

Polymers from Renewable Resources: Kinetics Studies of the Radiochemical Graft Copolymerization of Styrene onto Cellulose Extracted from Pine Needles and the Effect of Some Additives on the Grafting Parameters in an Aqueous Medium

GHANSHYAM S. CHAUHAN, SURYA K. DHIMAN, LALIT K. GULERIA, INDERJEET KAUR

Department of Chemistry, Himachal Pradesh University, Shimla, 171 005 India

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ABSTRACT: In an attempt to develop an alternative to petro-based polymers, we graft-copolymerized cellulose isolated from the needles of *Pinus roxburghii* with styrene in a limited aqueous medium in air by simultaneous irradiation using gamma rays as the initiator. The optimum conditions for obtaining maximum grafting were determined as a function of monomer concentration, total dose of irradiation, and amount of water. Maximum percentage of grafting (P_g ; 79.9) was obtained at a total dose of 1.152×10^4 Gy with 1.325×10^{-4} mol of styrene. The effect of methanol, LiNO_3 , $\text{Cu}(\text{NO}_3)_2$, Mohr's salt, H_2SO_4 , HNO_3 , and AcOH on P_g was studied. All the additives were found to decrease graft yield, contrary to some reported studies. Total percentage conversion and rates of polymerization, grafting, and homopolymerization were evaluated. Evidence of grafting was provided by the characterization of cellulose and its graft copolymers by Fourier transform infrared spectroscopy, thermogravimetry, and observation of the swelling behavior in some solvents. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1490–1500, 2002

Key words: graft copolymerization; pine needles; renewable resources; simultaneous method

INTRODUCTION

The grafting of styrene (Sty) onto cellulose has been reported, but not much information is available on the kinetics of graft copolymerization. Garnett and coworkers reported on the effects of mineral acids, organic solvents, and different alcohols and their binary mixtures and the effects of

pH on grafting reactions.^{1–4} Fazilat and Rostamine⁵ grafted Sty radiochemically and evaluated optimum conditions for maximum grafting on cellulose extracted from husks and stems of rice. The grafting of Sty by a simultaneous method onto cellulose derivatives has also been reported for cellulose acetate and butyrate,^{6,7} hydroxyethyl cellulose,⁸ and cellulose tricarbonyl.⁹ Recently, Ha et al.¹⁰ reported simultaneous and postirradiation grafting of Sty onto cotton cellulose and investigated the effects of total dose, dose rate, monomer concentration, and acidity of the reaction system on the molecular weight distribution.

To develop new polymeric materials for separation technologies, we attempted to utilize pine

Correspondence to: G. S. Chauhan (ghanshyam_in2000@yahoo.com).

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needles, a perennial forest waste of the Himalayas, as a renewable source of cellulose. We reported earlier on some work on the grafting of Sty by a potassium persulfate-ferrous ammonium sulfate redox system,¹¹ Sty-maleic anhydride,¹² and 4-vinyl pyridine (4-VP)¹³ by simultaneous gamma-ray irradiation onto the backbone polymer to get reactive polymers. The grafting of these monomers afforded functionalities useful in subjecting graft copolymers to postreactions. In this article, we report on the kinetics of the graft copolymerization of Sty by a simultaneous gamma-ray irradiation technique as a function of total dose, monomer concentration, and amount of water. The effects of some inorganic salts, mineral acids, and methanol were investigated under optimum conditions of grafting.

EXPERIMENTAL

Extraction of Cellulose

Cellulose was extracted by an improved ammonia digestion method as reported earlier.¹³ Pine needles were dried in an oven at 150°C and were crushed in a mixer to a fine powder. The powder was digested in a 1-L round-bottomed flask with liquor ammonia for 6–8 h at low pressure. The digested powder was repeatedly washed with water to ensure the removal of lignin and other water-soluble organic components and to get a clear supernatant liquid. The resulting mass was treated with calcium hypochlorite to remove any colored impurities. The excess bleaching powder was removed by treatment with dilute mineral acid. Cellulose thus obtained was stirred with solvents of varying polarities to ensure the extraction of any remaining impurities. Cellulose powder was dried to a moisture content of 5–10% at low temperature (30°C) because heating at a high temperature affected its reactivity adversely.

Graft Copolymerization

Cellulose (1 g) and the monomer (0.5 mL) in 10.0 mL of water were irradiated for 16 h at a dose of 0.048×10^4 Gy/h in a gamma chamber. We calculated the total dose of radiation by multiplying the dose rate per hour by the time of exposure. The samples containing both homopolymer and graft copolymers were filtered, dried, and weighed. We extracted the dried and weighed samples by stirring them in toluene for 2 h and, then, drying and weighing them. The process was

repeated to ensure complete removal of homopolymer until a constant weight was obtained. The amount of monomer was changed to 1.0, 1.5, 2.0, and 2.5 mL at the same total dose of radiation, with the amounts of cellulose and water kept constant. Similar experiments were performed at different times of radiation with the previously mentioned amounts of monomer for every time of irradiation and with the amounts of cellulose and water kept constant. The homopolymer was separated as stated previously.

Effect of Solvent

At a total radiation dose of 1.152×10^4 Gy and 131.25×10^{-4} mol of Sty, which afforded the maximum percentage of grafting (P_g), the effect of the amount of water was determined by variation of the amount of water between 5.0 and 20.0 mL at optimum values of monomer concentration and total radiation dose. The effect of methanol in a water-methanol system was studied at 1.152×10^4 Gy and 131.25×10^{-4} mol of monomer with the total solvent composition kept at 10.00 mL.

Effect of Additives

The effect of additives was studied at optimum values of all the three reaction conditions studied previously by the addition of 0.2M of H₂SO₄, HNO₃, AcOH, Mohr's salt, Cu(NO₃)₂, and LiNO₃. The weights of the homopolymer and graft copolymers are given in Table I.

Expressions Used for Grafting Parameters

Grafting parameters were obtained from the following relationships.¹²

Percentage Total Conversion (%C_t)

$$= \frac{\text{Weight of Polymer Grafted} + \text{Weight of Homopolymer Formed}}{\text{Weight of Monomer Charged}} \times 100$$

$$P_g = \frac{\text{Weight of Polymer Grafted}}{\text{Weight of Cellulose}} \times 100$$

Percent Grafting Efficiency (%GE)

$$= \frac{\text{Weight of Polymer Grafted}}{\text{Weight of Polymer Grafted} + \text{Weight of Homopolymer Formed}} \times 100$$

Rate of Polymerization (R_p) (mol L⁻¹ s⁻¹)

$$= \frac{\text{Weight of Polymer Grafted} + \text{Weight of Homopolymer Formed}}{\text{Molecular Weight of Monomer} \times \text{Time of Reaction (s)} \times \text{Volume of Reaction Mixture (mL)}} \times 100$$

Table I Effect of the Variation of the Amount of Water and Additives on Polymerization and Grafting Parameters of Poly(Sty) onto Cellulose

Serial No	Water (mL)	MeOH (mL)	Additive (0.2M) 10.0 mL	Weight of Graft Copolymer (g)	Weight of Graft Homopolymer (g)	%C _t	P _g	%GE	R _p × 10 ⁷ (mL ⁻¹ s ⁻¹)	R _g × 10 ⁷ (mL ⁻¹ s ⁻¹)	R _h × 10 ⁷ (mL ⁻¹ s ⁻¹)
1	5.0	—	—	1.079	0.146	16.48	7.90	35.11	38.53	13.53	24.98
2	10.0	—	—	1.799	0.359	84.83	79.90	68.99	112.06	77.32	34.74
3	15.0	—	—	1.28	0.612	65.38	28.00	58.45	32.31	18.88	13.42
4	20.0	—	—	1.288	0.128	30.47	28.80	69.23	21.53	14.91	6.62
5	25.0	—	—	1.268	0.171	32.16	26.80	61.04	18.43	11.25	7.18
6	8.0	—	—	1.644	0.235	79.34	64.40	59.46	104.80	62.32	42.48
7	6.0	—	—	1.467	0.514	71.86	46.70	47.60	94.93	45.19	49.74
8	4.0	—	—	1.305	0.017	23.58	30.50	94.72	31.16	29.5	1.64
9	2.0	—	—	1.281	0.004	20.87	28.10	98.59	27.58	27.19	0.387
10	0.0	—	—	1.00	0.232	16.99	0.00	0.00	22.45	0.00	22.45
11	10.0	—	H ₂ SO ₄	1.323	0.667	72.52	32.3	32.62	95.79	31.25	64.54
12	—	—	HNO ₃	1.09	0.283	27.32	9.0	24.12	36.08	8.7	27.34
13	—	—	AcOH	1.611	0.241	62.41	61.10	71.7	82.44	59.13	23.31
14	—	—	Mohr salt	1.699	0.316	74.37	69.9	66.69	98.51	65.71	32.80
15	—	—	LiNO ₃	1.029	0.235	19.34	2.90	10.98	25.55	2.81	22.74
16	—	—	Cu(NO ₃) ₂	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Cellulose = 1 g, total radiation dose = 1.152 × 10⁴ Gy, [Sty] = 131.25 × 10⁻⁴ mol.

$$\begin{aligned} \text{Rate of Grafting } (R_g) \text{ (mol L}^{-1} \text{ s}^{-1}) \\ = \frac{\text{Weight of Polymer Grafted}}{\text{Molecular Weight of Monomer} \\ \times \text{Time of Reaction (s)} \\ \times \text{Volume of Reaction Mixture (mL)}} \times 1000 \end{aligned}$$

$$\begin{aligned} \text{Rate of Homopolymerization } (R_h) \text{ (mol L}^{-1} \text{ s}^{-1}) \\ = \frac{\text{Weight of Polymer Grafted}}{\text{Molecular Weight of Monomer} \\ \times \text{Time of Reaction (s)} \\ \times \text{Volume of Reaction Mixture (mL)}} \times 1000 \end{aligned}$$

$$\begin{aligned} \text{Percentage Swelling } (P_s) \\ = \frac{\text{Weight of Swollen Polymer} \\ - \text{Weight of Dry Polymer}}{\text{Weight of Dry Polymer}} \times 100 \end{aligned}$$

Characterization of Cellulose and Graft Copolymer

Cellulose and its graft copolymers were characterized by elemental analysis on a Carlo Erba-1150, Fourier transform infrared (FTIR) spectra were obtained on a Nicolet FTIR spectrometer Series II, thermal analysis was carried out on a Shimadzu simultaneous thermogravimetry/differential thermal analysis analyzer in air, and swelling studies were carried out in different solvents by the equilibration method by immersion for 24 h at room temperature.

RESULTS AND DISCUSSION

In simultaneous irradiation, monomer radicals and active sites on the backbone are generated in the same reaction medium; hence, grafting can be initiated either by the growing polymeric radicals or from the active sites on the cellulose backbone as reported earlier for the grafting of 4-VP onto this backbone.¹³

Structural Aspects of Extracted Cellulose

Grafting reactions and the properties of the graft copolymers are affected by the structure of cellulose. In this case, the backbone got ammoniated during the extraction process. Elemental analysis of cellulose showed the presence of 1.55% N. It has been reported that ammoniation occurs in less ordered and high crystalline regions and leads to the increase of plane spacing up to 2.6 Å, thus, increasing the volume of unit cell from 671 cu. Å in native cellulose to 801 cu. Å in ammonia-

swollen cellulose. Furthermore, crystallinity determined from wide-angle X-ray diffraction studies showed that the extraction process opened up the cellulose matrix considerably, as percentage crystallinity was found to be just 31.00,¹⁴ against 59.0% for a commercial reference. However, attempts to determine its degree of polymerization by viscometry in FeTNa and Cu(en)₂ failed because cellulose behaves as a polyelectrolyte, suggesting that the oxidation of glycolic groups in the bleaching process occurs.

Effect of Total Dose and Monomer Concentration

Figures 1 and 2 represent P_g as a function of total dose and monomer concentration, respectively. P_g increased with increasing total dose for various monomer concentrations, giving a maximum at 1.152×10^4 Gy, except for the monomer concentration of 218.75×10^{-4} mol, which produced maximum grafting (21.5%) at 1.056×10^4 Gy. Beyond the maximum, P_g decreased for all monomer concentrations (Fig. 1). The maximum P_g (79.9%) was obtained at $[\text{Sty}] = 131.25 \times 10^{-4}$ mol. When P_g was studied as a function of monomer concentration at different total doses (Fig. 2), P_g increased with increasing monomer concentration, giving a maximum at $[\text{Sty}] = 175.0 \times 10^{-4}$ mol, and decreased thereafter. However, when 131.25×10^{-4} mol of Sty was used, a sharp increase in P_g was observed at a total dose of 1.152×10^4 Gy giving maximum grafting (79.9%), and then it decreased. At higher total dose of 1.248×10^4 Gy, maximum grafting (20%) was obtained at $[\text{Sty}] = 131.25 \times 10^{-4}$ mol. At higher monomer concentrations and higher total doses, P_g decreased due to preferential homopolymer formation. From various grafting parameters, an attempt was made to correlate $\%C_t$, $\%GE$, R_p , R_h , and R_g as functions of monomer concentration at different total doses. The results are presented in Figures 3–6. $\%C_t$ was higher at lower monomer concentrations and decreased with increasing $[\text{Sty}]$. This trend was followed, except for reactions carried out at a total dose of 1.152×10^4 and 1.248×10^4 Gy where $\%C_t$ increased with increasing monomer concentration, giving a maximum (84.83 and 54.34%) at $[\text{Sty}] = 131.25 \times 10^{-4}$ and 175.0×10^{-4} mol, respectively, and then decreased (Fig. 3). At very low total doses (0.768×10^4 and 0.96×10^4 Gy) and at higher monomer concentrations, $\%C_t$ was very low.

Figure 4 shows that that R_p at lower total doses (0.768×10^4 and 0.96×10^4 Gy) was very low. When grafting was carried out at higher total

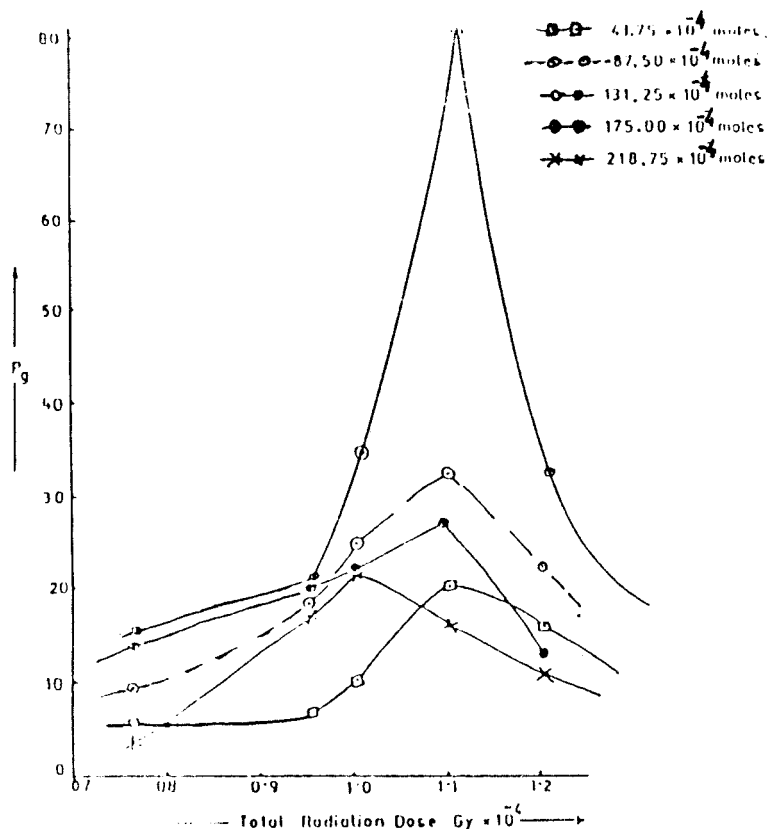


Figure 1 Effect of the total radiation dose on P_g at different monomer concentrations (cellulose = 1 g, water = 10.0 mL).

doses of 1.152×10^4 and 1.248×10^4 Gy, R_p increased with increasing [Sty], giving a maximum (112.06×10^{-7} and $84.7 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ at [Sty] = 131.25×10^{-4} and 175.0×10^{-4} mol, respectively. This trend was similar to that of % C_p , discussed previously. At a total dose of 1.056×10^4 Gy, R_p showed steady increase with increasing [Sty], reaching a maximum ($73.47 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$) before it started decreasing. Figure 6 shows that R_h , at lower monomer concentrations and lower total doses, decreased with increasing [Sty]. Under similar conditions, R_g showed an increase with increasing [Sty] and, then, decreased after reaching a maximum value (Fig. 5). The decrease in R_g was due to preferential homopolymer formation at higher monomer concentrations. It is again revealed from Figure 6 that R_h increased with increasing total dose of radiation and monomer concentration. At higher total doses (1.248×10^4 Gy), R_h increased with increasing [Sty] and gave a maximum value of $73.0 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ at [Sty] = 175.0×10^{-4} mol, whereas R_g was found to have a maximum ($77.32 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$) at a total dose of 1.152×10^4 Gy and at a monomer concentration [Sty]

= 131.25×10^{-4} mol. Thereafter, both these parameters showed a steep decrease. This behavior of R_h and R_g suggests their interdependency and supports the argument that at higher total doses and monomer concentrations, homopolymerization was the preferred process.

For all the grafting reactions carried out at different total doses, %GE increased with increasing monomer concentration and, then, decreased (Fig. 7). However, for the reaction carried out at an optimum total dose of 1.152×10^4 Gy, %GE was at a maximum at the lower monomer concentration, that is, at 43.75×10^{-4} mol, beyond which %GE decreased sharply. It is evident from Figures 5 and 6 that R_g and R_h were, respectively, maximum and minimum at this total dose and monomer concentration; hence, a higher value of %GE was expected under this set of reaction conditions.

Effect of the Amount of Water

The effect of variation of the amount of water on P_g is shown in Figure 8 and in Table I. At optimum conditions of total dose and monomer con-

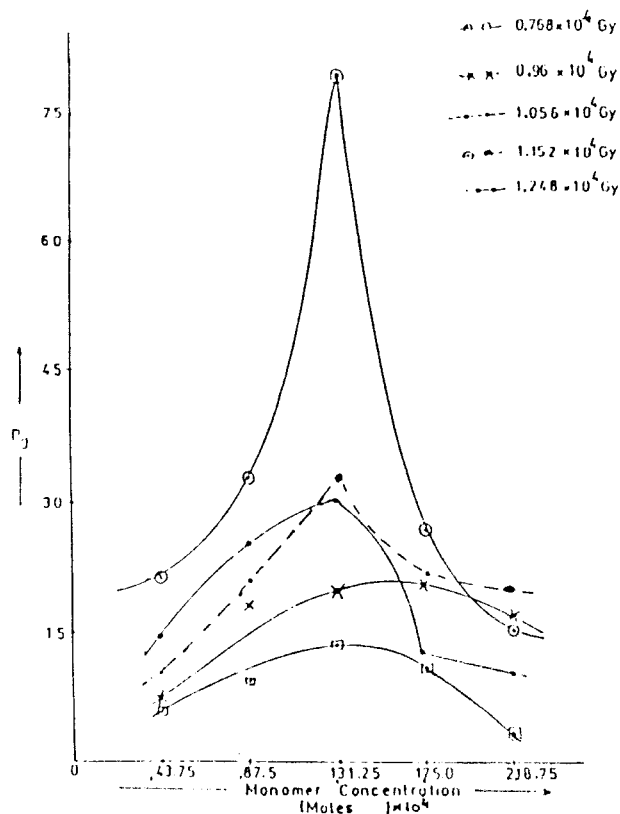


Figure 2 Effect of the monomer concentration on P_g at different total radiation doses (cellulose = 1 g, water = 10.0 mL).

centration, maximum P_g (79.9%) was obtained in 10.00 mL of water. Further increases in the amount of water led to a steep fall in P_g , and thereafter, it remained constant. An optimum

amount of water helped in the swelling of the polymer backbone, thus making it more accessible to the monomer. Increases in the amount of water above the optimum volume led to a de-

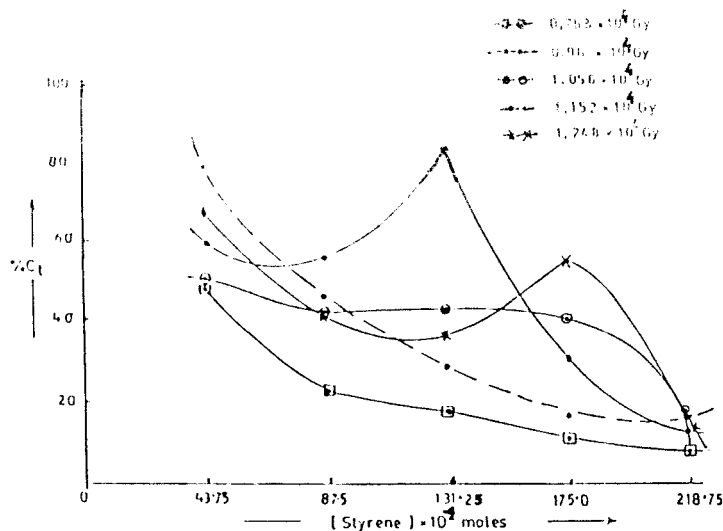


Figure 3 Total monomer conversion as a function of monomer charged at different total radiation doses (cellulose = 1 g, water = 10.0 mL).

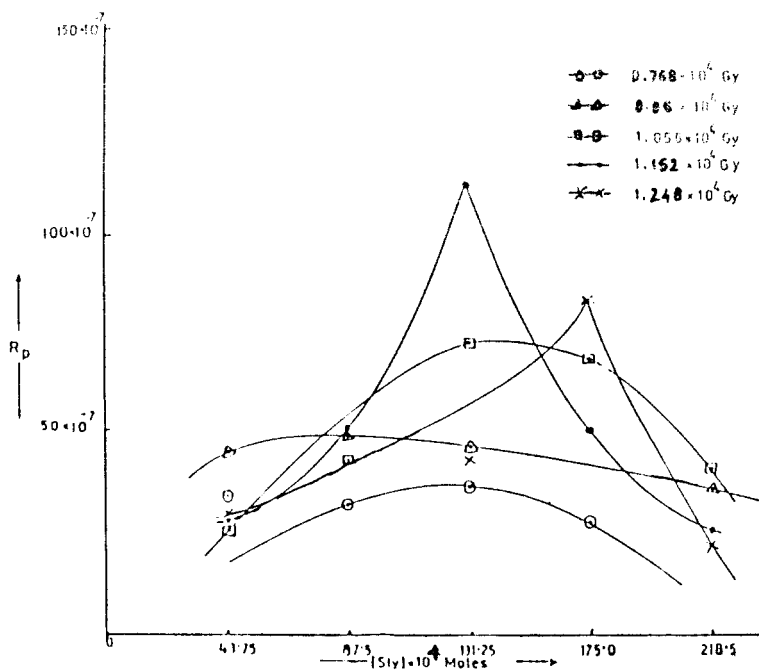


Figure 4 Effect of the monomer concentration on R_p at different total radiation doses.

crease in all the grafting parameters. R_p , R_h , and R_g fell sharply with increasing amounts of water, although P_g tended to remain constant. %GE was not much affected because the increasing amount of water resulted in lower yields of both graft and homopolymer.

Effect of Methanol

The addition of methanol to the reaction mixture decreased P_g uniformly (Fig. 9). As the solvent

composition varied from absolute water to 100% methanol, P_g fell from 79.9 to 0. A certain amount of methanol was reported to promote grafting;¹⁵ however, in this study, it failed to do so as all the grafting parameters showed a steady decrease in the presence of methanol (Table I). Only R_h increased from $34.47 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ in water medium to 42.48×10^{-7} and $49.74 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ in 8.0 : 2.0 and 6.0 : 4.0 water-methanol compositions, respectively. As the amount of methanol was further increased, R_h decreased

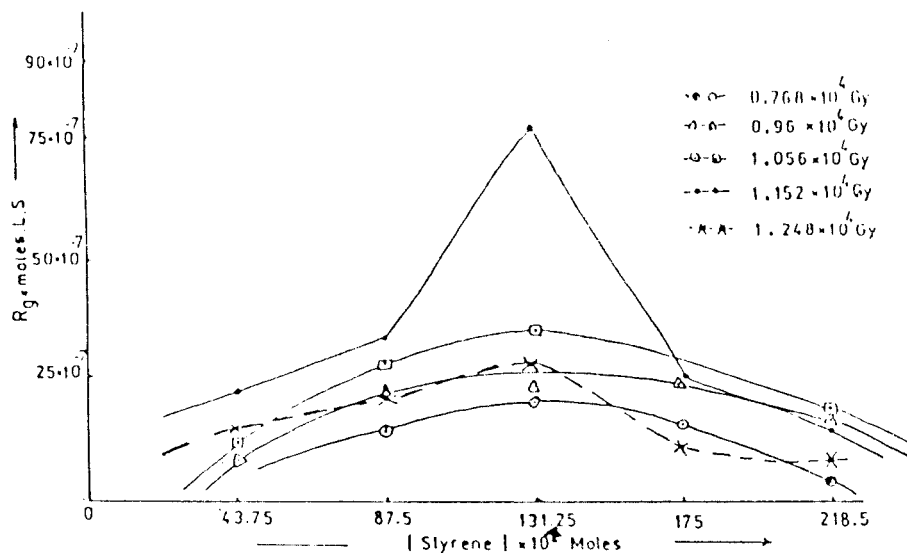


Figure 5 Effect of the monomer concentration on R_g at different total radiation doses (cellulose = 1 g, water = 10.0 mL).

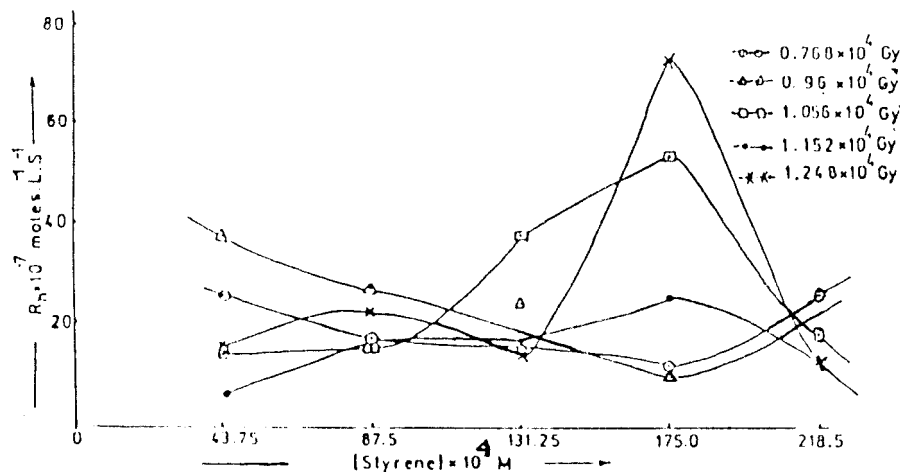


Figure 6 Effect of the monomer concentration on R_h at different total radiation doses (cellulose = 1 g, water = 10.0 mL).

more sharply compared to R_g ; hence, very high %GE (97.7 and 98.59, respectively, for water-methanol compositions 4.0 : 6.0 and 2.0 : 8.0) were observed. However, in absolute methanol, no

grafting was observed. This effect of methanol on polymerization parameters can be explained by its failure to swell the cellulose backbone compared to water where 33.5% swelling took place.

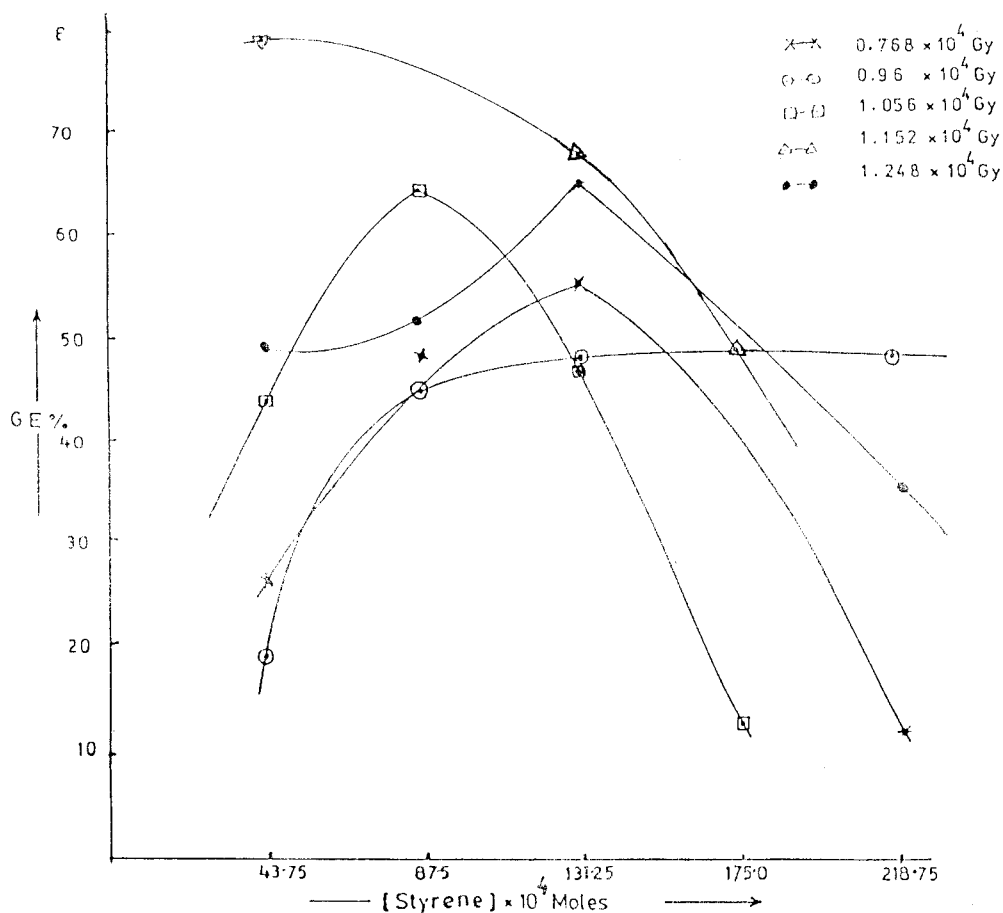


Figure 7 Effect of the monomer concentration on %GE at different total radiation doses (cellulose = 1 g, water = 10.0 mL).

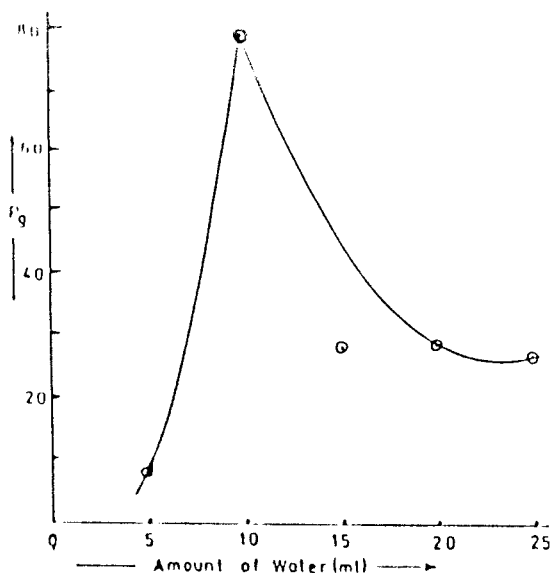


Figure 8 Effect of the amount of water on P_g (cellulose = 1 g, $[\text{Sty}] = 131.25 \times 10^{-4}$ mol, total radiation dose = 1.152×10^4 Gy).

Swelling enhances the accessibility of the monomer to the active sites. The role of swelling in grafting was well established by Garnett and co-workers.¹⁶ They also reported that a larger size of the diluent leads to lesser swelling of the backbone polymer and affects grafting in an adverse manner. Further, methanol is a good chain-transfer solvent. The solvent chain-transfer constant (C_s) of Sty to methanol ($C_s = 0.296 \times 10^{-4}$) is much higher than that of Sty to water ($C_s = 0.006 \times 10^{-4}$).¹⁷ This was supported by the fact that there was a sharp and steady fall in the $\%C_t$ when methanol was used as an additive to water or in absolute methanol. In the presence of methanol, various chain-transfer reactions were initiated that scavenged both monomer and backbone radicals as shown:



Such scavenging of the monomer and even backbone polymer radicals by solvent molecules was also reported by Harris and Arthur for the grafting of Sty onto preirradiated cotton and regenerated cellulose fabrics.¹⁸ Furthermore, they did not observe any add-on in methanol but readily did so with an 8% water-methanol mixture. In this study, the decrease of add-on to the cellulose backbone in methanol may also be at-

tributed to the distinct or fine structure of cellulose as it got ammoniated in the extraction process. The lower degree of order in the backbone polymer leads to the predominance of monomer radical-solvent reactions over radical-radical reactions.¹⁹

Effect of Additives

Some mineral acids and inorganic salts enhance grafting reactions and, in this study, the effects of some additives, such as H_2SO_4 , HNO_3 , AcOH , LiNO_3 , and known homopolymer suppressors such as Mohr salt and $\text{Cu}(\text{NO}_3)_2$,²⁰ on P_g at an optimum concentration of the monomer, total dose, and amount of water was studied. The results are presented in Table I. At the concentration studied, all the additives, contrary to their enhancing effect, decreased P_g . For acids, it seems more likely that the ammoniation of cellulose in the extraction process offset the advantages of acid catalysis. Nitric acid, being a strong oxidizing agent, produced a very low P_g (9%) compared to H_2SO_4 and AcOH (32.3 and 61.10%, respectively). Mohr salt, a known homopolymer inhibitor, also afforded lesser grafting P_g (67.9%), but R_h was lower (32.80×10^{-7} mol L^{-1} s^{-1} compared to 34.71×10^{-7} mol L^{-1} s^{-1} in its absence). A sharp decrease in P_g was observed with LiNO_3 , whereas with $\text{Cu}(\text{NO}_3)_2$, no grafting or homopolymer formation was observed. Cu^{+2} combined with the monomer to form a complex, thus, making it unavailable for either of the reactions. Cu^{+2} forms strong bonds with 2,3-hydroxyl groups of the pyranoside ring of cellulose,²¹ and

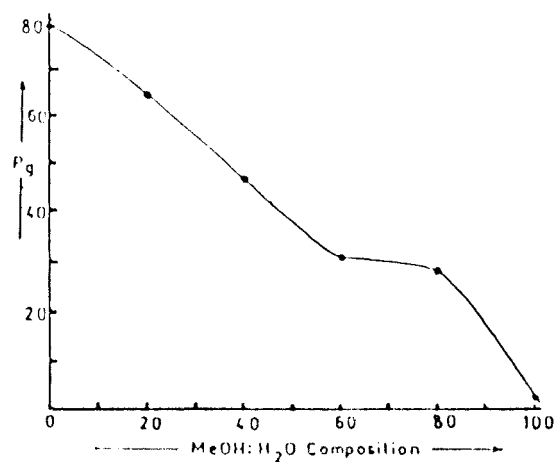


Figure 9 Effect of the amount of methanol-water composition on P_g (cellulose = 1 g, $[\text{Sty}] = 131.25 \times 10^{-4}$ mol, total radiation dose = 1.152×10^4 Gy).

bidentate- and tetradentate-coordinated Cu^{+2} becomes additionally stable.²² The formation of the complex in this study was confirmed by spectral studies. Garnett et al.²³ also reported that metal ions get adsorbed on the cellulose, which leads to their partitioning in the monomer system and backbone polymer. The role of the scavenging of monomer radicals and the partitioning of metal ions was reported by Collinson et al.²⁴ and Hoffman and Ratner.²⁵ In the case of Li^+ salts, it was reported that nontransition metal salts affect R_p and copolymer composition by complex formation with the monomer.²⁶ All the additives showed a decrease in all the grafting parameters (i.e., $\%C_t$, $\%GE$, P_g , R_p , and R_g). R_h , however, was enhanced (from 34.74×10^{-7} to 64.54×10^{-7} mol $\text{L}^{-1} \text{s}^{-1}$) in the presence of sulfuric acid.

Evidence of Grafting by the Characterization of Polymers

FTIR spectra of cellulose^{12,13} and cellulose-g-poly(Sty) were compared, and the IR spectrum of cellulose showed prominent peaks at 3471.89, 2927.66, 1165.16, 1016.8, and 871.67 cm^{-1} , corresponding to O—H, C—H, and C—O—C stretching and —OH bending, respectively. The peak assigned to O—H stretching (3471.89 cm^{-1}) was not only lower than expected for secondary and primary O—H groups but was also very broad. The presence of some native carboxylic groups was supported by the small shoulder peak at 1734.38 cm^{-1} corresponding to $>\text{C}=\text{O}$ absorption of acid. Cellulose-g-poly(Sty), on other hand, showed, in addition to the previous, peaks between 2847.03 and 2862.54 cm^{-1} due to C—H stretching and very sharp peaks between 759.3 and 755.56 cm^{-1} and 700.39 to 697.54 cm^{-1} in different cellulose-g-poly(Sty) copolymers. When the absorbance ratio of the monosubstituted benzene ring to the C—O—C stretching of the ether linkage of the anhydroglucose unit of cellulose (1068.07–1053.08 cm^{-1}) was plotted against the P_g , a straight line was obtained, which corroborated well with the P_g determined gravimetrically (Fig. 10).

Swelling studies of cellulose and cellulose-g-poly(Sty) were carried out in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), MeOH, and water. DMSO swelled the cellulose backbone more than water (Fig. 11). However, no swelling was obtained with DMF and MeOH. These results were expected in view of the contributions of solubility parameters (δH and δP), molar volumes both for protic and aprotic solvents. For

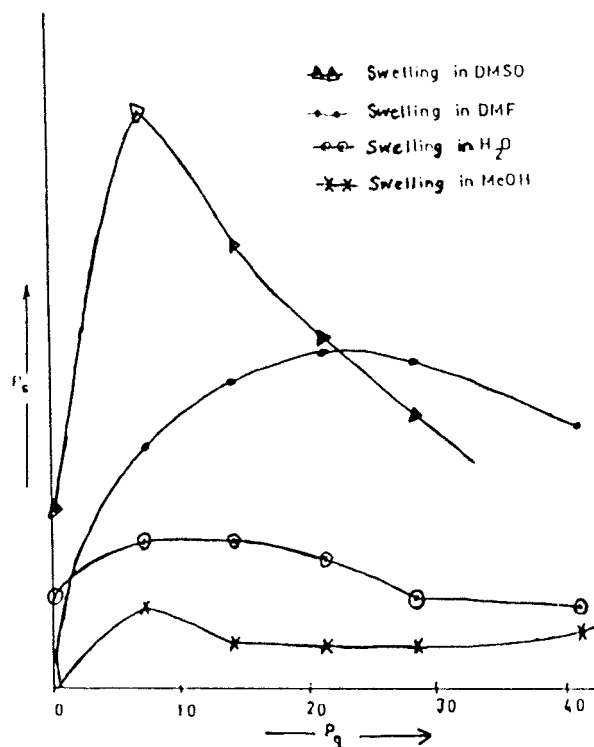


Figure 10 P_s of cellulose and cell-g-poly(Sty) in different solvents as a function of P_g (cellulose = 1 g, $[\text{Sty}] = 131.25 \times 10^{-4}$ mol, total radiation dose = 1.152×10^4 Gy).

cellulose-g-poly(Sty), P_s increased with increasing P_g and decreased at its higher values. The extent of swelling can be formulated as $\text{DMSO} > \text{DMF} > \text{H}_2\text{O} > \text{MeOH}$, and such trends were expected due to the opening of the cellulose matrix due to grafting; these voids could hold solvents. The solubilizing nature of DMSO and DMF toward poly(Sty) units was observed for modified cellulose.

Thermogravimetric analysis of cellulose and cellulose-g-poly(Sty) showed that the decomposition processes of these polymers were different. A primary thermogram of cellulose showed two stages of decomposition, whereas the graft copolymer degraded in a single stage.¹² The first stage of degradation in cellulose (222–372°C) was mainly related to the dehydration of —OH units and the formation of anhydride, followed by depolymerization above 300°C. In the next stage, pyrolysis to smaller products took place. The thermogram of the graft copolymer showed weight loss from 200°C with constant weight loss till 406°C. Poly(Sty) degraded between 300 and 400°C, with loss to dimers and trimers. A different pattern of thermal degradation arose due to

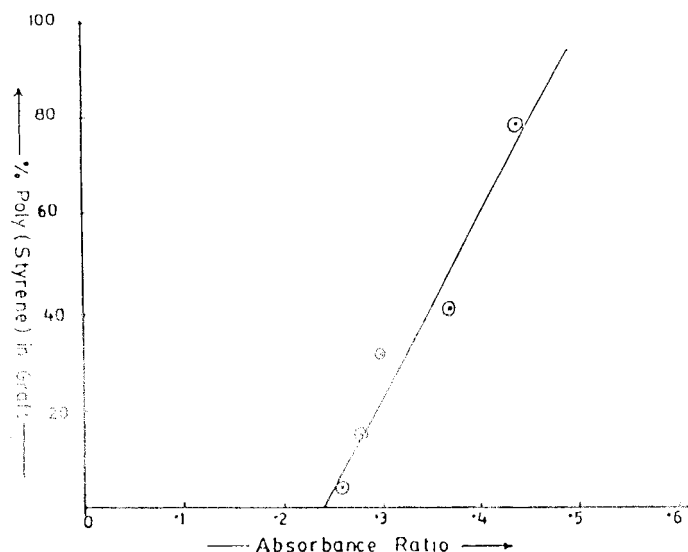


Figure 11 Correlation of the absorbance ratio of the stretching of C=C of Sty and COC of cellulose from FTIR spectra of different cell-g-poly(Sty).

opening of the cellulose matrix on grafting and the consumption of OH groups on grafting and incorporated polymers, and it provided evidence of grafting.

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