



Novel hybrid photosensitizers: Photoactive polymer–nanoclay

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ABSTRACT

A new type of hybrid photosensitizers was obtained by efficient adsorption of a photoactive polymer by an organically modified nanoclay. The polymer bore naphthyl and rose bengal chromophores, which absorbed light both in the ultraviolet and visible spectral region. Adsorption of the polymer on nanoclay prevented aggregation of chromophores. The obtained hybrid photosensitizer efficiently adsorbs hydrophobic compounds. It was also found to be an efficient photosensitizer in singlet oxygen generation. The hybrid photosensitizers combine the advantages of both component systems, i.e. possibility to attach a wide range of chromophores to the polymeric chain and resulting ability to photosensitize reactions, on one hand, and the ability to adsorb hydrophobic pollutants and easy separation from water characteristic of nanoclays, on the other.

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1. Introduction

The hybrid polymer–clay materials (polymer–clay nanocomposites, PCNs) have been known for more than two decades. The first material of this type was Nylon-6/montmorillonite and was first obtained in 1986 [1]. It was found that the addition of even very little amount of the clay to the polymer resulted in a significant improvement of polymer mechanical properties [2], heat resistance [3], and increased biodegradability [4]. The clays usually used to obtain PCNs are layered aluminosilicates. The examples of this type of clay are montmorillonite, bentonite, hectorite, and saponite. The layers in these clays are 1 nm wide while their lateral dimensions vary from 30 nm to several microns. The layers show ability to form stacked structures which can be broken (exfoliated). The gaps between the layers (galleries) are filled with water and cations which can be easily exchanged with organic cations and the materials obtained this way are called organoclays [5]. The remarkable consequence of the layered structure of the nanoclays is that the galleries can be intercalated by polymeric chains. However, while pristine clays can be intercalated only with hydrophilic polymers, organoclays may be intercalated also with hydrophobic polymers. Organoclays have found widespread applications. To date nanoclays have been used mainly as adsorbents or to modify or improve the properties of the polymers used as structural materials. This paper is, to our best knowledge, the first report on polymer–nanoclay hybrid materials in which the macromolecular

component of the hybrid material is a polymeric photosensitizer. Polymeric photosensitizers, i.e. polymers bearing chromophores able of photosensitizing useful reactions, have been intensively studied in our group for several years [6–12]. Water-soluble polymeric photosensitizers based on biodegradable natural polymers have been recently of our particular interest due to their potential application for the photodegradation of the pollutants in environmental conditions [6–10]. However, in some cases the polymeric photosensitizer, even nontoxic one, remaining in water after its purification, would be not acceptable. Hybrid polymer–nanoclay photosensitizers are a solution to the problem of the photosensitizer removal from water.

Organically modified nanoclays are excellent adsorbents, therefore many hydrophobic pollutants can be effectively removed from water by adsorption on the nanoclays [13]. However, this method does not actually detoxify the pollutants and a problem of the disposal of the organoclay containing adsorbed pollutant arises instead. Although methods of recovery of spent organoclays have been developed, including biological or photochemical degradation, chemical extraction/desorption, supercritical extraction, and thermal desorption [14], the problem of the pollutant disposal and detoxification remains. Since the hybrid photosensitizers described in this paper induce photodegradation of the adsorbed pollutants, they may provide a solution also to this problem.

Similar systems based on organoclays and low-molecular weight photosensitizers have been already developed [15,16]. However, metal-containing chromophores have been used to obtain them which may be of environmental concern. Moreover, the range of low-molecular chromophores which are able to intercalate into the nanoclays is limited while the application of a proper polymer as a chromophore carrier, which can be easily adsorbed by

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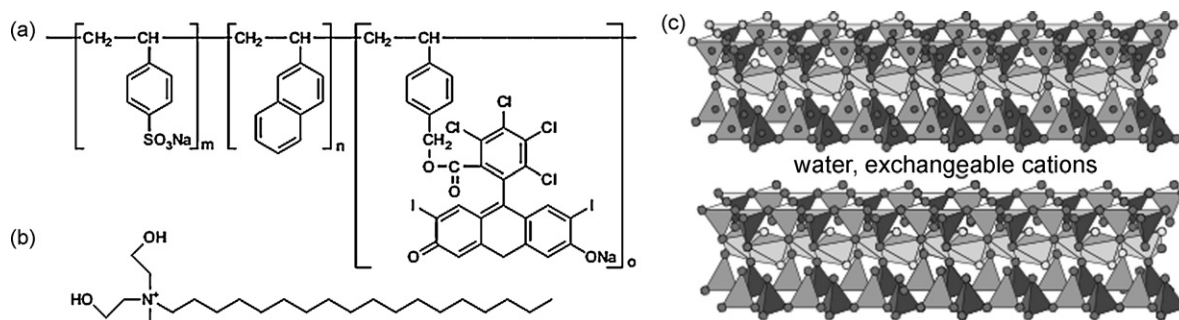


Fig. 1. The structure of (a) the polymeric photosensitizer (SNpRB), (b) ammonium surfactant intercalating C30B galleries, and (c) lamellar structure of montmorillonite—a lamella composed of two layers of tetrahedral silica sandwiching one layer of octahedral alumina.

the nanoclay, allows application of a much wider range of photosensitizing chromophores.

2. Experimental

2.1. Materials

Cloisite® 30B was a gift from Southern Clay Products, Inc., dimethyl sulfoxide (DMSO, Caledon, ACS reagent grade), methanol (analytical grade, Lach-Ner), 1-butanol (Caledon, reagent grade), tetrahydrofuran (THF, Caledon, glass distilled), calcium hydride (90–95%, Aldrich), sodium bicarbonate (analytical grade, POCh Gliwice), sodium carbonate (analytical grade, POCh Gliwice), phenol (pure, POCh Gliwice), and pentachlorophenol (PCP, 99%, Aldrich) were used as received. 2-vinylnaphthalene (2-VN, Aldrich) was purified by absorption chromatography using cyclohexane and alumina. Sodium styrenesulfonate (SSS, Monomer-Polymer & Dajac) was purified by three recrystallizations from a 9:1 (v/v) mixture of methanol and water, followed by two recrystallizations from pure methanol. Vinylbenzylchloride (VBC, Monomer-Polymer & Dajac) was washed three times with 2% NaOH and four times with distilled water. The monomers were dried over anhydrous CaCl_2 , and were distilled under reduced pressure before use. Rose bengal (RB, Aldrich, certified grade) was used as received. 1,3-Diphenylisobenzofuran (DPBF, Aldrich, Milwaukee, USA) was purified by recrystallizing three times from benzene in the dark. Anthracene-2-sulfonic acid, sodium salt (ANS), was prepared by reduction of anthraquinone-2-sulfonic acid, sodium salt (Aldrich), with Zn dust in the presence of NH_4OH . Benzoyl peroxide was purified by three recrystallizations from methanol.

2.2. Polymer synthesis (SNpRB)

The polymer was synthesized as described previously [17]. The composition of the polymer (mol%) obtained is as follows: SSS: 56.9, VN: 33.9, VBC: 2.23, RB: 0.97. M_w of the polymer (found using the sedimentation method) is 3.4×10^4 g/mol.

2.3. Synthesis of polymer–nanoclay hybrid photosensitizer

The example synthesis of the hybrid photosensitizer SNpRB-C30B was as follows. 2 mg of the polymer was dissolved in 10 ml of water and 150 mg of Cloisite 30B was added. The suspension was mixed in the dark for 5 days, centrifuged and washed with water until no polymer was detected in water used for washing by measuring its UV–Vis absorption spectrum.

2.4. Apparatus

The UV–Vis absorption spectra were recorded using a Hewlett-Packard HP 8452A diode-array spectrophotometer in 1-cm optical

path quartz cuvettes. The steady-state fluorescence spectra were recorded using a Perkin-Elmer LS-55 spectrofluorimeter in 1-cm optical path quartz cuvettes. Irradiations of the samples were performed using a 500 W xenon lamp. X-ray diffraction patterns of the samples were obtained with a Philips X'Pert APD diffractometer. HPLC analyses were performed using a Waters system equipped with a Waters 2996 PDA detector and a Symmetry C18 $5 \mu\text{m}$ ($4.6 \text{ mm} \times 150 \text{ mm}$) column. The eluent was 1:1 (v/v) mixture of water and acetonitrile containing 0.2 vol.% of acetic acid. The flow rate was 1.0 ml min^{-1} . A Malvern Nano ZS light scattering apparatus (Malvern Instrument Ltd., Worcestershire, UK) was used for dynamic light scattering (DLS) measurements.

3. Results and discussion

The hybrid photosensitizers studied are composed of a photoactive amphiphilic polymer and a nanoclay. The polymer used to obtain the hybrid photosensitizers is a terpolymer of sodium styrene sulfonate (SSS), 2-vinylnaphthalene (2-VN) and vinylbenzyl chloride (VBC). The rose bengal chromophores (RB) are attached to the VBC monomeric units [17] (Fig. 1a). The polymer containing 56.9 mol% of SSS, 39.9 mol% of 2-VN, 2.40 mol% of VBC, and 0.80 mol% of RB was used in the experiments.

The polymeric photosensitizer (hereafter referred to as SNpRB) contains a naphthalene chromophore which is responsible for the absorption of the light in the UV spectral region (a wide absorption shoulder at about 250–300 nm) and a rose bengal chromophore which absorbs the visible light (absorption maximum at about 540 nm) (Fig. 2). The polymer is therefore capable of absorbing in a wide range of solar light spectrum.

Both chromophores present in the polymer were found to be useful in photosensitizing reactions of practical interest. Polymers bearing the naphthyl chromophore are known to be efficient photosensitizers in electron-transfer-based photoreactions [9], including the dechlorination of chlorinated aromatic pollutants and oxidation of cyanides [10], and in energy-transfer-based photoreactions, e.g. isomerization of provitamin D_3 [18], while those bearing the

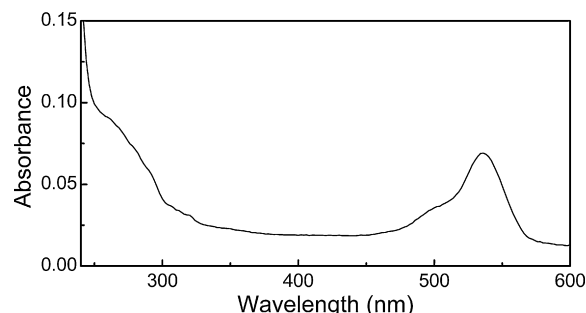


Fig. 2. UV–Vis absorption spectrum of SNpRB polymer in water ($c_{\text{pol}} = 5 \times 10^{-3}$ g/l).

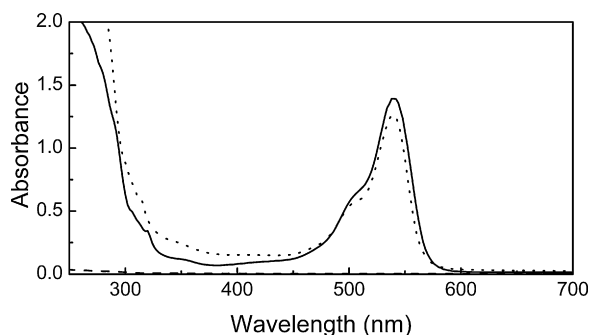


Fig. 3. UV-Vis absorption spectra of SNpRB in water ($c_0 = 0.12$ g/l) before (solid) and after addition of montmorillonite (dotted) and C30B (dashed). Concentration of clays is 0.1 g/l. The suspensions were stirred overnight and left for 1 h without mixing to sediment. The samples were filtered before the measurement.

rose bengal chromophore, a well-known singlet oxygen photosensitizer, may be applied in the photooxidation of phenols [11,12,19] and polycyclic aromatic compounds [8]. When considering the photophysics of this polymer it should be taken into account that both, naphthyl chromophore and rose bengal are efficient photosensitizers in singlet oxygen formation processes [20–22].

Moreover, naphthyl chromophore shows efficient intersystem crossing (quantum yield of 82% [23]) and the energy of its triplet level (255 kcal/mol) is much higher than that of rose bengal (164 kJ/mol) [23], thus a triplet–triplet energy transfer from the naphthyl chromophore to the rose bengal chromophore may follow the excitation of the naphthyl chromophore. The occurrence of the energy transfer in this polymer was indeed confirmed taking into account the comparatively high quantum yield of the oxidation of diphenylbenzofuran (DPBF), a well-known singlet oxygen scavenger [24], when naphthalene was excited [17]. It should be also pointed out that such a combination of chromophores makes it possible to utilize the energy from a wide spectral range to photosensitize various chemical processes. The polymer absorbs the light present in the solar spectrum which enables the SNpRB photosensitizer to be applied under environmental conditions.

The second component of the hybrid photosensitizers studied is Cloisite 30B® (hereafter referred to as C30B). This material, which is a layered nanoclay of the montmorillonite type organically modified with methyl tallow bis(2-hydroxyethyl) quaternary ammonium chloride (Fig. 1b) which intercalates between the clay lamellae (Fig. 1c). C30B was used as a support for the polymeric photosensitizer since it adsorbs SNpRB very quickly and efficiently, forming a hybrid photosensitizer, hereafter referred to as SNpRB-C30B. The adsorption process of the polymer by the nanoclay could be easily followed visually—the polymer is pink and the gradual discoloration of the polymer solution was observed when C30B was added, while the nanoclay turned pink. The amount of the polymeric photosensitizer adsorbed by C30B and by unmodified montmorillonite was compared by measuring the changes in the absorption spectra of the aqueous solution of SNpRB after addition of the same amount of C30B and unmodified clay (Fig. 3).

Montmorillonite K5, used as a model unmodified clay, adsorbed only about 9.5% of SNpRB within 10 days, while the addition of the same amount of C30B resulted in complete adsorption of the polymeric photosensitizer from the solution within 4 days. Thus, the adsorption of SNpRB by C30B could be ascribed solely to the hydrophobization of the nanoclay galleries by the surfactant.

It was checked if the adsorption of SNpRB did not result in the loss of the adsorptive properties of C30B relative to hydrophobic compounds of environmental interest. Therefore, the adsorption efficiency of pentachlorophenol (PCP), a model hydrophobic pollutant, of montmorillonite K5, C30B and SNpRB-C30B, was

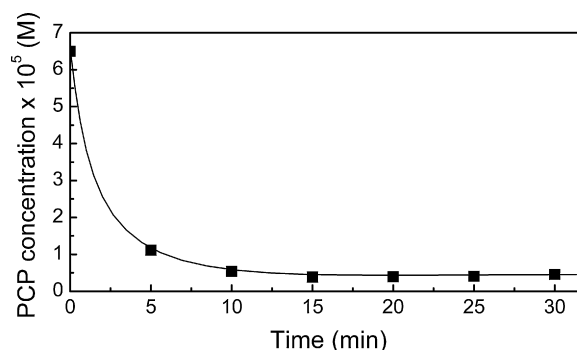


Fig. 4. Dependence of PCP concentration in water ($c_0 = 6.5 \times 10^{-5}$ M) on time after addition of 1.0 g/l C30B. PCP concentration was determined using HPLC system equipped with a UV-Vis absorption detector.

compared. Using HPLC analysis it was found that within 30 min 90% of PCP ($c_0 = 6.5 \times 10^{-5}$ M) was adsorbed by C30B, 37% by montmorillonite K5 and 66% by SNpRB-C30B. This indicates that the adsorptive capacity of the hybrid photosensitizer is lower than that of C30B, but still much higher than that of unmodified montmorillonite. Similar decrease of sorption capacity was observed when bentonite organically modified with cetyltrimethylammonium bromide (CTMA) was intercalated with aluminum phthalocyanine [16] and can be explained considering the saturation of the hydrophobic surfactant interlayer sites by the adsorbed polymer.

It was found that the adsorption process of PCP ($c_0 = 6.5 \times 10^{-5}$ M) by C30B (1.0 g/l) is complete within 15 min (Fig. 4). After that time 93% of PCP dissolved in water was adsorbed by the clay. The time dependence of PCP concentration (i.e. the rate and degree of adsorption) after addition of SNpRB-C30B was the same as for C30B (data not shown).

Considering the photosensitizing activity of the hybrid photosensitizer it is important to determine the location of the photoactive polymer and the adsorbed molecules of reactants. Thus, the first question which should be addressed is whether the polymer intercalates into the C30B galleries or it is adsorbed on the surface of nanoclay particles. One could expect that the polymer may intercalate into the galleries since it is an area where surfactant molecules are primarily located. There are, however, some reports that the surfactant may be also adsorbed onto the surface of the clay [25]. To solve that problem, the X-ray diffractograms of C30B before and after adsorption of SNpRB were obtained (Fig. 5). It was observed that they differ very little. The interlayer spacing for C30B was calculated to be 2.05 nm while for SNpRB-C30B, obtained by the adsorption of SNpRB in water, it was 2.10 nm.

At a first glance, such a small increase seems to exclude adsorption by intercalation of the polymer between the nanoclay galleries

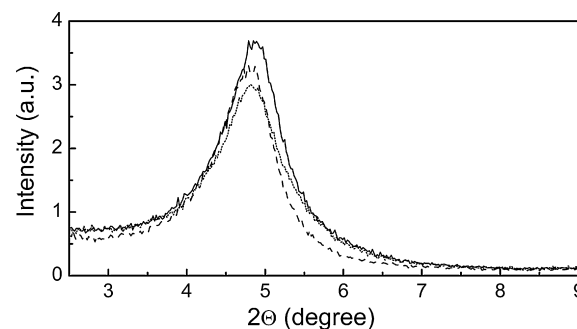


Fig. 5. X-ray diffractograms of C30B (solid) and SNpRB-C30B obtained from water (dashed) and methanol (dotted).

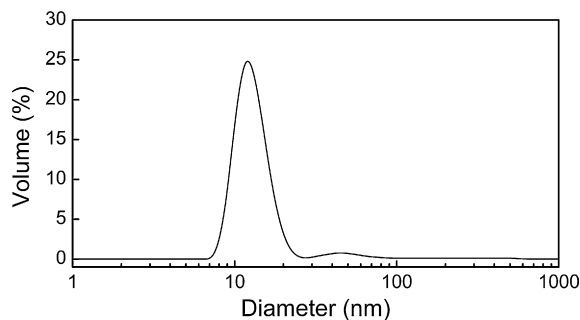


Fig. 6. The distribution of the aggregate size in the aqueous solution of SNpRB (1.0 g/l) obtained from the dynamic light scattering measurement. Ionic strength of NaCl added was 0.1.

and suggests adsorption of the polymer on the surface of the nanoclay packets. The adsorption of the polymer on the clay surface may be more probable than intercalation also due to the fact that in the aqueous solution the SNpRB polymer is expected to assume a compact pseudomicellar conformation with the diameter of micelles of the order of several nanometers, the behavior typical of the amphiphilic polyelectrolytes [26]. This assumption was confirmed by dynamic light scattering measurement (Fig. 6).

It has been shown that the size of the polymer aggregates in the aqueous solution is about 10 nm. The objects of this size are expected to be primarily unimolecular aggregates. Aggregates of that size are not able to intercalate unchanged into the galleries of montmorillonite. However, the small change in the interlayer spacing may be caused by the fact that the distance between galleries in C30B is already increased in comparison with that in unmodified montmorillonite, so the interlamellar volume may be large enough to accommodate the polymeric chains and therefore intercalation of the polymer, if occurs, may not result in considerable further increase of the spacing, provided the micelles may be disrupted in contact with the hydrophobized surface of the clay.

To find out which is the case, the material obtained by the adsorption of SNpRB by C30B in methanol solution was also prepared. In methanol, a good solvent for this polymer (both naphthalene and rose bengal are well-soluble in methanol), the polymeric chains are expected to assume random coil conformation which should enable their intercalation into the clay galleries. X-ray diffractogram of SNpRB-C30B with SNpRB adsorbed from methanol (Fig. 5) shows that the interlayer spacing is similar to that in water. This is an indication that polymeric chains dissolved in water intercalate into the galleries.

To get further insight into the structure of SNpRB-C30B the fluorescence measurements of SNpRB, both in the aqueous solution and adsorbed by C30B, were performed (Fig. 7). The fluorescence emission spectrum of SNpRB in water recorded using the light

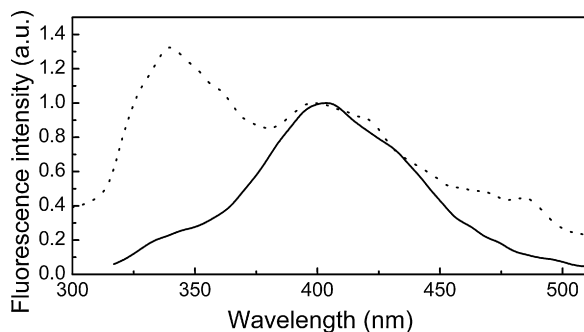


Fig. 7. The fluorescence emission of SNpRB in water ($c_{\text{pol}} = 5 \times 10^{-3}$ g/l, solid) and adsorbed by C30B (1.0 g/l, dashed) ($\lambda_{\text{ex}} = 297$ nm). The turbid samples of aqueous SNpRB-C30B suspension were mixed during measurement.

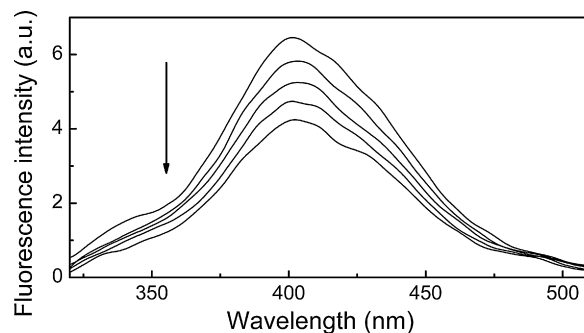


Fig. 8. Quenching of SNpRB emission ($\lambda_{\text{ex}} = 297$ nm) by 0, 2.2×10^{-5} , 4.0×10^{-5} , 6.0×10^{-5} , and 7.9×10^{-5} M PCP in water.

with the wavelength absorbed by the naphthyl chromophores ($\lambda_{\text{ex}} = 297$ nm) shows mainly excimer emission peaking at 402 nm and a very weak monomeric emission in the form of the shoulder at about 320 nm confirming that in the aqueous solution naphthalene chromophores are tightly packed inside the core of the aggregates. The spatial proximity of naphthalene chromophores within the aggregate cores results in the efficient excimer formation.

The respective spectrum of the turbid samples of SNpRB adsorbed within C30B (Fig. 7) is, however, very different. In this case the spectrum is dominated by the monomeric emission. This is an indication that the naphthalene chromophores have not enough rotational freedom to adopt a conformation necessary to form an excimer. This may result from the fact that the naphthyl chromophores are mostly located between the nanoclay layers and provides indirect indication, although still not conclusive, that the polymer undergoes intercalation into the galleries. It may be also expected that the efficiency of SNpRB-C30B in photosensitizing reactions via energy or electron transfer can be much higher compared to SNpRB in the aqueous solution due to much weaker tendency of the former to dissipate absorbed light energy by the excimer formation path.

Quenching of fluorescence of naphthalene chromophores was further studied using pentachlorophenol (PCP) as a quencher. It was found that in the aqueous solution of SNpRB PCP quenches both monomer and excimer emission of naphthalene (Fig. 8) with the same efficiency.

In the case of SNpRB-C30B, however, quenching is very efficient in the case of monomeric emission, while naphthyl excimer emission is almost unchanged (Fig. 9).

That may suggest that PCP is preferentially solubilized in the hydrophobic, spatially restricted areas of nanoclay galleries where excited naphthyl chromophores can emit only monomeric fluorescence. This is yet another indication that the polymer intercalates into the interlayer areas of the clay.

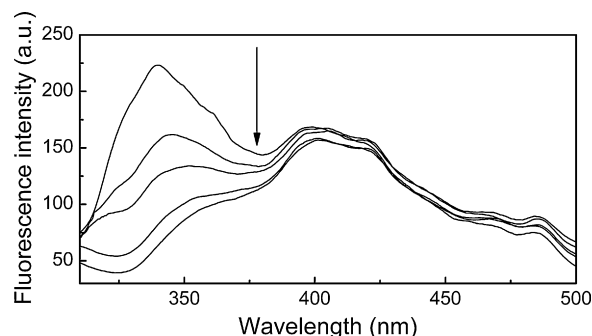


Fig. 9. Fluorescence quenching of SNpRB intercalated in C30B (1.0 g/l) by 0, 0.40×10^{-4} , 0.79×10^{-4} , 1.19×10^{-4} , and 1.57×10^{-4} M PCP ($\lambda_{\text{ex}} = 297$ nm).

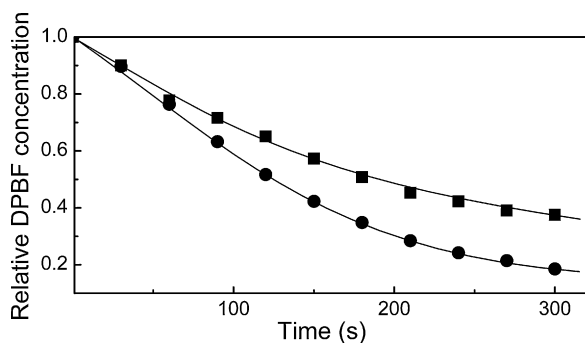


Fig. 10. The dependence of DPBF concentration ($c_0 = 1.0 \times 10^{-4}$ M) irradiated in methanol in the presence of SNpRB (1.0 g/l) dissolved in solution (●) or suspended SNpRB-C30B (■) (1.0 g/l, $\lambda_{\text{irr}} > 470$ nm). The concentration of DPBF was determined based on its UV-Vis absorption spectra.

The observation presented in Figs. 7–9 can be alternatively interpreted in terms of energy migration followed by trapping by excimer sites in SNpRB, which strongly depends on the compactness of a polymer chain. It has been demonstrated that the efficiencies of energy migration and trapping by excimer sites within the SNpRB polymer in aqueous solution are very high whereas they decrease when the polymer is hybridized with C30B. That can be explained considering the changes in the conformation of the polymer chain. In aqueous solution the polymer adopts a compact micelle-like conformation, which is favorable for the processes of energy migration and transfer occurring within the polymer chain. The observed decrease of their efficiency in the hybrid system suggests that the polymer assumes a loose conformation when intercalated with C30B.

To check whether singlet oxygen can be generated in the SNpRB-C30B system the model studies involving oxidation of DPBF as a singlet oxygen scavenger were carried out. The process was observed using homogenous SNpRB solution in methanol and suspension of SNpRB-C30B, both irradiated with light of $\lambda > 470$ nm, i.e. light absorbed by rose bengal chromophores and not absorbed by DPBF (Fig. 10). DPBF oxidation with singlet oxygen can be followed as a gradual decrease of its absorption band with a maximum at about 406 nm.

It was found that in both of these systems DPBF is efficiently oxidized, which confirms singlet oxygen formation. During 5 min of irradiation about 80% of DPBF was oxidized in SNpRB solution while 60% of DPBF was oxidized in SNpRB-C30B suspension. That high efficiency of the process suggests that the rose bengal chromophores present in the hybrid experience rather hydrophilic environment, similar to that of homogenous solution. In the case of SNpRB-C30B it may indicate that the rose bengal chromophores are located close to the surface of the clay packets.

In view of future potential applications as a photosensitizer for the degradation of water pollutants it was important to find out if the SNpRB-C30B photosensitizer is able of photosensitizing oxidation of hydrophilic compounds. To this end, 2-anthracene sulfonate (ANS) was irradiated in the presence of SNpRB-C30B with light of $\lambda > 470$ nm, absorbed by the RB chromophores and not absorbed by ANS. The photooxidizing efficiency of the hybrid photosensitizer was compared with the efficiency of homogenous aqueous solutions of SNpRB polymer and that of molecular RB. In order to make possible the comparison of the results of ANS photooxidation in these three systems, the SNpRB solution contained the same concentration of the polymer as the total concentration of SNpRB in the suspension of SNpRB-C30B and the concentration of molecular RB was adjusted to the same absorbance at the maximum of the 540 nm absorption band. The results are shown in Fig. 11.

It can be seen that the irradiation of ANS in the presence of RB and SNpRB polymer lead only to the small changes in ANS

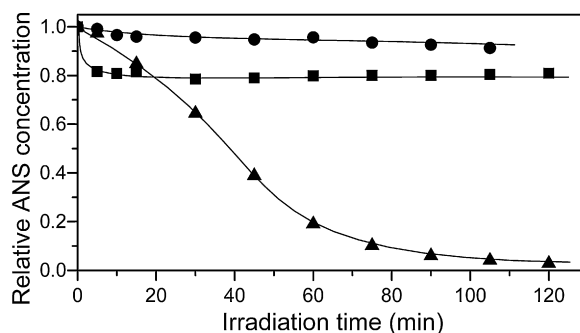


Fig. 11. The time dependence of relative ANS concentration ($c_0 = 4 \times 10^{-4}$ M) irradiated in the presence of RB (■), SNpRB (●), and SNpRB-C30B (▲). The SNpRB-C30B suspension contained 0.01 mg/ml of SNpRB and 1.43 mg/ml of C30B, $\lambda_{\text{irr}} > 470$ nm, $\lambda_{\text{ex}} = 365$ nm.

concentration (determined from ANS fluorescence emission measurements). This can be explained considering the aggregation of RB chromophores in these systems leading to the dissipation of excitation energy by excimer formation (see Fig. 7). In the presence of SNpRB-C30B, however, the irradiation of the ANS solution leads to its almost complete oxidation within 120 min. More efficient singlet oxygen formation in this case is due to decrease in aggregation of chromophores adsorbed by C30B. This is very promising result suggesting potential use of the hybrid photosensitizers composed of a nanoclay and a polymeric photosensitizer in the photodegradation of water pollutants.

4. Conclusion

A new type of a hybrid photosensitizer was obtained composed of a hydrophobically modified montmorillonite and a photoactive polymer containing both naphthalene and rose bengal chromophores. The hybrid photosensitizer adsorbs strongly hydrophobic compounds in the aqueous solution. On irradiation with light from the near UV-Vis spectral region it photosensitizes oxidation of both hydrophobic and water-soluble compounds. The process occurs with participation of singlet oxygen generated in the system.

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