

Semiconductor Photosensitized Grafting: Physicochemical Studies on Acrylamide Grafted CA Films

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SYNOPSIS

Grafting of acrylamide on cellulose acetate films was carried out in visible light using colloidal Fe_2O_3 as the photosensitizer. pH studies show that grafting is maximum at pH 6.0. Fourier transform infrared studies show that grafting occurs through the vinyl group of acrylamide. Grafting changes the tensile strength of the films, which has been probed through acoustic studies. X-ray diffraction studies show the amorphous nature of these films even after grafting. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In recent years the development of synthetic polymers by grafting monomers has attracted wide attention. Photoinitiated modifications of the surface properties of synthetic polymers by grafting vinyl monomers has been reported for the immobilization of ultraviolet (UV) stabilizers onto polymer films,¹ preparation of polymeric catalysts,² and a number of other applications.

Generally, in these reactions, absorption of photons leads to the formation of macroradicals on the polymer backbone onto which grafting of vinyl monomers takes place.³ When UV or visible light fails to rupture the bonds in the polymer backbone, the process may be promoted by using certain photosensitizers, e.g., benzophenone,^{4,5} *N,N*-diethyl dithiocarbamate,^{6,7} and others. Menon and Kapur⁸ used the water-soluble photosensitizer ferric chloride for grafting monomers onto natural rubber latex. Carbonyl methyl metal salts⁹ were also used as initiators of graft copolymerization. It has been shown that colloidal Fe_2O_3 can also photosensitize this grafting reaction utilizing visible light.¹⁰ When a polymer is grafted, side chains are added to the backbone. Such side chains may be located at the

surface or may be deeply penetrating. Monomer does not usually penetrate into the ordered crystalline region of the backbone polymer but enters the disordered amorphous regions due to irregularity of structure.¹¹ As a result, that portion of the total mechanical properties of the polymer which is controlled by the ordered zones will be little affected by grafting. But the addition of side chains in the amorphous region will impart its own characteristics to the grafted polymer. If the penetration of the side chains is deeper, major changes in the properties of the grafted polymer may develop. An attempt has therefore been made to investigate the chemical and mechanical aspects of acrylamide (AM)-grafted cellulose acetate films sensitized by colloidal Fe_2O_3 particles in visible light.

EXPERIMENTAL

Cellulose acetate (BDH, acetic acid content 53.5–54.5%) was purified by dissolving in acetone and adding methanol until precipitation was complete. Cellulose acetate films, (~ 0.10 mm thick) were prepared by slow evaporation from acetone solution on a mercury surface, washed thoroughly by Soxhlet technique using double-distilled water as extracting solvent, and dried under vacuum at 45°C. Acrylamide (BDH) was recrystallized three times from

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acetone and dried under vacuum before use. All solvents used were of Analar grade.

Colloidal Fe₂O₃ was prepared (particle size > 60 nm < 120 nm) by hydrolysis of FeCl₃ solution in a water bath for 7 days.¹² Methyl viologen (MV²⁺, Fluka, Switzerland) was used as received. pH of the solution was adjusted by dilute hydrochloric acid and dilute sodium hydroxide solutions. Acrylamide was grafted into the cellulose acetate films using visible light (>380 nm) from a 450-W Xenon lamp (ORIEL Corp., Stratford, CT)⁶ in the presence of colloidal Fe₂O₃ as photosensitizer at different pH values. The irradiated film was washed thoroughly by refluxing in a Soxhlet with double-distilled water to remove the polyacrylamide gel adhering to the film surface, and then vacuum-dried. The washing process was repeated until a constant weight of the grafted film was obtained.

The degree of grafting was measured as:

Degree of grafting (%)

$$= \frac{\text{wt of grafted film} - \text{wt of original film}}{\text{wt of original film}} \times 100$$

ANALYSIS

Elemental analysis was done by a 240C Element Analyzer. (Perkin-Elmer, Norwalk, CT). Small pieces from various regions of the grafted films were taken, weighed, and analyzed by the internal combustion method to measure the amount of nitrogen in the grafted films.

Fourier transform infrared (FTIR) spectra of the ungrafted and acrylamide grafted cellulose acetate films were taken using a Nicolet 710 FTIR spectrometer.

X-ray diffraction studies were performed on the cellulose acetate film, the grafted cellulose acetate films, and acrylamide powder using a Philips X-ray diffractometer to study the crystallinity and amorphousness of these samples. The scanning was performed from 4°C to 60°C, in steps of 0.02°, by Cu-K_α radiation.

ACOUSTIC STUDY

In this experiment, modulation of the constant input acoustic pulse by the films was studied by varying the grafting percentage, e.g., 10.60, 11.52, and 21.3%. The experiment was repeated 10 times with each of

the samples to obtain reproducible results. The thickness of the films used for acoustic study before and after grafting was almost same (thickness, ~ 0.10 ± 0.02 mm).

Two broad-band acoustic probes with central frequency of 10 MHz and crystal diameter of 12.5 mm were used. One probe was used as a transmitter of a short duration, normal longitudinal acoustic pulse, and the other probe was kept in tandem to receive this wave form after it is modulated by passing through the cellulose acetate films placed between them. The schematic diagram of the experimental setup is shown in Figure 1. High-vacuum silicone grease was used as couplant. Five hundred and twelve data points for each acoustic signal received were taken at a sampling rate of 10 ns. These data points were initially loaded in the digital memory of the oscilloscope and subsequently stored on the hard disk of a PC connected to the oscilloscope through an RS 232C interface. Fast Fourier transformation (FFT) was carried out on the time domain acoustic signals.

RESULTS AND DISCUSSION

When photons of band gap energy fall upon a semiconductor, an e⁻-h⁺ pair is produced.

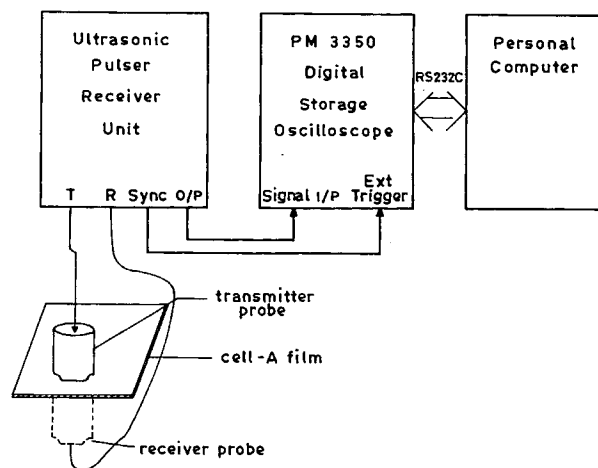


Figure 1 Experimental setup for the acoustic studies.

Table I Variation of [AM] Grafted with Degree of Grafting

Degree of Grafting (%)	Nitrogen Amount (%)	[AM] Grafted [(mol/g) × 10 ⁴]
0	0	0
10.60	2.13	8.38
11.52	2.33	9.32
21.30	4.01	17.39
30.33	5.25	24.50



where M = AM.

The h^+ abstracts a hydrogen atom from the base polymer cell-H and creates an active site onto which monomer AM is grafted. MV^{2+} takes up the conduction band e^- to prevent e^-h^+ recombination.

Table I shows the concentration of AM taken up by cellulose acetate films for various grafting percentages determined from the observed nitrogen

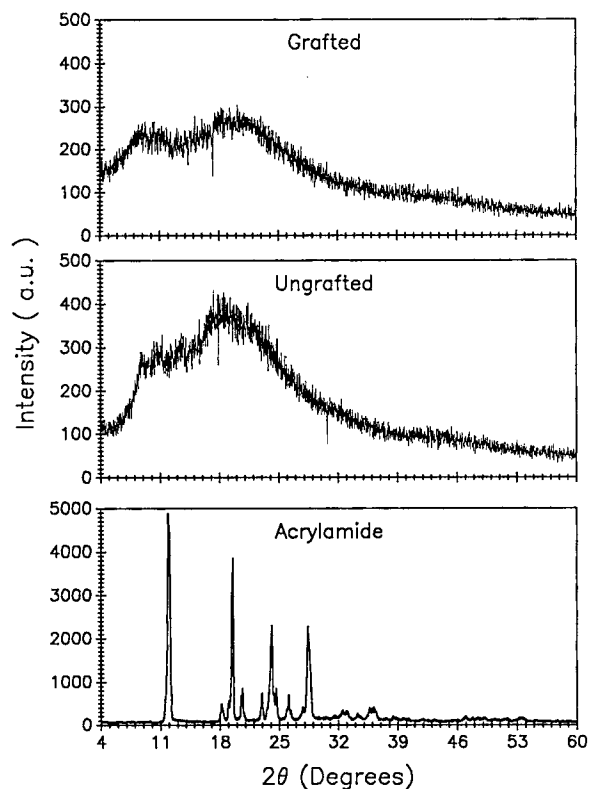


Figure 2 X-ray diffraction spectra of the ungrafted, grafted (10.6%) cellulose acetate films and acrylamide powder.

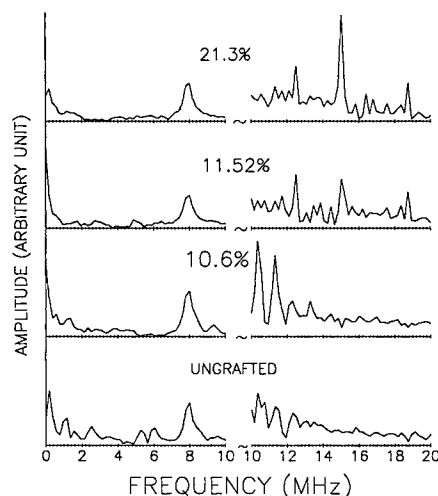


Figure 3 Frequency spectra of the modulated acoustic pulse for the ungrafted and grafted cellulose acetate films between 10 and 20 MHz.

contents in the grafted films. Because the AM molecule contains only one nitrogen atom, the amount of nitrogen is directly proportional to the amount of AM present in the grafted films. The elemental analysis was performed by taking samples from various regions of the grafted films. The result, shown in Table I, is the average value of 5 such estimations for each film. The values are almost identical in each estimation of a particular grafted film. As the amount of nitrogen present in each grafted film is proportional to the degree of grafting, the concentration of AM is also proportional to the grafting percentage. This shows clearly that grafting is homogeneous and uniform throughout the cellulose acetate film, and that AM is grafted and no polyacrylamide is occluded on the film surface, because in the case of the latter, nitrogen content in the grafted films would have been random.

It has been observed by Bhattacharyya and Maldas¹³ that since cellulose acetate and acrylamide are both polar molecules, acrylamide will have easy access to the interior of the trunk polymer due to the formation of hydrogen bonds. Thus, acrylamide grafting will change the mechanical properties of the virgin cellulose acetate film. Bhattacharyya and Maldas have also shown that the tensile strength of cellulose acetate films increases from 73.00 to 82.05 kg cm⁻² when the grafting percentage increases from 3.06 to 15.15 in the case of AM grafting. Giri, Sahoo, and Samal have shown that in the case of AM-grafted wool fiber, tensile strength of the sample increases with increased grafting percentage.¹⁴

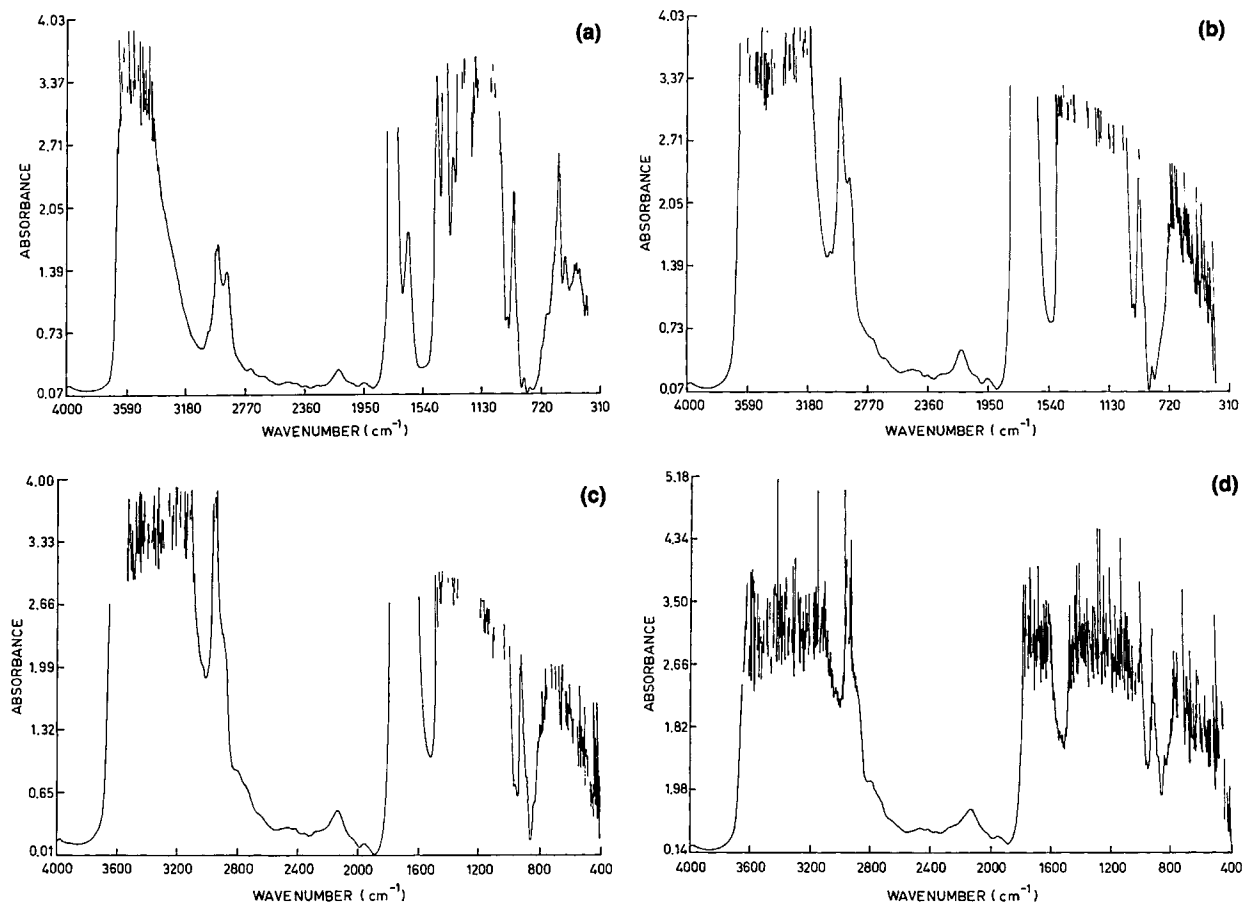


Figure 4 FTIR spectra of cellulose acetate films. (a) Ungrafted; and grafted; (b) 10.6%; (c) 21.3%; (d) 30.33%.

Figure 2 shows X-ray diffraction spectra of ungrafted, grafted (10.60%) cellulose acetate films and of AM powder. From the figure, it is evident that cellulose acetate is amorphous in nature and remains amorphous even after grafting, but AM powder is crystalline. Thus, in spite of the monomer AM being crystalline in nature, the polyacrylamide grafted chains are not. The crystallinity of AM is probably lost due to grafting. Because of the retention of this amorphousness, we presume that it was easy for AM to penetrate the trunk polymer and change its mechanical properties.

Figure 3 shows the variation of the modulated acoustic pulse in the frequency domain with the variation in the degree of grafting of the films up to 21.3%. Above this degree of grafting the film becomes brittle and uneven, hence the probes cannot be properly placed on it. The measurement of the acoustic wave velocity and attenuation was not attempted in these films because of their extremely low thickness. Hence we thought that it would be

interesting to investigate the variation of the modulated characteristics for the constant input acoustic pulse with the variation of film properties, by maintaining an almost-constant thickness of the films. The modulation properties of these acoustic pulses were found to enhance only in the frequency domain. FFTs of the time domain signals were performed for this purpose.

We observed that most of the energy of the received modulated acoustic signals was concentrated mainly in the 0–10 MHz range. But the variation of these frequency spectra with grafting in this frequency range was not very noticeable. On the contrary, in the frequency range from 10 to 20 MHz we could observe a systematic change, as shown in Figure 3.

It is reported^{15,16} that the mechanical properties of polymer change due to grafting. Several authors have observed this change by measuring acoustic velocity and attenuation. However, when thickness of the polymer film becomes too low, large errors

generate in these measurements and it becomes quite difficult to observe any change in these measurements with subtle variation of mechanical properties of the polymer. On the contrary, modulation of constant input acoustic pulse by the polymer films shows a promising way to observe indirectly the variation of the polymer's mechanical properties due to grafting. No attempt so far, to our knowledge, has been made to see the variation of the polymer's mechanical properties due to grafting from the modulation characteristics of the constant input acoustic pulse.

Bhattacharyya and Malda¹³ observed that tensile strength of irradiated, ungrafted cellulose acetate film was 72.68 kg/cm² and that there is a slow increase in tensile strength having gradient 0.38 with the variation of grafting percentage up to 33.54. The manifestation of this slow change in the mechanical properties would be very difficult to observe by conventional methods (i.e., by measuring the acoustic velocity and attenuation) because of the very small thickness of the films. However, through modulation measurements, we observed that with increase in degree of grafting, the peak in the frequency domain between 10 and 20 MHz shifts toward higher frequency.

This observation is explained as follows. From the X-ray patterns in Figure 2 it is evident that the polymer retains its amorphousness even after grafting. So the observed change in the acoustic pulse modulation characteristics in the frequency domain due to variation in the percentage of grafting does not necessarily result from the formation of crystallinity in these films due to grafting. On the other hand, when the polymer is grafted, rigidity of the molecular framework increases due to formation of polymer bridges of the polyacrylamide copolymers between the CA molecules, which is evident from the increase in tensile strength. As a result, attenuation for the high-frequency component of the pulse decreases. As the percentage of grafting increases, because of the progressive increase in rigidity, the higher frequency component started attenuating less. Films grafted above 21.3% became brittle because of the higher number of polymer bridges between the long chain molecules in the polymer, giving the molecules no space to slide over each other.

Figure 4 gives the FTIR spectra of ungrafted and grafted cellulose acetate films. Figure 4(a) shows the stretching vibrations of the carboxylate anion (1610–1550 cm⁻¹), and the O—H stretching vibrations of the polymeric association (3400–3200 cm⁻¹), which match well with that of cellophane. Figures 4(b), 4(c), and 4(d) are the FTIR spectra of AM-

grafted cellulose acetate films with grafting degrees of 10.6, 21.3, and 30.33%, respectively. All three of these spectra show N—H stretching vibrations of ~ 3370–3100 cm⁻¹, indicating that the amide group is grafted onto the backbone. Figure 4(d) shows C=O stretching vibrations at ~ 1670–1650 cm⁻¹ and a weak band at ~ 1620 cm⁻¹ due to N—H bending vibrations. From Figures 4(a) to 4(d), a gradual increase in absorption intensity at the band around ~ 2840 cm⁻¹ is observed. This is probably due to the alkane C—H stretching vibration which increases with increasing degrees of grafting. This corroborates the fact that grafting takes place through the vinyl group of AM, thereby destroying the double bond of the vinyl group.

Table II shows the grafting degree of AM at different pH with different initial concentrations. The data shows that at the three concentrations studied, grafting degree is maximum at pH 6.0. This is quite reasonable, because at high pH the hole-trapping efficiency of the colloid increases,¹² decreasing the number of valence band holes which actually initiate photografting. Again, at very low pH the conduction band position of Fe₂O₃ becomes unsuitable for e⁻ transfer to MV²⁺ present in the system, whence e⁻-h⁺ recombination occurs, thereby decreasing the number of holes responsible for initiation of grafting.

CONCLUSION

Grafting of AM onto cellulose acetate films is accomplished by using the semiconducting properties

Table II Variation of Grafting Degree with pH

Concentration of Acrylamide (M)	pH	Grafting Degree (%)
0.5	4.9	9.1
0.5	6.0	10.1
0.5	8.4	7.9
0.5	9.0	7.5
0.5	10.0	5.8
0.5	11.5	3.5
1.0	4.8	13.5
1.0	6.0	19.2
1.0	7.0	12.5
1.0	9.2	11.52
1.0	11.4	10.60
1.5	6.0	30.33
1.5	9.1	21.3
1.5	10.17	10.1

of colloidal Fe₂O₃ as a photosensitizing agent and is maximum at pH 6.0. The proportional increase in AM content in the grafted films with increasing degree of grafting shows that grafting is uniform throughout the films. FTIR studies show that grafting takes place through the vinyl group of AM. X-ray diffraction studies show that grafted polyacrylamide is amorphous, as is the polymer cellulose acetate. The amorphousness of the base polymer helps the monomer to penetrate deep inside the polymer, changing its mechanical properties (such as tensile strength). The effect of this change is correlated with the acoustic attenuation properties studied at higher frequency regions.

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