Grafting of a Styrene–Acrylonitrile Binary Monomer Mixture onto Cellulose Extracted from Pine Needles

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ABSTRACT: In an attempt to develop new reactive membrane materials, we graft-copolymerized styrene (Sty) and acrylonitrile (AN) onto cellulose extracted from pine needles by a chemical initiation method. The optimum grafting reaction conditions for Sty onto cellulose were earlier evaluated as [Sty] = 656.25 mmol/L and [potassium persulfate–ferrous ammonium sulfate] = 146.3:12.75 mmol/L in 20 mL of H_2O with a reaction time of 3 h and a reaction temperature of 60°C for 1 g of cellulose. Under these conditions, Sty was graft-copolymerized with AN at five different concentrations of the latter. Grafting parameters and different rates of concentration were evaluated. The effects of additives such as $ZnCl_2$, $LiNO_3$, and $Cu(NO)_3$ were studied at the best comonomer concentration of Sty–AN. In the presence of $ZnCl_2$, Sty–AN graft-copolymerized in an alternate way, thus, making it evident that $ZnCl_2$ coordinated to form a "complexomer," or complex of monomers $[Sty^-AN^+...ZnCl_2]$, of two monomers. Evidence of the structural characteristics of grafted chains were provided by characterization with elemental analysis, thermal analysis, and Fourier transform infrared spectroscopy. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2000–2007, 2002

Key words: binary monomer system; complexomer; graft chains; pine needles

INTRODUCTION

The formation of alternate copolymers by an electron donor monomer in the presence of Friedel Craft catalysts, some metal halides or organo aluminum halide, is presumed to proceed through homopolymerization of equimolar donor–acceptor monomer charge-transfer complexes.[1,2] Styrene (Sty) and methyl methacrylate (MMA) also yield an equimolar alternate copolymer in the presence of ethyl aluminum sesquichloride (EASC) at the

ratio 2:2:1 (Sty:MMA:Al).[3] Isoprene and maleic anhydride (MAnh) have been reported to copolymerize spontaneously at elevated temperatures (Ts) initiated by benzoyl peroxide (BPO), t-butyl perbenzoate, t-butyl peroxypivalate, and azobisisobutyronitrile.[4] Acrylonitrile (AN) and Sty have been found to yield alternating copolymer in the presence of $ZnCl_2$ initiated by $K_2S_2O_8$ at a Sty:AN molar ratio of 1:1 and a AN:$ZnCl_2$ ratio of 2:1.[5] Gaylord and coworkers graft-copolymerized poly(Sty-*alt*-MAnh) and poly(isoprene-*alt*-MAnh) onto poly(Sty) in the absence of any complexing agent and with BPO as the initiator.[6] Further, poly(Sty-*alt*-MMA) was grafted onto poly(butyl acrylate) and poly(Sty-*alt*-AN) onto poly(Sty) by initiation with BPO in the presence of EASC and $ZnCl_2$, respectively. Grafting of poly(Sty-*alt*-MMA)

onto poly(butyl acrylate-co-AN) was also carried with BPO as the initiator and EASC as the complexing agent.[7] Alternately, Sty and AN have been graft-copolymerized onto cellulose in the presence of $ZnCl_2$ with $K_2S_2O_8$ as the initiator and t-butyl peroxy pivalate as the catalyst.[8] Bohra et al.[9] grafted AN onto Sty–methacrylic acid copolymer by Ce^{4+}-ion initiation.

Cellulose and cellulosics constitute excellent membrane materials. However, these suffer from certain drawbacks such as low mechanical strength, poor weatherability, fouling, and consequent biodegradation. Membranes with some polymer grafted on are known to suffer minimum fouling. In addition, desired levels of solvent interaction characteristic of the membrane can be achieved by the grafting of hydrophobic or hydrophilic monomers. Tailor-made graft chains can be incorporated on the backbone polymer by grafting a suitable donor–acceptor monomer pair. We earlier synthesized well-defined graft copolymers of poly(Sty-*alt*-MAnh) onto cellulose extracted from pine needles.[10] We reported kinetics and provided evidence by Fourier transform infrared (FTIR) spectroscopy, thermal analysis, and swelling studies to support the structural aspects of the graft chains. In this article, we report on an investigation of the kinetics of the graft copolymerization of a binary mixture of Sty with AN attempted by a chemical initiation method. The grafting of these monomers led to the incorporation of well-defined graft chains. The grafted monomers were amenable to postreactions; hence, very exciting membrane materials may be realized. In this article, only the kinetics of the grafting of the Sty–AN monomer mixture is reported.

EXPERIMENTAL

Materials and Methods

Cellulose was extracted from pine needles by an improved ammonia digestion method.[11] Sty (Fluka Chemie AG, Buchs, Switzerland) was distilled at reduced pressure, and the middle fraction was used. AN (S. D. Fine, Poicha®, Mumbai, India) was used as received. $ZnCl_2$ was recrystallized from distilled water.

Graft Copolymerization

Five concentrations of AN (including 1:1) were graft-copolymerized at optimum reaction condi-

tions used earlier for the grafting of Sty by chemical initiation. These conditions included monomer (concentration = 656.25 mmol/L), initiator system (potassium persulfate–ferrous ammonium sulfate (KPS:FAS) = 146.3:12.75 mmol/L), water (20 mL), and a reaction T of 60°C and a reaction time (t) of 3 h, which were worked out for chemically initiated grafting of Sty onto cellulose. All experiments were carried in two sets. The homopolymer was separated by a solvent extraction method with a solvent system (dimethylformamide–benzene). Repeated extractions were carried until a constant weight was obtained.
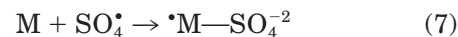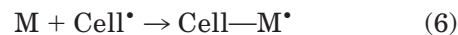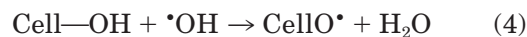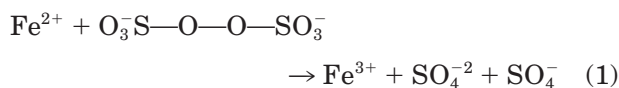
Effect of Additives

To affect changes in the grafting parameters, enhance grafting efficiency (GE), and change the nature of the graft chains, the effects of some additives such as $LiNO_3$, $Cu(NO_3)_2$, and $ZnCl_2$ were studied at the optimum conditions. These studies included 656.25 mmol/L each of Sty and the comonomer because at this concentration of the monomer system, the highest percentage grafting (P_g) was obtained. The effect of $ZnCl_2$ was studied at five different concentrations.

P_g and other parameters were defined by the usual relationship reported elsewhere.[10]

RESULTS AND DISCUSSION

The fundamentals of the mechanism of grafting reactions in the presence of $ZnCl_2$ can be explained by the following equations:
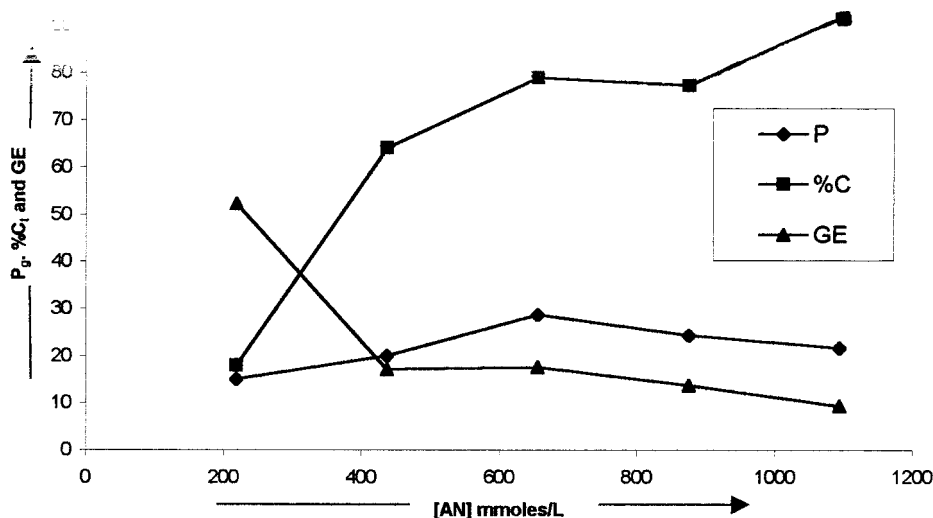
Initiation

$$Fe^{2+} + O_3^-S—O—O—SO_3^-$$
$$\rightarrow Fe^{3+} + SO_4^{-2} + SO_4^- \quad (1)$$

$$SO_4^- + H_2O \rightarrow HSO_4^- + {}^\bullet OH \quad (2)$$

$$Cell\text{-}OH + SO_4^\bullet \rightarrow CellO^\bullet + HSO_4^- \quad (3)$$

$$Cell—OH + {}^\bullet OH \rightarrow CellO^\bullet + H_2O \quad (4)$$

$$M + {}^\bullet OH \rightarrow {}^\bullet M—OH \quad (5)$$

$$M + Cell^\bullet \rightarrow Cell—M^\bullet \quad (6)$$

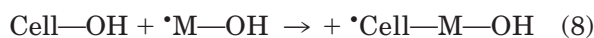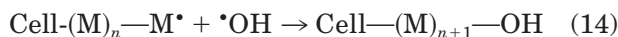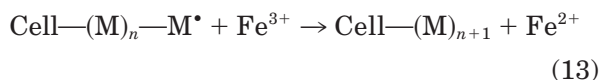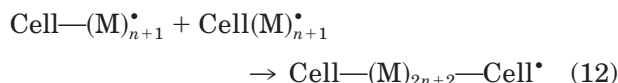$$M + SO_4^\bullet \rightarrow {}^\bullet M—SO_4^{-2} \quad (7)$$

Figure 1   Effect of [AN] on P_g, $\%C_t$, and GE ([Sty] = 131.25×10^{-4} mol, water = 20 mL, t = 3 h, T = 60°C, KPS = 146.3 mmol, and FAS = 12.75 mmol).

Propagation

$$\text{Cell—OH} + {}^{\bullet}\text{M—OH} \rightarrow + {}^{\bullet}\text{Cell—M—OH} \quad (8)$$

$${}^{\bullet}\text{Cell—OH} + n\text{M} \rightarrow \text{Cell—(M)}^{\bullet}_{n+1}\text{—OH} \quad (9)$$

$$\text{Cell}^{\bullet} + n\text{M} \rightarrow \text{Cell-(M)}^{\bullet}_n \quad (10)$$

$${}^{\bullet}\text{M—OH} + n\text{M} \rightarrow \text{HO-(M)}_n\text{-M}^{\bullet} \quad (11)$$

Termination

$$\text{Cell—(M)}^{\bullet}_{n+1} + \text{Cell(M)}^{\bullet}_{n+1}$$
$$\rightarrow \text{Cell—(M)}_{2n+2}\text{—Cell}^{\bullet} \quad (12)$$

$$\text{Cell—(M)}_n\text{—M}^{\bullet} + \text{Fe}^{3+} \rightarrow \text{Cell—(M)}_{n+1} + \text{Fe}^{2+} \quad (13)$$

$$\text{Cell-(M)}_n\text{—M}^{\bullet} + {}^{\bullet}\text{OH} \rightarrow \text{Cell—(M)}_{n+1}\text{—OH} \quad (14)$$

Where M represents the complexomer (Sty^+AN^- ... ZnCl_2) formed in the presence of ZnCl_2 that subsequently homopolymerizes. The grafting behavior of the monomers can be explained on similar lines as discussed for the radiation-induced grafting of binary monomer systems.[10] The formation of the complexomer by electron-acceptor and electron-donor monomers affords high kinetic and stoichiometric regularities. The alternation of monomers in graft chains affording high regularities is attributed to the homopolymerization of the complexomer. In the absence of complexomer formation, the structure of the graft chains is bound to be of an irregular nature because polymerization is dependent on reactivity ratio, and the product of the same does not approach zero as it does in the case of MAnh and Sty.

Analysis of Kinetic Data

The grafting behavior of the binary mixture of Sty and AN at the optimum reaction concentration conditions ([Sty] = 656.25 mmol/L, KPS = 146.3mmol/L, and FAS = 12.75 mmol, reaction t = 3 h, T = 60°C, water = 20 mL) is presented in Figures 1 and 2. P_g kept increasing with increasing [AN] (Fig. 1). Maximum P_g was observed at a 1:1 molar ratio of the monomers, and thereafter, it tended to remain constant. Percentage total conversion ($\%C_t$) showed a linear increase, as did the rate of polymerization (R_p) and the rate of homopolymerization (R_h), with increasing [AN] (Fig. 2). All grafting parameters, especially the rate of grafting (R_g), did not change appreciably with increasing [AN]. With increasing [AN], high values of $\%C_t$, R_p, and R_h and the linear increases of all these parameters were due to AN's preferred copolymerization with Sty. Due to unfavorable reactivity ratios in the case of Sty (M_1) and AN (M_2; r_1 = 0.36 and r_2 = 0.03 at 20°C, where r_1 and r_2 are the reactivity ratios of M_1 and M_2, respectively),[12] with increasing [AN], AN preferred to copolymerize more with Sty, leading to the increased formation of ungrafted copolymers.
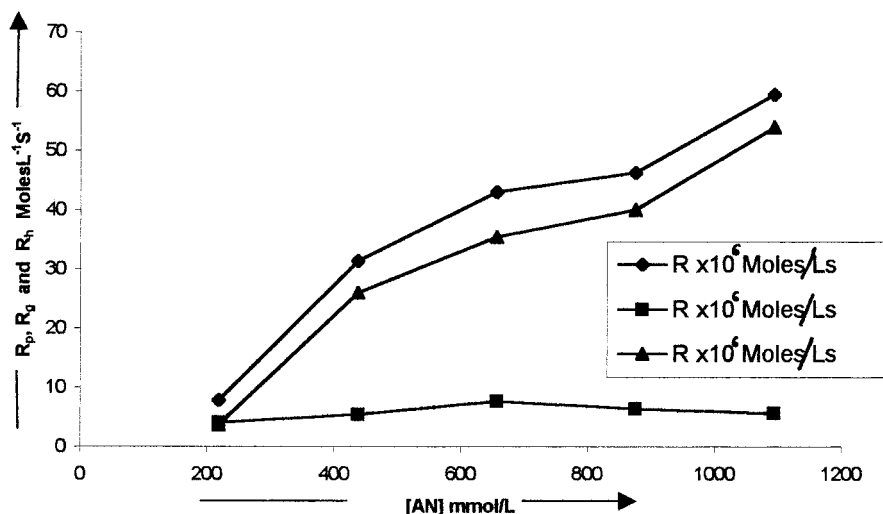
Figure 2 Effect of [AN] on R_p, R_g, and R_h ([Sty] = 656.25 mmol/L, water = 20 mL, t = 3 h, T = 60°C, KPS = 146.3 mmol/L, and FAS = 12.75 mmol).

Effects of Additives

The effects of some additives on grafting parameters were studied. As observed earlier for other binary monomer systems, the addition of $LiNO_3$ and $Cu(NO_3)_2$ led to a decrease in all the grafting parameters. This was explained by the fact that the metal ions (M^{+z}) had a tendency to combine with both the monomers and the cellulose. Metal ions formed complexes with Sty, AN, and cellulose, especially at the glycolic group of the latter. However, it seems that in this case, these preferentially got complexed with both the monomers and got partitioned more to form their complexes with the monomers as compared to cellulose,

which resulted in the observed decrease in the extent of the graft copolymer formed. Both $Cu(NO_3)_2$ and $LiNO_3$ again failed to promote grafting. R_h was not affected much by $LiNO_3$ as compared to $Cu(NO_3)_2$, which was an efficient homopolymer suppressor.[10]

Effect of ZnCl$_2$ on Grafting the Binary of the Monomer Mixture onto Cellulose

The addition of $ZnCl_2$ (in the concentration range of 81.8–327.2 mmol/L) to the binary mixture of Sty–AN at optimum reaction conditions decreased P_g and percentage grafting efficiency
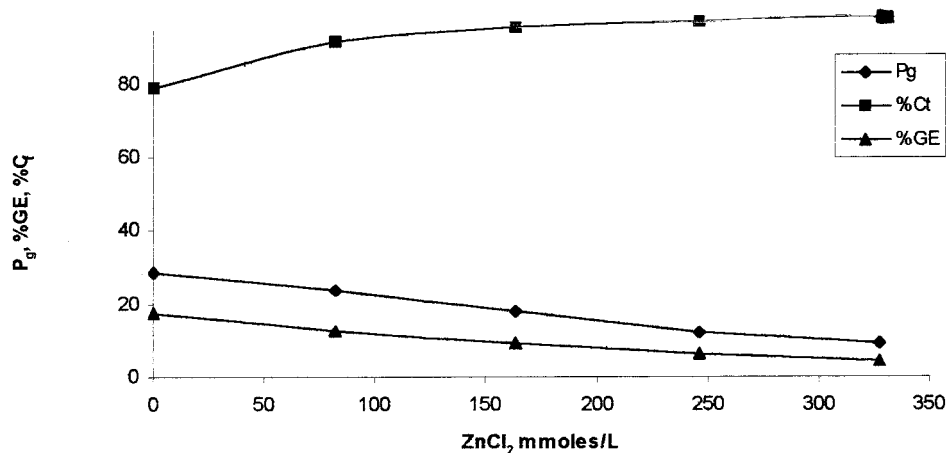

Figure 3 Effect of $ZnCl_2$ on P_g, %GE, and %C_t ([Sty] = 656.25 mmol/L, KPS:FAS = 146.3:12.75 mmol/L, water = 20 mL, t = 3 h, T = 60°C).
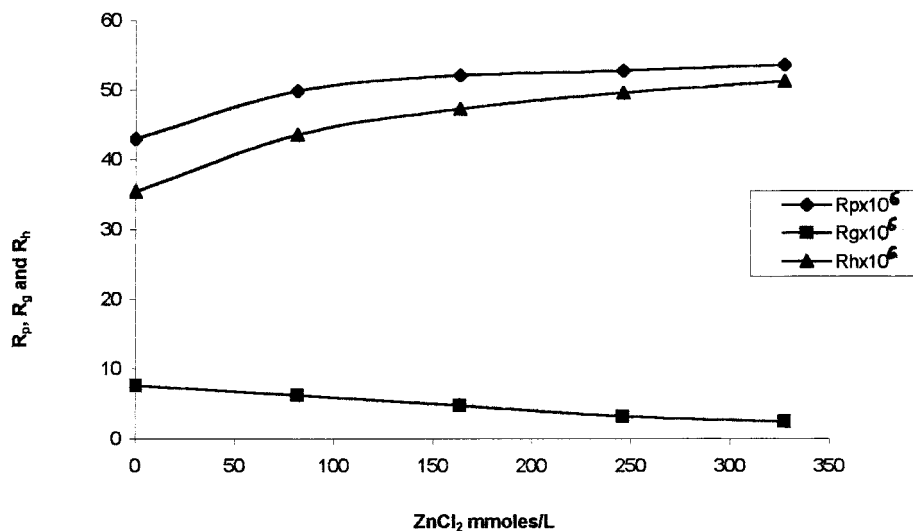
Figure 4 Effect of $ZnCl_2$ on R_p, R_g, and R_h ([Sty] = 656.25 mmol/L, KPS:FAS = 146.3:12.75 mmol/L, water = 20 mL, t = 3 h, T = 60°C).

(%GE; Fig. 3). P_g and %GE showed regular decreases, whereas %C_t increased regularly with increasing $ZnCl_2$ concentration. P_g fell from 28.7 in the absence of $ZnCl_2$ to 23.6, 18.0, 12.1, and 9.2 over the range of [$ZnCl_2$] studied. Similarly, %GE decreased steadily with [$ZnCl_2$] from 17.59 in its absence to 12.49, 9.13, 6.05, and 4.53. High values were observed for R_p and R_h in the presence of $ZnCl_2$. R_p had higher values from 42.98×10^{-6} to 49.78×10^{-6} mol L^{-1} s^{-1} on the addition of 81.8 mmol/L of $ZnCl_2$. It kept increasing but at very slow pace from 51.98×10^{-7} to 53.47×10^{-6} mol L^{-1} s^{-1} on further addition of $ZnCl_2$ (from 163.6 to 327.2 mmol/L). Similar behavior was observed for R_h, where values increased more or less corresponding to the lower and higher values from 35.41×10^{-6} mol L^{-1} s^{-1} in the absence of $ZnCl_2$ to 43.56×10^{-6} to 51.1×10^{-6} mol L^{-1} s^{-1} at the lowest and highest $ZnCl_2$ concentrations, respectively. R_p and R_h remained almost independent at higher $ZnCl_2$ concentrations. The increase in the values of these parameters, although progressive, was not very sharp. These had a tendency to remain almost constant or independent of $ZnCl_2$ at its higher concentrations. On the other hand, R_g decreased regularly to 6.21×10^{-6} to 2.42×10^{-6} mol L^{-1} s^{-1} in the presence of same concentration range of $ZnCl_2$ from 7.56×10^{-6} mol L^{-1} s^{-1} in its absence (Fig. 4).

These trends in the kinetic parameters in presence of $ZnCl_2$ provide evidence of kinetic regularity in the grafting reactions as $ZnCl_2$ formed a complexomer with Sty and AN (Sty$^+$AN$^-$ ...

$ZnCl_2$). This complexomer preferred to homopolymerize to give an alternate copolymer of poly(Sty-co-AN) rather than be grafted onto cellulose. The independence of different rates of reaction with increasing [$ZnCl_2$] was also explained by the fact that apart from complexing with monomers, $ZnCl_2$ also interacted with cellulose. $ZnCl_2$ was reported to affect grafting onto cellulose, especially of polar monomers, by decreasing its crystallinity and making its backbone more accessible for reacting sepcies.[13] It can also form donor–acceptor complexes with the polar monomers and, hence, activate the monomers for grafting. The possible equations for the termination of homopolymer [eqs. (11) and (12)] and grafting reactions [eqs. (13) and (14)] are presented in Scheme 1. It follows from the reaction scheme that the termination of growing chains adversely affects P_g, apart from the termination of the graft chains that is affected by the presence of $ZnCl_2$. The termination of growing macroradicals also influences homopolymer formation, also shown in Scheme 1.[14]

In this study, P_g decreased significantly in the presence of $ZnCl_2$. The fall of graft yield and increase in homopolymer formation with increasing $ZnCl_2$ concentration meant that processes 11 and 12 predominated in the case of these comonomer systems over processes 13 and 14.

Evidence of the Structural Aspects of Graft Chains by the Characterization of Graft Copolymers

The synthesized graft copolymers were characterized by some physical and chemical methods of
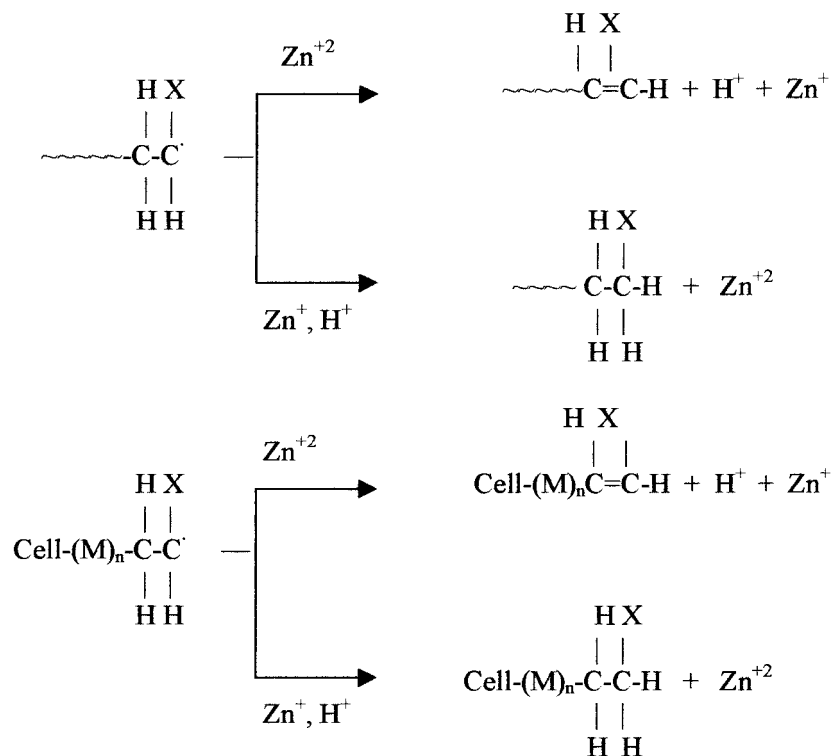
Scheme 1

analysis to investigate the structure of the graft chains. The characterization of these polymers provided evidence for the alternation of monomers in the graft copolymers in the presence of $ZnCl_2$.

Effect of AN Concentration on the Reactivity of Sty and the Structural Aspects of Graft Chains

Elemental analysis of cellulose revealed that the cellulose contained carbon (43.4%), hydrogen (4.16%), nitrogen (1.55%), carbon (57.86%), and hydrogen (6.1%; Table I). The presence of these elements corresponded to the structure of anhydroglucose units of the cellulose molecule. Further, the presence of nitrogen provided evidence that cellulose got ammoniated when pine needles were digested with ammonia. In the case of the graft copolymers [cellulose-g-poly(Sty)], %N was found to be negligible, meaning, thereby, that associated or trapped ammonia in the cellulose matrix got detrapped in the grafting process or

Table I   Elemental Analysis of Cellulose-*g*-poly(Sty-*co*-AN)

Serial Number	Weight of Graft Copolymer (mg)	P_g	% N (Analyzed)	Calculated Weight of N (g)	Calculated Weight of Poly(AN) (g)	Calculated Weight of Poly(Sty) (g)	AN Mole Fraction	Sty Mole Fraction
1	Cellulose	—	1.55	—	—	—	—	—
2	Cellulose-*g*-poly(Sty)	—	0.00	0.00	—	—	—	—
3	1.150	15.0	1.42	0.016	0.061	0.089	0.57	0.43
4[op,a]	1.287	28.7	2.46	0.032	0.122	0.165	0.59	0.41
5[ZnCl2,b]	1.121	12.1	1.00	0.01	0.04	0.08	0.49	0.51
6[ZnCl2,b]	1.236	23.6	1.68	0.031	0.08	0.156	0.50	0.50

[a] Synthesized optimum concentration of Sty and AN.
[b] Polymers synthesized in presence of $ZnCl_2$.
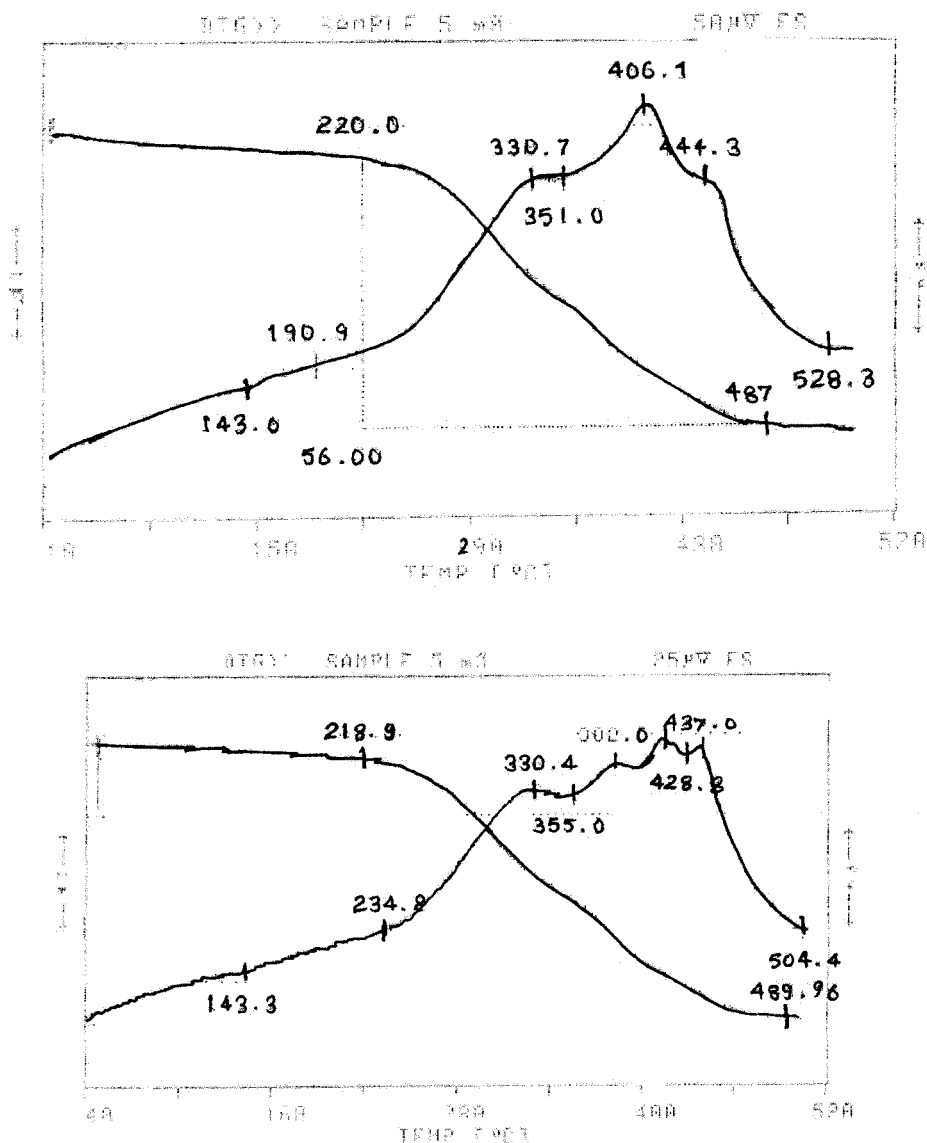[op], optimum grafting condition.

Figure 5 Thermograms of cellulose-*g*-poly(Sty-*alt*-AN).

the ammoniated groups may have as such been knocked off on initiation.

The graft copolymers of cellulose-*g*-poly(Sty-co-AN) were analyzed for the presence of nitrogen at higher and lower graft levels both prepared in the presence and in the absence of $ZnCl_2$. The reactivity ratios of Sty (M_1) and AN (M_2) favored more AN reactivity toward Sty as compared to itself.[12] For kinetic considerations, it was expected that the growing macroradicals from the binary monomer system would have higher amounts of AN as compared to Sty. As shown in Table I, as [AN] increased at constant [Sty], the amount of Sty increased in the graft copolymer along with that of AN, and this trend was observed in all the graft

copolymers studied. Mole fractions of these monomers tended to be constant and independent of [AN] in all the graft copolymers studied, although copolymer add-ons increased with increasing [AN]. Hence, high kinetic regularity or alternation of monomers in the graft chains is proposed for chemically initiated grafting. Elemental analysis could be applied to calculate the reactivity ratios of Sty and AN by applying different methods, and the rearranged copolymer equation $F_1(1 - f_1) = r_2 + [f_1^2(F_1 - 1)/F_1(1 - f_1)^2]r_1$, where f_1 and F_1 are the mole fractions of monomer M_1 in the feed solution and the graft copolymer, respectively. However, it was not attempted in this case because only two samples synthesized by partic-

Table II   Thermogravimetric Data of Cell-*g*-poly(Sty-*co*-AN)

Serial No.	Cellulosic with P_g	Degradation Stages	Weight Loss (%)	Residue (%)	Initial Decomposition Temperature (°C)	Final Decomposition Temperature (°C)	Main DTA Peaks (°C)	
							Exothermic	Endothermic
1	12.10	225.6–498.8	100.0	0.00	225.6	498.8	405.0	143.0
2	23.6	229.4–494.9	100.0	0.00	229.4	494.9	413.5	144.6

ular set of reactions were analyzed for the presence of nitrogen.

Thermogravimetric Analysis of Graft Samples

Thermograms of cellulose-*g*-poly(Sty-*co*-AN) are shown in Figure 5. The details of the degradation processes are given in Table II. Interestingly, the graft copolymers degraded in single step. The T range of the degradation, initial and final decomposition Ts of the graft copolymer, were very close in both of the thermograms. It was also matched by similarities in differential thermal analysis (DTA) peaks. Such close similarity in thermal behavior at different P_g's reflects on the regularity and identical structure of grafted chains.

FTIR Analysis of Graft Copolymers

FTIR spectra of cellulose-*g*-poly(Sty-co-AN) with an optimum P_g of 28.7 were recorded. Apart from the usual absorbance peaks of cellulose, main peaks at 2266 cm^{-1}, corresponding to AN (absorbance = 0.499), and at 1612 cm^{-1}, corresponding to C=C of Sty (absorbance = 0.5) were observed. The ratio of absorbance, thus, came to unity as expected for alternate copolymer chains of Sty and AN.

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