

Modification of Dextran Through the Grafting of *N*-Vinyl-2-Pyrrolidone and Studies of Physicochemical Phenomena in Terms of Metal-Ion Uptake, Swelling Capacity, and Flocculation

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Received 25 September 2007; accepted 20 May 2008

DOI 10.1002/app.28857

Published online 15 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The optimum conditions for grafting *N*-vinyl-2-pyrrolidone onto dextran initiated by a peroxydiphosphate/thiourea redox system were determined through the variation of the concentrations of *N*-vinyl-2-pyrrolidone, hydrogen ion, potassium peroxydiphosphate, thiourea, and dextran along with the time and temperature. The grafting ratio increased as the concentration of *N*-vinyl-2-pyrrolidone increased and reached the maximum value at 24×10^{-2} mol/dm³. Similarly, when the concentration of hydrogen ion increased, the grafting parameters increased from 3×10^{-3} to 5×10^{-3} mol/dm³ and attained the maximum value at 5×10^{-3} mol/dm³. The grafting ratio, add-on, and efficiency increased continuously with the concentration of peroxydiphosphate

increasing from 0.8×10^{-2} to 2.4×10^{-2} mol/dm³. When the concentration of thiourea increased from 0.4×10^{-2} to 2.0×10^{-2} mol/dm³, the grafting ratio attained the maximum value at 1.2×10^{-2} mol/dm³. The grafting parameters decreased continuously as the concentration of dextran increased from 0.6 to 1.4 g/dm³. An attempt was made to study some physicochemical properties in terms of metal-ion sorption, swelling, and flocculation. Dextran-*N*-vinyl-2-pyrrolidone was characterized with infrared spectroscopy and thermogravimetric analysis. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3455–3463, 2008

Key words: addition polymerization; graft copolymerization; swelling

INTRODUCTION

The graft copolymerization of vinyl monomers onto natural and synthetic polysaccharides has received widespread attention in recent years.^{1–3} Dextran has been chosen as a backbone; it is a nonionic and rigid natural polymer with a predominance of α -D-glucose (1–6) linkages. It is well known as a versatile material used in a variety of biomedical and industrial applications, such as drug carrier systems,⁴ pharmaceuticals,⁵ and food applications.⁶ *N*-Vinyl-2-pyrrolidone (NVP), which is a hydrophilic and nontoxic monomer, has various industrial applications.^{7,8} It has been used as the main component of temporary skin covers and wound dressings⁹ and also as the wrapping material of single-walled carbon nanotubes.¹⁰

The hitherto unreported graft copolymer (Dextran-*N*-Vinyl-2-pyrrolidone) was prepared with a peroxydiphosphate (PDP)/thiourea (TU) redox system.

The effects of the concentrations of potassium peroxydiphosphate, TU, hydrogen ion, dextran, and NVP along with the time and temperature on the

grafting parameters were studied. The graft copolymer was characterized with infrared (IR) spectroscopy and thermogravimetric analysis.

EXPERIMENTAL

Materials

NVP (Sigma-Aldrich Co. Ltd, Gillingham, Dorset, SP8 4XT, UK) was distilled under reduced pressure (11 mm) at 60°C, and the middle fraction was used in all experiments. Dextran (Sigma) and TU (Merck) were used as received. Potassium peroxydiphosphate was received as a gift sample from FMC (United States). Sulfuric acid (Merck) was used for maintaining the hydrogen-ion concentration. All other chemicals were analytical-grade. For the flocculation, coking and noncoking coals were received as gift samples from the Bokaro Steel Plant (India).

Procedure for the graft copolymerization

A dextran solution was prepared by the slow addition of a weighed amount of dextran to rapidly stirred, deaerated, triple-distilled water in a reactor. Calculated amounts of NVP, TU, and sulfuric acid solutions were added to the reactor at a constant

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temperature and degassed for half an hour. A known amount of a deaerated potassium peroxydiphosphate solution was added to initiate the reaction, and the reaction was carried out under a nitrogen atmosphere. After the desired time period, the reaction was stopped by air being allowed into the reactor. The graft copolymer was precipitated by the reaction mixture being poured into a water/methanol (1 : 5) mixture. The graft copolymer was separated, dried, and weighed, whereas the homopolymer remained in solution (filtrate). To the filtrate, a pinch of hydroquinone was added, and it was concentrated by distillation under reduced pressure. This concentrated solution was poured into an excess of pure methanol, and thus poly (*N*-vinyl-2-pyrrolidone) was separated, dried, and weighed.

RESULTS AND DISCUSSION

The graft copolymer was characterized according to Fanta's definition:¹¹

$$\text{Grafting ratio}(\%) = \frac{\text{Grafted polymer}}{\text{Weight of the substrate}} \times 100$$

$$\text{Add on}(\%) = \frac{\text{Synthetic polymer}}{\text{Graft copolymer}} \times 100$$

$$\text{Conversion}(\%) = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Grafting efficiency}(\%) = \frac{\text{Grafted polymer}}{\text{Polymer formed}} \times 100$$

$$\text{Homopolymer}(\%) = 100 - \text{Grafting efficiency}$$

The effects of the variation of the TU, PDP, NVP, hydrogen-ion, and dextran concentrations along with the time and temperature on the grafting parameters were studied.

Effect of the NVP concentration

The effect of NVP on the grafting parameters was studied through the variation of the concentration of NVP from 12×10^{-2} to 36×10^{-2} mol/dm³, and the results are shown in Figure 1. The grafting parameters increased when the concentration of NVP increased from 12×10^{-2} to 24×10^{-2} mol/dm³, but beyond 24×10^{-2} mol/dm³, these parameters decreased. The increases in the grafting ratio, add-on, and efficiency with the monomer concentration might be due to an accumulation of monomer molecules in close proximity to the backbone dextran. The monomer molecules in the immediate vicinity of the reaction sites became acceptors of dextran mac-

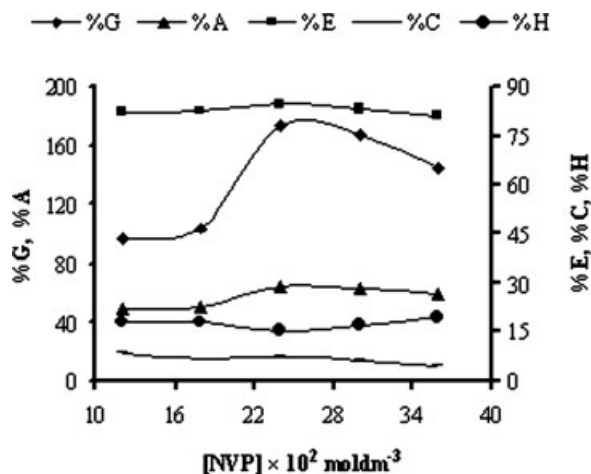
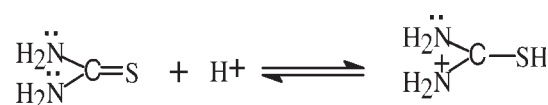


Figure 1 Effect of the *N*-vinyl-2-pyrrolidone concentration ([DOH] = 1.0 g/dm³; [TU] = 1.2×10^{-2} mol/dm³; time = 120 min; [H⁺] = 5×10^{-3} mol/dm³; [PDP] = 1.6×10^{-2} mol/dm³; temperature = 35°C). %G is the grafting ratio (%), %A is the add-on (%), %C is the conversion (%), %E is the grafting efficiency (%), and %H is the amount of the homopolymer (%).

roradicals, and this resulted in chain initiation; thereafter, they became free-radical donors to neighboring molecules. The decreases in the grafting ratio, add-on, and efficiency might be due to the formation of more homopolymer, which increased the viscosity of the reaction medium.

Effect of the hydrogen-ion concentration

The effect of the hydrogen-ion concentration on the grafting parameters was studied through the variation of the concentration of hydrogen ion from 3×10^{-3} to 7×10^{-3} mol/dm³ (Table I). The grafting ratio, add-on, and efficiency increased when the hydrogen-ion concentration increased from 3×10^{-3} to 5×10^{-3} mol/dm³, but beyond this range, these parameters decreased. The increase in the grafting parameters with the hydrogen-ion concentration up to 5×10^{-3} mol/dm³ was due to protonation of TU, and these protonated species reacted with the active species of the PDP ion (H₂P₂O₈²⁻) to give more primary free radicals; hence, an increase in the values of these parameters was observed:



However, beyond 5×10^{-3} mol/dm³, these parameters decreased with an increase in the hydrogen concentration, and this was attributed to the formation of less active species¹² of PDP such as H₅P₂O₈⁺ and H₆P₂O₈²⁺.

TABLE I
Effect of the Hydrogen-Ion Concentration

$[H^+] \times 10^3$ (mol/dm ³)	Grafting ratio (%)	Grafting efficiency (%)	Add-on (%)	Conversion (%)	Homopolymer (%)
3	109.9	79.8	52.4	5.2	20.2
4	133.1	81.9	57.1	6.0	18.1
5	173.9	84.6	63.5	7.7	15.5
6	131.0	82.7	56.7	5.9	17.3
7	115.1	80.5	53.5	5.4	19.5

$[DOH] = 1.0 \text{ g/dm}^3$; $[TU] = 1.2 \times 10^{-2} \text{ mol/dm}^3$; $[PDP] = 1.6 \times 10^{-2} \text{ mol/dm}^3$; $[NVP] = 24 \times 10^{-2} \text{ mol/dm}^3$; time = 120 min; temperature = 35°C.

Effect of the peroxydiphosphate concentration

The effect of the PDP concentration on graft copolymerization was studied at different concentrations of PDP (Fig. 2). The grafting ratio, add-on, and efficiency increased when the concentration of PDP increased from 0.8×10^{-2} to $2.4 \times 10^{-2} \text{ mol/dm}^3$. This increment was due to an increase in the rate of production of primary free radicals (R_1S^\bullet and $HPO_4^{\bullet-}$). When these radicals attacked the backbone, the number of grafting sites increased on the polymeric backbone, where grafting took place.

Effect of the TU concentration

The effect of the TU concentration on the grafting parameters was studied through the variation of the concentration of TU from 0.4×10^{-2} to $2.0 \times 10^{-2} \text{ mol/dm}^3$ (Table II). The grafting ratio, add-on, and efficiency increased when the concentration of TU increased up to $1.2 \times 10^{-2} \text{ mol/dm}^3$. The increase in the grafting parameters was attributed to the increase in the rate of production of primary free radicals with an increase in the TU concentration up to $1.2 \times 10^{-2} \text{ mol/dm}^3$. After this concentration, the concentration of PDP became less than that of TU, so the rate of production of primary free radicals decreased; therefore, an decrease in the grafting parameters was observed.

Effect of the dextran concentration

The effect of the dextran concentration on the grafting parameters was studied through the variation of the concentration of dextran from 0.6 to 1.4 g/dm³, and the results are presented in Figure 3. The grafting ratio, add-on, and efficiency decreased continuously when the concentration of dextran increased. This phenomenon could be explained by the fact that as the concentration of dextran increased, the viscosity of the reaction medium increased; this hindered the movement of NVP and dextran macroradicals, thereby reducing the grafting parameters.

Effect of the temperature

The effect of the temperature on the grafting parameters was studied from 25 to 45°C, and the results are presented in Table III. The grafting ratio, add-on, and efficiency increased continuously when the temperature increased, and this was due to the fact that the rate of production of primary free radicals increased. An increase in the temperature caused an increase in the movement of NVP molecules and dextran molecules, which resulted in an increase in the values of the grafting parameters.

Effect of the time

The effect of the time period on the grafting parameters was studied through the variation of the time period of the reaction from 60 to 180 min, and the results are shown in Figure 4. The grafting ratio, add-on, and efficiency increased continuously with an increase in the time period, and this led to an

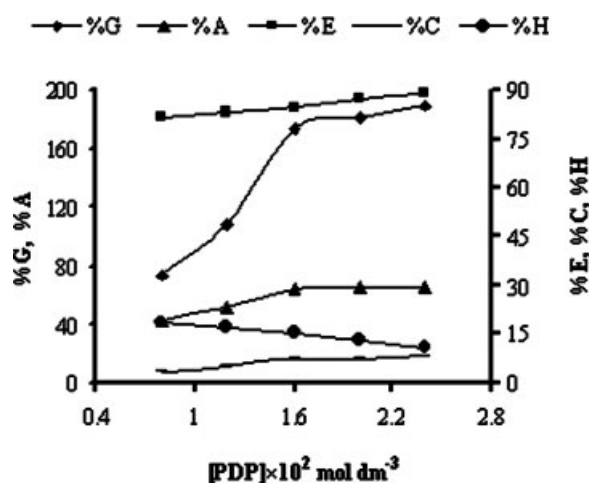


Figure 2 Effect of the peroxydiphosphate concentration ($[DOH] = 1.0 \text{ g/dm}^3$; $[TU] = 1.2 \times 10^{-2} \text{ mol/dm}^3$; time = 120 min; $[H^+] = 5 \times 10^{-3} \text{ mol/dm}^3$; $[NVP] = 24 \times 10^{-2} \text{ mol/dm}^3$; temperature = 35°C). %G is the grafting ratio (%), %A is the add-on (%), %C is the conversion (%), %E is the grafting efficiency (%), and %H is the amount of the homopolymer (%).

TABLE II
Effect of the TU Concentration

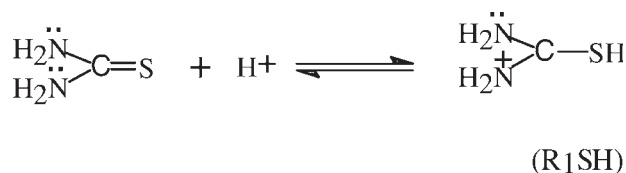
[TU] × 10 ² (mol/dm ³)	Grafting ratio (%)	Grafting efficiency (%)	Add-on (%)	Conversion (%)	Homopolymer (%)
0.4	141.8	82.9	58.6	6.4	17.0
0.8	167.3	83.5	62.6	7.5	16.5
1.2	173.9	84.6	63.5	7.7	15.5
1.6	146.0	81.8	59.4	6.7	18.2
2.0	138.9	79.6	58.1	6.5	20.5

[DOH] = 1.0 g/dm³; [PDP] = 1.6 × 10⁻² mol/dm³; [NVP] = 24 × 10⁻² mol/dm³; [H⁺] = 5 × 10⁻³ mol/dm³; time = 120 min; temperature = 35°C.

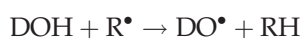
increase in the rate of production of radicals; hence, an increase in the grafting parameters was observed.

Mechanism

It is assumed that in the presence of hydrogen ion, TU can be protonated and react with active species of PDP¹³ (H₂P₂O₈²⁻) to produce free radicals (R₁S• and HPO₄^{•-}). These radicals extract hydrogen atoms from the dextran backbone, producing dextran free macroradicals. The monomer molecules, which are in close vicinity to the reaction sites, become acceptors of dextran macroradicals, resulting in chain initiation, and thereafter themselves become free-radical donors to neighboring molecules; thus, the grafted chain grows. The termination of chains by coupling yields the graft copolymer. The tentative mechanism can be represented as follows:



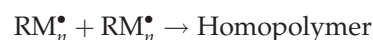
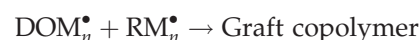
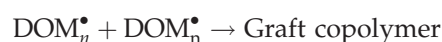
Initiation



Propagation



Termination



Evidence of grafting

IR spectra of ungrafted and grafted samples were recorded with a Jasco model FTIR-5300 in the range of 500–4000 cm⁻¹ to provide proof of grafting.

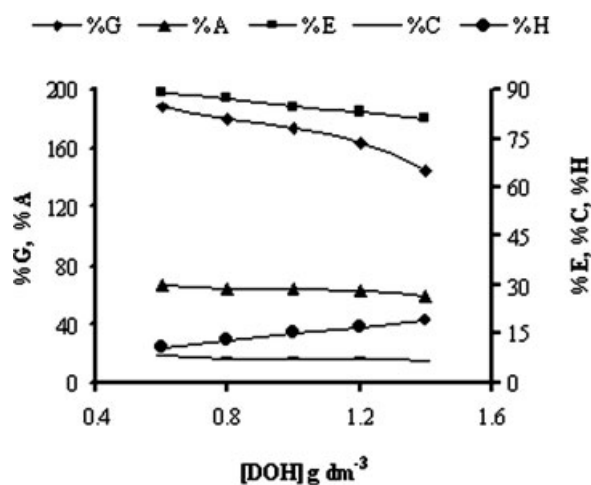


Figure 3 Effect of the dextran concentration ([DOH] = 1.0 g/dm³; [TU] = 1.2 × 10⁻² mol/dm³; time = 120 min; [H⁺] = 5 × 10⁻³ mol/dm³; [PDP] = 1.6 × 10⁻² mol/dm³; temperature = 35°C). %G is the grafting ratio (%), %A is the add-on (%), %C is the conversion (%), %E is the grafting efficiency (%), and %H is the amount of the homopolymer (%).

TABLE III
Effect of the Temperature

Temperature (°C)	Grafting ratio (%)	Grafting efficiency (%)	Add-on (%)	Conversion (%)	Homopolymer (%)
25	153.8	81.1	60.6	7.1	18.9
30	163.5	82.9	62.0	7.4	17.1
35	173.9	84.6	63.5	7.7	15.5
40	182.3	87.1	64.6	7.9	12.9
45	198.5	88.2	66.5	8.4	11.9

[DOH] = 1.0 g/dm³; [TU] = 1.2 × 10⁻² mol/dm³; [PDP] = 1.6 × 10⁻² mol/dm³; [H⁺] = 5 × 10⁻³ mol/dm³; [NVP] = 24 × 10⁻² mol/dm³; time = 120 min.

A comparison of the IR spectra of dextran and dextran-g-NVP (shown in Figs. 5 and 6) shows that a band at 3429.9 cm⁻¹ is due to the OH stretching vibration in the spectrum of dextran. There is a variation in the intensity of the OH stretching vibration, and a shifting of this peak from 3429.9 to 3222.9 and 3178.9 cm⁻¹ appears for dextran-g-NVP, indicating the participation of hydroxyl groups in the chemical reaction. The graft copolymerization is further confirmed by a characteristic absorption band at 1631.8 cm⁻¹ due to the >C=O stretching vibration and one at 1400.7 cm⁻¹ due to the -C≡N stretching vibration of the monomer molecule. The appearance of additional peaks in the spectrum of the graft copolymer and the disappearance of the OH out-of-plane bending vibration in the spectrum of dextran at 667.9 cm⁻¹ from the spectrum of dextran-g-NVP show that grafting might have taken place on OH sites of the dextran backbone.

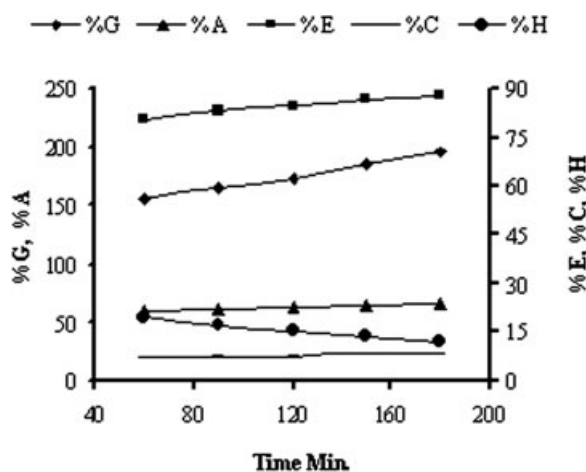


Figure 4 Effect of time ([DOH] = 1.0 g/dm³; [TU] = 1.2 × 10⁻² mol/dm³; [H⁺] = 5 × 10⁻³ mol/dm³; [NVP] = 24 × 10⁻² mol/dm³; [PDP] = 1.6 × 10⁻² mol/dm³; temperature = 35°C). %G is the grafting ratio (%), %A is the add-on (%), %C is the conversion (%), %E is the grafting efficiency (%), and %H is the amount of the homopolymer (%).

Thermal analysis

Thermograms were recorded on a Netzsch STA 409C/CD thermal analyzer from 0 to 1400°C at a heating rate of 15°C/min in a nitrogen atmosphere. The results are summarized in Table IV.

Dextran

A thermogravimetric trace showed that dextran started to degrade at about 112°C. The polymer decomposition temperature (PDT) was 120°C. The degradation of dextran occurred in a single step. The rate of weight loss increased with an increase in the temperature from 125 to 200°C and attained a maximum at 250°C. About 80.9% weight loss of dextran was found at 400°C. The temperature at which maximum degradation occurred (T_{max}) was 306°C; this was also confirmed by the endothermic peak present in the differential thermal analysis (DTA) curve of dextran at about 306°C, which showed that maximum degradation took place. The final decomposition temperature (FDT) was found at 500°C. In the DTA curve, additional peaks appeared with some fluctuation, which showed the gradual degradation of the polymeric backbone. The integral procedural decomposition temperature (IPDT) of dextran was found at 213.3°C. The thermogravimetric

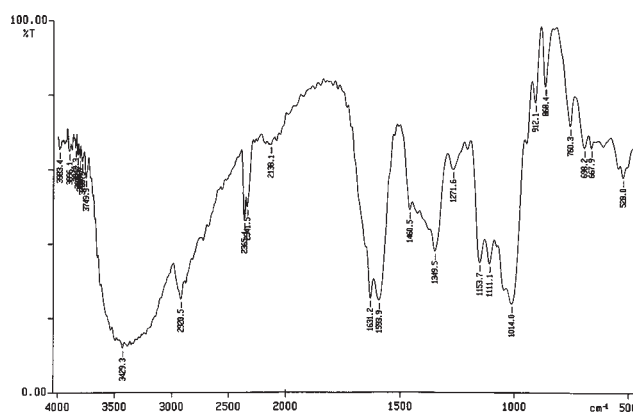


Figure 5 IR spectrum of dextran.

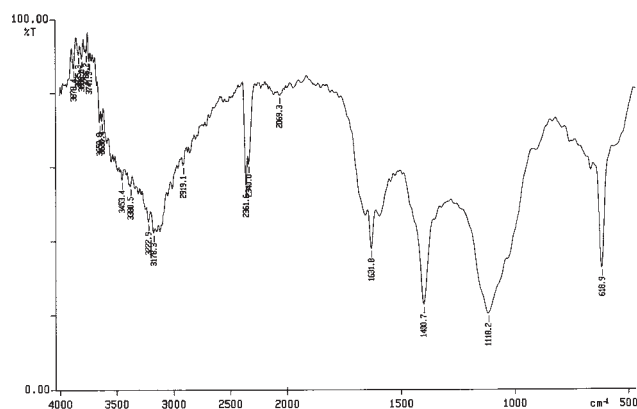


Figure 6 IR spectrum of dextran-g-NVP.

analysis trace and differential thermal trace of dextran are presented in Figures 7 and 8, respectively.

Dextran-g-NVP

A sharp peak at 106.25°C was due to the loss of absorbed water. The graft copolymer (dextran-g-NVP) started to degrade at about 112.3°C. The PDT was found at 114°C. The rate of weight loss increased with an increase in the temperature from 114 to 312.75°C, and thereafter, a decrease in the weight loss was observed. Two T_{\max} values of 206.3 and 312.3°C were found: maximum degradation occurred from 186.3 to 212.3°C and from 286.3 to 318.8°C, respectively. First, $T_{\max} = 206.3^\circ\text{C}$ indicated the elimination of the —OH group from the pendant chain attached to the polymeric backbone, and this was also confirmed by the endothermic peak present in the DTA curve between 200 and 206°C. The weight loss of the graft copolymer from 286 to 318.8°C was due to the elimination of the —NOC₄H₆ group. At 800°C, the maximum weight loss was found, that is, 63.7%; thus, the FDT was found at 1113°C. The IPDT was found at 217°C. The high FDT value and two-step degradation were indications of the stability of the graft copolymer in comparison with the parent backbone. The thermogravimetric analysis trace and differential thermal trace of dextran-g-NVP are presented in Figures 9 and 10, respectively.

Swelling study

To study the swelling behavior, different samples of the graft copolymer were synthesized with different concentrations of the monomer. The preweighed samples (20 mg each) were immersed in 20 mL of triple-distilled water and kept undisturbed for 10 h at room temperature until equilibrium swelling was reached. The swollen samples were then removed from triple-distilled water, quickly wiped with filter paper to remove droplets on the surface, and weighed. The swelling percentage and swelling ratio were calculated with the following expressions:¹⁴

$$\text{Swelling(\%)} = \frac{\text{Weight of swollen polymer} - \text{Weight of dry polymer}}{\text{Weight of dry polymer}} \times 100$$

$$\text{Swelling ratio} = \frac{\text{Weight of swollen polymer} - \text{Weight of dry polymer}}{\text{Weight of dry polymer}}$$

The swelling as a function of the monomer was investigated, and the results are given in Table V. The swelling percentage and swelling ratio increased as the concentration of NVP increased and reached the maximum values at $24 \times 10^{-2} \text{ mol/dm}^3$; this was due to the increase in the hydrophilicity of the graft copolymer, which in turn caused a stronger affinity for more absorption of more water.

Metal-ion uptake

The metal-ion-sorption studies were carried out with different samples of the graft copolymer synthesized with various concentrations of NVP ranging from 12×10^{-2} to $36 \times 10^{-2} \text{ mol/dm}^3$. For the metal-ion-sorption studies, 20 mg of the graft copolymer was placed in 10 mL of a metal-ion solution of a known concentration and kept there for 24 h. The strength of the unabsorbed metals ions was determined by a spectroscopic method.¹⁵ For the metal-ion-sorption studies, five metal ions—Cu²⁺, Ni²⁺, Zn²⁺, Pb²⁺, and Hg²⁺—were chosen. The sorption behavior of the polymeric backbone and graft copolymer for five

TABLE IV
Thermogravimetric Analysis of Dextran and Dextran-g-NVP

Sample code	PDT (°C)	IPDT (°C)	FDT (°C)	T_{\max} (°C)	DTA peaks	
					Exo peaks (°C)	Endo peaks (°C)
D	125	213.3	500	306.3	—	300.00
D _P	112.25	217.7	1113	206.3 312.3	—	200.00

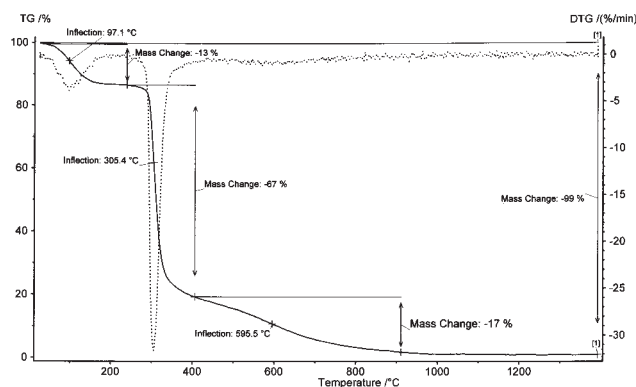


Figure 7 Thermogravimetric analysis of dextran (DTG = differential thermogravimetry; TG = thermogravimetry).

metal ions was investigated with the following expressions¹⁶ (Table VI):

Percentage uptake

$$= \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion in the feed}} \times 100$$

Partition coefficient

$$= \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion left in the solution}} \times \frac{\text{Volume of the solution (mL)}}{\text{Weight of the dry polymer (g)}}$$

Retention capacity

$$= \frac{\text{Amount of metal ion in the polymer (mequiv)}}{\text{Weight of the dry polymer (g)}}$$

The values of the ion-uptake percentage, partition coefficient, and retention capacity increased directly as the grafting percentage increased, and this was due to an increased number of pendent chains of NVP on the dextran backbone. The results also

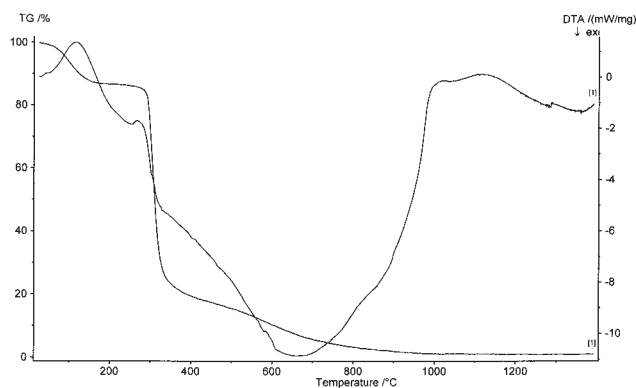


Figure 8 DTA of dextran (TG = thermogravimetry).

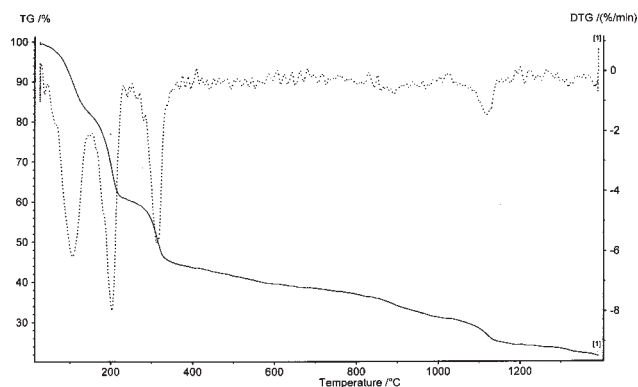


Figure 9 Thermogravimetric analysis of dextran-g-NVP (DTG = differential thermogravimetry; TG = thermogravimetry).

showed that Hg^{2+} was the ion least able to be uptaken.

Flocculation properties

Into a 1.0-L conical flask, 200 cc of a 1.0 wt % coal suspension was placed. The flask was placed on a flocculator, and the required quantity of the polymer solution was added to the flask to make the predetermined dose with respect to the suspension volume. After the addition of the polymer solution, the suspension was stirred at a constant speed for 15 min. The flocs were allowed to settle for half an hour. A clean supernatant liquid was drawn from a depth of 1.0 cm, and its turbidity was measured with a digital nephelometer [model 341 (EI), ISO-TECH Systems, Varanasi] to express the turbidity in nephelometric turbidity units. Dextran-g-NVP clearly showed better flocculation capability in bringing down the turbidity of supernatant liquids of coking and noncoking fine suspensions than dextran itself (Fig. 11). In dextran-g-NVP, dangling poly(*N*-vinyl-2-pyrrolidone) chains had better affinity to the

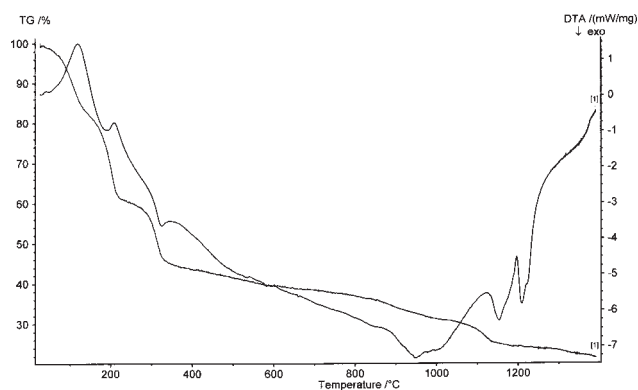


Figure 10 DTA of dextran-g-NVP (TG = thermogravimetry).

TABLE V
Swelling Study of Dextran-g-NVP

Sample code	[NVP] × 10 ² (mol/dm ³)	Grafting ratio (%)	Swelling (%)	Swelling ratio
D _{P1}	12	96.4	96	0.96
D _{P2}	18	103.7	152	1.52
D _{P3}	24	173.9	195	1.95
D _{P4}	30	167.2	188	1.88
D _{P5}	36	144.3	162	1.62

[DOH] = 1.0 g/dm³; [TU] = 1.2 × 10⁻² mol/dm³; [PDP] = 1.6 × 10⁻² mol/dm³; [H⁺] = 5.0 × 10⁻³ mol/dm³; time = 120 min; temperature = 35°C.

TABLE VI
Sorption Studies of Metal Ions on Dextran and Dextran-g-NVP

Sample code	[NVP] × 10 ² (mol/dm ³)	Grafting ratio (%)	Uptake (%)					Partition coefficient					Retention capacity				
			Cu ²⁺	Ni ²⁺	Zn ²⁺	Pb ²⁺	Hg ²⁺	Cu ²⁺	Ni ²⁺	Zn ²⁺	Pb ²⁺	Hg ²⁺	Cu ²⁺	Ni ²⁺	Zn ²⁺	Pb ²⁺	Hg ²⁺
D	—	—	2.3	1.9	1.5	1.9	0.8	11.7	9.4	7.7	10.1	4.1	1.1	0.9	0.8	1.0	0.4
D _{P1}	12	96.4	2.5	2.3	2.1	2.2	1.0	12.8	11.6	10.7	11.2	5.2	1.2	1.1	1.1	1.1	0.5
D _{P2}	18	103.7	5.4	4.5	3.8	4.4	3.7	28.5	23.7	19.8	22.8	19.1	2.6	2.2	2.0	2.2	1.8
D _{P3}	24	173.9	8.3	6.6	4.4	6.3	4.3	45.2	35.2	22.9	33.9	22.4	4.0	3.2	2.3	3.2	2.1
D _{P4}	30	167.2	4.1	3.7	2.9	3.6	2.2	21.6	19.2	14.7	18.5	11.5	2.0	1.8	1.5	1.8	1.1
D _{P5}	36	144.3	3.7	2.9	1.9	2.4	1.8	19.4	14.8	9.7	12.2	9.4	1.8	1.4	1.0	1.2	0.9

[DOH] = 1.0 g/dm³; [TU] = 1.2 × 10⁻² mol/dm³; [PDP] = 1.6 × 10⁻² mol/dm³; [H⁺] = 5.0 × 10⁻³ mol/dm³; time = 120 min; temperature = 35°C.

contaminant coal particles; a similar result was reported for acrylamide. Hence, its flocculation capability increased. The graft copolymer dextran-g-NVP may be used for the treatment of coal wastewater.

Viscosity measurements

The property of a liquid by virtue of the relative motion between its different layers is known as the

viscosity or internal friction. In other words, *viscosity* is the measure of the resistance to flow that a liquid offers when it is subjected to shear stress. With the help of an Ubbelohde capillary viscometer, the viscosity was measured. During the measurement, the temperature was maintained at 30 ± 0.1°C in a thermostat. From the efflux times of the polymer solution and solvent (1.0M NaCl), the relative viscosity ($\eta_{rel} = \eta/\eta_0$ [viscosity of polymer solutions/

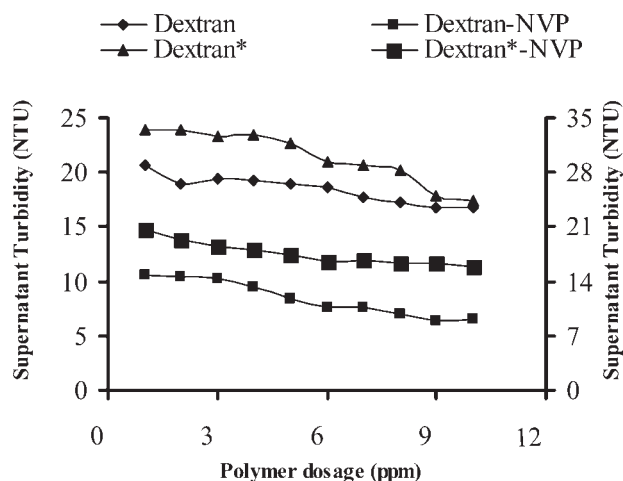


Figure 11 Effect of the polymer dosage on the turbidity for coking and noncoking coal. Noncoking coal is indicated by an asterisk.

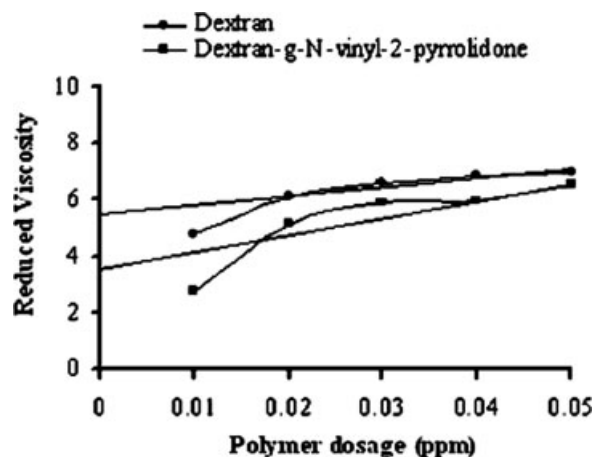


Figure 12 Reduced viscosity versus the polymer dosage (intrinsic viscosity of dextran = 4.8, intrinsic viscosity of dextran-g-N-vinyl-2-pyrrolidone-3.5).

viscosity of pure solvent]) was obtained. The specific viscosity (η_{sp}) was calculated as follows: $\eta_{sp} = \eta_{rel} - 1$. With knowledge of the concentration of the polymer solution (g/dL), the reduced viscosity was calculated for a set of five polymer concentrations. The intrinsic viscosity was then obtained from common ordinate intercepts on extrapolations of plots of the reduced viscosity versus the concentration (Fig. 12). It was observed that the intrinsic viscosity of dextran-g-NVP was lower than that of dextran. The graft copolymer of NVP showed lower intrinsic viscosity than the dextran backbone because longer grafted chains were available to make the molecules more flexible¹⁸ and thus reduced the intrinsic viscosity drastically.

CONCLUSIONS

1. A graft copolymer of dextran and NVP was synthesized with an efficient redox pair, that is, PDP/TU.
2. The spectroscopic data confirmed that the grafting of NVP occurred at the hydroxyl group of dextran.
3. The thermogravimetric analysis data showed that the graft copolymer of dextran was thermally more stable than ungrafted dextran.
4. The synthesized graft copolymer (dextran-g-NVP) showed good swellability toward water.
5. The synthesized graft copolymer showed better swelling, metal-ion-sorption, and flocculating properties.
6. Lower value of the intrinsic viscosity of the graft copolymer (dextran-g-NVP) indicated that

grafting took place on the —OH sites of the backbone.

One of the authors (K.B.) thanks University Grant Commission for an emeritus fellowship.

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