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Photosensitized dechlorination of polychlorinated phenols
2. Photoinduced by poly(sodium styrenesulphonate-co-*N*-vinylcarbazole) dechlorination of pentachlorophenol in water

Maria Nowakowska, Krzysztof Szczubiałka, Szczepan Zapotoczny
Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland

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Abstract

The photodechlorination of pentachlorophenol (PCP) solubilized in an aqueous solution of poly(sodium styrenesulphonate-co-*N*-vinylcarbazole) (PSSS-VCz) copolymer was studied. The reaction was found to be photoinduced by the polymeric carbazole chromophores. The products were identified using gas chromatography-mass spectrometry (GC-MS) analysis. It was found that the ultimate reaction product was unsubstituted phenol.

Keywords: Aqueous solution; Dechlorination; Pentachlorophenol; Photochemical reaction; Polymeric photosensitizer

1. Introduction

Pentachlorophenol (PCP) has been commonly used as a fungicide, bactericide, herbicide, molluscicide, algaecide and insecticide. Although the level of its application has declined somewhat in the last decade and its production and use have been forbidden by law in certain countries, PCP residues occur widely in the environment and it is considered to be a persistent environmental pollutant [1–4]. Thus it is desirable to develop a safe and effective method for its disposal. This problem has been studied in a number of laboratories and several different approaches have been suggested: incineration [5,6], chemical [7,8], microbiological [9–14] or photochemical [15–18] treatment. Incineration cannot be recommended because it is associated with the generation of HCl and detectable amounts of dioxins. Chemical methods, such as dechlorination using transition metal-promoted alkoxyborohydrides [8] or hydrodehalogenation by reaction with hydrogen in the presence of a Pt catalyst [7] can be useful for the disposal of considerable quantities of pure PCP or its concentrated solutions. Photochemical methods seem to be the most suitable for the removal of PCP from polluted water sources. Unfortunately, direct irradiation of PCP in water results in the formation of polychlorinated dibenzo-*p*-dioxins [18]. Much more promising results have been obtained during the photocatalytic degradation of PCP on titanium dioxide [15–17]. In the previous paper in this series, it has been demonstrated that carbazole acts as an efficient photosensitizer in the photodechlorination of PCP in acetonitrile solution [19]. The initial photochemical step of the reaction involves electron transfer from electronically excited carbazole to PCP.

In this paper, we report the photodechlorination of PCP in aqueous solution using a polymeric photosensitizer, poly(sodium styrenesulphonate-co-*N*-vinylcarbazole) (PSSS-VCz). The polymer belongs to the class of antenna polyelectrolytes, which have been shown to act as efficient photocatalysts [20–31].

2. Experimental details

2.1. Materials

PCP (Aldrich, 99%) and 2,3,5,6-tetrachlorophenol (Aldrich, 98%) were used as received. *N*-Vinylcarbazole (VCz) (Fluka, pure) was recrystallized twice under nitrogen. Sodium styrenesulphonate (SSS) (Du Pont, tech.) was purified by two crystallizations from a mixture of water and methanol (1 : 19 v/v) at 60 °C and dried in a vacuum oven. 2,2′-Azobis(isobutyronitrile) (AIBN) was purified by crystallization from ethanol (40–50 °C) under nitrogen and dried in a vacuum oven. Butanol (POCh, analytical grade) and sodium chloride (POCh, analytical grade) were used as obtained. Water was purified by fourfold distillation.

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2.2. Procedures

2.2.1. Polymer synthesis

PSSS-VCz copolymers were synthesized and purified according to the method described previously [27]. The contents of VCz in the polymers used in this work were determined to be equal to 8.5 mol.% in PSSS-VCz(8.5) and 13.7 mol.% in PSSS-VCz(13.7). The weight-average molecular weight, $\bar{M}_w$, was determined for PSSS-VCz(13.7) on a Beckman model E analytical ultracentrifuge. The value of $\bar{M}_w$ was found to be 11 000 for PSSS-VCz(13.7). The number average molecular weight, $\bar{M}_n$, of the polymer was estimated (assuming a polydispersity of two) to be 5500.

2.2.2. Preparation of the solutions

Aqueous polymer solutions of various concentrations (0.4–2.0 g l^{-1}) were prepared. All solutions used for irradiation contained the same initial concentration of PCP: $c^0_{PCP} = 1.8$ ppm $\cong 7.5 \times 10^{-6}$ M.

2.2.3. Solubilization of PCP

PCP solubilization for the determination of the distribution coefficient and for photochemical experiments was achieved by slowly injecting microlitre quantities of probe dissolved in acetone (7.5×10^{-2} M) to 5 ml aliquots of the polymers. The mixtures were shaken for 5 min, filtered and equilibrated in the dark for at least 1 h.

For the solubilization of PCP in aqueous polymer solutions used for fluorescence quenching measurements, solutions of PCP in acetonitrile were applied.

2.2.4. Irradiation of samples

Samples were irradiated using a Rayonet photochemical reactor (model RPR-100) equipped with eight RPR-3500 Å lamps of 24 W each. The intensity of the incident light produced was 1.05×10^{15} photons s^{-1} cm^{-3}, as measured using a ferrioxalate actinometer [32]. Polymer solutions containing solubilized PCP were deoxygenated by bubbling with argon for 15 min prior to irradiation. The solutions were mixed using a magnetic stirrer.

2.2.5. Gas chromatography analyses

The products formed on irradiation were analysed using an INCO GC-505M gas chromatograph equipped with an electron capture (EC) detector and a DB-608 capillary column (30 m, 0.32 mm inside diameter (ID), 0.5 μm film thickness). The parameters of the analyses were as follows: splitless injection; carrier gas, nitrogen at 38.7 cm^3 s^{-1} (1.86 ml min^{-1}); makeup gas, nitrogen at 40 ml min^{-1}; injector temperature, 250 °C; detector temperature, 300 °C; oven temperature, held isothermally at 180 °C; sample volume, 1 μl.

Samples for analysis were prepared as follows. The irradiated aqueous solutions were extracted with butanol. Butanol (1 ml) was added to a portion of the irradiated solution (2 ml), the mixture was shaken for 5 min and the organic phase was separated (NaCl was added for better phase separation). The organic phase was dried with anhydrous sodium sulphate. The resulting solution was concentrated (to 1 ml) and analysed.

2.2.6. Gas chromatography-mass spectrometry (GC-MS) analyses

GC-MS analyses were performed using a Hewlett-Packard 5890 GC-MS instrument equipped with a DB-5 capillary column (30 m, 0.32 mm ID, 0.25 μm film thickness). Samples for GC-MS analysis were prepared as follows. PCP was solubilized in 500 ml of 1.0 g l^{-1} PSSS-VCz(13.7) solution in water and irradiated for 5 min. The products were extracted with 100 ml of hexane and 100 ml of methylene chloride. The extracts were then combined, evaporated to a volume of several microlitres and analysed.

2.2.7. UV spectral measurements

The UV absorption spectra of the samples were measured using a Hewlett-Packard 8452A diode-array spectrophotometer.

2.2.8. Fluorescence spectral measurements

The steady state fluorescence spectra of the samples were recorded at room temperature on an MSF 102 spectrofluorimeter.

3. Results and discussion

3.1. Solubilization of PCP

The solubility of PCP in water is quite limited ($c \sim 6.9 \times 10^{-5}$ M at 20 °C) [33]. It increases considerably in the presence of PSSS-VCz. This is due to the solubilization of PCP in the hydrophobic microdomains created within the polymer as a result of the clustering of the hydrophobic carbazole units when the polymer is dissolved in water. Using a simple thermodynamic treatment described previously [34], the distribution coefficient (K) of PCP between water and the polymer pseudophase is estimated to be $(9.1 \pm 0.5) \times 10^5$ at 20 °C in an aqueous solution of PSSS-VCz(13.7) (the distribution coefficient K was defined as the ratio of the mole fraction of PCP in the polymer pseudophase ($x_{PCP}{}^{pol}$) to the mole fraction of PCP in water ($x_{PCP}{}^{aq}$): $K = x_{PCP}{}^{pol}/x_{PCP}{}^{aq}$. The solubilization of PCP results in a high local concentration of PCP in the restricted volume of the polymeric pseudophase and increases the probability of direct interactions between the PCP molecule and the VCz polymeric chromophores.

3.2. Photochemical reactions of PCP in water and in aqueous solutions of PSSS-VCz

Irradiation of deoxygenated solutions of PCP in water and of aqueous PSSS-VCz solutions containing solubilized PCP results in a decrease in the PCP concentration.

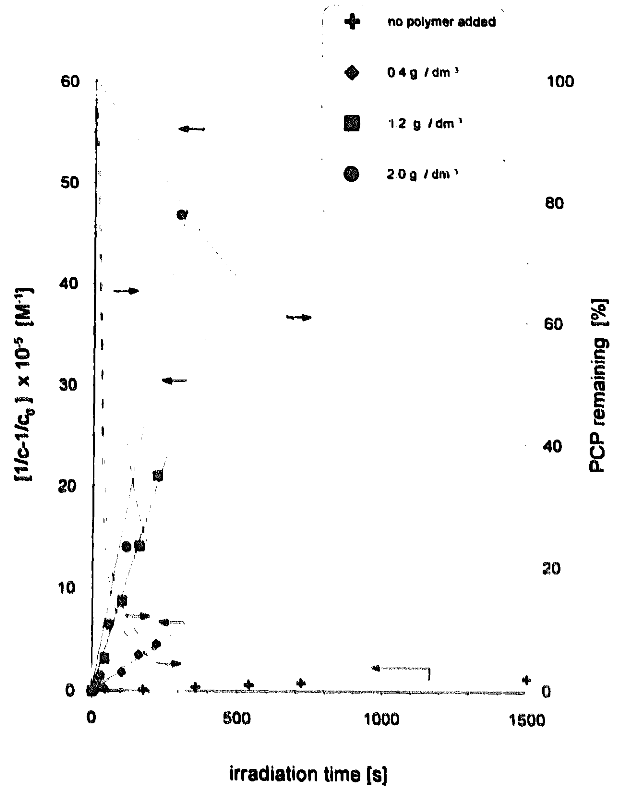

Fig. 1. Dependence of the PCP concentration on the irradiation time in solutions of various concentrations of PSSS-VCz(13.7) fitted to a second-order kinetic equation, and the dependence of the PCP concentration on the irradiation time.

However, the kinetics and mechanisms of the processes are considerably different in these two media. The data presented in Fig. 1 demonstrate that the consumption of PCP is much faster in the presence of the polymer and is strongly dependent on the polymer concentration (the total initial concentration of PCP in all systems studied was the same, $c_{PCP}^0 \cong 7.5 \times 10^{-6}$ M). In addition, the reaction carried out in an aqueous solution of PSSS-VCz(13.7) at a polymer concentration of 2.0 g dm^{-3} is over 150 times faster than in water at the same initial concentration of PCP. This is consistent with a reaction photoinduced by the excitation of carbazole chromophores present in the polymer. This is supported by the observation that the consumption of PCP is faster in the presence of the polymer richer in carbazole units, PSSS-VCz(13.7) (see Fig. 2).

GC-MS analysis shows that tetrachlorophenols are formed as the primary photochemical products under these conditions. 2,3,5,6-Tetrachlorophenol is the most abundant species formed in the system. In addition, prolonged irradiation results in the formation of secondary photochemical products, trichlorophenols. Further irradiation results in the formation of dichlorobenzenes and unsubstituted phenol as the final product of the dechlorination reaction. The quantum yield of PCP consumption in an aqueous solution of PSSS-VCz(13.7) (c_{pol} = 1.2 g l^{-1}) is estimated to be $(2.6 \pm 0.5) \times 10^{-3}$.

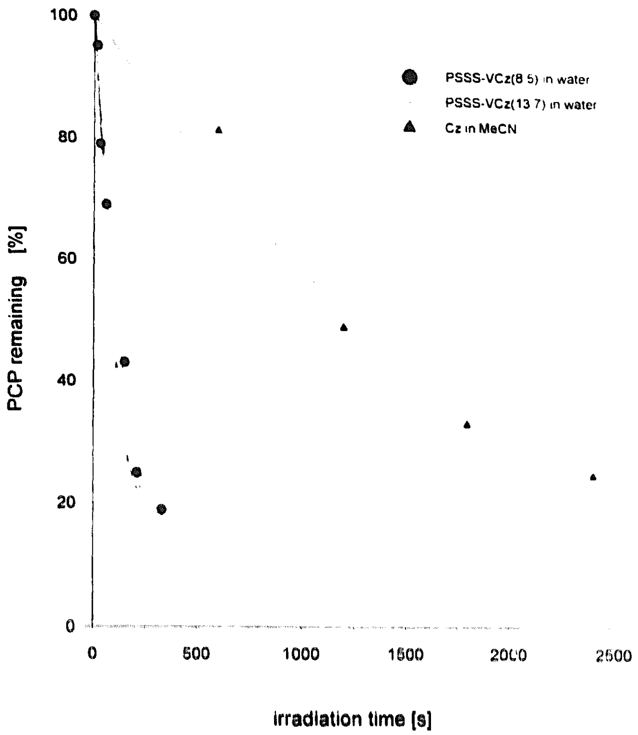

Fig. 2. Dependence of the PCP concentration on the irradiation time for solutions containing 0.4 g l^{-1} of different PSSS-VCz polymers and for a solution of carbazole in MeCN (details in text).

During the irradiation of PCP in water, tetrachlorophenols are also observed, but the major primary photochemical product formed is characterized by a higher retention time than that of PCP (see Fig. 3(b)). It is probably a condensation product, which has previously been reported as the major photochemical product formed during direct irradiation of PCP in water [35,36].

3.3. Studies of the mechanism of dechlorination of PCP solubilized in an aqueous solution of PSSS-VCz

Measurements of the steady state fluorescence spectra of PSSS-VCz in aqueous solution in the absence and presence of PCP have shown that PCP efficiently quenches the emission of polymeric carbazole chromophores (Fig. 4(A)). As shown in the previous paper [19], this effect can be explained by considering the electron transfer from excited carbazole to the PCP molecule. The quenching process can be described by the Stern–Volmer kinetic equation (see Fig. 4(B))

$$\frac{I_0}{I} = 1 + k_q \times \tau \times [\mathrm{PCP}]$$

where I_0 and I are the fluorescence intensities of the carbazole chromophores in the absence and presence of PCP, [PCP] is the concentration of PCP, k_q is the bimolecular rate constant for quenching of the carbazole chromophore by PCP and τ is the fluorescence lifetime of polymeric carbazole chromophores.

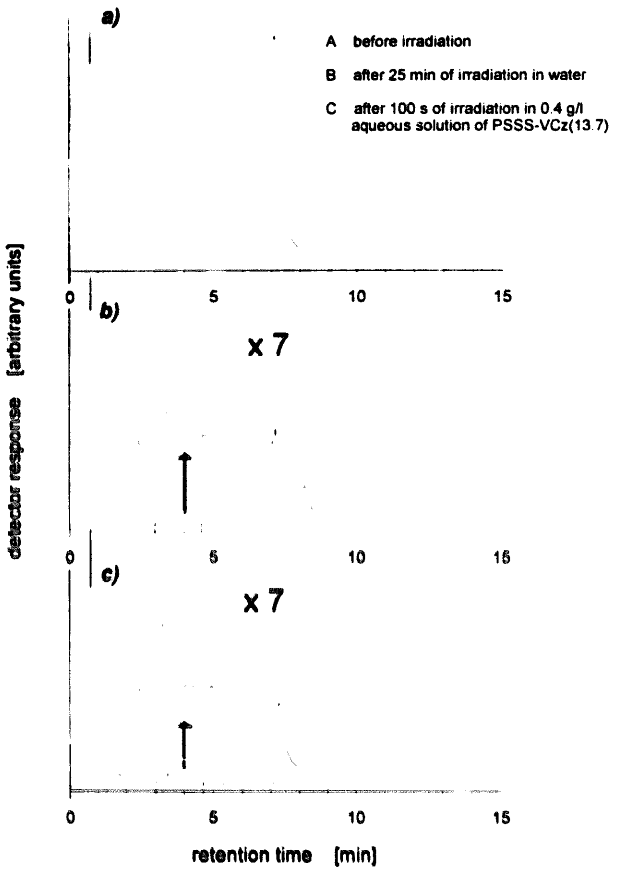

Fig. 3. GC traces of PCP before (a) and after irradiation in water for 25 min (b) and in 0.4 g l^{-1} aqueous solution of PSSS-VCz(13.7) for 100 s (c).

Assuming that the fluorescence lifetime for polymeric carbazole chromophores does not differ significantly from that of carbazole in polar solvents (τ= 15.2 ns), the rate constant for quenching is found to be 2.5×10^{11}. This value is considerably higher than that expected for a diffusion-controlled process. This may be rationalized in terms of the high local concentration of quencher molecules trapped in polymeric microdomains, thus confirming the actual location of PCP in the system studied.

4. Conclusions

PSSS-VCz is an efficient system for the photoinduced dechlorination of PCP in water. 2,3,5,6-Tetrachlorophenol is the main primary photochemical product formed during the irradiation of an aqueous solution of PSSS-VCz + PCP with light absorbed by the polymeric carbazole chromophores. Prolonged irradiation of the reaction mixture results in the formation of trichlorophenols, dichlorobenzenes and phenol. The rate of dechlorination increases with increasing polymer concentration and with increasing content of carbazole units in the polymer chain.

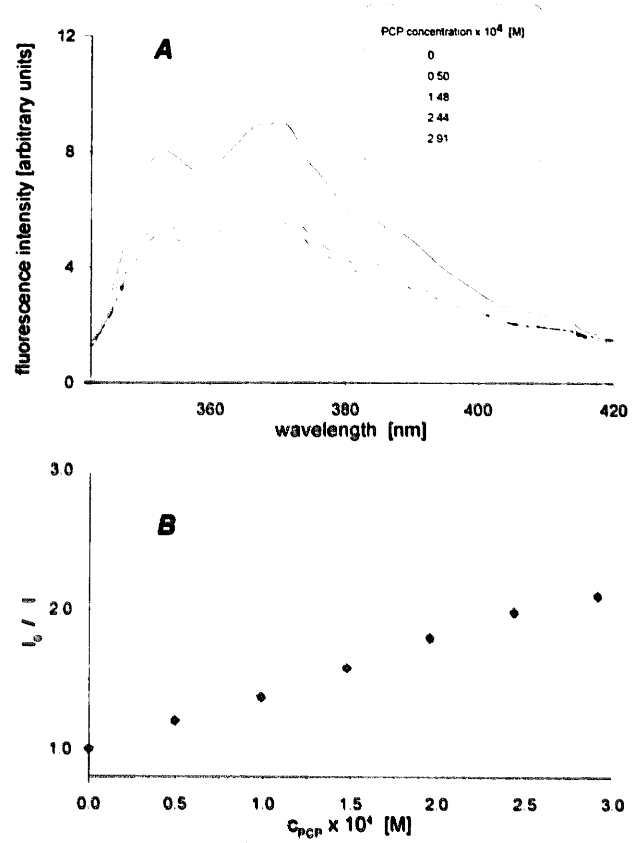

Fig. 4. (A) Steady state fluorescence spectra of an aqueous solution of PSSS-VCz(13.7) in the absence and presence of PCP at various concentrations. (B) Stern–Volmer plot for PSSS-VCz(13.7) fluorescence quenching by PCP in water (I_0/I is the ratio of the PSSS-VCz(13.7) fluorescence intensity in the absence (I_0) and presence (I) of PCP).

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