

# Effect of the Nature and Degree of Crosslinking on the Rose Bengal Uptake by DVB-, NNMBA-, HDODA-, and TTEGDA-Crosslinked Aminopolyacrylamides

M. G. Gigimol, Beena Mathew

School of Chemical Sciences, Mahatma Gandhi University, Kottayam 686560, Kerala, India

Received 27 July 2006; accepted 24 October 2006

DOI 10.1002/app.25970

Published online 28 February 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Polyacrylamides with 2–20 mol % divinyl benzene (DVB), *N,N'*-methylene-bisacrylamide (NNMBA), 1,6-hexanediol diacrylate (HDODA), and tetraethyleneglycol diacrylate (TTEGDA) crosslinking and without crosslinking were prepared by free radical solution polymerization. Amino functions were incorporated into these polymers by transamidation with excess ethylenediamine. The dye uptake of nonprotonated and protonated aminopolyacrylamides was followed by batch equilibration method towards Rose Bengal (RB), Methyl Orange (MO), Methyl Red (MR), and Methylene Blue (MB). RB uptake by the polyacrylamide-supported systems is higher than other dyes. Generally the dye uptake by the protonated systems is higher than the nonprotonated systems. To optimize the conditions of dye uptake, the effect of the concentration of RB solutions,

temperature, and pH were followed. Kinetic studies showed that the uptake of RB by both nonprotonated and protonated crosslinked aminopolyacrylamides is a phase boundary process followed by three-dimensional diffusion. The extent of RB uptake by the various systems depends on the nature and degree of crosslinking, and the relative rigidity/flexibility of the polyacrylamide support. Thus, the dye uptake followed the order: linear > NNMBA- > DVB- > TTEGDA- > HDODA-crosslinked system. The dye uptake followed the same trend as the variation of amino capacity with degree of crosslinking in the respective crosslinked system. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2856–2867, 2007

**Key words:** crosslinking; hydrophilic polymers; supports; swelling

## INTRODUCTION

The synthesis and applications of functional polymers have received considerable attention in recent years.<sup>1</sup> Some of the important fields in which the chemistry of functional polymers bears relevance are the design of polymeric functional reagents and catalysts, organic synthesis, enzyme immobilization, and chelating polymers.<sup>2,3</sup> The use of functional polymer depend on the physical properties and chemical constitution of the polymers. The ease of chemical modification and its adaptability under different conditions to which it is subjected is governed by the microstructure of the polymer. The dependence of the reactivity of the attached functional groups on the nature of the polymer matrix like the polarity of the support, molecular character and extent of crosslinking, and the overall topographical nature has been reported from this laboratory.<sup>4–6</sup> The main

advantages of crosslinked polymer-supported solid phase organic reagents over their monomeric counterparts in organic synthesis are the ease of separation and reusability.<sup>7–9</sup> In addition, the polymer matrix can provide a specific microenvironment that might induce selectivity in a chemical reaction due to the steric factors arising from the macromolecular structure, crosslink density, and pore size in the case of crosslinked polymer or a dilute distribution of reactive functions on the polymer chain. Organic dyes find extensive use as sensitizers in photooxygenation reactions.<sup>10–14</sup> Polymer bound Rose Bengal (RB) was first reported by Neckers and coworkers in 1973.<sup>15</sup> Polymer bound RB is effective in photooxidation reactions.<sup>16–23</sup>

In the present study, we are investigating the interaction of dyes with 2–20 mol % divinyl benzene (DVB)-, *N,N'*-methylene-bisacrylamide (NNMBA)-, 1,6-hexanediol diacrylate (HDODA)-, tetraethyleneglycol diacrylate (TTEGDA)-crosslinked, and linear polyacrylamide-supported nonprotonated and protonated amines. For this, we have selected dyes like RB, Methyl Orange (MO), Methyl Red (MR), and Methylene Blue (MB). Of these, RB is found to be effectively interacted with our polymeric systems. This article describes the dependence of the nature

Correspondence to: B. Mathew (beenamj@yahoo.com).

Contract grant sponsor: Council of Scientific and Industrial Research (CSIR).

and degree of crosslinking on the interaction of RB with the polyacrylamide support. Photooxidation reactions using this polymer bound RB is not intended in this article.

## EXPERIMENTAL

### Materials

Rose Bengal (RB) was purchased from BDH, UK. Acrylamide, *N,N'*-methylene-bisacrylamide (NNMBA), ethylenediamine, Methyl Orange (MO), Methyl Red (MR), and Methylene Blue (MB) were obtained from SRL, Mumbai, India. Divinyl benzene (DVB), 1,6-hexanediol diacrylate (HDODA), and tetraethylene-glycol diacrylate (TTEGDA) were purchased from Aldrich Chemical Company (St. Louis, MO). All low molecular weight compounds were commercially available and were purified by distillation or recrystallization unless, otherwise stated.

### Instrumental

The IR spectra were recorded on a Shimadzu IR-470 Spectrophotometer using KBr pellets. Electronic spectra were recorded on a Shimadzu 160 A UV/vis Spectrophotometer. SEM photographs were taken on a Hitachi S-2400 instrument.

### Preparation of linear, DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamides

The linear, DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked polyacrylamides were prepared by free radical solution polymerization.<sup>24</sup> Amino functions were incorporated into crosslinked polyacrylamides by transamidation with excess ethylenediamine at 80°C for 20 h. The amino functions were detected by the semiquantitative ninhydrin reaction<sup>25</sup> and estimated by acid titration.

### Preparation of the protonated aminopolyacrylamides

Aminopolyacrylamide (100 mg) was equilibrated with 0.02N HCl for 24 h. Excess HCl was removed by washing with distilled water until the washings were free from any acid.

### Dye uptake by crosslinked nonprotonated and protonated aminopolyacrylamides: General procedure

Dye uptake by crosslinked nonprotonated and protonated aminopolyacrylamides were carried out by equilibration of the polymers with dye solutions. A mixture of the required concentration of aqueous solution of dye was equilibrated with crosslinked non-

protonated and protonated aminopolyacrylamides (0.075 g) in a water bath shaker for 8 h. The polymer attached dye was collected by filtration and washed with distilled water to remove the uncomplexed dye. The polymer was further Soxhlet extracted with different solvents like methanol, acetone, and chloroform to remove the remaining dye, which was admixed with the polymer. The concentration of dye solution before and after the uptake was followed using UV/vis. spectrophotometer. The amount of dye bound by the polymer was calculated from the differences in the concentrations of the dye solution before and after uptake. The concentration of the dyes in water were calculated by using the molar absorption coefficient of  $100,000 \text{ cm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 549 nm for RB.<sup>24</sup> From this, dye bound by 1 g of the polymer was calculated.

### Time-course of dye uptake

To investigate the optimum time required for uptake, 0.075 g of crosslinked aminopolyacrylamide (4 mol %) was shaken with dye solution ( $70 \times 10^{-6} \text{ M}$ , 75 mL) in a thermostated water bath at regular intervals of time. The concentrations of the dye solutions at regular intervals were followed spectrophotometrically.

### Kinetics of RB uptake

For the kinetic studies of RB uptake by DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked (4 mol %) aminopolyacrylamides, the polymer (0.075 g; 100–200  $\mu\text{m}$  spherical shape) was equilibrated with RB solution ( $7.4 \times 10^{-5} \text{ M}$ , 75 mL) for different time intervals in a thermostatically controlled system. Kinetic studies of protonated and nonprotonated systems were done at 302 K. The extent of uptake was found out spectrophotometrically as described earlier.

### Adsorption studies of uptake of RB

The required amount of protonated and nonprotonated (4 mol %) DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamide (100–200  $\mu\text{m}$ ) was equilibrated by shaking with RB solutions of varying concentrations for 8 h at room temperature (302 K). The same experiment was repeated to follow the dependence of temperature on the adsorption of RB on DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamides by carrying out the experiments at varying temperatures.

### Effect of pH on the uptake of RB

The experiments were carried out at different pH of phosphate buffer [ $\text{Na}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ , 0.025M] at

room temperature. The extent of dye uptake was found out spectrophotometrically as described earlier.

### Swelling studies

Hundred milligram each of the different polymer was equilibrated with 10 mL distilled water for 48 h. The swollen resins were collected by filtration, excess water was removed by centrifuging and the swollen weight was determined. The samples were then dried in vacuum. The equilibrium water content (EWC) was calculated as the ratio of the water in the gel to the total weight of the hydrated gel expressed as percentage by the equation.

$$\text{EWC} = \frac{\text{wt. of wet resin} - \text{wt. of dry resin}}{\text{wt. of wet resin}} \times 100$$

### Effect of the nature and degree of crosslinking on the uptake of RB

Two to 20 mol % of protonated and nonprotonated DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamide (100–200  $\mu\text{m}$ ) with equimolar amount of reactive sites were equilibrated with RB solution for 8 h. The extent of RB uptake was found out spectrophotometrically as described earlier.

## RESULTS AND DISCUSSION

### Synthesis of linear, DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamides

Two to 20 mol % DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked polyacrylamides were prepared by free radical solution polymerization at 80°C as represented in Scheme 1. The hydrophilic-hydrophobic nature of the polymeric support can be changed by choosing appropriate crosslinking agents. The different crosslinking agents selected for preparing crosslinked polyacrylamides are divinylbenzene (DVB), NNMBA, HDODA, and TTEGDA. The criteria for the selection of these crosslinking agents are the difference in their relative rigidity/flexibility and polarity. Incorporation of these crosslinking agents in different proportions changes the physicochemical characteristics of the hydrophilic polyacrylamide support. To investigate the effect of the nature and degree of crosslinking on dye uptake, polymers with 2, 4, 8, 12, and 20 mol % DVB, NNMBA, HDODA, and TTEGDA crosslinking were prepared by varying the relative amount of acrylamide and the respective crosslinking agent. A linear polyacrylamide was also synthesized to investigate the possibility of multi transamidation of amide groups of polyacrylamide with ethylenediamine.

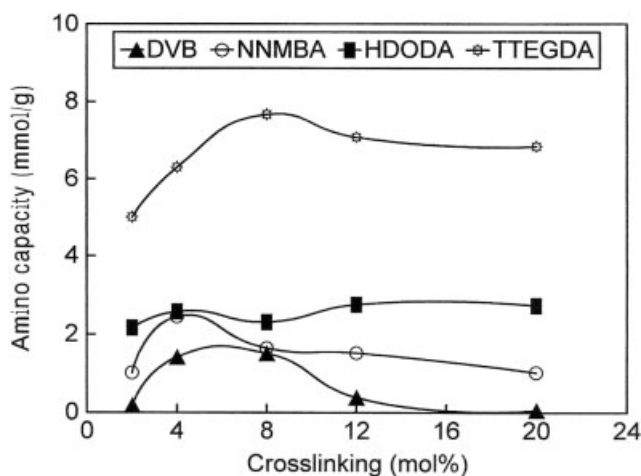
Amino functions were incorporated into linear, DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked polyacrylamides with the amide functions in varying structural environments by transamidation with excess ethylenediamine at 80°C for 20 h (Scheme 2).

The amino functions were detected by the semi-quantitative ninhydrin reaction and estimated by acid titration. The possibility of the reaction of the free amino group of the attached ethylenediamine is less, because of the increased basicity of the excess free ethylenediamine, which is acting as the solvent itself, the chance for the second coupling is less. In the DVB-, NNMBA-, and HDODA-crosslinked systems, the extent of incorporation of the amino functions increased till 4 mol % and decreased further. While in the TTEGDA-crosslinked system, the capacity increases till 8 mol % and decreased further.

The DVB-crosslinked systems have the decreased amino capacities because of the lowest availability of the reactive sites by the extremely rigid and hydrophobic nature of the DVB crosslinks. While the semi rigid and semi hydrophilic NNMBA-crosslinked systems have amino capacities higher than that of DVB-crosslinked systems. The HDODA-crosslinked systems have the amino capacities in between that of TTEGDA- and NNMBA-crosslinked systems. On comparing the amino capacities of four systems, it is found that amino capacity is highest for TTEGDA-crosslinked system because of its high hydrophilic and flexible nature (Fig. 1). To investigate the possibility of transamidation of the second amino group of the bound ethylenediamine, transamidation of linear polyacrylamide was also carried out. The polymer obtained was soluble and separation of the transamidated polymer from the reaction mixture was very difficult and the separable yield was very less. This suggests that the second coupling is negligible. The capacity of the linear system is 8.2 mmol  $\text{g}^{-1}$ . This higher capacity originates from the easy accessibility of the reactive sites for transamidation in the linear system. In crosslinked polymers higher capacity would be expected for the low crosslinked systems because of the increased availability of the reactive sites for the substrates in the solution phase. The variation of the amino capacity could originate from the heterogeneity developed in the crosslinked polymer resulting in the formation of microdomains with region of increased crosslinking in the support.<sup>26</sup> This would result in an unpredictable variation in the extent of functionalization.

To investigate the influence of quaternary ammonium ion in dye uptake, aminopolymers were equilibrated with excess dil. HCl and excess HCl was removed by washing with distilled water until the washings were free from any acid (Scheme 3).





**Figure 1** Aminocapacities of 2–20 mol % DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamides.

pathic substrate with ionic and hydrophobic uptake sites. Both electrostatic and hydrophilic/hydrophobic interactions are operative in the uptake of RB on the polymer support. In the case of MR, the uptake on the polymer support is lowest because of the steric hindrance which is highest for MR because of the presence of an *o*-substituted carboxyl, and this prevents the orientation of the uptake sites of the dye molecules.

Figure 2 shows the time-course of dye uptake by polyacrylamide-supported amine. The uptake of RB, MO, and MR requires much less time compared with MB. This also depends on the hydrophilic/hydrophobic balance between the polymer and the dye molecule, and the extent of orientation of their uptake sites for a more stable uptake.

#### Comparison of uptake of RB by linear, and 2–20 mol % DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked nonprotonated and protonated aminopolyacrylamides

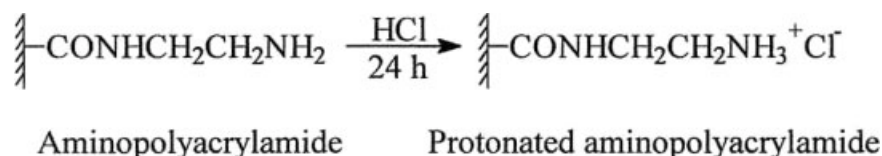
Because of the high uptake of RB than other dyes, the interdependence of the nature and the degree of crosslinking on dye uptake was investigated towards RB only. Among the linear protonated and nonprotonated systems, RB binding by the protonated system is higher than the nonprotonated system. On comparing the linear systems with crosslinked

systems, RB binding of linear systems is higher than crosslinked systems (protonated 217 mg g<sup>-1</sup>; nonprotonated 193 mg g<sup>-1</sup>). This arises from the easy accessibility of the binding sites for RB molecules. Because of the very low amount of the separated linear amino polyacrylamide, its binding studies were restricted to this extent only. In all the crosslinked aminopolyacrylamides, the amount of dye bound is higher for the protonated system than that for the nonprotonated system. The reason for higher dye uptake by the protonated system is the effective interaction between the dye molecules in the aqueous solution with the protonated lipophilic ammonium ions in the crosslinked polyacrylamides. RB uptake by 2–20 mol % crosslinked protonated and nonprotonated aminopolyacrylamides is given in Figure 3. Generally the reactivity of a crosslinked polymeric system decreases with increasing crosslink density. But an anomalous observation of the increase of reactivity of crosslinked polyacrylamides with a certain degree of crosslinking (4–10 mol %) are reported.<sup>8</sup>

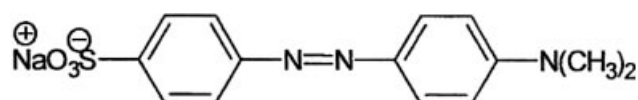
#### Time-course and kinetics of RB uptake on nonprotonated and protonated aminopolyacrylamides

The time-course of dye-polymer support interaction is of considerable importance in the uptake of dye on a polymer-support. To optimize the time necessary for maximum uptake, batch studies were carried out by equilibrating RB solutions with 4 mol % DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked protonated and nonprotonated aminopolyacrylamide. Figure 4 shows the time-course of RB uptake by 4 mol % protonated and nonprotonated DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamide.

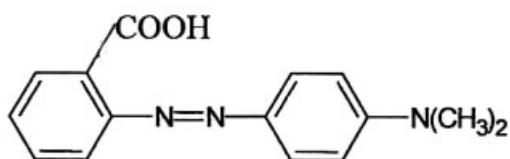
The dye uptake of the protonated system is higher than the nonprotonated systems. The uptake of RB on DVB-crosslinked protonated aminopolyacrylamide was completed within 45 min and for its nonprotonated form, the time required was 60 min. In the case of NNMBA-crosslinked systems, the uptake of RB on protonated form was completed in less than 30 min and for its nonprotonated form, the time required was 70 min. The HDODA-crosslinked aminopolyacrylamide required less than 10 min for the protonated form and 60 min for the nonpro-



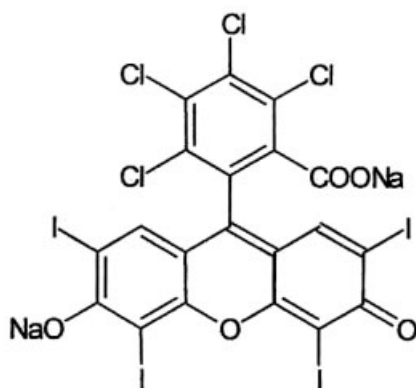
**Scheme 3** Preparation of protonated aminopolyacrylamide.



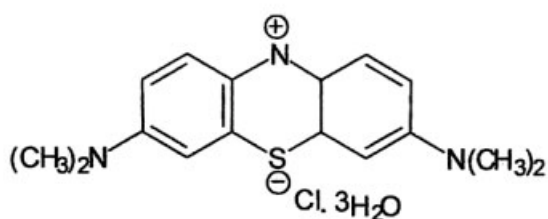
Methyl Orange



Methyl Red



Rose Bengal



Methylene Blue

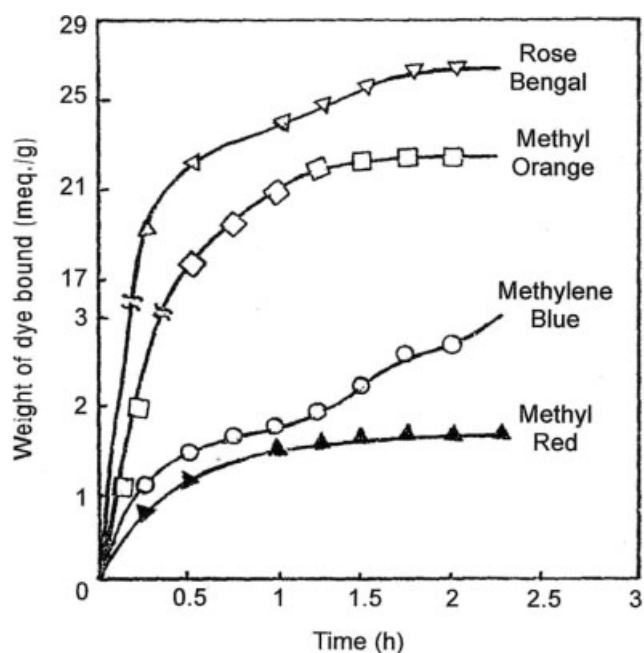
**Scheme 4** Structure of Methyl Orange, Methyl Red, Rose Bengal, and Methylene Blue.

nated form. TTEGDA-crosslinked protonated aminopolyacrylamide required 45 min and the nonprotonated form required 30 min for optimum uptake of RB.

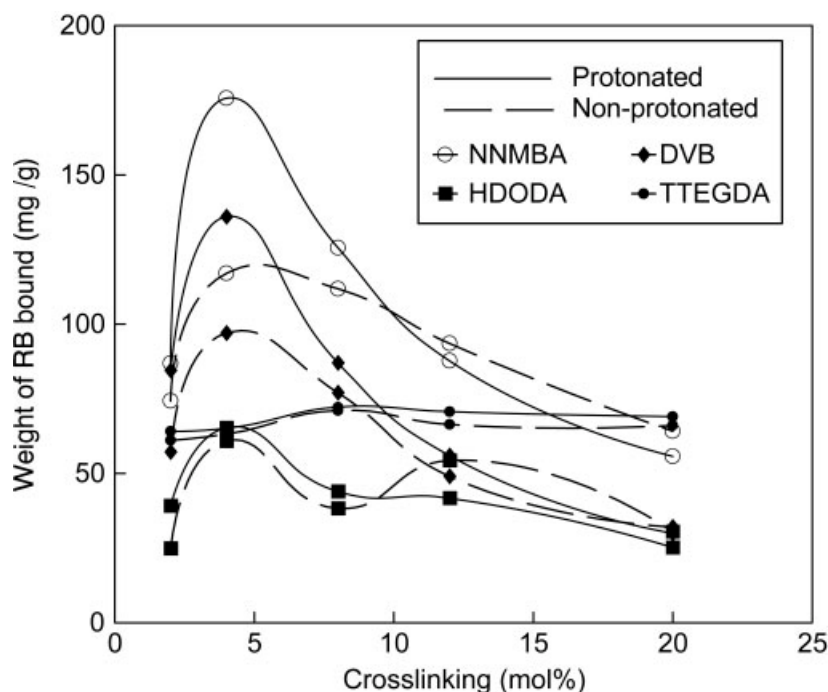
Kinetic studies of the RB uptake on 4 mol % DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamides showed that these reactions do

not follow any of the first, second, or third order reactions. Here the polymer-support is in the solid phase and RB is in the solution phase. For such heterogeneous reaction, the uptake occurs at solid-liquid interface, which can be regarded as a phase-boundary process involving the adsorption of the dye molecules by the easily available surface reactive sites<sup>27</sup> followed by the diffusion of the dye molecule to the interior of the three-dimensional support for the uptake by the functional groups flanked by the crosslinks. In general, for such a phase boundary process, the kinetic equation<sup>28</sup> is  $[1-(1-\alpha)^{1/3}] = KT$  and for the diffusion process, the kinetic equation is  $[1-(1-\alpha)^{1/3}]^2 = KT$ ; where  $\alpha$  = fraction adsorbed at time  $T$ ;  $K$  = Rate constant.

The first stage corresponds to the phase boundary process. Small deviations are observed after these times, which are due to change in the local polarity and differences in pore size both leading to the inaccessibility of the uptake sites buried within the crosslinks for the RB molecules. This hindrance is also supported by the already occupied RB molecules in the surface of the polymer-support.<sup>29</sup> In such cases, the dye has to penetrate into the polymer matrix to reach the uptake sites. This necessitates a three-dimensional diffusion.<sup>30</sup> Hence the uptake of RB on both nonprotonated and protonated crosslinked aminopolyacrylamide is a phase boundary process followed by a three-dimensional diffusion. Kinetics of RB uptake by NNMBA-crosslinked nonprotonated and proto-



**Figure 2** Time course of dye uptake by 8 mol % NNMBA-crosslinked aminopolyacrylamide.



**Figure 3** Variation of Rose Bengal uptake with the nature and degree of crosslinking by the 2–20 mol % DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked protonated and nonprotonated aminopolyacrylamides.

nated aminopolyacrylamide is shown in Figures 5 and 6.

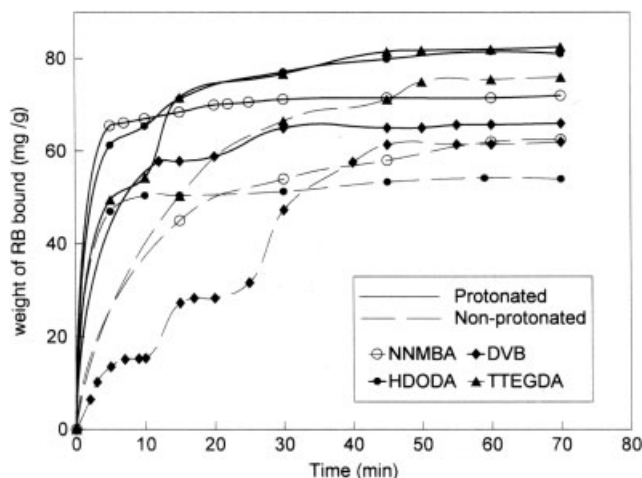
### Characterization of the RB bound nonprotonated and protonated aminopolyacrylamides

#### IR spectra

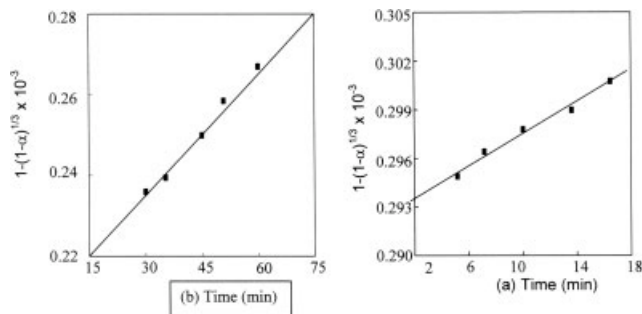
The spectrum of the crosslinked polyacrylamide showed the characteristic absorption of the C–N stretch of the amide group at  $1445\text{ cm}^{-1}$ . The peak at  $1660\text{ cm}^{-1}$  is due to C=O group and is overlapped with the bending mode of N–H band. In TTEGDA-

crosslinked polyacrylamide, the absorptions at  $1740$  and  $1100\text{ cm}^{-1}$  indicate the presence of ester and ethylene oxide linkages of the crosslinking agent TTEGDA. The band corresponding to the aromatic ring of the DVB-crosslinking is observed at  $800\text{ cm}^{-1}$ . The absorptions in the region  $1570$ – $1500\text{ cm}^{-1}$  arise from the N–H bending and C–N stretching of the C–N–H group of the secondary amide groups in the NNMBA-crosslinked polyacrylamides.

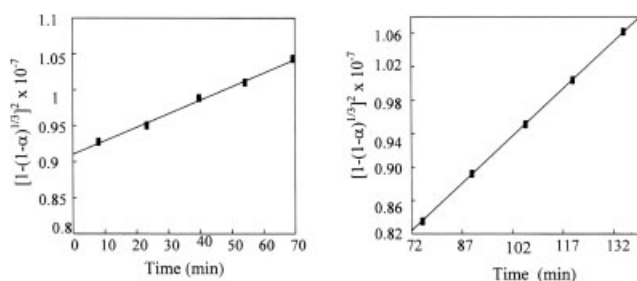
In the case of aminopolyacrylamide, the free N–H peak around  $3300\text{ cm}^{-1}$  appears as an extremely weak shoulder. The broad N–H peak centered around  $3500\text{ cm}^{-1}$  appears to be an indication of high degree of hydrogen bonding. The shoulder at  $1638\text{ cm}^{-1}$  is the N–H bending of the  $\text{NH}_2$  on the amide group. The carbonyl peak at  $1660\text{ cm}^{-1}$  was observed in the same region as of polyacrylamides.



**Figure 4** Time-course of Rose Bengal uptake by 4 mol % protonated and nonprotonated DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamide.



**Figure 5** Phase boundary adsorption of Rose Bengal by NNMBA-crosslinked aminopolyacrylamide: (a) nonprotonated and (b) protonated systems.



**Figure 6** Three-dimensional diffusion of Rose Bengal by NNMBA-crosslinked aminopolyacrylamide: (a) nonprotonated and (b) protonated systems.

The weaker band near  $1250\text{ cm}^{-1}$  results from the interaction between the N—H bending and C—N stretching. The broad band in the region  $900\text{--}400\text{ cm}^{-1}$  is because of N—H wagging. The absorption between  $1590$  and  $1500\text{ cm}^{-1}$  is characteristic of the secondary amide groups. This is due to the N—H bending and C—N stretching of the C—N—H groups in amides and amines. The very small absorptions in the unfunctionalized polyacrylamide are intensified in the amino resins since transamidation leads to secondary amides.

RB bound systems showed a decrease in the intensity of bands around  $3400$  and  $2900\text{ cm}^{-1}$  than those of free amines. There is an additional peak at  $950\text{ cm}^{-1}$  corresponding to the aromatic rings of RB. The splitting of the N—H peak at  $3300$  and  $3400\text{ cm}^{-1}$  indicated the incorporation of the amino groups for uptake with RB preventing hydrogen bonding between the amino groups.

#### UV-visible spectra

The solid state UV-vis spectrum of RB exhibits  $\lambda_{\text{max}}$  at  $570\text{ nm}$ . Uptake of RB on nonprotonated aminopolyacrylamide results in the blue shift of the  $\lambda_{\text{max}}$  of RB to  $563\text{ nm}$  as shown in Figure 7. Uptake to the protonated amino resin results in the blue shift to  $567\text{ nm}$ . As the absorption of RB in this region originates because of the  $n \rightarrow \pi^*$  transitions, the blue shift indicates the presence of dye chromophore in more polar environment on uptake.

#### Scanning electron microscopy

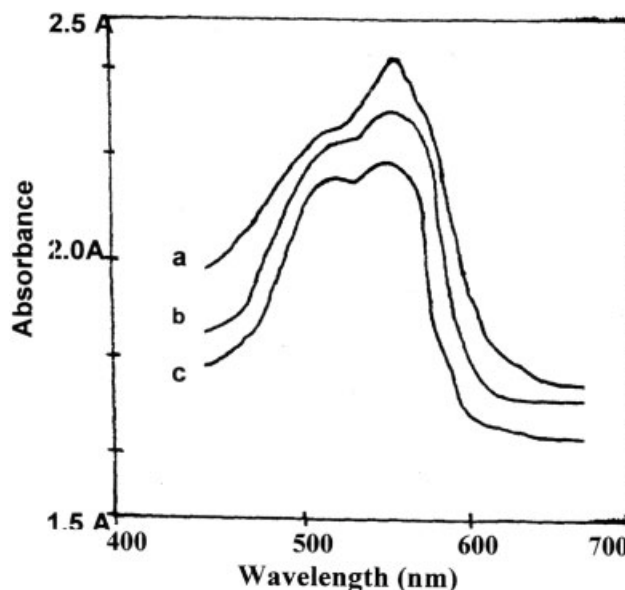
The morphological variation in crosslinked polymers can be correlated with their molecular architecture, reactivity, and physical properties using Scanning Electron Microscopy (SEM). The morphological features of the various crosslinked polymer supports have been investigated by making use of this technique. SEM is the most widely used technique to study the shape, size, morphology, and porosity of polymers.<sup>31–34</sup> In the present study, SEM was used to probe the change in morphological features of the crosslinked polymers on

uptake with the dye RB. The SEMs of NNMBA-crosslinked aminopolyacrylamide system and the RB adsorbed form are given in Figure 8.

The surface morphology of RB adsorbed polymers is different from the corresponding free polymers. The SEMs of free polymers have glassy and rough appearance. When the dye RB is bound on these polymers, the glassy and rough appearance is lost and surface of bound polymer seems smooth. This suggests higher strain energy regions on the surface of the unbound polymer. Uptake would occur in these regions, which lowers the surface energy. Hence the surface gets smoothed in the adsorbed polymer.<sup>35</sup>

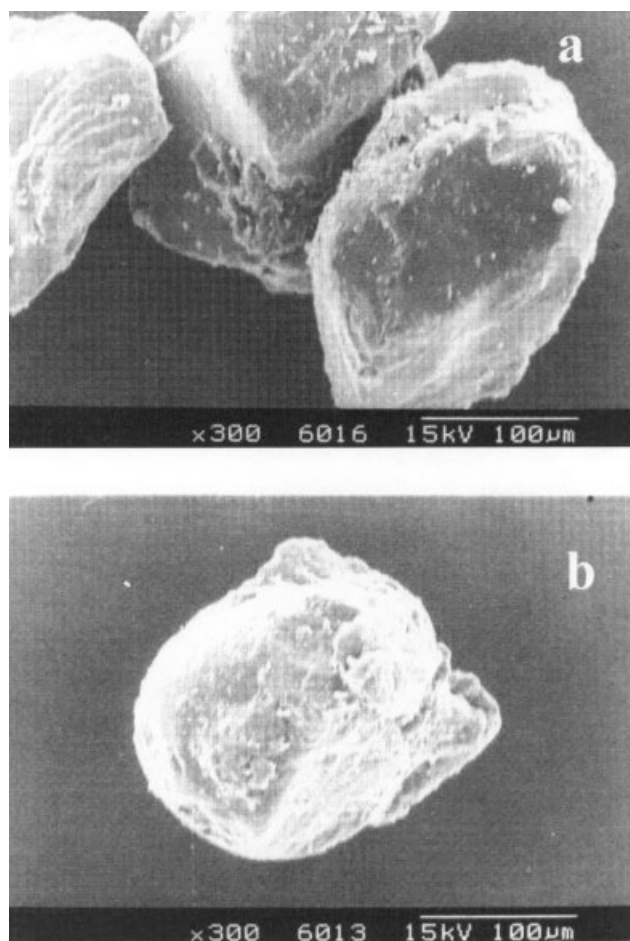
#### Swelling studies

The extent of swelling in water is represented as equilibrium water content (EWC). The water intake by the DVB-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamide systems decreases with the extent of crosslinking. As the degree of crosslinking increases from 2 to 20 mol %, the availability of polar reactive sites for the water molecules is decreased by the consecutive crosslinking points and there by decreasing the swelling and solvation characteristics. The water intake by the semirigid and semihydrophilic NNMBA-crosslinked aminopolyacrylamide systems increases with the extent of crosslinking till 4 mol % and thereafter decreases. The swelling of TTEGDA-crosslinked aminopolyacrylamide system is higher than the DVB-, NNMBA-, and HDODA-crosslinked systems. This is due to the increased flexibility and hydrophilic nature of TTEGDA cross-



**Figure 7** UV-vis. spectra of (a) Rose Bengal, (b) Rose Bengal bound on protonated aminopolyacrylamide, and (c) Rose Bengal bound on aminopolyacrylamide.





**Figure 8** SEM of (a) NNMBA-crosslinked aminopolyacrylamide and (b) Rose Bengal bound on NNMBA-crosslinked aminopolyacrylamide.

linking agent resulting in its increased capacity to hold more water molecules in the crosslinked network through hydrogen bonding with the oxygen atom of the ethylene oxide units of the TTEGDA. The swelling of the bound resin followed the same order as the unbound polymer. But the swelling of the RB bound polymer is less. After uptake with the dye RB on polymers, the polar functional groups of the polymers are less accessible for water. Also the presence of the aromatic moiety reduces the swelling in water. A comparison of the swelling and characteristics of 4 mol % DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamide indicated the following order of the swelling: DVB- < HDODA- < NNMBA- < TTEGDA-crosslinked system (Fig. 9).

#### Effect of the variables of uptake condition on the adsorption of RB

The effect of variables like time, temperature, concentration of RB solution, and pH were found to have vital roles on the adsorption of RB on polymers. Nonprotonated and protonated amino

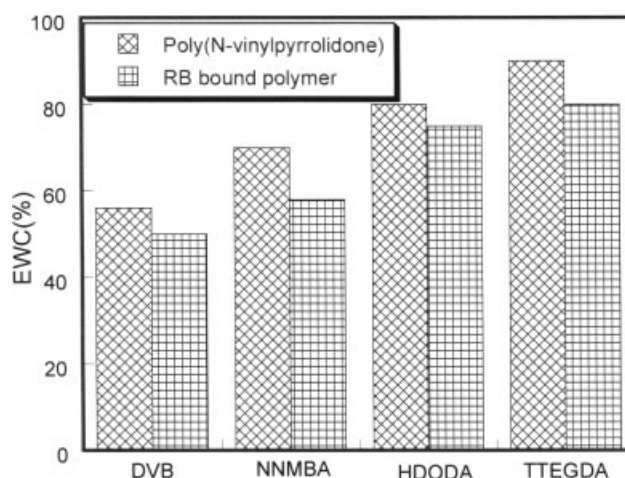
functionalized DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked (4 mol %) polyacrylamide (0.075 g) was equilibrated with RB solution (100 mL) of varying concentrations in a water bath shaker for 8 h. Here polymers of size between 100 and 200  $\mu\text{m}$  were used. The whole sets of experiments were done at room temperature (302 K) for nonprotonated and protonated aminopolyacrylamides. Concentration, temperature, and pH dependence on the adsorption of the dye RB on nonprotonated and protonated systems were found out.

#### Concentration dependence

As the concentration of dye solution increased, the amount of dye adsorbed on the polymer also increased. This increase could also be verified by visual observation. The lightly loaded polymers are purple while the highly loaded polymers are dark brownish red in color. When the dye was lightly loaded on the polymer, the RB moieties are far apart and are "site isolated", i.e., the probability of repulsion of near-by dye molecules is less because of the large distance between two dye molecules. For the heavily loaded resin, the effective distance between the immobilized dyes are diminished and is controlled by the coiling of the interspersed polymer chain and the extent of repulsion is directly controlled by the extent of polymer chain loading with the dye.<sup>26</sup> A general representation of the concentration dependence on the adsorption of RB on 4 mol % HDODA-crosslinked nonprotonated and protonated aminopolyacrylamides is shown in Table I.

#### Temperature dependence

RB ( $1.90 \times 10^{-4} \text{M}$ , 100 mL) was equilibrated with a definite amount of DVB-, NNMBA-, HDODA-, and



**Figure 9** EWCs of 4 mol % DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamides and Rose Bengal bound polymers.

**TABLE I**  
Concentration Dependence on the Adsorption of Rose Bengal by 4 mol % HDODA-Crosslinked Nonprotonated and Protonated Aminopolyacrylamides

Concentration of dye ( $10^{-6}$ M)	Amount of Rose Bengal bound (mg/g)	
	Nonprotonated aminopolyacrylamide	Protonated aminopolyacrylamide
30	58	60
50	73	78
70	99	101
100	115	135
125	160	165

TTEGDA-crosslinked (4 mol %) nonprotonated and protonated aminopolyacrylamide for 8 h at different temperatures, such as 294, 304, 314, 324, and 334 K. At all temperatures, dye uptake is higher for protonated system than for the nonprotonated system (Table II). The lower dye uptake at higher temperature arises from the exothermicity of the uptake process. This leads to an overall decrease in the rate of uptake. Uptake of RB on DVB-crosslinked nonprotonated and protonated aminopolyacrylamides is highest at 334 K and lowest at 294 K. For the two NNMBA-crosslinked systems, one interesting thing observed was that the amount of dye adsorbed on polymer is highest at room temperature (302 K) and lowest at 294 K. Uptake of RB on HDODA-crosslinked nonprotonated and protonated aminopolyacrylamides is highest at 324 K and lowest at 294 K. RB uptake on TTEGDA-crosslinked nonprotonated and protonated aminopolyacrylamides is highest at 314 K and lowest at 294 K.

#### pH dependence

To investigate the optimum pH of uptake, the experiments were carried out at different pHs of phosphate buffer ( $\text{Na}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ , 0.025M) at room temperature. Investigation of the effect of pH on dye uptake is limited to alkaline pH, since the pink colored RB becomes colorless at acidic pH.

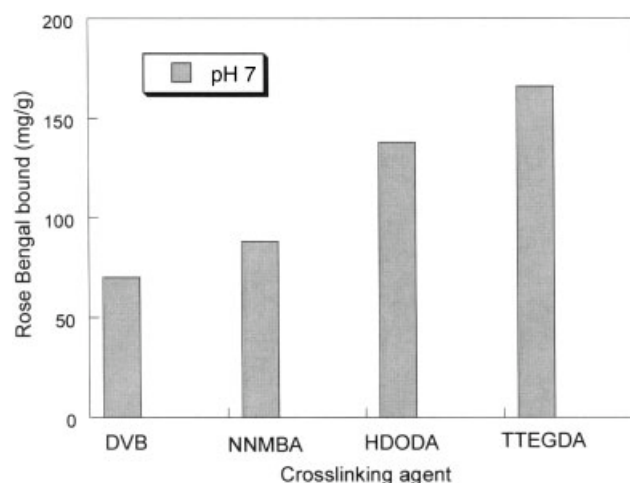
**TABLE II**  
Temperature Dependence on Rose Bengal Uptake by 4 mol % NNMBA-Crosslinked Nonprotonated and Protonated Aminopolyacrylamides

Temperature (K)	Amount of Rose Bengal bound (mg/g)	
	Nonprotonated aminopolyacrylamide	Protonated aminopolyacrylamide
294	203.05	205
304	256.9	258
314	206.1	207.5
324	214.2	242.2
334	248.5	258.3

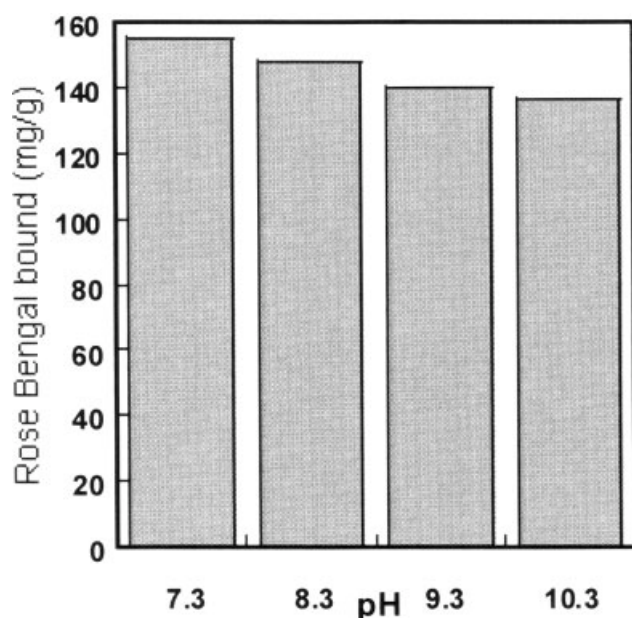
It was found that the RB uptake is maximum at pH 7.3. Though at pH 7.3, RB uptake on DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked (4 mol %) nonprotonated and protonated amino polyacrylamide is higher than that of other pHs, the dye uptake was found to be highest (Fig. 10) when the reaction was carried out in aqueous medium. While we are using the buffer, there are different ions and these ions would have some interfering effect on the uptake of RB. That may be the reason for the low uptake in the presence of buffer. A general representation of the effect of pH on the uptake of RB by 4% NNMBA-crosslinked aminopolyacrylamide is shown in Figure 11.

#### Effect of the nature and degree of crosslinking on uptake of RB by 2–20 mol % DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked nonprotonated and protonated aminopolyacrylamides

A polymer support must possess a structure that permits adequate diffusion of the reagents into the reactive site. This depends on the extent of swelling or solvation, the effective pore size and pore volume, and the chemical and mechanical stability of the resins under the reaction conditions. These in turn depend upon the degree of crosslinking of the resins and the conditions employed for the preparation of the resin. For the nonprotonated and protonated DVB-, NNMBA-, and HDODA-crosslinked aminopolyacrylamides, the dye uptake increased with increasing crosslinking till 4 mol % and decreased thereafter (Fig. 3). The RB uptake by the nonprotonated and protonated systems are in same range suggesting that the quarternary ammonium ion has no significant effect on RB uptake. The anomalous observation of 4 mol % crosslinking arises from the



**Figure 10** Uptake of RB by 4 mol % DVB-, NNMBA-, HDODA-, and TTEGDA-crosslinked aminopolyacrylamides at pH 7.



**Figure 11** Variation of Rose Bengal uptake with pH non-protonated 4 mol % TTEGDA-crosslinked aminopolyacrylamide.

heterogeneity developed in these particular crosslinked systems. For the TTEGDA-crosslinked system, the dye uptake increased till 8 mol % and thereafter decreased. The low degree of RB uptake on the high crosslinked system arise from the decreased accessibility of the uptake sites for the RB molecules by the higher concentration of consecutive crosslinking points. Moreover, the possibility of uptake sites will be higher on the surface of the polymer and this results in the repulsion between the bound dye molecules.<sup>36</sup>

On comparing the various crosslinked systems, the RB uptake followed the order: NNMBA- > DVB- > TTEGDA- > HDODA-crosslinked system. Generally, high RB uptake would be expected for the highly flexible and polar TTEGDA-crosslinked system. The observation of low uptake of RB by system with high amino capacity arises from the incompatibility between RB and the polymer support, and inaccessibility of the nearby uptake sites for the uptake with the large RB molecules. The hydrophobic and rigid DVB-crosslinked and semirigid and semihydrophilic NNMBA-crosslinked systems are more compatible with the RB moieties than the HDODA- and TTEGDA-crosslinked systems.

Usually, as the degree of crosslinking is increased, the mobility of the polymer chain is reduced resulting in decreased interaction of the substrate in solution with the reactive function in the solid polymer-support. The access of reactive groups in highly crosslinked networks is considerably diminished as they are flanked by large number of crosslinks leading to a decreased reactivity.<sup>37,38</sup> The low dye uptakes of the 2 and 20 mol % crosslinked system

arise from the lower concentrations of the uptake sites.

## CONCLUSIONS

Linear and differently crosslinked polyacrylamides were prepared by free radical solution polymerization and functionalized by transamidation with excess ethylenediamine. The interaction of the amino functions with dyes like RB, MO, MR, and MB was followed and the RB adsorption was found to be higher than other dyes. Also RB uptake by the protonated systems is higher than the nonprotonated systems. The conditions of RB uptake were optimized. Kinetic studies showed that the uptake of RB by the polymeric systems is a phase boundary process followed by a three-dimensional diffusion. The RB uptake by the linear systems is higher than crosslinked systems. The binding of crosslinked systems varied with the relative rigidity/flexibility as well as the extent of crosslinking in the polymer support. The trend in RB uptake with degree of crosslinking is similar to the variation of amino capacity with the degree of crosslinking in the respective crosslinked system.

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