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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Gigimol, M. G. , Jose, Jincy and Mathew, Beena(2006) 'Dye Binding Characteristics of N,N'-Methylene-bis-acrylamide (NNMBA)-Crosslinked Polyacrylamide-Supported Amine and its Photooxidizing Ability', Journal of Macromolecular Science, Part A, 43: 4, 689 – 694

To link to this Article: DOI: 10.1080/10601320600602571

URL: <http://dx.doi.org/10.1080/10601320600602571>

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Dye Binding Characteristics of N,N'-Methylene-bis-acrylamide (NNMBA)-Crosslinked Polyacrylamide-Supported Amine and its Photooxidizing Ability

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The dye binding characteristics of 8 mol% NNMBA-crosslinked polyacrylamide-supported amine is investigated with Rose Bengal (RB), Methyl Orange (MO), Methylene Blue (MB) and Methyl Red (MR). The influence of the concentration of dye solution on dye binding, time course of dye binding and characterization were explored. It is observed that binding is higher in the case of Rose Bengal and dye binding depends on the polarity, as well as the size of the dye molecule. The photooxidation property of polymer bound RB was investigated towards the oxidation of benzoil to benzil. RB bound polymer acts as an efficient heterogenous photooxidizing agent.

Keywords polyacrylamide-supported, dye binding, time-course, characterization

Introduction

In the recent past, the chemistry and application of functional polymers is an area which has achieved rapid progress (1). Chemical modification is used extensively to modify the properties of polymers for various applications (2). Some of the important fields where the chemistry of functional polymers bears relevance are organic synthesis, design of polymeric reagents and catalysts, chelating polymers and biomimetic chemistry (3–5). The nature of the polymeric backbone, conformation of the macromolecular chain, micro-environment of the reactive functional groups, relative occurrence of the functional groups in the polymer chain, stereochemistry around the functional groups, and the overall topology of the macromolecular matrix decide the reactivity of a functional group attached to the macromolecular backbone (6–8). Polyacrylamide and poly(N-vinyl pyrrolidone) are used to bind molecules for specific purposes (9, 10).

The present paper describes the dye binding characteristics of 8 mol% NNMBA-crosslinked polyacrylamide-supported amine towards Rose Bengal (RB), Methyl Orange (MO), Methylene Blue (MB) and Methyl Red (MR). The photooxidation behavior of the Rose Bengal anchored on polyacrylamide support was also investigated.

Received July 2005; Accepted September 2005.

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Experimental

Synthesis of 8 mol% NNMBA-Crosslinked Polyacrylamide

For the preparation of 8 mol% NNMBA-crosslinked polyacrylamide, acrylamide (13.064 g) and NNMBA (2.4667 g) were dissolved in water (400 ml) and kept at 80°C. The potassium persulphate (500 mg) initiator was added and the mixture was heated with stirring at 80°C for 4 h. The polymer was collected by filtration, washed with water, ethanol, methanol, and acetone. The lumps were powdered and dried at 70°C, giving a 13.65 g product yield.

Preparation of NNMBA-Crosslinked Polyacrylamide-Supported Amine

Crosslinked polyacrylamide (10 g) was added slowly to ethylenediamine (100 ml) and kept at 100°C with stirring. Heating and stirring were continued for 20 h, the reaction mixture was then poured into distilled water containing crushed ice. The resin was filtered, and washed with aqueous NaCl (0.1 M) until the washings were free from ethylenediamine as indicated by the absence of any blue coloration with ninhydrin reagent. The gel was washed with distilled water to remove chloride ions until the filtrate gave a negative test for chloride ions. Finally, the product was washed with methanol and acetone and dried in an oven at 50°C.

Dye Binding Studies of 8 mol% NNMBA-Crosslinked Polyacrylamide-Supported Amine

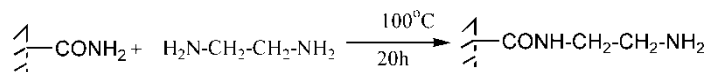
A mixture of amino polyacrylamide (0.075 g) and 30×10^{-6} M of each dye such as Rose Bengal, Methylene Blue, Methyl Orange and Methyl Red were combined in a reagent bottle covered with black paper and shaken well in a water bath shaker at 80 rpm for 5 h (11). The dye bound polymer was collected by filtration and washed with distilled water and Soxhlet extracted to remove the uncomplexed dye. The amount of dye bound to the polymer support was followed spectrophotometrically by calculating the difference in the optical densities of the dye solution before and after binding.

In order to investigate the optimum time required for binding, the aminopolyacrylamide (0.06 g, 100–200 μ m) was equilibrated with dye solutions [30×10^{-6} M, 50 ml) for different time intervals in a thermostatically controlled system. Concentration dependence of the binding was determined by equilibrating amino polyacrylamides with dye solutions of concentrations ranging from $8\text{--}26 \times 10^{-6}$ M for 5 h at room temperature (302 K).

Photooxidation by Rose Bengal Supported on Polyacrylamide-Supported Amine

Benzoin was dissolved in 20 ml CH₃OH, and a known amount of the RB bound aminopolyacrylamide was added. Photooxidation by RB bound aminopolyacrylamide was carried out by irradiating the reaction mixture using a 125W lamp. During the reaction O₂ was bubbled through the reaction mixture. 0.5 ml of the reaction mixture was withdrawn at intervals, using a micropipette and care was taken that no solid particles were removed with the solution.

The aliquot thus withdrawn was carefully evaporated on a rotary evaporator and the residue was dissolved in 5 ml of CH₃OH. The absorbance was measured at 390 nm with a



Scheme 1. Transamidation of NNMBA-crosslinked polyacrylamide with ethylenediamine.

Shimadzu 160A UV/vis Spectrophotometer. The initial rates were obtained from graphs of a concentration of Benzil against time. The extent of the reaction was also followed by TLC. The product benzil was characterized by comparing M.P, IR, and TLC with those of an authentic sample.

Measurements

The IR spectra were recorded on a Shimadzu IR 470 Spectrometer using KBr pellets. Electronic spectra were recorded on a Shimadzu 160A UV/vis Spectrophotometer.

Results and Discussions

The incorporation of amino functions to the NNMBA-crosslinked polyacrylamide is depicted in Scheme 1. The extent of amination was followed by acidic titration and was found to be 1.652 mmol/g.

The dye bindings on 8 mol% NNMBA-crosslinked polyacrylamide-supported amine decreased in the order: RB > MO > MB > MR (Table 1). This variation in the amount of dye bindings on polymer support can be attributed to the difference in the structure (Figure 1) and binding abilities of the dye molecules in addition to their hydrophilic/hydrophobic characteristics. With an increasing concentration of dye solution, the binding increased and this was profoundly higher in the case of Rose Bengal. RB is an anionic amphipathic substrate with ionic and hydrophobic binding sites. Both electrostatic and hydrophilic/hydrophobic interactions are operative in the binding of RB on the polymer support. In the case of MR, the binding of the polymer support is lowest because of the steric hindrance, which is highest for MR due to the presence of an *o*-substituted carboxyl group, and this prevents the orientation of the binding sites of the dye molecules.

Table 1
Concentration dependence of dye binding on NNMBA-crosslinked polyacrylamide-supported amine

Concentration of dye solution ($\times 10^{-6}$ M)	Amount of dye bound ($\times 10^{-2}$ mequi/g)			
	RB	MO	MB	MR
8	78.5	43.5	10.7	9.5
11	104.5	58.8	23.5	10.0
14	137.4	79.4	28.7	10.6
17	167.0	101.0	33.5	10.9
20	196.5	105.5	37.4	13.6
23	226.1	122.0	61.57	13.5
26	256.2	138.6	67.5	15.5

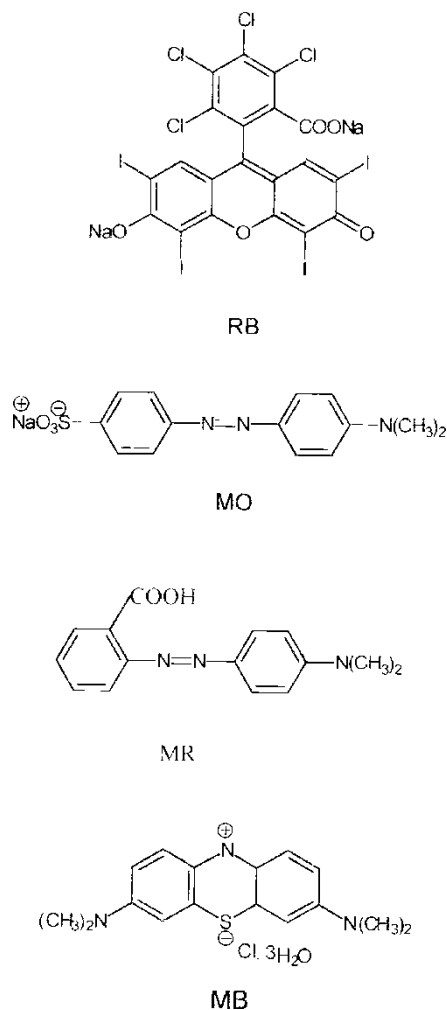


Figure 1. Structures of RB, MO, MR, and MB.

UV spectra of dyes and polymer bound dyes are shown in the Figure 2. RB exhibits λ_{max} at 570 nm, MB at 676 nm, MO at 460 nm, and MR at 481 nm. Binding of these dyes on aminopolyacrylamide resulted in a blue shift to 563, 600, 422 and 464 nm, respectively for RB, MB, MO, and MR. The blue shift indicates the presence of dye chromophore in a more polar environment on binding with this polymer support.

The IR spectra of the NNMBA-crosslinked polyacrylamide showed the characteristic absorptions of amide-NH and C=O around 3400 and 1660 cm^{-1} , respectively and a secondary amide of the crosslinking agent in the region $1540\text{--}1500\text{ cm}^{-1}$. In the case of amino resin, the N-H peak at 3400 cm^{-1} was broadened by the extensive degree of hydrogen bonding. A decrease in the intensity of the band around 3400 cm^{-1} and splitting of the N-H peak to 3300 and 3400 cm^{-1} indicated the incorporation of the amino groups for dye binding. Figure 3 shows the time-course of dye binding by polyacrylamide-supported amine. The binding of RB, MO and MR requires much less time compared to MB. This also depends on the hydrophilic/hydrophobic balance between

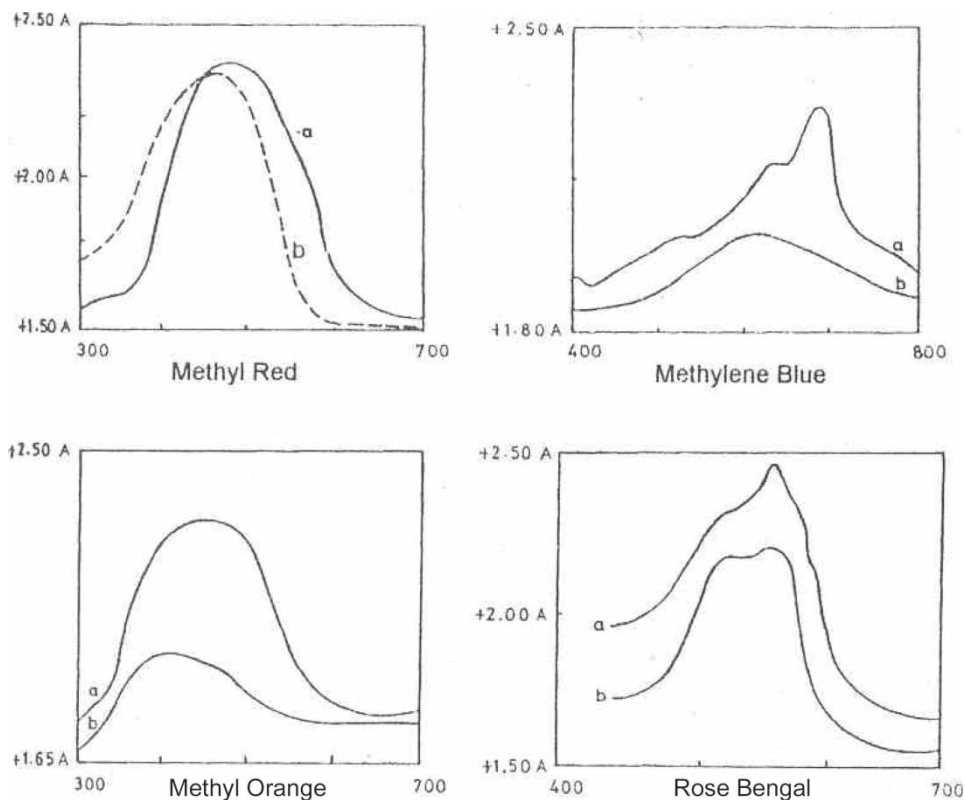


Figure 2. UV spectra of dyes and polymer bound dyes: (a) Dye; (b) Polymer bound dye.

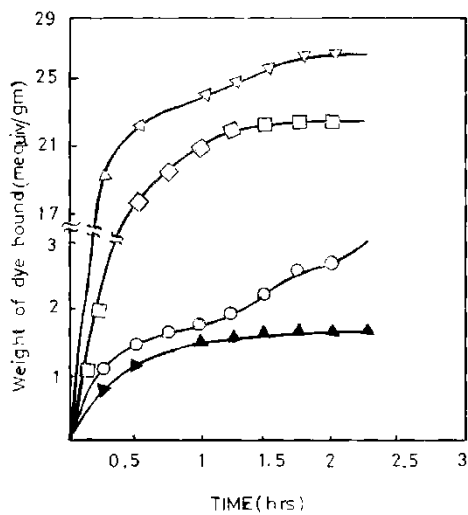


Figure 3. Time course of dye binding by polyacrylamide-supported amine \square -MO; ∇ -RB; \circ -MB; \blacktriangle -MR.

the polymer and the dye molecule and the extent of orientation of their binding sites for a more stable binding.

Thus, polyacrylamide-supported amine was found to be effective as a support for the binding of dyes and because of the polar nature, the polyacrylamide itself and its chemically modified form can bind a number of ions and dye molecules, and the application of this system as a heterogenous photooxidizing agent is in progress.

As described in the experimental part, the photooxidation reactions were carried out. In order to remove any residual soluble organic substrate or product, the spent polymer samples were collected from the reaction mixture and washed thoroughly with the solvent. The products were characterized by noting their physical constants and characterized by IR and UV spectra. It is found that polyacrylamide bound RB is an effective singlet oxygen producer and an efficient heterogeneous photooxidizing agent. Polymer supported RB can be recycled without the loss of efficiency.

Conclusions

The preceding investigations on the interaction of polyacrylamide-supported amine with various dyes revealed that they could be effectively bound on the polar polyacrylamide system. The binding of Rose Bengal was more effective, showing this system can act as an efficient heterogeneous photooxidizing agent.

Acknowledgment

One of the authors, M.G.Gigimol, is thankful to the Council of Scientific and Industrial Research (CSIR), Government of India for the financial support as Senior Research Fellowship.

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