Graft Copolymerization of 2-Acrylamido-2-methyl Propane Sulfonic Acid on Dimethyl Sulfoxide Pretreated Poly(Ethylene Terephthalate) Films Using Cerium Ammonium Nitrate as Initiator

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ABSTRACT

In this study, graft polymerization of 2-acrylamido-2-methyl propane sulfonic acid (AMPS) on poly(ethylene terephthalate) (PET) films using cerium ammonium nitrate (CeAN) as an initiator was investigated. Before the polymerization reaction was carried out, films were swelled in dimethyl sulfoxide (DMSO) at 140°C for 1 h. The effect of polymerization temperature, time, initiator, and monomer concentrations on the graft yield were investigated. It was observed that the graft yield was initially increased with increasing temperature, monomer, and initiator concentrations; and then decreased. Graft yield was found to increase with increasing polymerization time up to 5 h, then remain constant. The effects of monomer and initiator inclusions on the grafting yield were also examined. Optimum conditions for grafting were found to be $[AMPS] = 1.0$ M, $[Ce^{4+}] = 1.5 \times 10^{-2}$ M, $T = 85°C$ and $t = 5$ h. The rate of grafting was found to be proportional to the 0.1 and 0.4 powers of monomer and initiator concentrations, respectively. The overall activation energy for the grafting was calculated to be 11.4 kcal mol^{-1}. The effect of grafting on PET film properties such as intrinsic viscosity and water absorption capacity were determined. The grafted PET films were characterized with FTIR spectroscopy and scanning electron microscopy (SEM).

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Key Words: Graft copolymerization; Poly(etheylene terephthalate) film; 2-Acrylamido-2-methyl propane sulfonic acid; Swelling assisted polymerization.

INTRODUCTION

Poly(ethylene terephthalate), (PET) is the most widely used synthetic polymer in industry for fiber, film, and plastics. It forms excellent films, however, a few disadvantages exist with respect to surface properties mostly originating from its low water wettability, poor adhesion, and high static electrification. One way to improve the poor features of PET is graft copolymerization. Introduction of hydrophilic groups by vinyl grafting not only improves the poor features of PET, but broadens their use as membranes (ion exchange, ultrafiltration, pervaporization) in separation technology.

There are numerous reports concerned with the grafting of vinyl monomers onto PET films either by radiation,[1–8] or by chemical means.[9–13] The chemical initiation method has been found best fitting for this purpose due to the low degradation of the parent polymer. 2-Acrylamido-2-methyl propane sulfonic acid (AMPS) is one of the monomers which can be used for this purpose. By grafting of the ionic monomers onto PET, surface charged molecules such as dyestuff surfactants and proteins would be able to interact strongly with the grafted PET surfaces. However, there are only a few studies concerning the use of AMPS for this purpose.

Burr and co-workers[14] grafted mixtures of acrylonitrile and AMPS onto starch using cerium ammonium nitrate (CeAN) initiator and Fanta et al.[15] studied graft copolymerization of AMPS together with acrylamide onto starch by cobalt-60 irradiation and determined the water absorbency and water solubility of the resulting products. Uchida et al.[9] used AMPS as an ionic monomer to graft onto the surface of PET film with simultaneous UV irradiation method and characterized the surface structure of the films and reported that the graft copolymerization took place not merely on the outermost surface but also within the surface region of PET film without any change in the bulk properties.

There is no study concerning the grafting of AMPS onto PET film by chemical means in the literature. In the present study we have investigated the graft copolymerization of AMPS using CeAN as initiator which is a versatile oxidizing agent capable of reacting with almost all types of functional groups and has been extensively used for polymerization of vinyl monomers.[16,17] However, the grafting of vinyl monomers onto PET meets with some difficulties. First, the chemical nature of PET does not allow formation of its macrochains of an appreciable quantity of radicals that initiate the grafting. Second, high extend of the crystallization and ordering of the amorphous regions of the industrial samples retard monomer diffusion.

One way that affects the grafting reactions is the pretreatment of the film, before the reaction is started. These pretreatments have primarily involved swelling solvents, which open up the physical structure of the PET for the diffusion of monomer and initiator into the film. Studies concerning the use of swelling agents have shown that the grafting yield is improved by suitable swelling agents.[1,6,10,12] In our previous studies, we have also examined the effect of various solvents in the copolymerization of acrylamide,[11,18] 4-vinyl pyridine,[13] and *n*-vinyl-2-pyrrolidone[19] and dimethyl sulfoxide (DMSO) was found to be the most suitable swelling agent among the solvents studied and reported that

the pretreatment of the films in DMSO for 1 h at 140°C is the best condition.[11] In this study, we have also used this condition before the graft copolymerization was carried out.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) films (Hoksp) of 50 μm thickness were used for grafting. All reagents were Merck products and used as received.

Graft Polymerization

Poly(ethylene terephthalate) films were cut to dimensions of about 40×60 mm and swelled in DMSO for 1 h at 140°C,[11] blotted between a filter paper, and put into a polymerization tube containing a known concentration of aqueous AMPS solution. The polymerization tube and the contents were brought to a predetermined constant polymerization temperature and nitrogen gas was allowed to pass through the solution for 45 min. After thermal equilibrium was reached, the required amount of aqueous CeAN (prepared in 1 N HNO_3) was added. The polymerization reaction was allowed to proceed for a specified period of time under nitrogen atmosphere. At the end of predetermined polymerization time, grafted films were removed from the polymerization medium. The residual solvent, homopoly(AMPS) and unreacted monomer were removed from the grafted film surface by washing in distilled water at 50°C for 5 h with continuous stirring. The washing water was changed at least five times. The grafted PET films were then vacuum dried at 50°C for 72 h and weighed. The grafting yield (%) was calculated from the weight gain of the films as follows:

$$\text{Grafting yield } (\%) = \left[\frac{w_g - w_i}{w_i} \right] \times 100 \qquad (1)$$

where w_i and w_g denote the weights of the ungrafted and AMPS grafted PET films, respectively.

The rate of grafting (R_g) was determined from Eq. (2).[20]

$$R_g = \frac{(w_g - w_i) \times 100}{M_w + t \times V} \qquad (2)$$

where M_w is the molecular mass of AMPS, t is the polymerization time (s), and V is the volume (mL) of the overall polymerization medium.

Water Absorption Capacity Measurements

Ungrafted and AMPS grafted PET films were immersed in thermostatted distilled water at 20°C ± 0.1°C for 48 h, then removed from the medium, blotted between a filter paper and weighed. This procedure was followed by vacuum drying at 50°C for 96 h

until a constant weight. Water absorption capacity was determined from the weight gain of the films.

Intrinsic Viscosity Measurements

Intrinsic viscosity measurements of PET films were carried out in *m*-cresol using a Ubbelohde capillary flow viscometer mounted in a water bath maintained at $25°C \pm 0.1°C$.

Infrared Spectroscopy

FTIR spectra of PET films were recorded using a Mattson Model 1000 FTIR spectrometer. Samples were analyzed as films cast from phenol/tetrachloroethane (1 : 1, v/v) onto NaCl plates.

Scanning Electron Microscopy

Scanning electron micrographs of PET films were obtained using a JEOL Model JEM-100 CX II microscope. Poly(ethylene terephthalate) samples were coated with gold by a Polaron SC 502 Sputter Coater for examination.

RESULTS AND DISCUSSION

Effect of Polymerization Temperature

The effect of temperature on the graft copolymerization of AMPS on PET films was studied within the range of 50–95°C by keeping monomer and initiator concentrations and polymerization time constant as $0.5\,M$, $2.0 \times 10^{-2}\,M$ and $1\,h$, respectively (Fig. 1). As seen from Fig. 1, the temperature increase from 50°C to 85°C was accompanied with a sharp increase in the grafting yield (6.8%). A further increase in temperature caused a slight decrease in the yield.

The increase in the grafting yield with increasing temperature may be attributed to: (a) increase in the swellability of films with increasing temperature; (b) increase in the mobility of monomer and initiator molecules in the polymerization medium; (c) increase in the diffusion of monomer and initiator to the PET backbone; and (d) increase in the initiation and propagation rates of grafting. On the other hand, since the high temperature also causes an increase on the rates of chain termination reactions, a decrease was observed over 85°C.

Similar results were reported in the benzoylperoxide initiated graft copolymerization of 2-hydroxy ethylmethacrylate,[8] acrylamide,[11] 4-vinylpyridine[13] onto PET films and other vinyl monomers on PET fibers.[21]
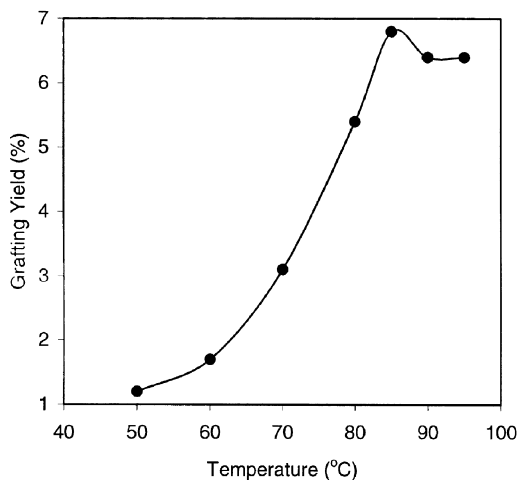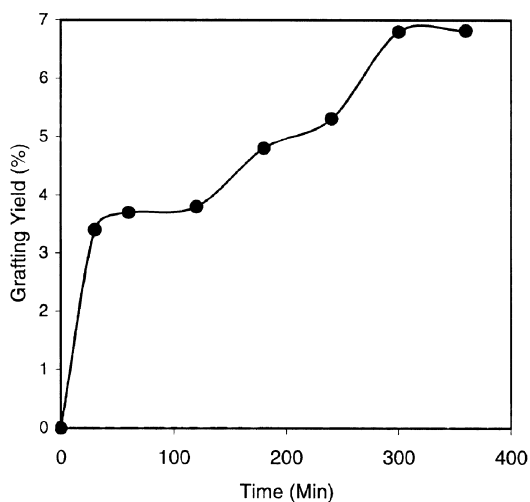
Figure 1. Change of grafting yield with temperature. $[AMPS] = 0.5\,M$, $[Ce^{4+}] = 2 \times 10^{-2}\,M$, $t = 1\,h$.

Effect of Time on Grafting Yield

The effect of polymerization time on grafting yield is presented in Fig. 2. The saturation grafting value of 6.5% was reached after 5 h of polymerization time for concentrations of $[AMPS] = 0.5\,M$, $[Ce^{4+}] = 2.0 \times 10^{-2}\,M$ at 85°C.

The leveling off after 5 h is probably due to the saturation of active PET backbone by homopoly(AMPS) which forms a diffusion barrier. Similar results were reported for the

Figure 2. Effect of time on grafting yield. $[AMPS] = 0.5\,M$, $[Ce^{4+}] = 2 \times 10^{-2}\,M$, $T = 85°C$.

graft copolymerization of 2-hydroxy ethylmethacrylate[8] on PET films and methylmetha-crylate[22] and acrylamide[23] on PET fibers.

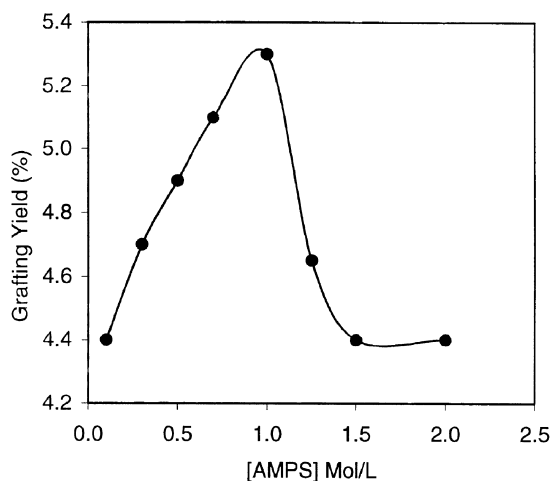### Effect of Monomer Concentration on Grafting Yield

The variation of the grafting yield with the concentration of AMPS was investigated by changing the monomer concentration from 0.1 to 2.0 M, keeping the initiator concentration, temperature, and time constant as $[Ce^{4+}] = 2.0 \times 10^{-2}$ M, $T = 85°C$, and $t = 5$ h respectively (Fig. 3).

As seen from the graph, as the AMPS concentration was increased from 0.1 to 1.0 M, the grafting yield was also increased and reached a maximum of 5.3%. This may be attributed to the increased diffusion rate of monomer molecules into PET backbone, which leads to a higher grafting yield. A further increase in AMPS concentration beyond 1.0 M caused a decrease on the grafting yield. This could be associated with the excess adsorption of AMPS and homopoly(AMPS) on PET surface, which will hinder the diffusion of initiator molecules. Such behaviors were also obtained in other studies in the literature.[12,23,24]

Effect of Initiator Concentration

The effect of CeAN concentration on the percent grafting is shown in Fig. 4. The increase in the concentration of initiator up to 1.5×10^{-2} M results in an increase on the grafting percentage and a further increase in CeAN concentration decreased the percent grafting.

Since the Ce^{4+} ions have high oxidation potential and PET chains have no functional groups to be oxidized; active sites on PET backbone can only be created by the interaction

Figure 3. The variation of grafting yield with monomer concentration. $[Ce^{4+}] = 2 \times 10^{-2}$ M, $T = 85°C$, $t = 5$ h.
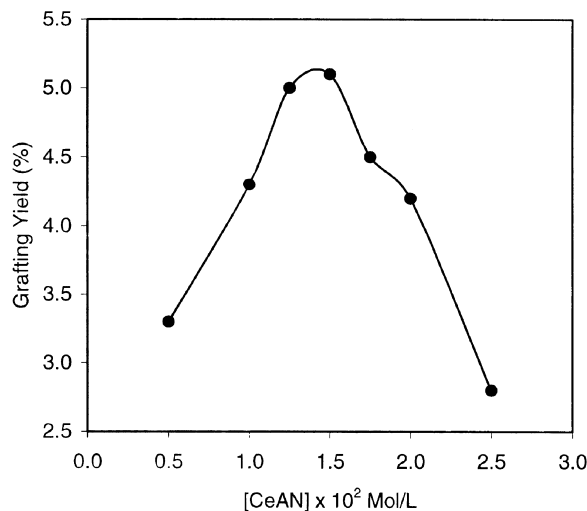
Figure 4. The effect of initiator concentration on grafting yield. $[AMPS] = 1.0\,M$, $T = 85°C$, $t = 5\,h$.

of Ce^{4+} ions by PET matrix. As $[Ce^{4+}]$ increases, the number of active sites on PET backbone and number of active AMPS radicals increases, which result in an increased grafting yield. A further increase in $[Ce^{4+}]$ will enhance the grafting reactions as well as homopolymerization and termination reactions. These terminated graft copolymer and homopoly(AMPS) chains will hinder the diffusion of Ce^{4+} and AMPS molecules onto PET matrix and cause a decrease on the grafting yield value. This behavior was reported by numerous other researchers.[8,11,13,25–28]

Effects of Monomer and Initiator Diffusions

Pretreated PET films were dipped into a $1.0\,M$ AMPS and $1.5 \times 10^{-2}\,M$ Ce^{4+} solutions for 1–4 days at $20°C$ before graft polymerization reactions were carried out. It was observed that, monomer, and initiator inclusions of PET films caused no further increase on the grafting yield. This may be attributed to the opening up of the PET film structure by preswelling in DMSO, which causes rapid diffusion of AMPS and Ce^{4+} to the PET backbone. These results are not consistent with the previous studies on the graft copolymerization of vinyl monomers onto PET film.[8,18,19]
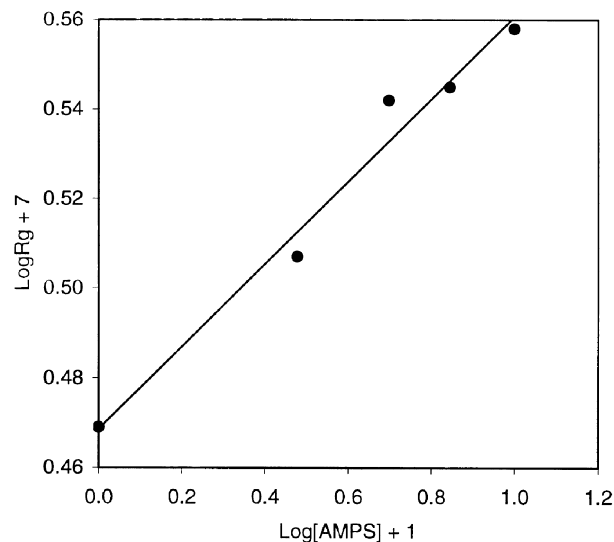
Kinetics of Grafting

The relation between the rate of grafting (R_g) and [AMPS] and $[Ce^{4+}]$ can be written as:

$$R_g = k[AMPS]^m[Ce^{4+}]^n \tag{3}$$

where m and n can be experimentally determined.

Figure 5. The change of rate of grafting with monomer concentration. $[Ce^{4+}] = 1.5 \times 10^{-2}$ M, $T = 85°C$, $t = 5$ h.

The change in initial rate of grafting with AMPS concentration was determined changing [AMPS] between 0.1–1.0 M, by keeping other variables constant (Fig. 5). The slope of $\log R_g$ vs. log[AMPS] graph reflects that the rate of grafting is proportional to 0.1 power of [AMPS].

The rate of grafting was determined for different CeAN concentrations ranging 0.5×10^{-2}–1.25×10^{-2} M, and the plot of $\log R_g$ vs. log[CeAN] (Fig. 6) were found to be a straight line with a slope of 0.4, indicating 0.4 power dependence of [CeAN] on R_g.

From these results, it was concluded that the grafting rate of AMPS and PET films using Ce^{4+} as the initiator can be written as:

$$R_g = k[AMPS]^{0.1}[Ce^{4+}]^{0.4} \tag{4}$$

The overall activation energy for grafting was determined to be 11.4 kcal mol^{-1} from the Arrhenius plot of $\log R_g$ vs. $1/T$ (Fig. 7).

There are no kinetic data concerned with the grafting of AMPS using Ce^{4+} ions in the literature. There are reports on the grafting of various vinyl monomers onto PET films and fibers, using different initiators that, the dependence of the rate of grafting on monomer and initiator concentrations varies with the types of monomers and initiators used for grafting.[8,19,23,29,30–34]
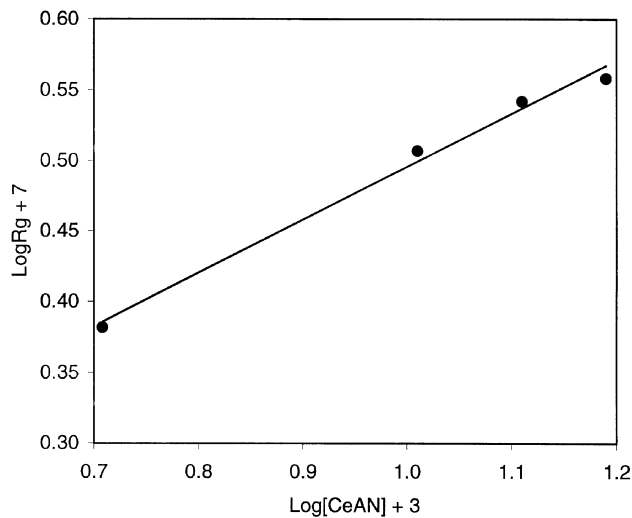
Figure 6. The change of rate of grafting with initiator concentration. $[AMPS] = 1.0\,M$, $T = 85°C$, $t = 5\,h$.

Intrinsic Viscosity Measurements

Limit viscosity numbers, $[\eta]$, of ungrafted and AMPS grafted PET films are shown in Table 1. As seen from the table, $[\eta]$ were increased with an increasing grafting yield,
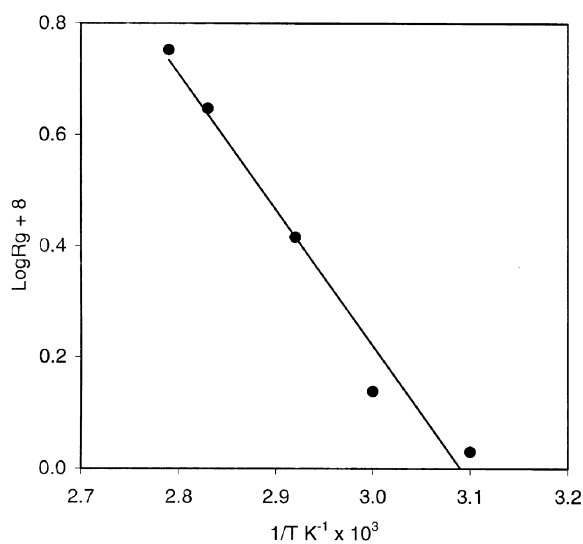
Figure 7. Effect of temperature on the rate of grafting. $[AMPS] = 1.0\,M$, $[Ce^{4+}] = 1.5 \times 10^{-2}\,M$, $T = 85°C$, $t = 5\,h$.

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Table 1. Intrinsic viscosities of AMPS grafted PET films.

Grafting yield (%)	$[\eta]$ dL g^{-1}
0.0	0.23
2.5	0.24
4.4	0.36
6.4	0.37

showing evidence of grafting. Similar results were reported for the grafting of various vinyl monomers onto PET films and fibers in the literature.[18,23,35]

Water Absorption Characteristics

Water absorption capacity results of ungrafted and AMPS grafted PET films are given in Table 2. As reflected from the table, water absorption capacity of grafted films were increased with increasing grafting yield, and reached a 28% water absorption capacity at 6.4% grafting yield. Water absorption capacity of PET film is directly related to the number of hydrophilic groups introduced into the PET matrix by grafting AMPS, which has a hydrophilic nature. Furthermore, the opening up of the PET backbone by the grafting process also causes an increase in the water uptake of the films. Similar results are reported in the literature.[18,19]

FTIR Spectrum

The FTIR spectrum of AMPS grafted PET film was presented in Fig. 8. Besides the well known, expected distinctive absorptions of PET,[8] AMPS grafted PET film contained additional peaks at 1720 cm^{-1} (—C=O amide I band stretchings), at 1640 cm^{-1} (amide II band stretchings) and at 3470 cm^{-1} (—N—H stretchings). This was taken to be additional proof of grafting.

Table 2. Water absorption capacities of AMPS grafted PET films.

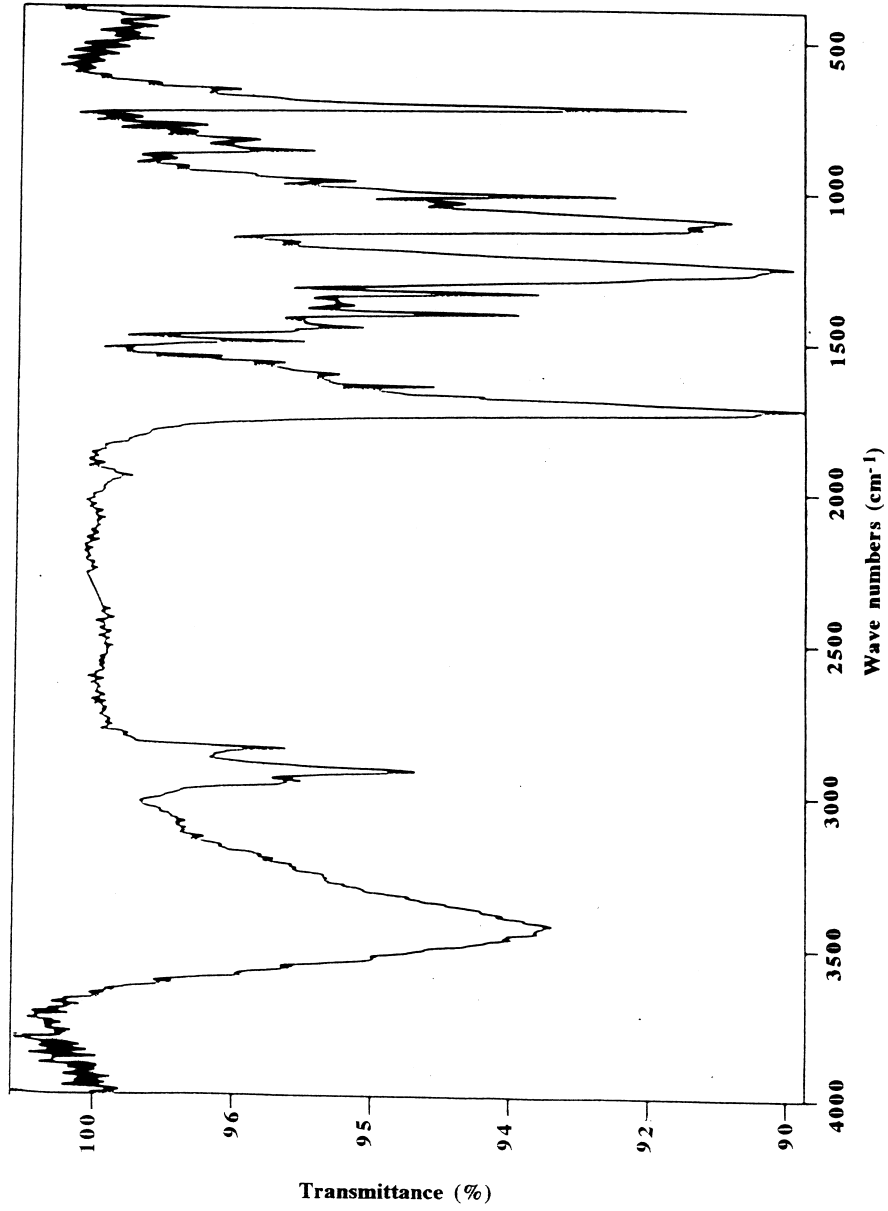| Grafting yield (%)	Water absorption capacity (%)
0.0	0.6
1.2	12
1.7	14
2.8	18
3.7	19
4.8	21
6.4	28

Figure 8. FTIR spectrum of AMPS grafted PET film.
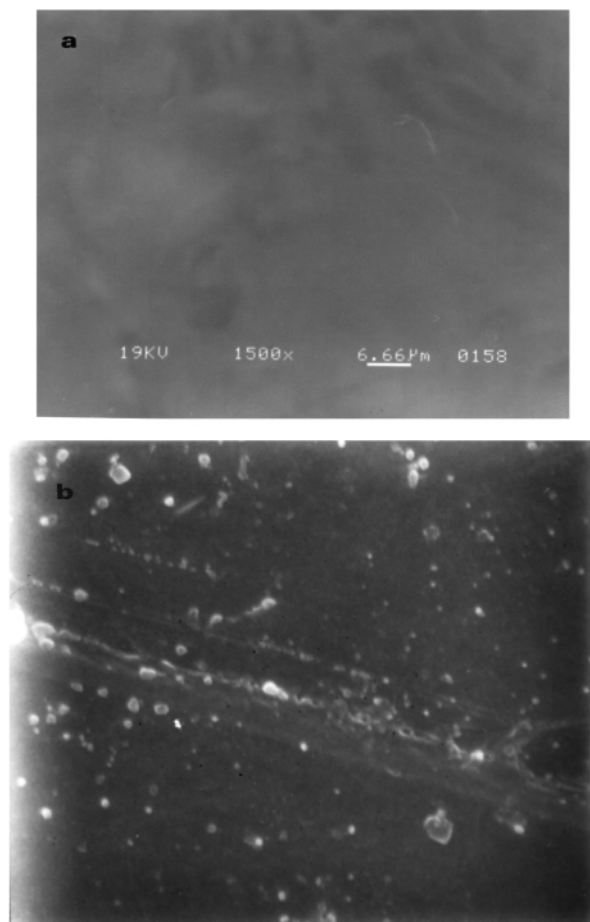
Figure 9. Scanning electron micrographs obtained from (a) ungrafted (1500×), and (b) AMPS grafted (1000×) PET films.

Microstructure of Grafted PET Films

Scanning electron micrographs of ungrafted and AMPS grafted PET films were shown in Fig. 9. It was observed from the scanning electron microscopy (SEM) results that the ungrafted PET film surface [Fig. 9(a)] has a smoother and more homogeneous surface. After the graft copolymerization procedure, AMPS units were attached to the PET backbone as side chains, and seem to form microphases in the graft copolymer [Fig. 9(b)]. This heterogeneous appearance of PET surface shows additional evidence of grafting.

CONCLUSION

The present work relates to the graft polymerization of AMPS onto DMSO pretreated PET films using CeAN initiator. The following conclusions were drawn from the experimental results.

The optimum conditions for maximum grafting were found to be 85°C polymerization temperature, 5 h of polymerization time, 1.0 M [AMPS] and 15×10^{-2} M [Ce^{4+}].

The rate of grafting was found to be proportional to the 0.1 and 0.4 powers of monomer and initiator concentrations, respectively, and the overall activation energy for the grafting was determined to be 11.4 kcal mol^{-1}.

The water absorption capacity and the intrinsic viscosity of the films were increased as the grafting yield increased.

ACKNOWLEDGMENT

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