Synthesis, Characterization, and Flocculation Characteristics of Polyacrylamide-Grafted Glycogen

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ABSTRACT: The synthesis of glycogen-g-polyacrylamide (Gly-g-PAM) was carried out by a ceric ion-induced solution polymerization technique. Six grades of graft copolymers were synthesized by the variation of catalyst and monomer concentrations. These graft copolymers were characterized by intrinsic viscosity measurements, FTIR spectroscopy, and X-ray diffraction techniques. Flocculation performance of these graft copolymers were done in kaolin suspension. Of the above grades, the graft copolymer Gly-g-PAM 5, which has longer PAM chains, showed best flocculation performance. The flocculation performance of the graft copolymer was compared with commercial flocculants and other PAM-grafted flocculants developed so far in the authors' laboratory. In all the cases, it was found that the graft copolymer performed the best. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 773–778, 2007

Key words: FTIR; graft copolymer; polysaccharides; viscosity; water-soluble polymers

INTRODUCTION

Over recent years, considerable attention has been focused upon the treatment and disposal of wastewater sludges.[1–3] Polymeric flocculants are extensively used for the treatment of industrial effluents and mineral water.[4,5] Among natural and synthetic polymers, synthetic polymers are very effective due to their versatile tailorability, but they have poor shear stability. Natural polymers are of low cost, shear stable, nontoxic, and highly biodegradable. Therefore, it has been possible to develop efficient, shear stable, and less biodegradable flocculants by grafting synthetic polymers onto the backbone of natural ones.[6–8]

Earlier in the authors' laboratory, many graft copolymers have been synthesized by grafting polyacrylamide (PAM) onto amylopectin, carboxymethyl cellulose, starch, guar gum,[9–11] etc. The PAM-grafted polysaccharides exhibit synergistic characteristics in flocculation. It was postulated by one of the authors (R. P. Singh) that graft copolymers are more effective flocculants when compared with the linear polymers, because of the greater approachability of the dangling flexible PAM chains grafted onto rigid polysaccharide branches to the contaminant particles in suspension.[12,13] These PAM-grafted polysaccharides are nonionic in nature and are effective flocculants for the relatively low negatively charged colloids.

Among the PAM-grafted polysaccharides so far developed, PAM-grafted amylopectin was the most efficient flocculant, which can be attributed to its highly branched structure.[14]

Glycogen is a high molecular weight highly branched storage polysaccharide. The structure of glycogen is similar to amylopectin, in that it is a heavily branched molecule containing straight chains of glucose units connected by $\alpha 1 \rightarrow 4$ linkages.[15] The branching that results from $\alpha 1 \rightarrow 6$ linkages is much more frequent in glycogen than in amylopectin, occurring every 8–12 glucose units. It is highly soluble and has very good hydrodynamic behavior. In the present case, glycogen is grafted with PAM and various grades of graft copolymer are synthesized by varying the reaction parameters.

EXPERIMENTAL

Materials

Materials for synthesis

Glycogen was procured from Sigma Chemicals, USA. Acrylamide was procured from E Merck, Germany. Ceric ammonium nitrate (CAN) was obtained from Loba Chemie, Bombay, India. Acetone of laboratory grade was procured from E Merck, Bombay, India.

TABLE I
Synthetic Details of Graft Copolymers of Glycogen

Polymers	Polysaccharide (g)	Acrylamide (mol)	CAN (10^{-5}) (mol)	Conversion (%)	Intrinsic viscosity (dL/g)
Gly-g-PAM 1	0.25	0.063	3.6	84	9.0
Gly-g-PAM 2	0.25	0.049	3.6	81	9.1
Gly-g-PAM 3	0.25	0.035	3.6	83	7.8
Gly-g-PAM 4	0.25	0.049	5.4	90	8.1
Gly-g-PAM 5	0.25	0.049	2.7	75	9.3
Gly-g-PAM 6	0.25	0.049	2.0	70	8.7

% Conversion = [(wt. of graft copolymer − wt. of polysaccharides)/wt. of acrylamide monomer] × 100.

Material for flocculation

Kaolin was supplied by C D pharmaceutical works, Howrah, India. The average particle size of kaolin is 4.79 nm and the suspension ζ potential is −2.2 mV at pH 6.82.

Flocculants

The source of commercial flocculants like Rishfloc 440 HV and Rishfloc 226 LV are Rishav Chemicals, India. Magnafloc 351 and Magnafloc LT22 were procured from Allied Colloids, England.

Synthesis

Grafting reaction was carried out by ceric ion-induced redox initiation method.[16–18] The details of the synthesis and the reaction conditions are as follows: 0.25 g of glycogen is dissolved in 30 cc distilled water. Required amount of acrylamide is dissolved in 30 cc distilled water and mixed with glycogen solution. Nitrogen is purged through the reaction mixture for 30 min followed by addition of CAN solution. Nitrogen gas is again purged for 30 min. The reaction is allowed to continue for 24 h, after which it is terminated by adding saturated solution of hydroquinone. At the end of the reaction, polymer is precipitated by adding excess of acetone. It is then dried in vacuum oven; subsequently it is sieved and pulverized. The reaction temperature is always maintained at (28 ± 0.01)°C. The synthetic parameters are given in Table I.

Purification of graft copolymer by solvent extraction

The extraction of occluded polyacrylamide (PAM) was carried out by solvent extraction using a mixture of formamide and acetic acid (1 : 1 by volume).[19]

Characterization

Viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelohde viscometer (CS/

S: 0.003899) at 25°C. The viscosities were measured in dilute aqueous solution. The pH of the aqueous solution is neutral. The intrinsic viscosities were evaluated as described earlier,[19] which is a standard procedure for measurement of intrinsic viscosity with an Ubbelohde viscometer. The intrinsic viscosities of all the graft copolymers are also reported in Table I.

Elemental analysis

The elemental analysis of all the samples, namely, glycogen and their graft copolymers, is performed with a Carlo Erba 1108 elemental analyzer. The estimation of only three elements, that is, carbon, hydrogen and nitrogen, is undertaken. The results are shown in Table II.

X-ray diffraction analysis

Glycogen, PAM, and graft copolymer glycogen-g-polyacrylamide 5 (Gly-g-PAM 5) are used for XRD analysis. A PW 1840 diffractometer and PW 1729 X-ray generator (Philips, Holland) are used for this study using Co Kα radiation. The scattering angle (2θ) is varied from 10° to 45°. The X-ray diffractograms of glycogen, Gly-g-PAM 5, and PAM are shown in Figure 1.

FTIR analysis

A Thermo Nicolet FTIR Spectrophotometer (Model–Nexus 870 FTIR) was used. The potassium bromide

TABLE II
Results of Elemental Analysis

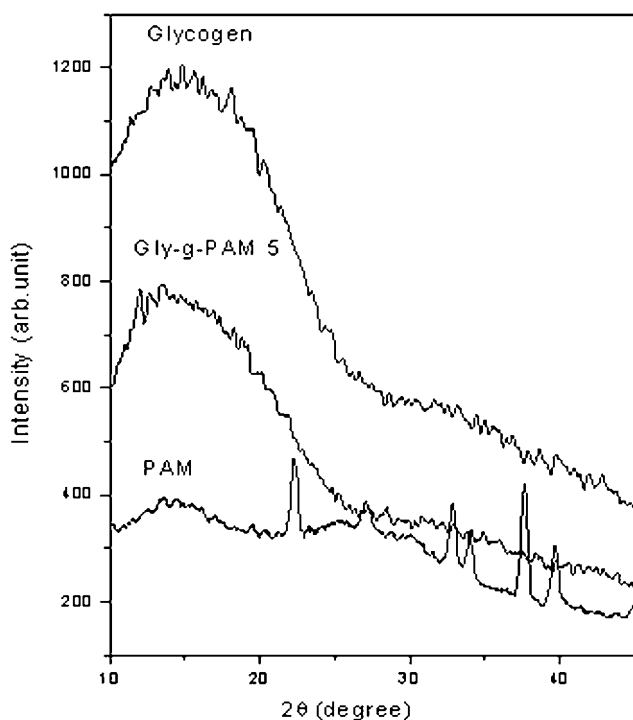| Polymers	% Carbon	% Hydrogen	% Nitrogen
Glycogen	38.3	6.29	0.25
Gly-g-PAM 1	42.5	7.2	14.68
Gly-g-PAM 2	40.5	7.0	14.9
Gly-g-PAM 3	41.27	6.7	14.15
Gly-g-PAM 4	42.1	7.1	14.21
Gly-g-PAM 5	43.38	7.4	15.12
Gly-g-PAM 6	42.5	6.8	14.48

Figure 1 X-ray diffractograms of glycogen, Gly-*g*-PAM 5, and polyacrylamide.

(KBr) pellet method was used for FTIR study. The FTIR spectra of glycogen, Gly-*g*-PAM 5, and PAM are shown in Figure 2.
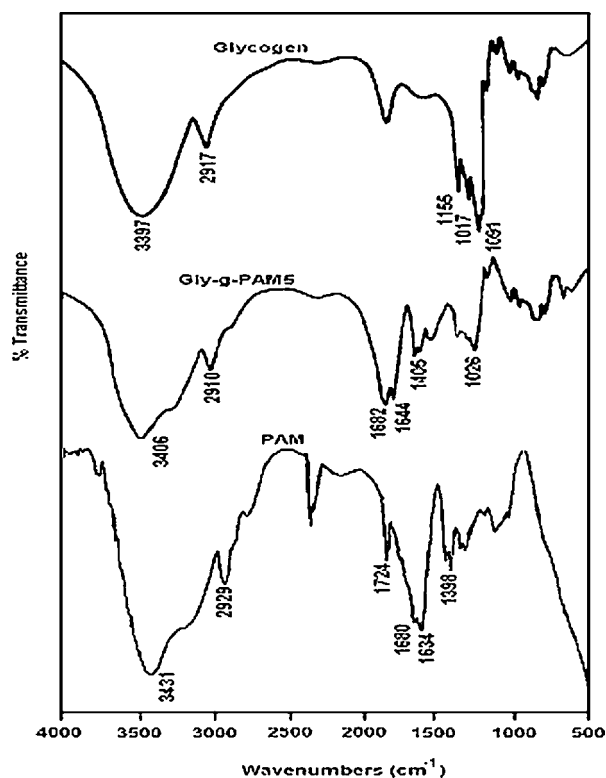

Figure 2 FTIR spectrums of glycogen, Gly-*g*-PAM 5, and polyacrylamide.

Determination of weight average molecular weight by SLS analysis

The weight average molecular weight (M_w) of glycogen and Gly-*g*-PAM 5 are determined by DLS-7000 Super Dynamic Light Scattering Spectrophotometer. Ar$^+$ (λ = 488 nm) laser was used for study with toluene as the reference liquid.[20] The results are given in Table III.

Flocculation studies

Flocculation characteristics of the polymers were measured in 5 wt % kaolin suspensions by settling test in a 100 mL stoppered graduated cylinder. The flocculation performances of all the grades of graft copolymer were compared and the grade showing best settling efficiency was determined. The flocculation efficiency of best grafted grade was compared with those of several commercial flocculants like Magnafloc 351, Magnafloc LT22, Rishfloc 440 HV, and Rishfloc 226 LV. The flocculation efficiency of Gly-*g*-PAM 5 was also compared with other PAM-grafted polysaccharides developed so far in the authors' laboratory.

RESULTS AND DISCUSSIONS

Synthesis and intrinsic viscosity

The details of the graft copolymerization reaction and the evaluated percentage of grafting are given in Table I. In the present investigation, two series of graft copolymers of glycogen and PAM have been synthesized by grafting PAM branches onto glycogen, using ceric ion initiator. In the first series (Gly-*g*-PAM 1–Gly-*g*-PAM 3), the acrylamide concentration was varied by keeping the concentrations of glycogen and catalyst constant. In the second series (Gly-*g*-PAM 4–Gly-*g*-PAM 6), the catalyst concentration was varied keeping the concentrations of glycogen and acrylamide constant.

The mechanism of ceric ion initiation involves the formation of chelate complex that decomposes to generate free radical sites on the polysaccharide backbone. These active free radicals in the presence of acrylic monomers generate graft copolymers.[21] The average number of grafting sites per backbone molecule depends on the ceric ion concentration to glyco-

TABLE III
Results of SLS Analysis

Polymers	Molecular weight, M_w (g/mol)
Glycogen	5.741×10^6
Gly-*g*-PAM 5	1.478×10^7

gen. A relatively low concentration of catalyst will initiate few grafting sites, resulting in longer PAM chains against shorter PAM chains at higher PAM concentration. This is reflected in their corresponding intrinsic viscosity values. Intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which in turn depends upon its molecular weight, structure, nature of the solvent, and the temperature of the medium. For two polymers of approximately same molecular weight, the branched polymer will have lower hydrodynamic volume compared to its linear counterpart and thus have lower intrinsic viscosity value.[22] Further, in the case of branched polymers, the longer is the branching, higher will be its intrinsic viscosity and *vice versa*. This has been observed in the present case (Table I). Highest intrinsic viscosity is observed in case of Gly-*g*-PAM 5, which is having longer PAM chains.

Elemental analysis

The results of element analysis of glycogen and all its graft copolymers are listed in Table II. Glycogen does not show any significant presence of nitrogen. However, the negligible amount of nitrogen in glycogen is because of the presence of trace quantities of unisolated proteins in the polysaccharide. It has been found that there is a considerable percentage of nitrogen in the grafted copolymers, which can be accounted for the presence of grafted PAM chains. In the series of graft copolymers based on glycogen, the variation in the nitrogen content, although not much, is significant in case of Gly-*g*-PAM 5. The higher percentage of nitrogen may be due to the increased PAM content in the graft copolymer.

X-ray diffractometry

X-ray diffractograms of glycogen, Gly-*g*-PAM 5, and PAM are shown in Figure 1. In the case of PAM, the crystalline peaks appear in 2θ range of 20°–40°. But in the case of glycogen and Gly-*g*-PAM 5, there is no considerable peak of crystallinity, which is further proof of grafting.

FTIR analysis

The FTIR spectra of glycogen, Gly-*g*-PAM 5, and PAM are shown in Figure 2. It can be seen that a broad absorption band in glycogen at 3397 cm^{-1} is due to the stretching frequency of the O—H groups. The bands at 1155 and 2917 cm^{-1} are assigned to C—O stretching and C—H stretching, respectively. Two peaks at 1091 and 1017 cm^{-1} are due to CH_2—O—CH_2 stretching vibrations.

In the case of PAM, a broad absorption at 3431 cm^{-1} is for the N—H stretching frequency of the am-

ide group. Two strong bands around 1680 and 1634 cm^{-1} are due to amide-I (CO stretching) and amide-II (NH bending). Another band at 1724 cm^{-1} is due to the presence of free acid groups. The bands around 1398 and 2929 cm^{-1} are for the C—N and C—H stretching vibrations.

In the FTIR spectrum of Gly-*g*-PAM 5, O—H stretching band of hydroxyl group of glycogen and N—H stretching band of amide group of PAM overlap with each other and lead to a broad band appearing at 3406 cm^{-1}. Two bands around 1682 and 1639 cm^{-1} are due to amide-I and amide-II bands of the amide group of PAM. C—N and C—H stretching bands appear at 1405 and 2910 cm^{-1}, respectively.

It is observed that almost all the characteristic peaks of glycogen and PAM are present in the FTIR spectra of Gly-*g*-PAM 5. As PAM was initially removed from the reaction products, the presence of the above bands in the graft copolymer is a strong evidence of grafting.

SLS analysis

The weight average molecular weight of glycogen and Gly-*g*-PAM 5 are determined by SLS analysis. The molecular weight of graft copolymer is more than the original polysaccharide. The results are given in Table III.
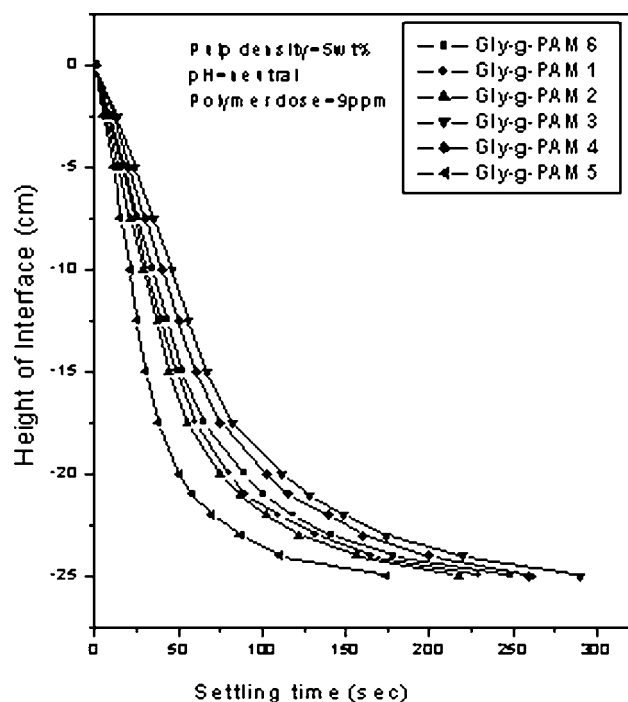

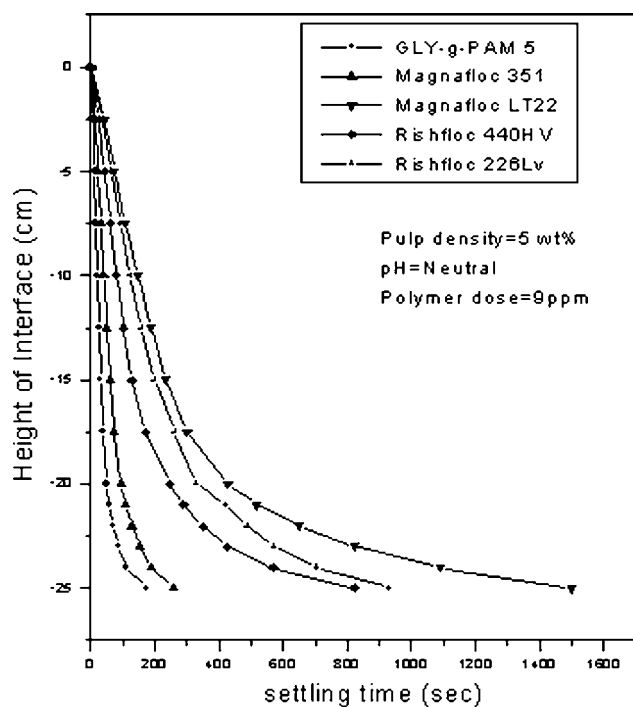**Figure 3** Comparison of flocculation efficiency of various grades of Gly-*g*-PAM in 5 wt % kaolin suspension.

Figure 4 Comparison of flocculation efficiency of Gly-*g*-PAM 5 and some commercial flocculants in 5 wt % kaolin suspension.

Flocculation studies

The flocculation performance of glycogen and its graft copolymers are compared in kaolin suspensions. The results are shown in Figures 3–5. In these figures, the
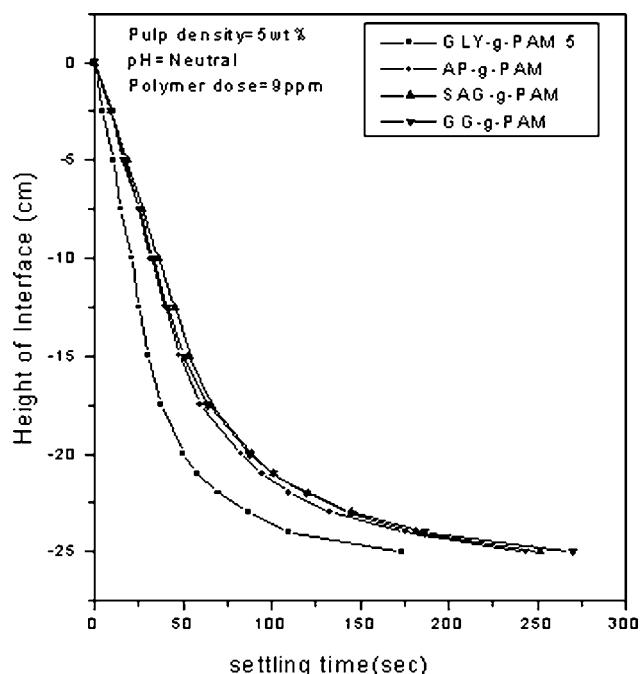
TABLE IV
Settling Velocity of Various Flocculants

Polymers	Settling velocity (cm/s)
Gly-*g*-PAM 1	0.25
Gly-*g*-PAM 2	0.266
Gly-*g*-PAM 3	0.178
Gly-*g*-PAM 4	0.196
Gly-*g*-PAM 5	0.4
Gly-*g*-PAM 6	0.224
Magnafloc 351	0.212
Magnafloc LT22	0.046
Rishfloc 440 HV	0.081
Rishfloc 226 LV	0.061
Ap-*g*-PAM	0.240
SAG-*g*-PAM	0.224
GG-*g*-PAM	0.227

height of the interface between the solid and liquid is plotted against time. The flocculation performance of a particular polymer could be correlated with the settling time. The lesser the settling time, the better is the flocculation performance. In Figure 3, the flocculation performance of all the graft copolymers are compared. It is observed that Gly-*g*-PAM 5 performs better than the other grades. It has also the highest settling velocity as given in Table IV. This can be attributed to the longer PAM chains present in Gly-*g*-PAM 5, which is also evident from intrinsic viscosity values from Table I.

In Figure 4, the flocculation performance of Gly-*g*-PAM 5 is compared with commercial flocculants like Magnafloc 351, Magnafloc LT22, Rishfloc 440 HV, and Rishfloc 226 LV. Here also the performance of Gly-*g*-PAM 5 is superior to other flocculants.

Figure 5 is a comparison of flocculation performance of Gly-*g*-PAM 5 with other PAM-grafted polysaccharides developed so far in the authors' laboratory like Ap-*g*-PAM, SAG-*g*-PAM, and GG-*g*-PAM. It is observed that Gly-*g*-PAM is the best performing flocculant. This can be explained by Singh's Easy Approachability Model. According to the model, the polysaccharide chain transforms to a comblike structure after grafting. This leads to better approachability of branched PAM chains toward the colloidal contaminants thereby increasing the flocculation efficiency. A highly branched polysaccharide will therefore lead to a highly branched graft copolymer whose flocculation efficiency would exceed its linear counterparts. Thus glycogen being a highly branched polysaccharide, when grafted with PAM branches leads to a highly efficient flocculant.

CONCLUSIONS

By varying the reaction parameters, a series of graft copolymers of glycogen and PAM are prepared. These grades are characterized by FTIR, SLS analysis, elemental analysis, XRD analysis, and intrinsic viscosity

Figure 5 Comparison of flocculation efficiency of Gly-*g*-PAM 5 and some grafted polysaccharides in 5 wt % kaolin suspension.

measurements. From the flocculation studies, it is evident that the graft copolymer Gly-*g*-PAM 5 having fewer and longer PAM branches performs better than the other grades. Gly-*g*-PAM 5 exhibits better flocculation performance than several commercial flocculants. When compared with the other flocculants based on PAM-grafted polysaccharides so far developed in the authors' laboratory, Gly-*g*-PAM 5 appears to be the best flocculant. As glycogen has the highest molecular weight and highly branched structure and its graft copolymer giving the best performance, it provides confirmation to Singh's Easy Approachability Model.

References

1. Zhao, Y. Q. Sep Purif Technol 2004, 35, 175.
2. Rey, P. A.; Varsanik, R. G. In Water Soluble Polymers, Beauty with Performance; Glass, J. E., Ed.; 1984; p 113.
3. Bolto, B. A. American Chemistry Society, Washington DC. Prog Polym Sci 1995, 20, 987.
4. Bratby, J. Coagulation and Flocculation; Uplands Press: Cryodon, UK, 1980.
5. Gregory, J. In Solid/Liquid Dispersions; Tadros, T. F., Ed.; Academic Press: London, 1987, 163.
6. Swanson, C. L.; Shogren, R. L.; Fanta, G. F.; Imam, S. H. J Environ Polym Degrad 1993, 1, 155.
7. Singh, R. P.; Karmakar, G. P.; Rath, S. K.; Karmakar, N. C.; Pandey, S. R.; Tripathy, T.; Panda, J.; Kannan, K.; Jain, S. K.; Lan, N. T. Polym Eng Sci 2000, 40, 45.
8. Singh, R. P.; Nayak, B. R.; Biswal, D. R.; Tripathy, T.; Banik, K. Mat Res Innovat 2003, 7, 331.
9. Rath, S. K.; Singh, R. P. J Appl Polym Sci 1997, 66, 172.
10. Deshmukh, S. R.; Sudhakar, K.; Singh, R. P. J Appl Polym Sci 1991, 43, 1091.
11. Deshmukh, S. R.; Singh, R. P. J Appl Polym Sci 1987, 33, 1963.
12. Singh, R. P. In Polymers and Other Advanced Materials: Emerging Technologies and Business Opportunities; Prasad, P. N., Mark, J. E., Fai, T. J., Eds.; Plenum: New York, 1995; p 227.
13. Singh, R. P.; Tripathy, T.; Karmakar, G. P.; Rath, S. K.; Karmakar, N. C.; Pandey, S. R.; Kannan, K.; Jain, S. K.; Lan, N. T. Curr Sci 2000, 78, 798.
14. Rath, S. K.; Singh, R. P. J Appl Polym Sci 1998, 70, 1795.
15. Matsui, M.; Kakut, M.; Misaki, A. Carbohydr Polym 1996, 31, 227.
16. Nayak, B. R.; Singh, R. P. Eur Polym J 2001, 37, 1655.
17. Owen, D. R.; Shen, T. C. In Structure Solubility Relationships in Polymers; Harris, F. W., Seymour, R. B., Eds.; Academic Press: New York, 1977.
18. Arslan, H.; Hazer, B. Eur Polym J 1999, 35, 1451.
19. Nayak, B. R.; Singh, R. P. J Appl Polym Sci 2001, 81, 1776.
20. Teraoka, I. Polymer Solutions: An Introduction to Physical Properties; John Wiley and Sons, Inc.: New York, 2002; p 108.
21. Simon, J.; Bajpai, A. Eur Polym J 2003, 39, 2077.
22. Rath, S. K.; Singh, R. P. Colloids Surf A 1998, 139, 129.