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# Energy and Electron Transfers in Photosensitive Chitosan

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Polymer materials that have specific properties such as photo-activity, in particular the ability to participate in energy or electron transfer processes, have become increasingly important in recent years.[1] Thus far, most of the studies have been carried out with synthetic polymers.[2-4] However, there is a growing interest in natural polymers for practical applications, in particular in bio-technology and environmental protection.[5-7] A unique feature of natural polymers compared with synthetic ones is their ability to undergo biodegradation.[8,9] Among various natural polymers, one of the most obvious choices for these applications is polysaccharide, the most abundant polymer in the biosphere.

Chitosan, a fully or partially deacetylated product of its parent polysaccharide chitin, has attracted significant interest in the broad range of scientific research, including biomedical, agriculture, and environmental protection fields, because of its biodegradability, biocompatibility, and bioactivities.[10-12] Chitosan is hydrophilic; a large number of its hydroxyl and amino groups provide the sites for numerous attractive chemical modifications.[11-15] Photosensitive natural polymers (e.g., natural polymers containing various chromophores) for photodecomposition of various toxins have been gaining attention recently.[16,17] In this study, we synthesize a novel photosensitive polymer based on chitosan (anthracene chromophore containing chitosan). The anthracene moieties play the role of photosensitizer. Because of the presence of anthracene chromophores, the polymer absorbs light from the UV−vis spectral region. Electronically excited polymeric chromophores participated in energy and electron transfer processes to the molecules of suitable acceptors. The photosensitive chitosan developed herein could lead to the application of the environmentally friendly photocatalytic system operating with visible light to conduct an efficient degradation of a wide range of pollutants.

Under acidic conditions (in a homogeneous solution of methanesulfonic acid in this experiment), the amino groups are protonated, and this is disadvantageous for the nucleophilic displacement reaction. Hence, the substitution is supposed to happen preferentially onto the hydroxyl groups (see Scheme 1). This has been confirmed by FTIR, $^1$H NMR, and $^{13}$C NMR spectra.

**Scheme 1.** Synthesis of Photosensitive Chitosan
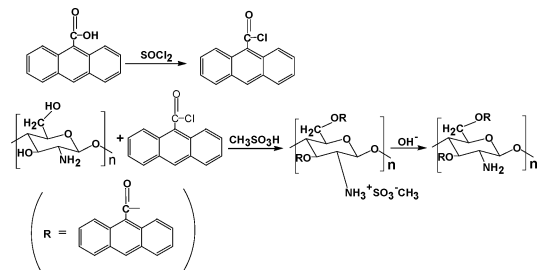


In the IR spectrum of the anthracene-containing chitosan, a strong absorption band around 1715 cm$^{-1}$ can be observed, which can be attributed to the ester carbonyl group, and the bands at about 3080
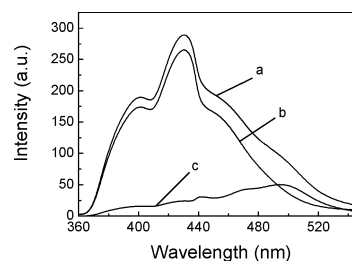


**Figure 1.** Emission spectra of the modified chitosan and anthracene-9-carboxylic acid. Curve a: modified chitosan; curve b: anthracene-9-carboxylic acid; curve c: difference spectrum; $\lambda_{ex}$ = 350 nm.

and 910 cm$^{-1}$ are associated with the aromatic ring. An enhancement of the bands around 1240 cm$^{-1}$ (C−O) and 1110 and 1050 cm$^{-1}$ (C−O−C) can be observed from the comparison of the IR spectra of the modified chitosan and the starting material chitosan. The IR spectrum of anthracene-containing chitosan also exhibits an amino absorption band around 1600 cm$^{-1}$, but no amide absorption can be observed. These results indicate that the anthracene moieties are introduced onto the positions of the hydroxyl groups of chitosan, and substitution does not happen to the amino groups of chitosan. $^1$H NMR spectrum exhibited the signals in the range of 7−9 ppm, assigned to the aromatic protons of anthracene moieties. The $^{13}$C NMR (deuterated DMSO) spectrum of the polymer shows resonance signals at chemical shift 122−135 ppm associated with the carbons on the aromatic ring. The signal around 167 ppm is attributed to the carbonyl group (C=O). These results again confirm that sutstitution happens to the hydroxyl groups on the glucosamine unit of chitosan.

To further investigate the microscopic structure of the polymer, fluorescence emission spectra were measured. Figure 1 shows the emission spectra of the polymer and anthracene-9-carboxylic acid in DMSO and 30 wt % water (polymer: 1 × 10$^{-6}$ g/g). By comparing the emission spectra, one might conclude that the fluorescence of polymeric chromophores is dominated by the monomer emission (around 430 nm) with small contribution of excimer emission around 500 nm.

The pendatnt chromophore groups along the polymer chain may interact with one another to form a stable ground-state dimer (static excimer) or a dynamic excimer or both. The former originates from the aggregation of chromophores, and the latter arises from the interaction of an excited chromophore and a ground-state one. Usually, a static excimer shows a red-shift excitation spectrum, while a dynamic excimer has the same excitation spectrum as that of the monomer emission.[18] The excitation spectrum monitored at $\lambda_{em}$ = 500 nm gave almost the same results as that monitored by the monomer emission at $\lambda_{em}$ = 430 nm. Therefore, the absence of an aggregate of the ground-state dimer was confirmed, and the emission at 500 nm is attributed to the excimer emission between an excited chromophore group and a ground-state one.

The ability of anthracene-containing chitosan to participate in the energy transfer process was investigated by using perylene (PE)
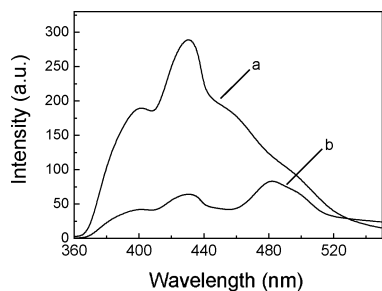
**Figure 2.** Fluorescence emission of the chromophore-containing chitosan before and after the addition of perylene. Curve a: emission without addition of perylene; curve b: emission in the presence of perylene; $\lambda_{ex}$ = 350 nm.



**Figure 3.** UV−vis absorption spectra of the chromophore-containing chitosan in the presence of $MV^{2+}$ as a function of irradiation time: Curve a: 200 s; curve b: 100 s; curve c: 0 s.

as the energy acceptor because of the thermodynamic feasibility for the singlet−singlet energy transfer, and the energies of excited singlet states of anthracene (AN) and PE are as follows: $E_s$(AN) = 3.31 eV, $E_s$(PE) = 2.9 eV.[19] Figure 2 shows the fluorescence emission of the chromophore-containing chitosan before and after the addition of perylene. The fluorescence of the chromophore-containing chitosan was efficiently quenched by the addition of perylene into the solution (PE concentration = $5 \times 10^{-8}$ M), and the emission of the energy acceptor (PE) appeared in the region of 460−520 nm. This indicates that the energy transfer occurs from anthracene moieties to the energy acceptor PE. Thus, the chromophore-containing chitosan could act as efficient photosensitizer.

To investigate the ability of the chromophore-containing chitosan to participate in the electron-transfer process, methyl viologen dichloride ($MV^{2+}$) was used as the electron acceptor. The excitation spectra recorded for this system indicated that the ground electronic states AN and $MV^{2+}$ did not form any complex, since the excitation spectra for the polymer system with and without $MV^{2+}$ show almost the same results. The fluorescence emission is quenched in the presence of $MV^{2+}$. The energy transfer from AN to $MV^{2+}$ is unfavorable because of the difference between energy levels of the molecules. The energy of the excited singlet states of $MV^{2+}$ and AN were 4.8 and 3.31 eV, respectively.[19] The energies were estimated based on absorption spectra. Hence, the quenching of fluorescence emission could be the result of possible electron transfer from the singlet excited state of AN to $MV^{2+}$. This electron transfer process could be described as follows: AN + $MV^{2+}$ → $AN^{\bullet+}$ + $MV^{\bullet+}$. $MV^{\bullet+}$ shows characteristic maximum absorption around 400 and 600 nm.[20,21] Figure 3 shows the UV−vis absorption spectra of the chromophore-containing chitosan in the presence of $MV^{2+}$ as a function of irradiation time (modified chitosan and $MV^{2+}$ concentration: $5 \times 10^{-4}$ g/g). As the time of irradiation ($\lambda$ = 360 nm) increases, the polymer system's absorption at 400 and 600 nm increases, and this indicates that the electron transfer process proceeds continuously. The experimental results indicate that the energy and electron transfers could occur from the polymeric chromophores to suitable acceptor molecules, and these energy and electron transfer processes could be used to induce photochemical reactions of organic compounds. Hence, the anthracene-containing chitosan could act as a promising photosensitizer for the reaction of organic compounds and has the potential in the applications of
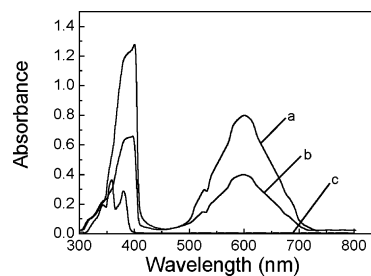
the environmentally friendly photocatalytic system for efficient degradation of a wide range of pollutants.

**Supporting Information Available:** Experimental section, FTIR spectra, ^{1}H NMR spectrum, ^{13}C NMR spectrum, UV−vis spectrum, the fluorescence excitation spectra, and the fluorescence emission spectra for the polymer system with and without $MV^{2+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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