problems related to the limited and steadily decreasing volume of natural resources, develop technologies which will save and/or improve the quality of the environment (especially water), and search for new energy sources. All these issues are interconnected and they are subjected to the studies in number of research laboratories around the world. In practical terms they point out to the need of wider use of the renewable resources, both as materials and as a source of energy.

Current paper addresses some of these issues. We present here our attempts for development of family of novel photosensitizers based on biodegradable polymers from renewable resources. Photosensitizers are the compounds which absorb radiation in a defined spectral region and use that acquired energy to induce photophysical and/or photochemical reactions in another molecular entity present in a system which is not able to absorb directly the incident radiation. The primary photophysical steps involve energy or electron transfer between these species. Many photochemical processes of practical importance have to be photosensitized. In our previous studies we have demonstrated that the application of polymeric photosensitizers helps to avoid some problems observed when low-molecular-weight sensitizers are used.[1] Here we demonstrate that the polysaccharides can be used as carriers of chromophores. Polysaccharides have a lot of advantages: they are the most abundant natural polymers in biosphere, they are renewable, cheap, can be easily modified (a number of functional groups) and are biodegradable. The chromophores which absorb the light from the nUV/Visible spectral region (ideally solar light) can be covalently attached to the polysaccharide chain. Recently we have developed and studied number of photosensitizers based on polysaccharides.[2–6] For the clarity of the presentation we will describe that new family of photosensitizers using anthracene-modified dextran as an example.

Experimental Part

Instruments

The UV-Vis absorption spectra were measured using HP 8452A Diode Array spectrophotometer (Hewlett-Packard, USA).

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^1H NMR spectra of the polymers were measured in DMSO-d_6, solution using a Bruker AMX 500 spectrophotometer (Bruker, Germany. The IR spectra were recorded in KBr pellets using a Bruker IFS-48 spectrophotometer (Bruker, Germany). The steady-state fluorescence and lifetime measurements were done using SLM Aminco 8100 spectrofluorimeter (SLM, USA). GPC/HPLC analyses were carried out using Waters system (Waters, USA). For GPC measurements detection was done using Waters 2410 Refractive Index Detector and Waters 2996 Photodiode Array Detector. For HPLC UV and fluorescence detectors were applied. Depending on a system studied, irradiation was performed using mercury lamp with interference filter at 365 nm or using Rayonet photochemical reactor equipped with RPR-3500A or RPR-3000A lamps.

Materials

Dextran, M = 10 000 g/mol, 98% (DX), 9-chloromethylanthracene, 98% (9CMA), 9-methylanthracene, 99% (9MA), perylene, 99% (Pe), all from Aldrich, Milwaukee, USA were used as received. 4,4′-Bipyridinium-1,1′-bis(trimethylenesulfonate) (SPV) was prepared according to procedure described in literature.[7]

Synthesis of Anthracene Substituted Dextran (DXA)

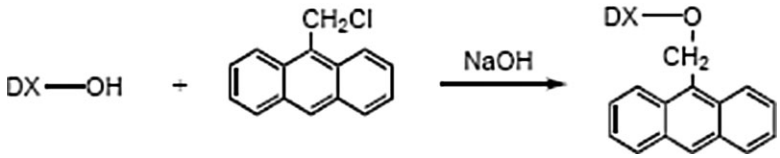
A series of DXA polymers characterized by different content of anthracene were synthesized. The polymers were obtained in a two phase etherification reaction between DX and 9CMA (Scheme 1):

The detailed information on procedures of synthesis, purification and characterization was given elsewhere.[3]

Results and Discussion

A series of dextran substituted with anthracene chromophores (DXA) (with degree of substitution, DS, of 0.2–6.5%) was obtained and studied. All polymers were soluble in DMSO. They were also soluble in water when the degree of substitution was lower than 3. Thus we have used in further studies mainly the polymers of the degree of substitution DS $\leq$ 2.5. Comparison of the GPC traces for starting material and for DXA recorded using simultaneously RI and UV ($\lambda = 375$ nm absorption maximum for anthracene (An)) detectors, confirmed that An is indeed attached to the polymer chain. It has been demonstrated that the attachment of An to the dextran chain does not influence considerably the photophysical properties of the chromophores. The absorption and emission spectra of DXA in aqueous solution display the bands characteristic of An chromophores (see Figure 1A and 1B). They are red-shifted in comparison with model compound 9MA which reflects the difference in the environment experienced by the chromophores. What is important, the vibronic structure of the spectra, characteristic of anthracene chromophores, is preserved. The emission, excitation and synchronous spectra (data not shown) recorded for the polymers indicated that there is no considerable aggregation of chromophores or formation of excimers which would lower the photosensitizing activity of the DXA sensitizers. It is important that DXA polymers absorb light from the visible spectral region.

Taking into account the well known behavior of the amphiphilic polymers in water one could expect that DXA polymer chain adopts a compact conformation in



Scheme 1.
Substitution reaction of dextran with anthracene chromophores.

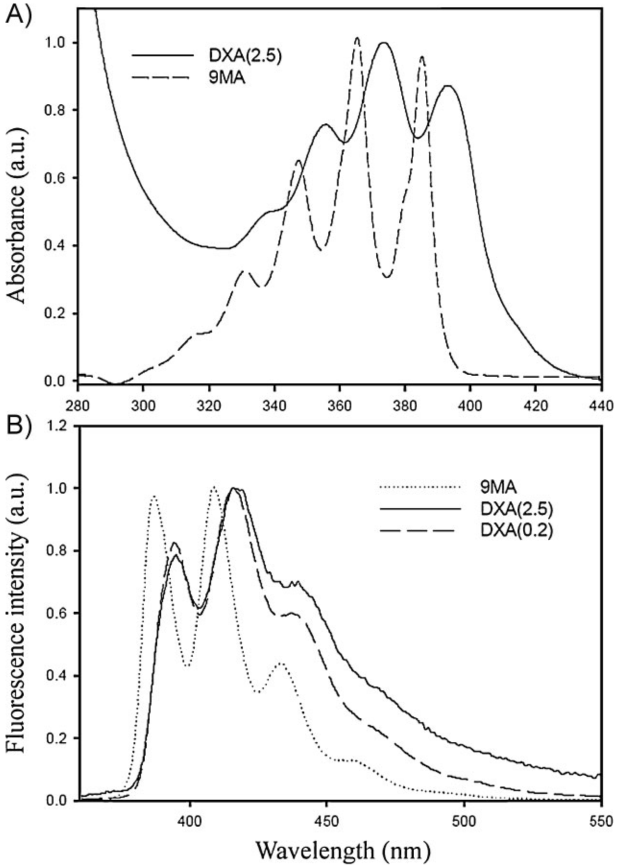


Figure 1.

A) Normalized electronic absorption spectra of 9MA in methanol and DXA(2.5) in aqueous solution; B) Normalized steady-state emission spectra for DXA(2.5) and DXA(0.2) in aqueous solutions and 9MA in methanol.

aqueous solution. Large hydrophobic anthracene chromophores cluster together and form hydrophobic nanodomains surrounded by the segments of dextran chain providing them protection from contact with water and improving the solubility of polymer in water. That is evidenced by the observation of solubilization of large hydrophobic molecules in the aqueous solutions of DXA. We have demonstrated that using perylene as a molecular probe. Perylene is useful for these studies as its solubility in water is extremely low ($\sim 10^{-9}$ M). Additionally, it aggregates in water and the aggregates do not display fluorescence. In hydrophobic medium perylene fluorescence is very strong (the quantum yield ~ 0.9). Thus, a very sensitive fluorescence technique can be used to determine the concentration of perylene in the system. Based on experimental results and using a simple two-phase model,[8] we have determined the distribution coefficient for perylene, K, defined as a ratio of the molar fraction of Pe present in polymer pseudophase to the molar fraction of perylene in water (Equation 1):

$$K = w_p / w_{aq} \qquad (1)$$

where w_p is the molar fraction of probe in the polymer pseudo-phase and w_{aq} is the molar fraction of probe in the aqueous phase.

The values of the distribution coefficient are high and they are a function of the content of An chromophores present in polymer and they are growing with increase in DS. For example, for DXA(2.5) the K value was found to be equal to $(1.88 \pm 0.20) \times 10^7$. The high hydrophobicity of these domains, comparable with that of toluene, was confirmed using pyrene as a molecular probe and measuring its emission spectrum (more specifically the ratio of the vibronic bands I to III which strongly depends on polarity of the medium, increasing while polarity is increasing). Fluorescence anisotropy measurements for solubilized perylene or rhodamine B indicated that the microviscosity of the polymeric microdomains is quite high; the microviscosity is close to that of glycerol at 25 °C. Based on the above mentioned experiments one can visualize that the DXA dissolved in water exists in a form of photo-nanoreactors with hydrophobic interiors (in which hydrophobic molecules can be solubilized) dispersed in aqueous phase. How do they work as photosensitizers? In order to answer that question the photophysical and photochemical properties of the DXAs were determined.

Photophysical/Photochemical Activity of DXA

Steady-state fluorescence polarization measurements performed for Pe solubilized in aqueous solution of DXAs indicated significant depolarization of emission of the Pe emission when excited indirectly (by energy transfer from An, $\lambda_{ex} = 345$ nm). That suggests that energy migration between An chromophores occurred in the polymers prior to the energy transfer to Pe. The energy transfer from the An chromophores to Pe was confirmed by observation of decrease of emission intensity in aqueous solution of DXA in the presence of Pe at very low concentration (see Figure 2).

The quenching process could be described by the Stern-Volmer kinetic equation (see Equation 2):

$$I_0/I = 1 + k_q \tau [Q] \qquad (2)$$

where: I_0 and I are the fluorescence intensities in DXA in the absence and in the presence of Pe, respectively, τ is the lifetime of the energy donor species (anthracene chromophores in DXA), and [Q] is a concentration of Pe.

From the slope of the Stern-Volmer plot (Figure 3), and using experimentally

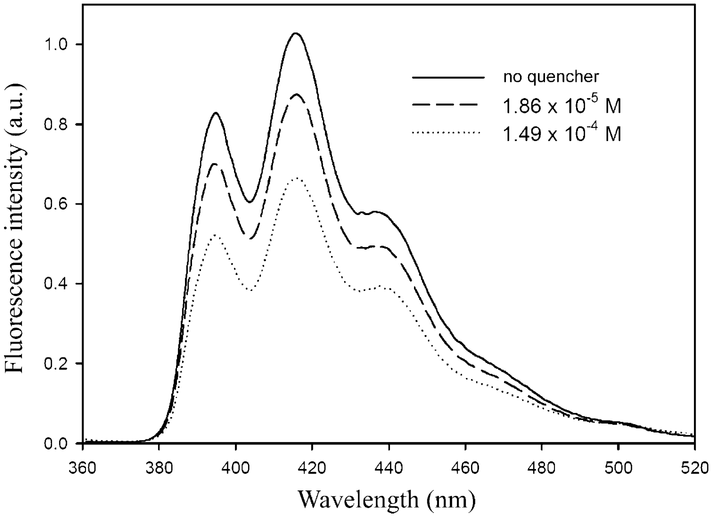


Figure 2.
Steady-state fluorescence spectra of DXA(2.5) in aqueous solution ($c_P = 0.1$ g/L) in the absence and in the presence of perylene.

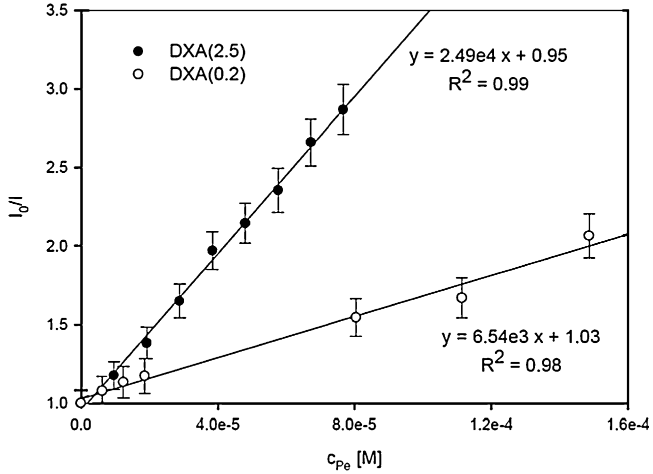


Figure 3.
Stern-Volmer plots for quenching of DXA in aqueous solution with Pe, $c_{DXA} = 1$g/L.

determined value of 6.9 ns for the lifetime of An chromophores in DXA the rates constant for the energy transfer from the An to Pe chromophores were calculated. They are equal to $(4.09 \pm 0.02) \times 10^{12}$ M^{-1} s^{-1} and $(1.07 \pm 0.01) \times 10^{12}$ M^{-1} s^{-1} for the higher substituted polymer, DXA(2.5) and lower substituted one, DXA(0.5), respectively. Similar values were obtained from the Stern-Volmer equation fitted to the experimental data obtained by measurements of the An fluorescence lifetimes as a function of Pe concentration. That confirms that there is no static quenching between these chromophores. High values of k_q, exceeding the values expected for a diffusion controlled process, suggest that the long-range resonance (Förster) type mechanism is involved in An-Pe energy transfer in aqueous solutions of DXA containing solubilized Pe. The radius of interaction (R_0) for the pair An-Pe calculated from the Förster equation is quite large, $R_0 = 43 \pm 0.4$ Å.[9] Differences in the k_q values obtained for DXA polymers of different degree of substitution confirms that the Pe is solubilized in nanodomains formed by An chromophores. Their structure and properties strongly depend on the number of An units involved in their formation.

The quantum efficiency of energy transfer (χ) was determined from the experimental data using the well known equation (Equation 3):[10]

$$\chi = 1 - I_a/I_0 \qquad (3)$$

where I_0 and I_a are the fluorescence intensities in the absence and in the presence of energy acceptor, respectively.

The values of quantum efficiency of energy transfer was found to be 0.50 ± 0.05. Such a high value of energy transfer can be explained considering the high thermodynamic feasibility for singlet-singlet energy transfer between An and Pe (energies of excited singlet states: E_S (An) = 3.31 eV, E_S (Pe) = 2.9 eV)[11] as well as proximity of the molecules (Pe is solubilized inside the microdomains formed by An chromophores).

It was observed that the addition of viologen (SPV) to the aqueous solution of DXA leads to the efficient quenching of An fluorescence. The process was explained considering the photoinduced electron transfer from excited An to SPV (the energy transfer is excluded due to the energy levels of the compounds; E_S (An) = 3.31 eV,[11] E_S (SPV) = 4.8 eV, as determined experimentally). The driving force (ΔG^0) for photoinduced electron transfer was determined using a Rehm-Weller equation (Equation 4):[12]

$$\Delta G^0 = E_D^{ox}(An) - E_A^{red}(SPV) - E^* - C \quad (4)$$

where $E_D^{ox}(An)$ is the oxidation potential of the donor (An), $E_A^{red}(SPV)$ is the reduction potential of the acceptor (SPV), E^* is the energy of electronically excited singlet state of the donor (An), and C is an electrostatic term.

The value of ΔG^0 for the pair An-SPV was found to be −1.88 eV, indicating that the process is highly thermodynamically favorable. The occurrence of that process was confirmed by observation of the characteristic blue color of the DXA + SPV SPV solution irradiated with the light absorbed selectively by An ($\lambda = 365$ nm) indicating formation of semi-reduced $SPV^{\bullet -}$. The reaction was followed by the measurements of the characteristic absorption spectrum of $SPV^{\bullet -}$ with the maxima at 395 and 600 nm and confirmed the efficient charge separation in the system, which can be explained considering that An chromophores reside in polymeric microphase while SPV molecules preferentially in water.

The above mentioned experiments confirmed that DXA polymers could potentially act as efficient photosensitizers both via energy and electron transfer to the suitable energy/electron acceptors.

Application of DXA

While searching for possible practical applications of DXAs, their ability to sensitize two types of processes, i.e. oxidation of perylene (a representative of polynuclear aromatics) and degradation of Parathion ethyl (PTE) (a representative of pesticides), was studied. Both groups of the compounds, polynuclear aromatics and pesticides are among the most dangerous pollutants of environment, especially water.

It was found that irradiation of the aqueous solutions of DXA containing solubilized Pe and saturated with oxygen with light at $\lambda = 365$ nm, absorbed exclusively by the anthracene chromophores, leads to oxidation of Pe with formation of perylenequinones (PQ), as shown schematically in Scheme 2 below:

The process could be easily followed by the fluorescence measurements as the highly fluorescent Pe was transformed to non-fluorescent products. The kinetics of the photosensitized oxidation of Pe could be fitted to the pseudo-first order kinetic equation (see Figure 4).

Based on the experimental results and literature data the following mechanism of Pe oxidation was proposed:

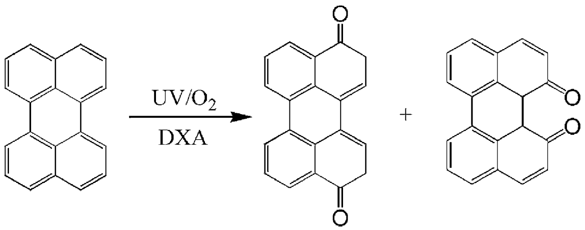
$$An^* + Pe \rightarrow An + Pe^*$$

$$Pe^* + An \rightarrow Pe^{*+} + An^{*-}$$

$$An^{*-} + O_2 \rightarrow An + O_2^{*-}$$

$$Pe^{*+} + O_2^{*-}(\text{or } O_2) \rightarrow Pe\ oxidation\ products$$

The first step involves energy transfer from the An chromophores to solubilized Pe molecules. That is followed by photoinduced electron transfer from the electronically excited Pe to An chromophores, as suggested earlier.[13] The process is thermodynamically possible because the value of



Scheme 2.
Photosensitized oxidation of perylene.

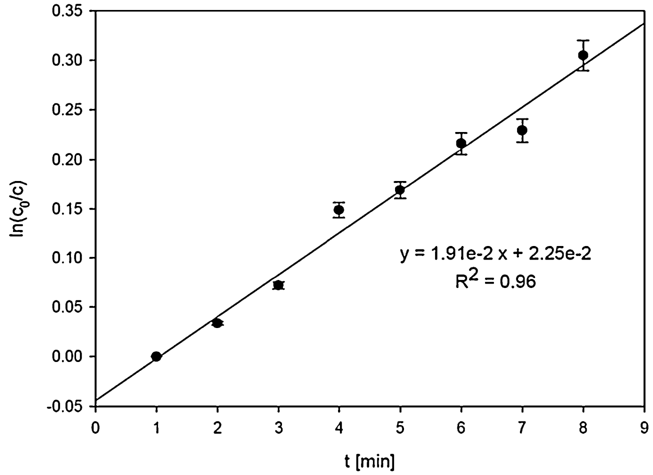


Figure 4.
Kinetics of Pe oxidation in aqueous solution photosensitized by DXA(2.5) ($c_{DXA} = 0.1$ g/L, $c_0 = 2.66 \cdot 10^{-6}$ M, $\lambda_{irr} = 365$ nm) fitted to the pseudo-first order kinetic equation.

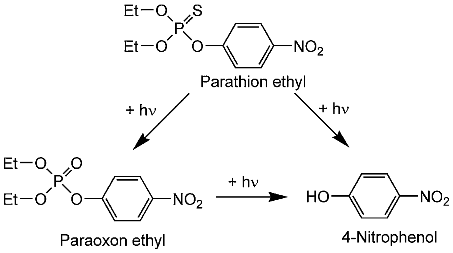
$\Delta G^0 = -0.39$ eV as was calculated using a Rehm-Weller equation (Equation 4) and substituting: $E_D^{ox}(Pe) = 0.85$ eV[13], $E_A^{red}(An) = -1.76$ eV,[14] $E^*(Pe) = 2.9$[9] eV and $C = 0.1$ eV. The An and Pe radical-ions undergo secondary reactions with participation of oxygen, finally leading to the formation of PQ. PQ are considerably less dangerous for the environment as they can be eliminated by photodegradation and biodegradation.[15] In the next step the photosensitized degradation of Parathion ethyl (PTE), a well known pesticide, was studied. It was found that irradiation of aqueous solution of DXA containing PTE with light at 365 nm (absorbed only by the anthracene chromophores) leads to the degradation of pesticide. The mechanism of that photosensitized degradation process is different than that for degradation of PTE induced by direct excitation with light absorbed by that compound ($\lambda = 280$ nm). The final product of the reaction initiated by direct excitation is 4-nitrophenol (NP), compound characterized by high stability and high toxicity (see Scheme 3).

That compound is also formed in the photosensitized reaction but it is only an intermediate product and it is degraded when the irradiation is prolonged resulting in its complete mineralization. Photoinduced electron transfer from electronically excited anthracene chromophores to PTE was postulated as a primary photophysical step in photosensitized reaction:

$$An^* + PTE \rightarrow An^{\bullet +} + PTE^{\bullet -}$$

The process is thermodynamically feasible, $\Delta G^0 = -1.58$ eV (calculated from the Rehm-Weller equation (Equation 4), where $E_D^{ox}(An) = 1.16$ eV,[16] $E_A^{red}(PTE) = -0.67$ eV,[17] $E^*(An) = 3.31$ eV[11] and $C = 0.1$ eV).

The charge separation is effective due to the physical separation of electron donor and electron acceptor, which are in two different phases (anthracene in polymeric



Scheme 3.
The mechanism of photodegradation of PTE pesticide (irradiation with light at $\lambda = 280$ nm).

microdomains and PTE in water).

$$An^{*} + PTE \rightarrow An^{*+} + PTE^{*-}$$

$$PTE^{*-} + O_2 \rightarrow PTE\ oxidation\ products$$

$$PTE^{*-} + O_2 \rightarrow PTE + O_2^{*-}$$

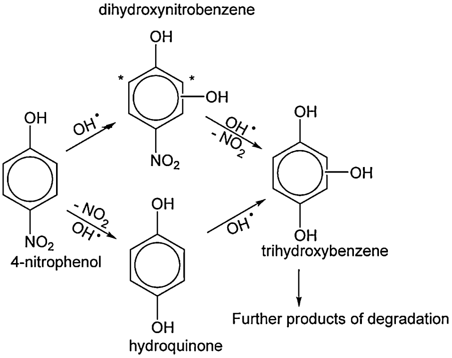
$$An^{*+}(An) + O_2^{*-}(or\ O_2) \rightarrow An\ oxidation\ products$$

As was already mentioned NP is one of the PTE oxidation products. It was, however, observed that irradiation of NP solubilized in aqueous solution of DXA saturated with oxygen leads to its degradation. The mechanistic studies of that process revealed that the reaction is initiated by photoinduced electron transfer from the excited An chromophores to the NP. The value of free energy (ΔG^0) for the process:

$$An^{*} + NP \rightarrow An^{\bullet +} + NP^{\bullet -}$$

calculated from the Rehm-Weller equation (Equation 4), based on literature values of the oxidation potential of the donor ($E_D^{ox}(An) = 1.16$ eV[16]) and the reduction potential of the acceptor ($E_A^{red}(NP) = -0.86$ eV[18]) was found to be equal to -1.39 eV.

Based on our experimental results and literature data one can suggest the following scheme for degradation of NP in the presence of DXA photosensitizers (Scheme 4):



Scheme 4.
Photosensitized degradation of NP

Thus, one may conclude that the DXA photosensitized degradation of PTE pesticide in aqueous solution leads to its total mineralization.

Degradation of DXA

One of the most important aspect of using the photosensitizers based on natural polymers was their degradability. We have found that our modified polysaccharides

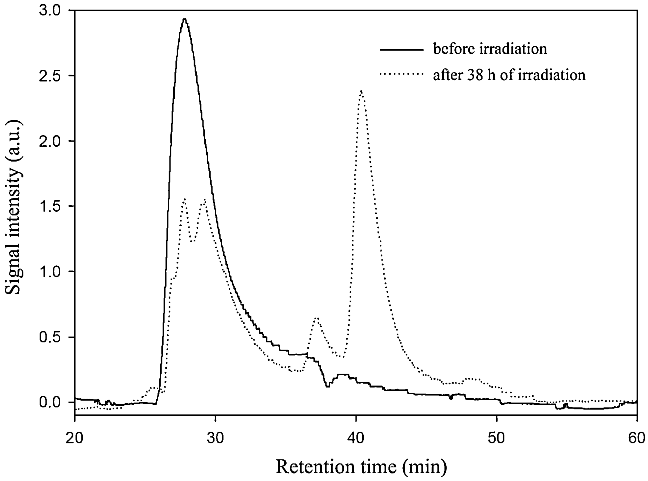


Figure 5.
GPC traces of polymeric photosensitizers studies before and after irradiation with 300 nm UV light.

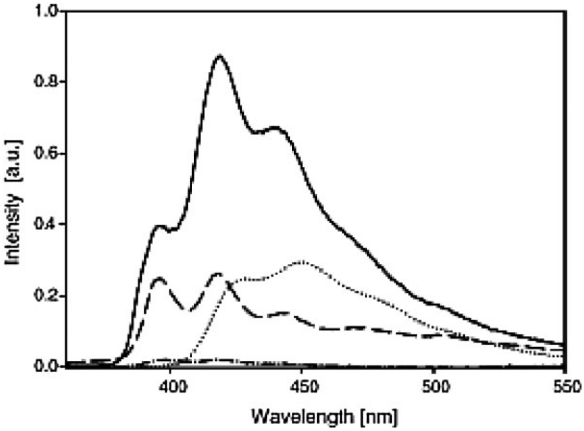


Figure 6.
Emission spectra of DXA before (—) and after irradiation with light $\lambda_{irr} = 350$ nm (-.-.-), after reduction with isopropanol (- - -) and the emission spectrum of 9-hydroxyanthracene in isopropanol solution) (……).

are degradable. Firstly, they undergo photodegradation. The prolonged irradiation of DXAs in their aqueous solutions leads to the chain scission as detected by GPC (Figure 5) and to (photo)oxidation of anthracene chromophores (Figure 6). The biodegradability of the photosensitizers was monitored using a Zahn-Wellens test. The studies were performed using a microflora of the active sludge obtained from a sewage treatment plant. It was found that the DXA undergoes biodegradation, although the rate of the process is somewhat slower than that for a virgin dextran.

Conclusion

Novel dextran-based photosensitizers were prepared to sensitize reactions of various organic compounds in water with the use of light from the visible spectral region. The sensitizers contained various amounts of anthracene chromophores. It was found that they are active even when the content of chromophores is very low. The photosensitizer chains adopt a compact conformation in aqueous solution which allows solubilization of large hydrophobic molecules and facilitates processes of energy migration/transfer as well as electron transfer. The sensitizers can find practical applications in purification of water from the toxic compounds such as PNA and pesticides. What is important, the DXAs can be degraded in aqueous solution after usage.

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