

Graft Copolymerization of Nitrile Monomers onto Sulfonated Jute-Cotton Blended Fabric

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ABSTRACT: Graft copolymerization of nitrile monomers, such as acrylonitrile and methacrylonitrile, onto bleached sulfonated jute-cotton blended fabric was carried out in an aqueous medium using potassium permanganate as an initiator under the catalytic influence of sulfuric acid in a nitrogen atmosphere. The effect of concentrations of monomer, permanganate, sulfuric acid, reaction time, and reaction temperature on the percent graft yield was studied. The percent graft yield was found to be dependent on the above-mentioned variables. On the basis of experimental findings, an optimum condition for effective grafting is suggested. As

evidence of polymer grafting, some instrumental analyses, such as thermogravimetric analysis, infrared spectroscopy, and X-ray diffractometry were carried out. Grafting improved the thermal stability, protected from photo-oxidative degradation, affected dyeability, and had a positive impact on color fastness. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2262–2266, 2003

Key words: grafting; nitrile monomer; sulfonation; jute; cotton; blended fabric

INTRODUCTION

Chemical modification through grafting of vinyl monomers onto jute and cotton fibers has been receiving considerable interest in recent years. Although jute fiber possesses high dimensional stability, certain unfavorable textile properties such as high stiffness, very low elasticity, and susceptibility toward sunlight have tremendously limited their use. Therefore, to minimize their undesirability and to enhance their effectiveness for intensified textile uses, graft copolymerization of vinyl monomers onto jute fiber has been attempted during recent years using chemical,^{1–5} photochemical,⁶ and radiation-induced^{7–10} methods of initiation where the grafted fiber show improved tenacity, dyeability and tensile properties. Furthermore, among the methods of initiation, chemical method of initiation of grafting involving oxidizing agents such as KMnO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, $\text{K}_2\text{S}_2\text{O}_8$, and KHSO_5 are promising from the economic point of view and are quite selective in nature. Among the chemical initiators, permanganate has an identity of its own. Permanganate ions are known to act as strong oxidizing agents in an aqueous solution, and alone or in the presence of an activator they have been used to initiate graft copolymerization onto various cellulose substrates.^{11–14}

In the present investigation an effort was made to modify bleached sulfonated jute-cotton blended fabric with vinyl monomers such as acrylonitrile and methacrylonitrile, initiated by a $\text{KMnO}_4/\text{H}_2\text{SO}_4$ redox system. To make the modification process more economical, an attempt also was made to find out the optimum modification conditions depending on concentrations of monomer, initiator, catalyst, reaction time, and temperature. Grafting was determined on the basis of the weight increase of the fabric treated. Some instrumental analyses such as infrared spectroscopy, X-ray diffractometry, and thermogravimetric analysis (TGA) were done to identify graft on fabric.

EXPERIMENTAL

Materials

Loomstate bleached sulfonated jute-cotton blended (BSJCB) fabric was used as a material for the investigation. Acrylonitrile (AN) and methacrylonitrile (MAN) were used fresh after distillation under a reduced pressure. All other chemicals used were of C.P. grade and were used as such without further purification.

Production of fabric

Jute fiber was sulfonated with sodium sulfite.¹⁵ Sulfonated jute fiber was blended with 40% cotton for the production of 60×60 plain woven fabric. Sulfonated jute-cotton blended fabric was bleached with hydro-

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gen peroxide in a high-pressure rapid lab deep machine.^{16,17}

Graft copolymerization

The treatment of BSJCB fabric was carried out in a 100-mL stoppered Erlenmeyer flask. Polymerization was done with 20%–90% monomer, 0.0%–1.5% permanganate as initiator, and 0.0%–1.5% sulfuric acid as catalyst based on the weight of fabric at 40°C–100°C for 0.5–3.0 h in the fabric : liquor ratio of 1 : 30. At the end of the desired reaction period, the BSJCB fabric was thoroughly washed with boiling soap solution (2.0%) to removed the loosely adhering polymer, washed, and dried.^{5,18,19} Percent graft yield was calculated according to

$$\% \text{ graft yield} = \frac{B - A}{A} \times 100$$

where A is the weight of ungrafted BSJCB fabric before treatment and B is the weight of the grafted BSJCB fabric after treatment.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) of the fabric sample was done using a Mettler TG-50 (Shimadzu, Kyoto, Japan). The heating rate throughout the study was 10°C /min. The measurement was made under a constant flow rate (20 mL/min) of nitrogen.²⁰

IR spectroscopy

Fabric sample was mixed with KBr in the ratio 1:100, and a pellet was prepared. Then, the IR spectra of this KBr pellet was recorded with IR-470 infrared spectrometer (Shimadzu, Kyoto, Japan).

X-ray diffractometry

X-ray diffraction of the fabric sample was measured using a Phillips diffractometer. The dried isotropic sample was compressed as a pellet into the pore of a disk with a diameter of 2 mm and a thickness of 1 mm, and its X-ray diagrams were made with Ni-filtered Cu α radiation at 30 kV and 20 mA. Crystallinity of the fabric sample was determined by Segal et al.²¹

Measurement of breaking strength

The breaking strength of the fabric sample was measured by the tensile strength tester (Torsee's Schopper type OS-100).²²

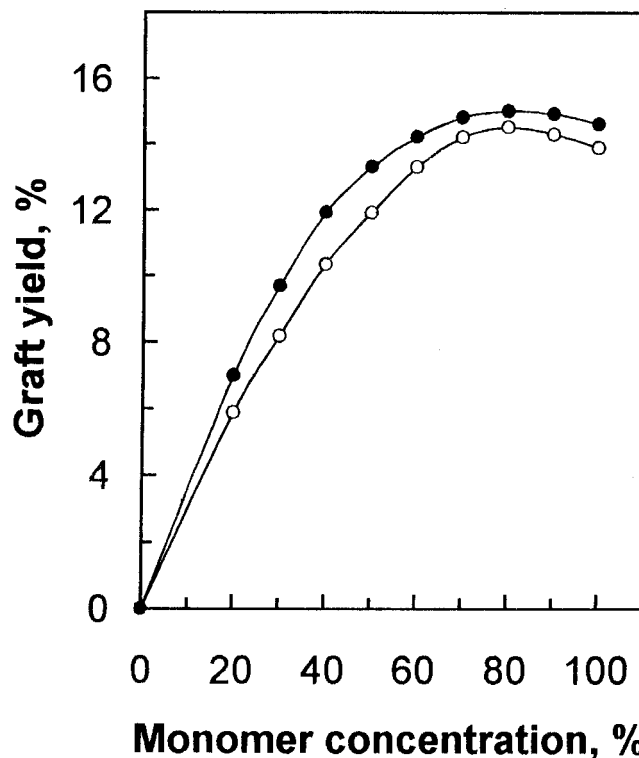


Figure 1 Effect of monomer concentration on percent graft yield of nitrile monomers onto BSJCB fabric (○: acrylonitrile, ●: methacrylonitrile).

RESULTS AND DISCUSSION

Effect of monomer

The effect of AN and MAN concentrations on its polymerization with BSJCB fabric using $\text{KMnO}_4 / \text{H}_2\text{SO}_4$ redox system is shown in Figure 1. From Figure 1 it can be seen that the percent graft yield increased with the increase of monomer concentration, and with more than 80% monomer, the percent graft yield decreased. This may be because of the higher availability of monomer molecules in the vicinity of immobile cellulose macroradicals as well as a higher monomer concentration in the polymerization medium. The greater availability of the monomer in the polymerization medium acted in favor of molecular collision,^{5,23} thereby enhancing polymerization in general or homopolymer formation in particular. The decreased percent graft yield of more than 80% suggests that homopolymerization prevails over grafting at a higher monomer concentration.

Effect of initiator

The effect of variation of initiator, that is, KMnO_4 concentration on the percent graft yield, is shown in Figure 2. It can be observed from Figure 2 that percent graft yield and homopolymer were 0 when BSJCB fabric was grafted with AN and MAN in the absence

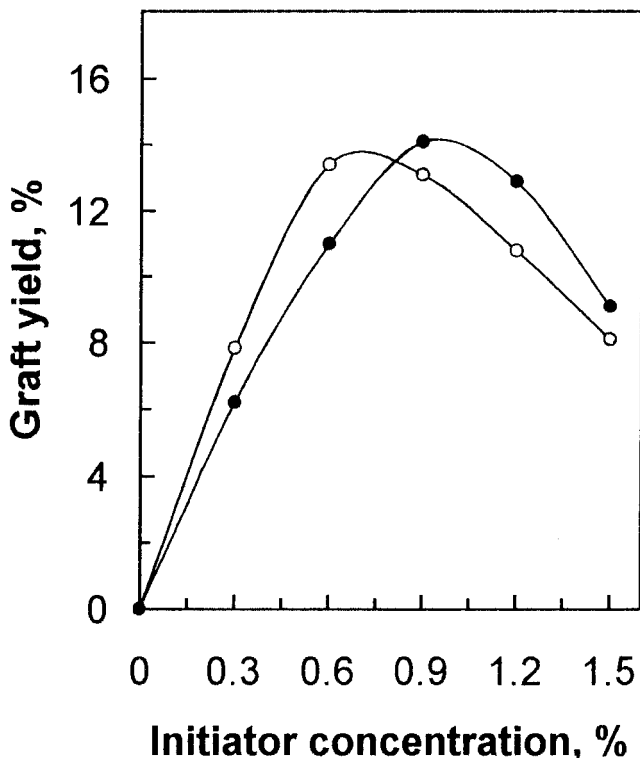


Figure 2 Effect of initiator concentration on percent graft yield of nitrile monomers onto BSJCB fabric (○: acrylonitrile, ●: methacrylonitrile).

of KMnO_4 . This is because in the absence of KMnO_4 in the polymerization medium, cellulose as well as monomer were not converted to their radicals.²³ However, the percent graft yield increased with the increase of permanganate concentration up to 0.6%–0.9%—that is 0.6% for AN and 0.9% for MAN and beyond this range, the graft yield decreased. A similar behavior also was true for homopolymer. The increasing trend of percent graft yield might be a result of the formation of a great number of grafting sites on the fiber backbone of BSJCB fabrics through a reduction of KMnO_4 to Mn(III) or Mn(II). The grafting sites, that is, cellulose macroradicals in the presence of vinyl monomers, induced grafting.^{5,24} Another explanation is that a significant amount of graft formation occurred in the presence of KMnO_4 because a certain amount of MnO_2 deposited on the BSJCB fabric.

Again, the decrease of percent graft yield observed at above 0.6%–0.9% KMnO_4 concentration could be interpreted in terms of retardation of monomer diffusion and faster rate of their termination. Besides impeding monomer diffusion at higher KMnO_4 , the deposited MnO_2 colloidal particles on the fabric act as a source of excess Mn(IV) which may contribute to oxidation of BSJCB fiber macroradicals, and termination of growing poly-AN or poly-MAN chain. However, abundance of primary free radicals may also lead to termination by coupling, thereby decreasing the overall polymerization yield.

Effects of time and temperature

The effect of the rise of reaction temperature on percent graft yield is shown in Figure 3. From Figure 3 it can be seen that the percent graft yield increased with the increase of the temperature up to 50°C for AN and up to 60°C for MAN and beyond which it decreased. The increase in percent graft yield at high temperature may be a result of the increase in the rate of production of active free radicals, which increased the number of grafting sites at a higher rate. In addition, the rate of graft initiation and the increase in temperature also increased the rate of diffusion of monomer into the fiber matrix, where grafting was also initiated by complexed monomer. The decrease in percent graft yield beyond 50°C and 60°C for AN and MAN, respectively, may be the result of an increase in the formation of homopolymer and the premature termination of growing grafted chains by excess Mn(III) or Mn(II) ions produced on oxidation of Mn(IV) ions.

Effect of catalyst

The effect of catalyst, that is, H_2SO_4 concentration, on the percent graft yield of BSJCB fabric is shown in Figure 4. The percent graft yield increased with the increase of sulfuric acid concentration up to 1.2% for AN and 1.0% for MAN and then it decreased gradually as the acid concentration was increased. The plau-

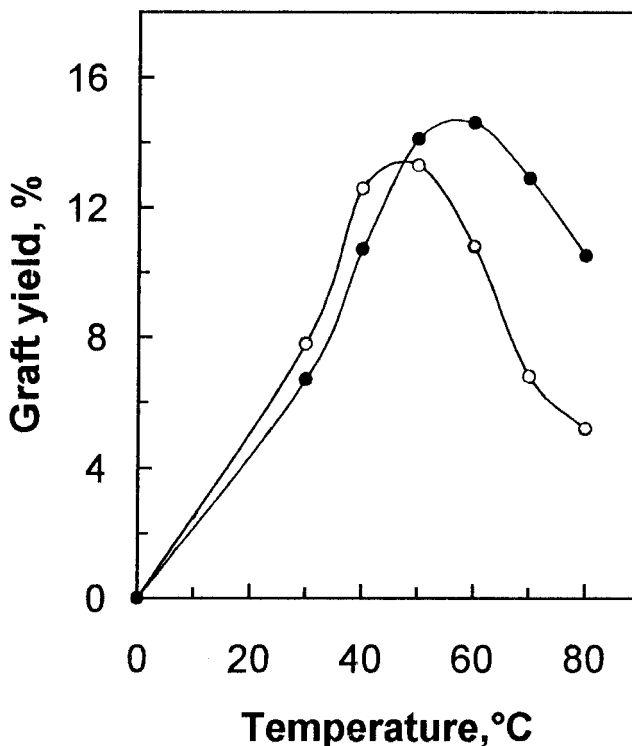


Figure 3 Effect of reaction temperature on percent graft yield of nitrile monomers onto BSJCB fabric (○: acrylonitrile, ●: methacrylonitrile).

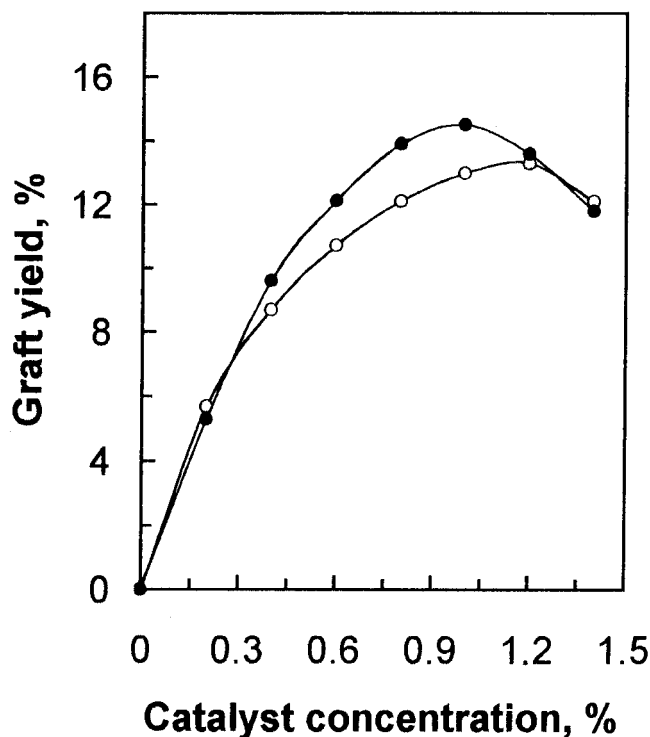


Figure 4 Effect of catalyst concentration on percent graft yield of nitrile monomers onto BSJCB fabric (○: acrylonitrile, ●: methacrylonitrile).

sible explanation of such behavior is that sulfuric acid in the grafting medium assisted the grafting, both by causing inter- and intracrystalline swelling of the substrate and by acting as a catalyst in the hydrolysis of cellulose, leading to uncoiling of the chains and improvement of the monomer accessibility. On the other hand, the experiment showed that homopolymer formation was also enhanced in the presence of acid. A higher concentration of acid, however, may cause degradation of the backbone chain of cellulose as well as of the graft chains. Thus, with the increase in the amount of sulfuric acid in the polymerization medium, the percent graft yield was decreased.

Thermogravimetric analysis

The thermal behavior of BSJCB and its AN- and MAN-grafted fabrics was examined by a study of their TGA thermograms. From the results, listed in Table I, it can

be observed that the loss in weight up to 289°C in the TGA curves was 7.7%–10.0%, which is a result of the desorption of adsorbed water and volatile matters. The actual pyrolysis started at around 285°C and ends at around 392°C. The blended fabric that lost its weight at 384°C was at 64.6%. The char residue at 600°C of blended fabric was lower (13.8%) than that of grafted fabric (15.1%–16.7%). The grafted fabric's moisture content, which was lower than that of the ungrafted fabric, and char residue, which was higher than its grafted counterpart, are related to the monomer that pertains to the grafting. The TGAs of grafted and ungrafted BSJCB fabrics suggest that the thermal stability of grafted fabric is higher than that of ungrafted fabric.

IR spectroscopy

The infrared spectra of the BSJCB fabric (control) and grafted BSJCB fabrics are shown in Figure 5. Figure 5 shows that the absorption bands of hydroxyl and carboxyl groups are around 3315–3455 and 1639–1725 cm^{-1} , respectively. However, an additional peak obtained for AN- and MAN-grafted fabrics at 2230–2235 cm^{-1} was observed. This peak is characteristic of the nitrile group corresponding to AN- and MAN-grafted onto BSJCB fabric. This ultimately shows that BSJCB fabric is being grafted with acrylonitrile and methacrylonitrile.

X-ray diffractometry

To define the crystalline structure of AN- and MAN-grafted BSJCB fabrics before and after grafting, X-ray diffraction patterns were analyzed. The degree of crystallinity of BSJCB fabric and their AN- and MAN-grafted fabrics was 73.9%, 69.4%, and 66.5%, respectively. This may be explained by the grafting with acrylonitrile and methacrylonitrile, which reduces the crystallinity of the BSJCB fabric because of the incorporation of amorphous copolymers. This may mechanically bind the cellulosic chains, confirming the additional strength to the fabric.

Characteristics

The breaking strength of grafted BSJCB fabric is higher than that of ungrafted fabric. Again, the loss in break-

TABLE I
TGA of Ungrafted and Grafted BSJCB Fabrics

Fabric sample	Initial weight loss region (°C)	Weight loss (%)	Actual pyrolysis region (°C)	Weight loss at end of pyrolysis (%)	Char decomposition region (°C)	Decomposed char (%)	Residual char (%)
Ungrafted	25–289	10.4	289–384	64.6	384–600	11.2	13.8
AN grafted	25–285	8.1	285–384	62.0	384–600	12.6	17.3
MAN grafted	25–287	7.7	287–392	63.5	392–600	12.1	16.7

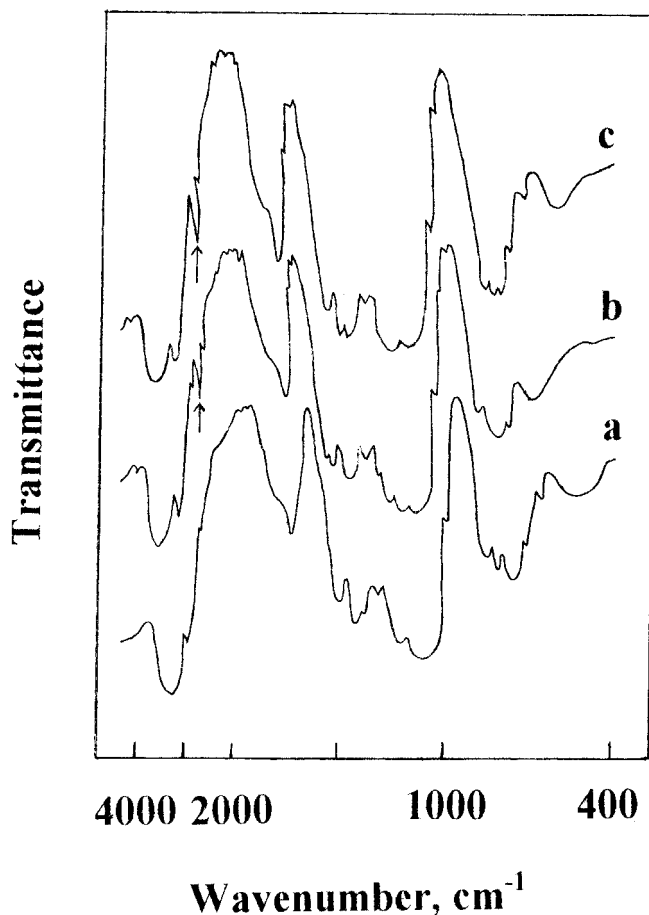


Figure 5 FTIR spectrographs of ungrafted and grafted BSJCB fabrics: (a) BSJCB fabric; (b) AN-grafted BSJCB fabric; (c) MAN-grafted BSJCB fabric.

ing strength of grafted BSJCB fabric on exposure to sunlight in air for 300 h was 5.0%–10.0% lower than that of BSJCB fabric. This means that the grafting of BSJCB fabric with acrylonitrile and methacrylonitrile decreases the loss in breaking strength by photooxidative degradation. The incorporation of monomer through grafting increases breaking strength as well as decreasing the photooxidation degradation that occurs by sunlight.

The BSJCB and their modified fabrics were dyed (2.0% dye) with Direct Yellow 29 and Direct Red 39 at

100°C for 60 min in the fabric : liquor ratio of 1 : 30. The dye absorption of the grafted fabric was 10.0%–15.0% lower than that of ungrafted fabric, meaning that grafting increased the hydrophobicity of the grafted fabric. The graft copolymerization had a positive impact on colorfastness to sunlight in air, on wash fastness to a soap medium up to 100°C, and on colorfastness to some common acids and alkalis.

References

1. Haque, M. M.; Habibuddowla, Md.; Mahmood, A. J.; Mian, A. J. *J Polym Sci, Polym Chem Ed* 1980, 18, 1447.
2. Trivedy, M.; Metha, P. C. *Cellul Chem Technol* 1973, 7, 401.
3. Ghosh, P.; Ganguly, R. K. *Polymer* 1994, 35, 383.
4. Moharana, S.; Tripathy, S. S. *J Appl Polym Sci* 1991, 42, 1001.
5. Sikdar, B.; Basak, R. K.; Mitra, B. C. *J Appl Polym Sci* 1995, 55, 1673.
6. Ghosh, P.; Paul, S. K. *J Macromol Sci, Chem* 1983, A20, 169.
7. Majumdar, S. K.; Rapson, W. H. *Text Res J* 1964, 34, 1007.
8. Ghosh, P.; Bandyopadhyay, A. R.; Das, S. *J Macromol Sci, Chem* 1983, A19, 1165.
9. Al-Siddique, F. R.; Khan, A. U.; Sheikh, R. A. *J Bangladesh Acad Sci* 1983, 7, 87.
10. Imrisova, D.; Maryska, S. *J Appl Polym Sci* 1968, 12, 2007.
11. Singh, B. C.; Mohanty, A. K. *J Appl Polym Sci* 1987, 33, 2809.
12. Kulkarni, A.; Chitale, A. G.; Vaidya, B. K.; Metha, P. C. *J Appl Polym Sci* 1968, 7, 1581.
13. Gaylor, N. G.; Tomono, T. *J Polym Sci, Polym Lett Ed* 1975, 13, 698.
14. Samal, R. K.; Sahoo, P. K.; Samantaray, H. S. *J Mol Sci—Rev, Macromol Chem Phys* 1986, C26, 81.
15. Janson, J.; Sjostron, E. *Svensk Paperstidn* 1966, 69, 107.
16. Salam, M. A.; Abdullah, A. B. M.; Khan, N. N. *Bangladesh J Sci Ind Res* 1978, 13, 181.
17. Sarkar, P. B.; Chatterjee, H. *J Text Inst* 1948, 39, T274.
18. Abou-Zeid, N. Y.; Higazy, A.; Hebeish, A. *Angew Makromol Chem* 1984, 121, 69.
19. El-Rafie, M. H.; Abdul Hafiz, S. A.; Hassan, S. M.; Hebeish, A. *Polym Polym Comp* 1994, 2, 99.
20. Varma, D. S.; Narasimhan, V. *J Appl Polym Sci* 1972, 16, 3225.
21. Segal, L.; Creely, J. J.; Martin, A. E.; Conrad, C. M. *Text Res J* 1959, 29, 786.
22. International Standard ISO 5081-1977(E) (Stip method) International Standardization for Organization, Switzerland, 1977.
23. El-rafie, M. H.; Abdel Hafiz, S. A.; Hassan, S. M.; Hebeish, A. *Polym Polym Comp* 1994, 2, 2.
24. Samal, R. K.; Samantaray, H. S.; Samal, R. N. *Polym J* 1986, 18, 471.