Radiation-Induced Grafting of *N,N'*-Dimethylaminoethylmethacrylate onto Chitosan Films

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ABSTRACT: Chitosan films were grafted with *N,N'*-dimethylaminoethylmethacrylate using the ^{60}Co gamma irradiation method. The effect of solvent composition, monomer concentration, dose rate, and total dose on grafting was studied. The solvent composition has a marked effect on the degree of grafting. Maximum yield was obtained in the water–methanol (1 : 1) system. The percent grafting increased with monomer concentration and was found to be higher at a lower dose rate for a constant total dose of 0.216 Mrad. The tensile strength, crystallinity, and degree of swelling of grafted films decreased on increasing graft level. However, the graft copolymers showed improved thermal stability. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 869–877, 1997

INTRODUCTION

Chitosan, a polyaminosaccharide, is derived from chitin, which is the exoskeleton of crustaceans, molluscs, fungi, etc. This natural polymer is nontoxic, biodegradable, and biocompatible. These useful characteristics allow its use in the area of biomedical, biotechnological, and industrial applications. Its biomedical uses, such as wound-healing accelerator, artificial kidney membrane, in drug delivery systems, absorbable sutures, and as an antihypocholestermeric agent, are of special interest.[1–3] The structure of chitosan is similar to cellulose except for the hydroxy group at carbon-2, which is replaced by an amino function. These amino functions are easily accessible for modification with a variety of chemical reagents.

Considerable interest has grown in the modification of chitosan through grafting of vinyl monomers. The combination of natural and synthetic polymers by a grafting process yields hybrid materials which could manifest desirable properties. Graft copolymerization of chitosan with acrylonitrile, methylmethacrylate (MMA), and methacrylic acid using azobisisobutyronitrile (AIBN),[4,5] MMA using Fenton's reagent as redox initiator,[6] 2-hydroxyethylmethacrylate (HEMA), and acrylamide using ceric(IV) salt as redox initiator[7,8] and styrene, vinyl acetate, acrylamide, MMA, and HEMA using the gamma irradiation method, have been reported in the literature.[9,10]

This article presents the grafting of chitosan with *N,N'*-dimethylaminoethylmethacrylate (DMAEMA) using the ^{60}Co gamma irradiation technique and the effect of percent grafting on physicochemical properties of modified chitosans.

EXPERIMENTAL

Materials

Chitosan (mol wt 2.5×10^5 and degree of deacetylation 83%) used in this study was prepared[10] from prawn shell chitin. DMAEMA monomer (E. Merck, Germany) was distilled at 70°C/20 mmHg

and stored at 4°C.[11] Methanol (A.R. Grade) was obtained from BDH Chemicals, India, and used without any further purification.

Radiation Source

The irradiation of samples was carried out in a ^{60}Co gamma chamber supplied by Bhabha Atomic Research Centre, Bombay, India.

Preparation of Films

Chitosan films were prepared by dissolving the material in 1% acetic acid solution and subsequently spreading it on a glass plate maintained at room temperature in a dust-free environment for 72 h, followed by immersing in 10% aqueous sodium hydroxide solution. The thickness and area of all chitosan films under study were kept constant.

Grafting Procedure

Graft copolymerization was carried out in standard joint borosil glass tubes of 13×2.8-cm size. All the samples were kept in glass tubes for equilibrium swelling in water–methanol solvent for 20 h before grafting. The monomer was added just before the irradiation of samples. The monomer concentration was kept at 10 vol % in most of the experiments, unless otherwise specified. The system was deoxygenated by slow bubbling of nitrogen gas through the solution for 5 min in an ice bath. The sample tubes were irradiated for a specified time in a gamma radiation chamber. After irradiation, the reaction was stopped by addition of a large volume of methanol to the reaction mixture in the tubes. The homopolymer formed during reaction was removed by soxhlet extraction in methanol for 24 h. All the samples were then dried under vacuum at 50°C until a constant weight was attained. The weight of dry grafted samples was measured and the percentage of grafting was calculated using the following relationship:

$$\% \text{ grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are the weights of original and grafted samples, respectively.

CHARACTERIZATION

Swelling Studies

The swelling studies of original and modified samples were carried out in phosphate buffer solution (pH 7.4, 0.1M) at 37°C as a function of time. The degree of swelling of these samples was calculated using the following equation:

$$\text{Degree of swelling } (Q) = \frac{W_s - W_d}{W_d}$$

Where W_s and W_d are the weights of swollen and dry samples, respectively.

Infrared Spectroscopy

The infrared spectra of grafted chitosan films were recorded on an FTIR spectrophotometer (Nicolet-5DX). The films of uniform thickness were dried over P_2O_5 in vacuum before recording spectra.

Thermal Properties

Thermal properties of original and modified samples were studied by a Du Pont differential scanning calorimeter (DSC-2000) at a heating rate of 10°C min^{-1} from 50 to 400°C. The DSC unit was precalibrated with indium for the entire working range and the base line was obtained using an empty aluminum pan.

Thermogravimetric analysis (Du Pont TGA-980) was performed in the temperature range from 50 to 600°C at a heating rate of 10°C min^{-1} in nitrogen atmosphere (60 cm^3 min^{-1}).

Mechanical Properties

The tensile properties of original and modified samples were measured using an Instron tensile tester (UTM, 1112) under the following conditions. Crosshead speed, 2.5 cm/min; gauge length, 3.0 cm; temperature, 25°C; and relative humidity, 65%. The ultimate tensile strength and percent elongation at break were calculated.

X-Ray Diffraction Studies

The wide angle x-ray diffraction (WAXD) patterns were obtained on a Rigaku diffractometer

using nickel-filtered CuK$_\alpha$ radiation at a scanning speed of 2°/min in the 2θ range from 10 to 35°.

The diffraction patterns were resolved into two parts corresponding to scattering by amorphous (A_a) and crystalline (A_c) phases. The ratio of area corresponding to the crystalline phase (i.e., area under sharp peaks) to the total area [$A_c/(A_c + A_a)$] was taken as the degree of crystallinity. Percent crystallinity was calculated as follows:

$$\% \text{ Relative crystallinity} = \frac{A_c}{(A_c + A_a)} \times 100$$

RESULTS AND DISCUSSION

Chitosan films were found to be transparent and flexible. No change in appearance of films was observed upon storage in the dry state. However, with increasing graft level of DMAEMA, modified films became brittle in the dry state.

Effect of Solvent Composition

In the present system, the role of the water–methanol mixture is not only to provide a homogeneous medium for the DMAEMA monomer, but also to act as swelling agent for chitosan films, so as to make available a greater surface area on the film for grafting.

The effect of solvent composition on the grafting of DMAEMA onto chitosan film is shown in Figure 1. It may be observed that the percent grafting in pure water as well as pure methanol is very low (<7%). The addition of water in methanol (MeOH) had a marked effect on the degree of grafting of DMAEMA onto chitosan. The percent grafting increases with the increase of water content in the water–methanol mixture and maximum grafting for DMAEMA (39%) was observed in a 1 : 1 water–MeOH system. The low level of grafting in pure MeOH may be due to the formation of a homopolymer during graft copolymerization which remains in solution. This increases the viscosity of the solution and subsequently reduces the migration of DMAEMA molecules onto chitosan surface. The addition of water reduces the rate of homopolymerization and retards the viscosity increase of the solution. These results also reveal the importance of water for grafting of DMAEMA onto chitosan. Besides this, it appears that, in the process of grafting, the presence of
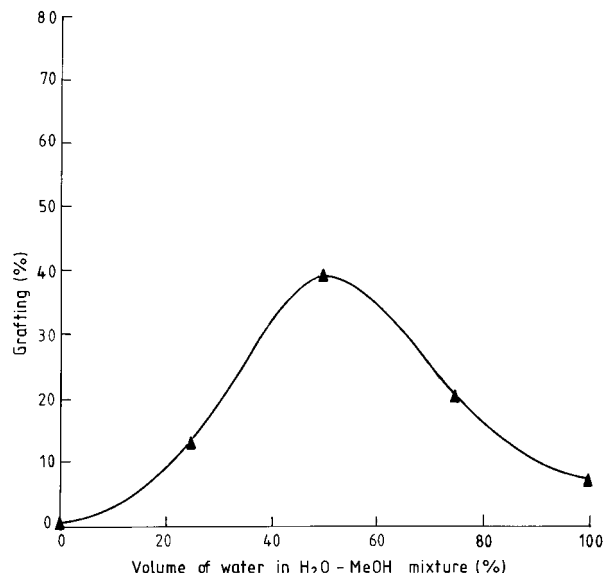

Figure 1 Effect of solvent composition on grafting. Monomer concentration, 10 vol %; dose rate, 90 r s^{-1}; total dose, 0.216 Mrad.

water would also be responsible for the rupture of intermolecular hydrogen bonds in chitosan molecules; as a consequence of which, DMAEMA molecules can diffuse readily to them. Similar behavior was also reported by Shigeno, Kondo, and Takemoto[9] for chitin. The percent grafting decreases on increasing water content beyond 50% in the water–MeOH system. The higher content of water in the solvent mixture appears to act as an inhibitor, which reduces not only the homopolymerization but also grafting level.

Effect of Monomer Concentration

The relation between percent grafting and monomer concentration is shown in Figure 2. Grafting was carried out at room temperature at a dose rate of 90 rad/s (r s^{-1}) for a total dose of 0.216 Mrad in a water–methanol (1 : 1) mixture. The results show that there is an increase in the percent grafting with monomer concentration of the DMAEMA system. These results show a very general trend which has been found in other grafting systems. During the grafting process, monomer continuously diffuses into the polymer matrix. The ability of chitosan macroradicals to capture DMAEMA would depend on the availability of DMAEMA molecules in their vicinity. The increase in monomer concentration will therefore lead to an increase in graft content.
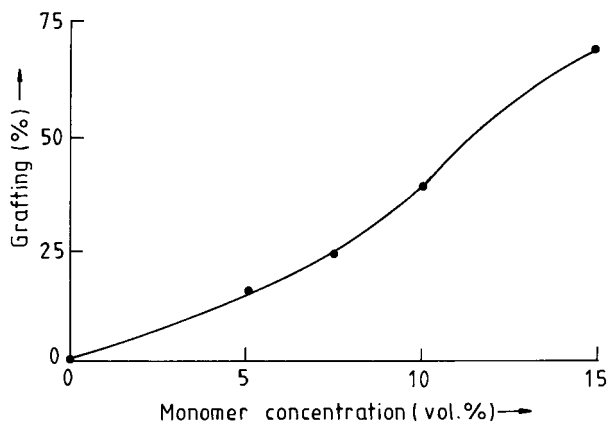
Figure 2 Effect of monomer concentration on grafting. Solvent, $H_2O-MeOH$ (1 : 1); dose rate, 90 r s^{-1}; total dose, 0.216 Mrad.

Effect of Dose Rate and Time

Grafting was studied at different dose rates (22.5, 45.0, and 90.0 r s^{-1}) in a water–methanol (1 : 1) system. The results are depicted in Figure 3. At a constant total dose of 0.216 Mrad, grafting was found to be higher (63%) at lower dose rates (22.5 r s^{-1}) for chitosan samples. This is expected behavior for radiation grafting systems.[12] It has been reported that, during irradiation, a number of free radical species are formed and 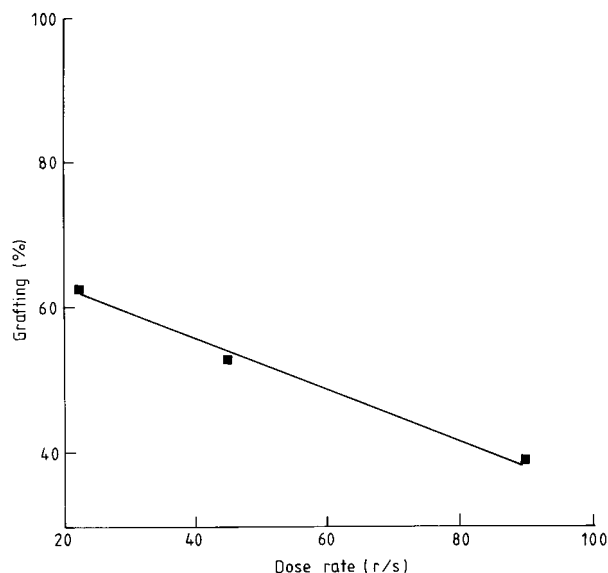their number increases with dose rate.[13] The monomer and radical species may react either with the polymer backbone (grafting) or with each other (homopolymerization).[14] During the graft copolymerization process, monomer molecules will continuously diffuse into the polymer matrix at a constant rate, irrespective of irradiation dose rate. Under such conditions, the greater availability of free radicals at a higher dose rate will increase the rate of homopolymerization. As a result of this, the relative rate of grafting will decrease appreciably at higher dose rate.

The extent of graft copolymerization as a function of time at various dose rates for the DMAEMA system on chitosan samples is presented in Figure 4. All the plots pass through the origin, indicating that the grafting proceeds without any induction period. All the curves in the figure show that the percent grafting increased with the irradiation time and leveled off at a certain graft content for the DMAEMA system.

The results of the rate of grafting (R_g, %/h) at various dose rates for a total dose of 0.216 Mrad for DMAEMA grafting onto chitosan films were calculated from Figure 4. The relationship between rate of grafting (R_g) and dose rate (I) is expressed as:
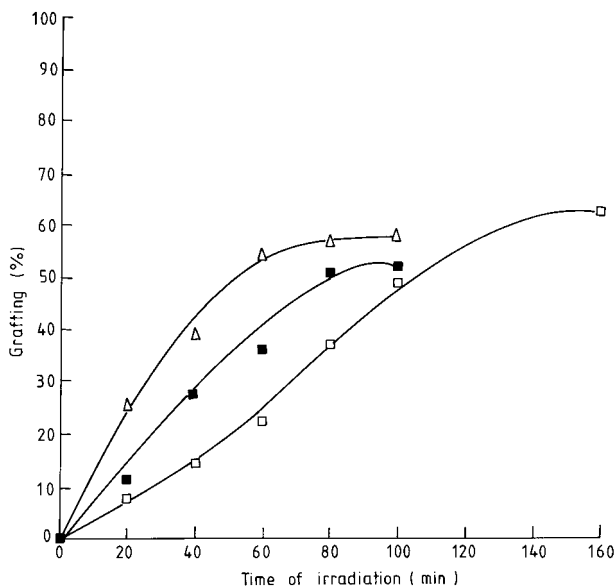
$$\log R_g = \log K + n \log I$$

Figure 3 Effect of dose rate on grafting. Monomer concentration, 10 vol %; solvent, $H_2O-MeOH$ (1 : 1); total dose, 0.216 Mrad.

Figure 4 Effect on time of irradiation on grafting. Monomer concentration, 10 vol %; solvent, $H_2O-MeOH$ (1 : 1); dose rate, (△) 90 r s^{-1}, (■) 45 r s^{-1}, (□) 22.5 r s^{-1}.

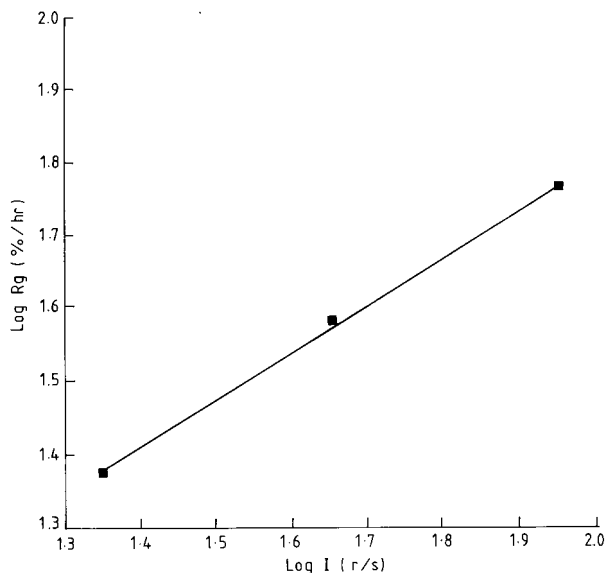**Figure 5** Variation of rate of grafting with dose rate.

Where K is a constant and n is the order of rate of grafting.

The log R_g versus log I plot is presented in Figure 5. The order of dependence (n) of rate of DMAEMA grafting system was found to be 0.66. The dependence of rate of grafting on dose rate has also been found to vary widely, namely between 0.31 and 0.90.[15-17]

Effect of Total Dose

The effect of total dose on grafting is presented in Figure 6. A total dose up to 0.54 Mrad was used at a dose rate of 90 r s^{-1}. The figure exhibits an increase in percent grafting with the increase in dose of irradiation up to 0.324 Mrad; beyond this there is marked decrease in the rate of grafting and tendency to level off. During the graft copolymerization reaction, the availability of monomer is higher in the initial stages and hence, the monomer can diffuse very easily to the grafting sites and grafts readily onto chitosan film. The rate of homopolymer formation does not have much effect on grafting kinetics. Both homopolymerization and copolymerization reactions proceed simultaneously up to a total dose of 0.324 Mrad. Beyond this limit a decrease in the percent grafting results in the increase of the rate of homopolymerization as compared to the rate of grafting. The increasing content of grafted poly(DMAEMA) may act as a barrier against the diffusion of monomer into the polymer matrix, resulting in an in-

crease in the rate of homopolymerization and decrease in the graft content.

Mechanism of Grafting

Grafting and homopolymerization of DMAEMA may be initiated by different free radicals. Chitosan molecule contains two reactive groups at C-2 and C-6 positions, which are expected to play important roles of active sites. Chitosan radicals react with DMAEMA to initiate graft copolymerization. DMAEMA free radicals react with other DMAEMA molecules, resulting in the formation of homopolymer. The graft copolymerization propagated by continuous transfer of DMAEMA monomer to the vicinity of macroradicals of chitosan. However, the transfer of DMAEMA monomer is dependent on various factors, e.g., availability of monomer, diffusion of monomer, solvent, homopolymer formation, etc. Effects of solvent, radiation dose rate, and total dose/time on either one or more of these factors indirectly affects the rate of grafting and homopolymerization.

Swelling Studies

The rate of swelling of original and modified samples is presented in Figure 7. The original and irradiated samples reaches an equilibrium state within 3 h. However, the degree of swelling of
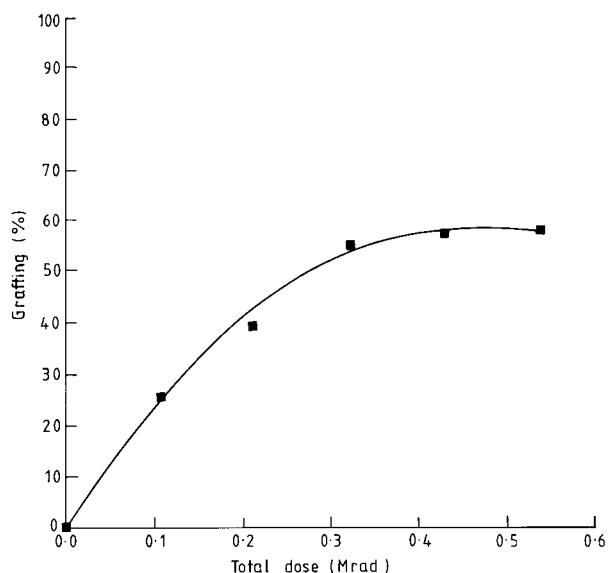

Figure 6 Effect of total dose on grafting. Monomer concentration, 10 vol %; solvent, H$_2$O−MeOH (1 : 1); dose rate, 90 r s^{-1}.
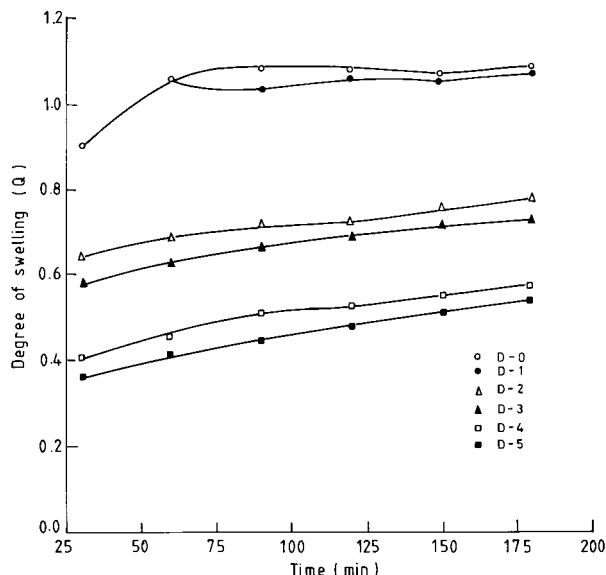
Figure 7 Swelling kinetics of DMAEMA-grafted chitosan.

grafted samples decreases from 0.78 to 0.54 as a function of DMAEMA graft level from 12 to 54%. The crosslinking of DMAEMA molecules in the polymer network may be responsible for the decrease in swelling of grafted samples. The hydrophilic nature of chitosan is due to the presence of free amino groups at the C-2 carbon atom. During the grafting process, a substantial number of free
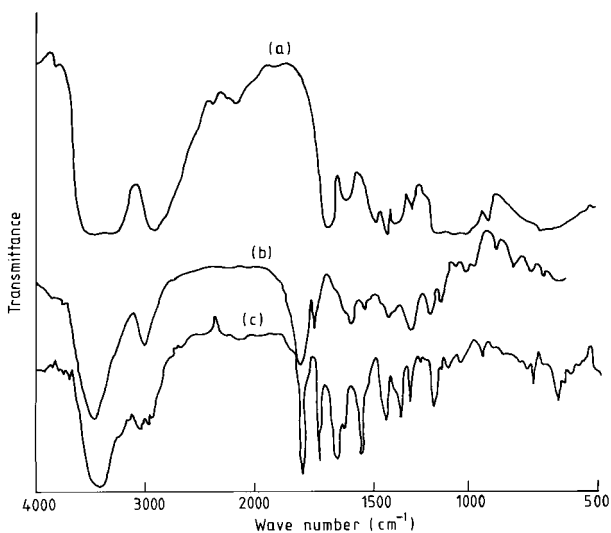

Figure 8 FTIR spectra of (a) chitosan, (b) Poly-(DMAEMA), and (c) DMAEMA-*g*-chitosan (graft level 16%).

amino groups are blocked by the growing chains of poly(DMAEMA). These changes are also responsible for the decrease in the degree of swelling of grafted chitosan.

Infrared Spectroscopy

The FTIR spectra of chitosan and DMAEMA grafted chitosan are presented in Figure 8. The most significant peaks appearing at 1665, 1590, and 1313 cm^{-1} in the chitosan spectra may be assigned to $C=O$ stretching, $C-N$ bond, and CH_2 wagging, respectively. Chitosan does not show any significant change in spectrum upon ir-
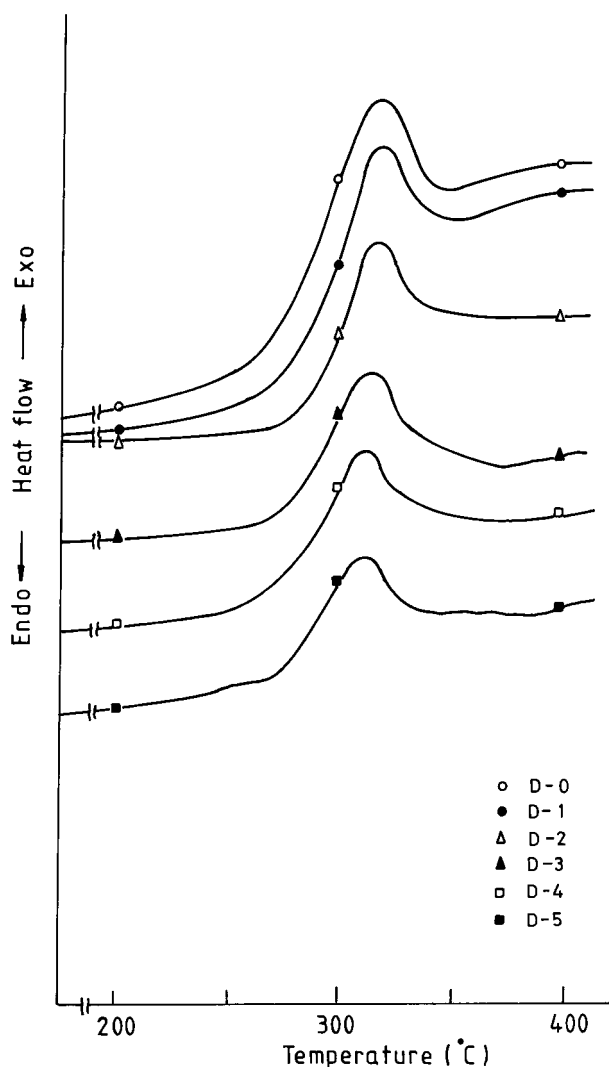

Figure 9 DSC thermograms of DMAEMA-grafted chitosan.

Table I Thermal Properties of Original and DMAEMA-Grafted Chitosan

Sample	Grafting of DMAEMA (%)	Decomposition Temperature (°C)	Enthalpy Change (J g⁻¹)	IDT (°C)	FDT (°C)
D-0[a]	—	273.5	141.8	270.7	329.4
D-1[b]	—	273.6	141.7	270.7	329.4
D-2	12	271.2	120.5	272.9	429.4
D-3	25	270.1	106.2	273.3	431.5
D-4	41	268.4	97.6	275.2	447.8
D-5	54	266.8	78.8	280.4	467.5

[a] Original.
[b] Irradiated.

radiation up to a total dose of 0.54 Mrad. A peak at 1730 cm⁻¹ in the grafted sample may be due to the carbonyl function of poly(DMAEMA). There is a shift in peak (3200 cm⁻¹) toward a higher wave number. This may be due to substitution of DMAEMA molecules onto amino groups of chitosan.

Thermal Properties

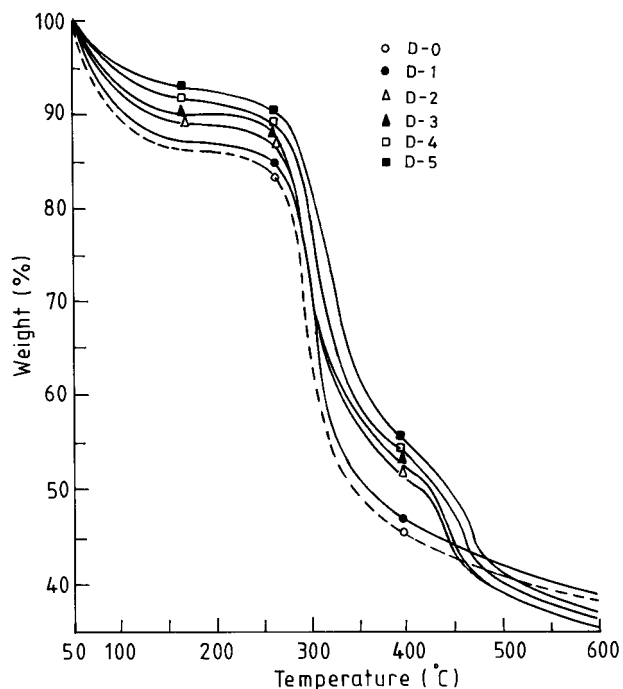DSC thermograms of original and DMAEMA-grafted chitosan are shown in Figure 9 and the

values of decomposition temperature and enthalpy change are summarized in Table I. No significant change is observed in the decomposition temperature upon grafting with DMAEMA, whereas enthalpy of grafted samples decreases from 120.5 to 78.8 J g⁻¹ when the graft level of DMAEMA increases from 12 to 54%. This may be due to two-step decomposition of the grafted sample. The formation of a crosslinked network structure in DMAEMA-grafted chitosan would contribute to the above-mentioned fact.

Thermograms of unmodified and DMAEMA-grafted chitosan samples are presented in Figure 10. The values of initial decomposition temperature (IDT) and final decomposition temperature (FDT) are listed in Table I. An increasing trend is observed in IDT and FDT with the level of DMAEMA grafting onto chitosan. This increase
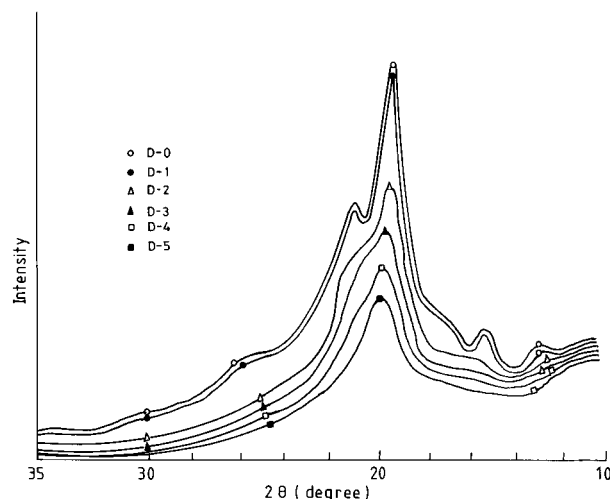

Figure 10 TGA thermograms of DMAEMA-grafted chitosan.

Figure 11 X-ray diffraction patterns of DMAEMA-grafted chitosan.

Table II Mechanical Properties and Crystallinity of Original and DMAEMA-Grafted Chitosan Films

Sample	Grafting of DMAEMA (%)	Crystallinity (%)	Tensile Strength (kg/cm^2)	Elongation (%)
D-1[a]	—	56.2	281.6	3.1
D-1[b]	—	56.2	280.3	3.1
D-2	12	48.6	330.9	3.2
D-3	25	44.3	279.6	2.7
D-4	41	38.7	217.8	2.5
D-5	54	31.9	178.7	2.2

[a] Original.
[b] Irradiated.

may be attributed to the formation of a DMAEMA cyclic structure of grafted chitosan as a result of partial decomposition of a side group of the DMAEMA molecule.

X-ray Diffraction Studies

Diffractograms of DMAEMA-grafted chitosan are presented in Figure 11. The diffractograms show a major peak at 19° whose relative intensity decreases sharply on increasing graft level of DMAEMA. The value of percent relative crystallinity is listed in Table II. It appears that relative crystallinity decreases from 48.6 to 31.9 as a function of graft level of DMAEMA from 12 to 54%. This decrease of relative crystallinity may be due to interference of bulky pendant chains of poly(DMAEMA) grafted onto the chitosan molecule.

Mechanical Properties

The tensile properties of original and modified samples were evaluated in the dry state, and results are listed in Table II. No significant change is observed in the tensile properties upon gamma-ray irradiation (0.54 Mrad). However, in case of DMAEMA-grafted chitosan films, tensile strength first increases up to the 12% graft level and then decreases with increasing amount of grafting. A decrease is observed in percent elongation at break (29%) on increasing the graft level of DMAEMA from 12 to 54%. The increase in tensile strength at 12% graft level may be attributed to the branching effect of poly(DMAEMA) in chitosan matrix. It was observed from X-ray diffraction studies that crystallinity of grafted chitosan decreases with increasing graft level. The reason for

the decrease in tensile strength above the 12% graft level may be due to an increase of the amorphous region in the grafted sample.

CONCLUSIONS

From the above study it can be concluded that a desired level of grafting of DMAEMA onto chitosan films can be achieved by appropriate selection of grafting conditions, namely solvent composition, monomer concentration, dose rate, and total dose. The degree of swelling, crystallinity, and tensile strength decreased by 51, 43, and 37%, respectively, at a graft level (54%) of DMAEMA, whereas modified films showed improved thermal stability.

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