Research Article

Synthesis and Characterization of Graft Copolymer of Dextran and 2-Acrylamido-2-methylpropane Sulphonic Acid

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A novel biodegradable graft copolymer of dextran (Dx) and 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS) was synthesized by grafting poly-AMPS chains onto dextran backbone by free radical polymerization using ceric ammonium nitrate (CAN) as an initiator. Different amounts of AMPS were used to synthesize four different grades of graft copolymers with different side chain lengths. These grafted polymers were characterized by elemental analysis, FTIR, 1HNMR, rheological technique, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and X-ray diffractometry (XRD). They exhibited efficient flocculation performance in kaolin suspension.

1. Introduction

Water soluble polymers have received a great attention in recent years. Carbohydrate polymers are often preferred over synthetic polymers due to their nontoxic, low-cost, ease of availability, and biodegradability characteristics [1–3]. They are used in pharmaceuticals, detergents, cosmetics, textiles production, and in waste-water treatment (flocculation) [4].

The choice of dextran relies on several aspects [5–8]. First, dextran of various molecular weights is commercially available. Second, the degree of branching of the dextran can be as low as 0.5%, making them ideal molecular model for scientific studies. Third, dextran possesses high water solubility, is stable under mild acid and basic conditions, and contains a large number of hydroxyl groups for conjugation [9–11]. Dextran (Dx) (C₆H₁₀O₅)ₙ has been successfully used in the medical and biomedical fields for more than four decades. Dextran is the generic term for a family of neutral water soluble polysaccharides consisting (95%) of α-(1→6) linked D-glucose main chain with varying branches, and 5% branches may arise from α-(1→2), α-(1→3), and α-(1→4) glycosidic linkages. It has common solubility in water and dipolar aprotic solvents [12]. It is biocompatible and biodegradable and can lead to biopolymers derivatives with balanced hydrophobic/hydrophilic character [13].

Among polymeric flocculants, the synthetic polymers can be tailor-made by controlling molecular weight, molecular weight distribution, the structure of polymers, and the nature and percentage of ionic groups. Thus, the synthetic polymers are very efficient flocculants [14–16]. It has been observed from rheological studies that grafting of shear degradable polymers onto the rigid polysaccharides backbone provides fairly shear stable systems [17].

In this paper, we aim to report the synthesis and characterization of graft copolymers based on poly 2-acrylamido-2-methyl-1-propane sulphonic acid (PAMPS) and dextran by ceric ammonium nitrate (CAN) induced solution polymerization technique [18–20]. Four grades of graft copolymers (Dx-g-PAMPS1 to Dx-g-PAMPS4) were synthesized by varying the amount of AMPS in the reaction feed [21]. The graft copolymers were characterized by elemental analysis, FT-IR, FT-1H-NMR, rheological technique, scanning electron microscopy (SEM), thermal analysis (TGA), and X-ray diffractometry (XRD). The flocculation efficiencies of graft...
2. Experimental

2.1. Materials. Dextran (average $M_w = 482000$ Da) was procured from Sigma-Aldrich chemicals, USA, 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS) was procured from Sigma-Aldrich chemicals, Germany. CAN was procured from Loba Chemie, Mumbai. Acetone and hydroquinone were procured from E. Merck, Mumbai. Kaolin is a gift from Rajmahal Quartz-Sand, Kolkata, India.

2.2. Synthesis of Graft Copolymers. Four grades of graft copolymers (Dx-g-PAMPS1 to Dx-g-PAMPS4) of Dx and PAMPS were synthesized by Ce (IV) induced solution polymerization technique. In a 50 mL conical flask, 1 g of dextran was taken and it was dissolved in 25 mL of water and after a clear solution chulk it downs the amount of AMPS. The mixture was stirred continuously for 30 min under nitrogen atmosphere and heating the reaction mixture up to 50 $^\circ$C, then 20 mg of CAN was added. The reaction was carried out for 3 hrs until the solution become viscous. The graft copolymers were precipitated with acetone and washed 10 times by acetone for removal of unreacted AMPS. The resultant graft copolymer was dried under vacuum at 50 $^\circ$C. The synthesis details of the graft copolymers are summarized in Table 1.

2.3. Characterization

2.3.1. Elemental Analysis. The elemental analysis of dextran and all the graft copolymers was performed by using CHN analyzer, CE-440 Elemental analyzer, Mexico. The estimated analysis of three different elements, carbon, hydrogen and nitrogen, was undertaken. The results are shown in Table 2.

2.3.2. Intrinsic Viscosity Measurement. Intrinsic viscosity measurements of the aqueous solution of all Dx and graft copolymers were carried out with the help of Ubbelohde viscometer (CS/S: 0.00386) 25 ± 0.1 $^\circ$C. Intrinsic viscosity of all the samples was determined from the point of intersection of two extrapolated (to zero concentration) plots, that is, inherent viscosity versus concentration ($\eta_{inh}$ versus $C$) and reduced viscosity versus concentration ($\eta_{red}$ versus $C$). The standard method used to evaluate intrinsic viscosity has been described earlier [7]. The intrinsic viscosities of all the graft copolymers are reported in Table 1.

2.3.3. FTIR Spectroscopy. A Thermo Nicolet FT-IR spectrophotometer (Model JASCO FT-IR-5300) was used to record the IR spectra within the range of 4000–400 cm$^{-1}$. The IR spectra (Figure 1) of dextran, PAMPS, and graft copolymer (Dx-g-PAMPS3) were recorded in solid state using a KBr pellet method.

2.3.4. $^1$H FTNMR Spectroscopy. $^1$H NMR spectra (Figure 2) of samples were recorded by JEOL AL 300 FT-NMR spectrometer with sample solution in dimethyl sulphoxide-$d_6$ (DMSO-$d_6$) and tetramethylsilane (TMS) was used as an internal reference [22, 23].

2.3.5. Rheological Measurements. The rheological (viscosity versus shear rate) measurements (Figure 3) of aqueous solutions of dextran and graft copolymers (Dx-g-PAM1 to Dx-g-PAMPS4) were carried out using controlled stress Brookfield DV-III Ultra, programmable rheometer. A 2° cone of diameter 4 cm and with truncation of 46 $\mu$m was used for the measurements.

2.3.6. Scanning Electron Microscopy (SEM). For this study, dextran was used in powder form, whereas the PAMPS and graft copolymer (Dx-g-PAMPS3) were in the form of small granules (Figure 4). A HRSEM SUPRA 40, ZEISS (Germany) was used for the above study.
2.3.7. Thermal Analysis. The thermogravimetric analysis (TGA) of Dx, PAMPS, and its graft copolymer (Dx-g-PAMPS3) was carried out with a TGA-DTA, METTER-TOLEDO (Germany) instrument. Analysis of the samples (Figure 5) was performed up to a temperature of 600°C, starting from 50°C in nitrogen atmosphere [24, 25]. The heating rate was uniform in all cases at 10°C per minute.

2.3.8. X-Ray Diffractometry. Dextran, PAMPS, and the graft copolymer (Dx-g-PAMPS3) were subjected to XRD analysis (Figure 6). An 18-KW Cu-rotating anode Rigaku (Tokyo, Japan) X-ray powder diffractometer was used.

3. Flocculation Study

Jar test method was employed to estimate flocculation performance of synthesized graft copolymers. In 1 L beaker, 1 wt% kaolin suspension was taken. The beaker was placed on flocculator dipping the stirrer blade in the suspension. Under a low stirring condition, required quantity of polymer solution was added to beaker to make predetermined dose with respect of suspension volume. After the addition of polymer solution, the suspension was stirred at 185 RPM for 2 min followed by 100 RPM for 5 min. The flocs were allowed to settle down for 10 minutes. Clean supernatant liquid was drawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (digital nephelometer model, Bellstone Hitech International) to express the turbidity in nephelometric unit (NTU). A comparison of flocculation efficiency of Dx-g-PAMPS1 to Dx-g-PAMPS4 is shown in Table 2.

4. Results and Discussion

4.1. Synthesis of Graft Copolymers. Table 1 shows the synthetic details of the graft copolymers based on dextran and PAMPS by radical polymerization technique in aqueous medium using a ceric ammonium nitrate initiation system. The mechanism of ceric-ion-induced initiation involves the formation of chelate complex that decomposes to

**Figure 1:** FT-IR spectra of Dx, PAMPS, and Dx-g-PAMPS3.

**Figure 2:** FT-1H NMR of Dx, PAMPS, and Dx-g-PAMPS3.

**Figure 3:** Viscosity versus shear rate curves of graft copolymers.
generate free radical sites on the polysaccharide backbone. Four grades of graft copolymers (Dx-g-PAMPS1 to Dx-g-PAMPS4) were synthesized by varying the amount of 2-acrylamido-2-methyl-1-propane sulphonic acid. The amount of AMPS was varied in order to observe the effect with varying chain length of grafted PAMPS. At fixed concentration of CAN, fixed number of grafting sites on the polysaccharide backbone was expected. Thus, difference in AMPS concentration will lead to different chain length of PAMPS. At high concentration of AMPS, longer PAMPS chains were expected, whereas shorter chains were expected at lower concentration of AMPS. At optimum concentration of AMPS, longest PAMPS chains were obtained. Therefore, it was determined by intrinsic viscosity. In this case, Dx-g-PAMPS3 is the grade showing highest intrinsic viscosity of 15.3 dL/g having maximum chain length.

4.2. Elemental Analysis. The results of elemental analysis of Dx and its graft copolymers are given in Table 2. Dextran does not show any significant presence of nitrogen. In case of graft copolymers, it was found that there is considerable percentage of nitrogen proving the grafting of PAMPS chains on the polysaccharides backbone. In the series of graft copolymers with Dx, highest percentage of nitrogen was observed in case of Dx-g-PAMPS3. Since this graft copolymer showed highest intrinsic viscosity and maximum grafting efficiency (GE), the highest percentage of nitrogen can be explained on the basis of longer branches of PAMPS on the dextran backbone.

4.3. Intrinsic Viscosity Measurement. The intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which in turn is a function of the polymer molecular weight, its structure, nature of solvent, and the temperature of the medium. Keeping the other factors
constant, for two polymers of approximately similar molecular weight, a branched polymer will have lower hydrodynamic volume and hence a lower intrinsic viscosity as compared to its linear counterpart. Further, along a series of branched polymers, the longer the branches, the higher will be the intrinsic viscosity and vice versa. This has been observed in practice.

In the series of graft copolymers (Dx-g-PAMPS1 to Dx-g-PAMPS4), the graft copolymer Dx-g-PAMPS3, having optimum AMPS concentration at a fixed CAN concentration, has higher intrinsic viscosity indicating that it has longer PAMPS chains. The intrinsic viscosity values of all graft copolymers are reported in Table 1.

4.4. FTIR Spectroscopy. FTIR spectra of the dextran and Dx-g-PAMPS3 are shown in Figure 1. The IR spectra of Dx, AMPS, and Dx-g-PAMPS3 are shown in Figure 2. In the IR spectrum of Dx, a broad peak present at 3423 cm\(^{-1}\) and is due to the stretching of –OH. Due to hydrophilic nature of Dx, a peak shows at 1647 cm\(^{-1}\) and is due to the stretching of –CH\(_2\) group. A band at 1157 cm\(^{-1}\) confirms the presence of glycosidic linkage (C–O–C) in dextran. The band in the region of 1016 cm\(^{-1}\) is due to the C–O stretching. In case of AMPS spectrum, a broad band at 3448 cm\(^{-1}\) is due to the collapse of –NH and –OH (–SO\(_3\)H) stretching frequency. The peaks present at 3039 cm\(^{-1}\) and 2992 cm\(^{-1}\) represent the stretching and bending frequency of –S–O–C group. The presence of all the peaks is due to water molecule. The peaks present at 2929 cm\(^{-1}\) and 1458 cm\(^{-1}\) represent the stretching and bending frequency of –CH\(_2\) group. A band at 1157 cm\(^{-1}\) confirms the presence of glycosidic linkage (C–O–C) in dextran. The band in the region of 1016 cm\(^{-1}\) is due to the C–O stretching. In case of AMPS spectrum, a broad band at 3448 cm\(^{-1}\) is due to the collapse of –NH and –OH (–SO\(_3\)H) stretching frequency. The peaks present at 3039 cm\(^{-1}\) and 2992 cm\(^{-1}\) represent the stretching and bending frequency of –S–O–C group. The presence of all the peaks is due to water molecule. The peaks present at 2929 cm\(^{-1}\) and 1458 cm\(^{-1}\) represent the stretching and bending frequency of –CH\(_2\) group. A band at 1157 cm\(^{-1}\) confirms the presence of glycosidic linkage (C–O–C) in dextran. The band in the region of 1016 cm\(^{-1}\) is due to the C–O stretching. In case of AMPS spectrum, a broad band at 3448 cm\(^{-1}\) is due to the collapse of –NH and –OH (–SO\(_3\)H) stretching frequency. The peaks present at 3039 cm\(^{-1}\) and 2992 cm\(^{-1}\) represent the stretching and bending frequency of –S–O–C group. The presence of all the peaks is due to water molecule. The peaks present at 2929 cm\(^{-1}\) and 1458 cm\(^{-1}\) represent the stretching and bending frequency of –CH\(_2\) group. A band at 1157 cm\(^{-1}\) confirms the presence of glycosidic linkage (C–O–C) in dextran. The band in the region of 1016 cm\(^{-1}\) is due to the C–O stretching. In case of AMPS spectrum, a broad band at 3448 cm\(^{-1}\) is due to the collapse of –NH and –OH (–SO\(_3\)H) stretching frequency. The peaks present at 3039 cm\(^{-1}\) and 2992 cm\(^{-1}\) represent the stretching and bending frequency of –S–O–C group. The presence of all the peaks is due to water molecule. The peaks present at 2929 cm\(^{-1}\) and 1458 cm\(^{-1}\) represent the stretching and bending frequency of –CH\(_2\) group. A band at 1157 cm\(^{-1}\) confirms the presence of glycosidic linkage (C–O–C) in dextran. The band in the region of 1016 cm\(^{-1}\) is due to the C–O stretching. In case of AMPS spectrum, a broad band at 3448 cm\(^{-1}\) is due to the collapse of –NH and –OH (–SO\(_3\)H) stretching frequency. The peaks present at 3039 cm\(^{-1}\) and 2992 cm\(^{-1}\) represent the stretching and bending frequency of –S–O–C group. The presence of all the peaks is due to water molecule. The peaks present at 2929 cm\(^{-1}\) and 1458 cm\(^{-1}\) represent the stretching and bending frequency of –CH\(_2\) group. A band at 1157 cm\(^{-1}\) confirms the presence of glycosidic linkage (C–O–C) in dextran. The band in the region of 1016 cm\(^{-1}\) is due to the C–O stretching. In case of AMPS spectrum, a broad band at 3448 cm\(^{-1}\) is due to the collapse of –NH and –OH (–SO\(_3\)H) stretching frequency. The peaks present at 3039 cm\(^{-1}\) and 2992 cm\(^{-1}\) represent the stretching and bending frequency of –S–O–C group. The presence of all the peaks is due to water molecule. The peaks present at 2929 cm\(^{-1}\) and 1458 cm\(^{-1}\) represent the stretching and bending frequency of –CH\(_2\) group. A band at 1157 cm\(^{-1}\) confirms the presence of glycosidic linkage (C–O–C) in dextran. The band in the region of 1016 cm\(^{-1}\) is due to the C–O stretching.
been found that graft copolymer Dx-g-PAMPS3 shows better performance (lesser turbidity over lowest polymer dose) than other graft copolymers. This could be explained due to the fact that in graft copolymer, the dangling longer poly-PAMPS chains have better approachability to the contaminant.

6. Conclusion

From the results, it can be concluded that PAMPS is grafted on Dx. Variation in the synthetic parameters results in a series of graft copolymers with varying length of PAMPS chains. The FTIR and FT³H NMR spectra provide a strong proof of grafting. Rheological investigation shows that the graft copolymer having longer PAMPS chains has more shear viscosity. TGA results show that the graft copolymer has more thermal stability than corresponding Dx and PAMPS. Shear viscosity of the aqueous solution of the graft copolymer Dx-g-PAMPS3 is larger than the other graft copolymers. Morphology variation of Dx, PAMPS, and graft copolymers supports the above conclusion. X-ray diffraction pattern shows the amorphous nature of graft copolymer and absence of AMPS in the grafted product. Estimation of flocculation performance in kaolin suspension shows the graft copolymer Dx-g-PAMPS3 as the most effective flocculant. Thus, the graft copolymer in every way is more stable than the base polysaccharide. Thus, by grafting PAMPS onto dextran, shear stable efficient flocculants have been obtained and they can be used for the treatment of wastewater.

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References


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