Radiation-grafting of *N,N*-dimethylaminoethylmetacrylate onto polyethylene film by preirradiation method

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Summary

Radiation-induced graft polymerization of N,N-dimethylaminoethyl-metacrylate onto low density polyethylene (LDPE) film by the preirradiation method in presence of air was investigated. The appropriate reaction conditions at which the graft polymerization was carried out are reported.

Introduction

A recent concept in developing novel functional materials is based on the use of strong noncovalent interactions for holding together molecular components (1-4). The system consists in mixing one functional homopolymer and one functional compound. The main application of this concept is the design of polymeric liquid crystalline materials, however, homopolymers which form salts with liquid crystal compounds are often hygroscopic and present poor mechanical properties; graft copolymers of dimethylaminopropylmetacrylamide (DMAPMAA) and dimethylaminoethylmetacrylate (DMAEMA) with less hydrophilic polymers such as polyethylene are therefore of interest.

Graft polymerization is a well-known method for the modification of chemical and physical properties of polymeric materials. Although graft polymerization can be achieved by ionizing radiation, ultraviolet light or chemical initiators, radiation grafting is one of the most promising methods due to its extensive penetration in the polymer matrix and its rapid and uniform formation of active sites for initiating grafting throughout the matrix.

The radiation-induced grafting of acrylic acid (AA) and methacrylic acid onto polyethylene (PE) was studied in some detail by several authors (5-9). The synthesis of modified polymers of PE with grafted chains of polyacrylamide (PAA) has essential practical interest. These polymers can be used, among other applications, as coatings for metals, as separation membranes and as a biomaterials with thromboresistant properties when they have polybases on the surface (10-12). However, to the best of our knowledge, grafting of DMAEMA onto PE films has not yet been done.

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The aim of the present work is an investigation of preirradiation induced grafting of DMAEMA onto PE and the study of structural, morphological and phase peculiarities of the grafted copolymers; it is focused on the search for appropriate conditions to obtain the graft copolymer.

The next step in this investigation will be the formation of a salt with functionalized mesogens of benzoic acids derivatives. The study of these compounds in conjuction with graft copolymers is expected to lead to electrostatic complexation between complementary functional groups via ion-ion interactions.

Experimental

PE film from PEMEX of 0.07 mm thickness was grafted with distilled DMAEMA from Aldrich Chemical Co. Inc.. PE films were cut into 1 cm wide and 5 cm long pieces; their exact weight and thickness were recorded.

All samples of PE films were exposed in air at room temperature, to cobalt-60 gamma rays, at a dose rate of 6.2 kGy/h, using a Gammabeam 651 PT from Nordion International Inc., to form peroxides and hydroperoxides in the polymer film. After irradiation, duplicate samples were introduced in glass ampoules which contained solutions of freshly distilled monomer (60% by volume in benzene). The ampoules were connected to a vacuum line and degassed by repeated freezing and thawing. They were sealed under vacuum, placed in thermostat water baths at different temperatures from 45 to 75 °C for various periods of time to insure grafting of the monomer onto the PE films.

After grafting, the ampoules were opened and the films were extracted with benzene for 24 hours to dissolve homopolymer formed in the reaction; the grafting yield was determined gravimetrically, by the following equation, where W_o is the initial weight of PE film and W the final weight of the grafted sample.

$$\% \text{ grafting} = \frac{W - W_o}{W_o} x 100$$

The percentage of grafting was determined as a function of : a) preirradiation dose at a constant dose rate (6.2 kGy/h), constant monomer concentration (60% monomer, 40% benzene) constant reaction temperature and different heating time; b) reaction time at constant solution concentration, preirradiation dose, dose rate and temperature; c) reaction temperature at constant solution concentration, preirradiation dose, dose rate and different reaction time; and d) monomer concentration in the solution at a constant temperature, dose rate, preirradiation dose and different reaction time.

The activation energy (E_a) of the grafting system was calculated with help of the Arrhenius equation:

$$E_a = 2.303 \ x \ \frac{1.987 \ (\log V_2 - \log V_1)}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

where V_1 and V_2 are the rates of grafting in %/h, at T_1 and T_2 temperatures respectively.

Swelling was determined gravimetrically. The film was immersed in a swelling solvent (dichloromethane) at 35 °C for a given time and then weighed immediately after the solvent remaining on the surface had been wiped off with filter paper. FTIR with attenuated total reflection (ATR-FTIR) spectra were recorded on a Perkin-Elmer Model 1600 spectrophotometer. Thermal analysis was performed using a differential scanning calorimeter (DSC) model 2910 TA Instruments, at 10 °C/min. Scanning electron microscopy (SEM), was performed in a JOEL microscope JSM-5200. The crystalline structure of the films was analyzed by X-ray diffraction, using a SIEMENS D-500 diffractometer with Cu K_α radiation of 1.5406 A° wavelength.

Results and discussion

Grafting temperature was determined in the range of 45 to 75 °C.

The reaction temperature is an important factor to control grafting. As shown in Figure 1, grafting rate increases with temperature in samples preirradiated at 200 kGy with a concentration monomer of 60%, at a dose rate of 6.2 kGy/h. This effect was different at a monomer/solvent concentration of 80/20 and preirradiation dose of 250 kGy; in this case the grafting rate decreased with the increase in temperature from 45 to 75 °C (Figure 2) because the radicals trapped in the bulk of the film partially decayed before grafting took place due to mutual recombination, and because higher monomer concentration delayed the diffusion of the monomer/solvent solution into the PE film. The limited (maximum) grafting percentage vs. temperature is plotted in Figure 2. This effect was also observed by Shinohara and Tomioka (1960) who studied the grafting of N-vinylpyrrolidone onto PE.

It seems that higher amounts of solvent enhanced monomer diffusion and the effect of recombination of growing radicals decreased, increasing the grafting percentage and the length of the grafted chains.

The rate of reaction (%graft/h) of the samples irradiated at a monomer concentration of 60% was calculated by plotting in log-log scale the percent of graft versus time; the activation energy was calculated from the slope of the Arrhenius plot (grafting rate *vs* 1/temperature), and the overall activation energy of the grafting at this monomer concentration was determined to be approximately 5.35 kcal /mol (22.4 kJ/mol).
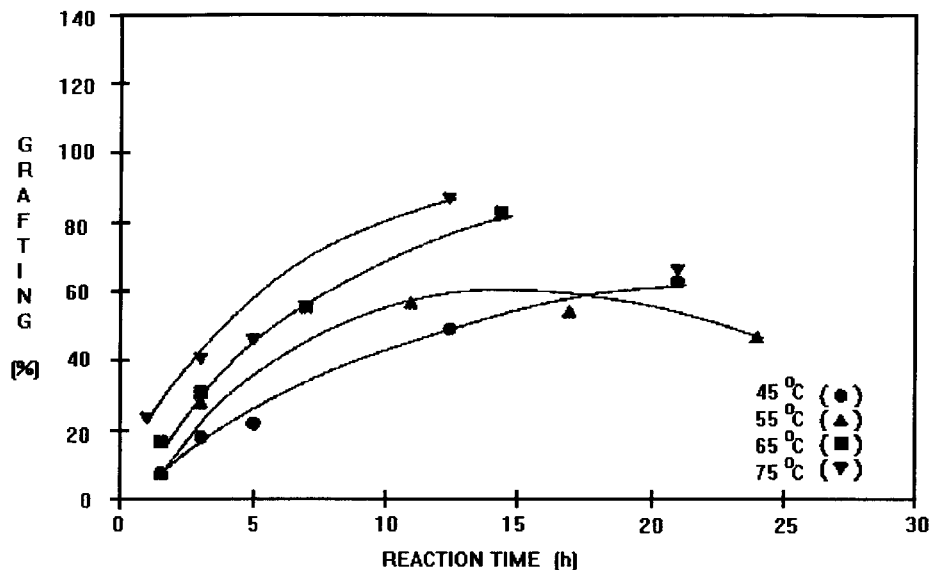
Figure 1. Graft % as a function of reaction time, at different graft temperatures; preirradiation dose 200 kGy.
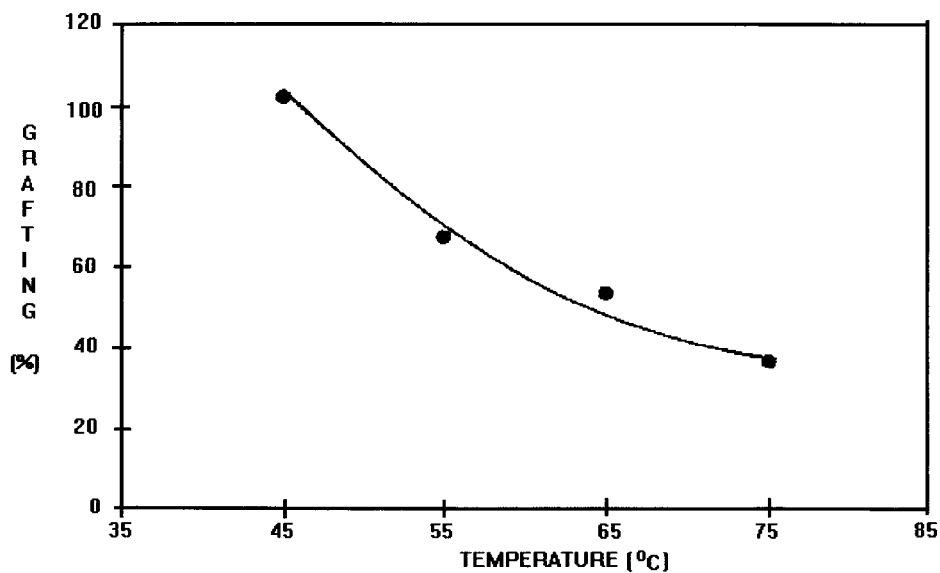

Figure 2. Graft % as a function of temperature, monomer concentration 80%; and preirradiation dose 250 kGy.

Monomer concentration. The effect of DMAEMA concentration in benzene (%/volume) on grafting percent was studied. Results are shown in Figure 3 for samples irradiated at 200 kGy at 55 °C. The plot shows that grafting percent increases with concentration in all ranges studied, but 60% was chosen because the homopolymer and gel formation increase with the rise in monomer concentration, and the separation of the grafted film became difficult.
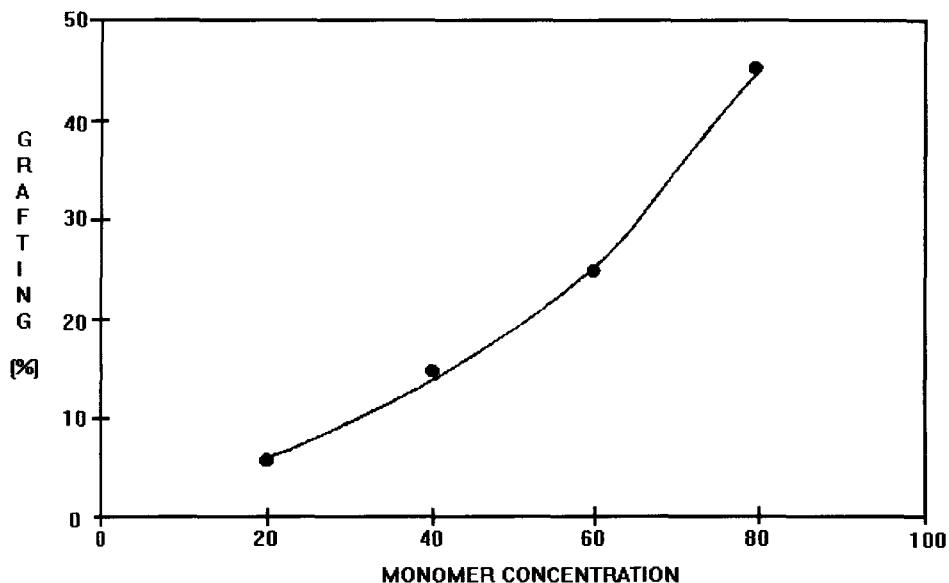

Figure 3.   Graft % as a function of concentration, graft temperature 55°C, preirradiation dose 200 kGy.

Preirradiation dose. Dependence of grafting on the preirradiation dose was investigated between 200 and 300 kGy. Figure 4 shows typical curves of grafting percent vs. reaction time for samples heated at 55 °C with 60/40 monomer/solvent.

The grafting degree increased with time and seemed to level off at a certain value, called "limited percent grafting". The limited percent grafting increased with the rise in preirradiation dose, however, above 250 kGy, the curves crossed. This crossing-over effect at a certain preirradiation dose was also found by Hoffman et al. (13). They found a maximum in grafting of methacrylic acid onto polypropylene (PP) and PP/PE copolymer films.

The grafting percentage decreases in films irradiated for longer periods indicating that the active sites may be degraded by recombination of primary radicals faster than they interact with growing radicals of the monomer.
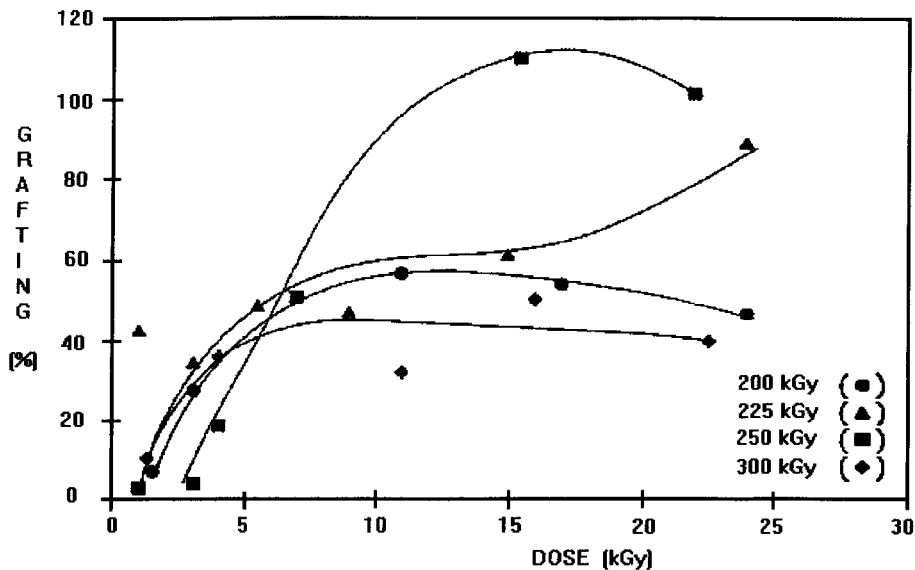
Figure 4.   Graft %   as a function reaction time, graft temperature 55 °C; at different preirradiation dose.
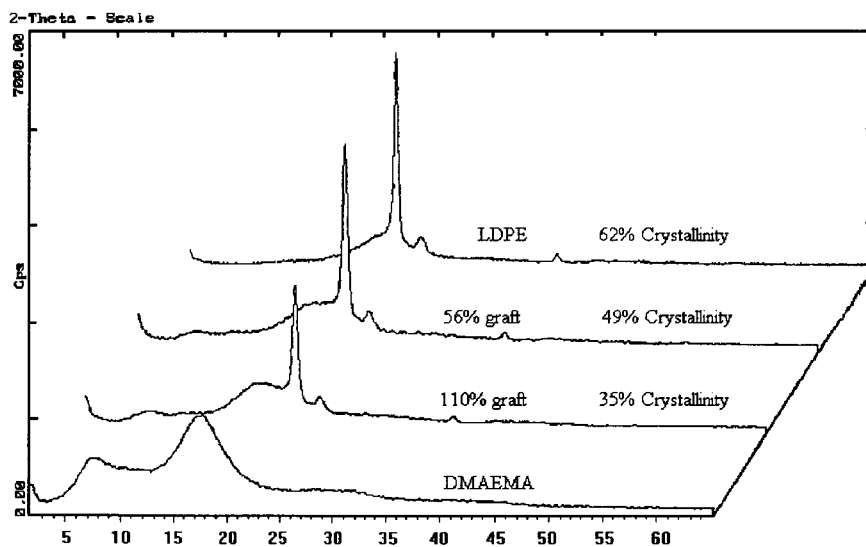

Figure 5.   X ray diffraction of DMAEMA, 56% grafted, 110% grafted and LDPE.

<u>Crystallinity</u>. The crystallinity decreased as the grafting percentage increased, as shown by the X-ray diffractogram (Fig. 5).

<u>Surface structure</u>. Scanning electron micrograph (SEM) of the surface of the grafted films shows small globules scattered on the surface. These globules increase in both number and size with increasing degree of grafting.

<u>FTIR-ATR spectra</u>. To confirm the surface structure of the grafted films, they were examined by infra-red spectrophotometry. The starting PE film has strong bands at 2930 and 2950 cm^{-1} due to stretching, 1460 and 1470 cm^{-1} due to CH_2 bending and 720 and 730 cm^{-1} due to CH_2 rocking.

After grafting, the spectra showed characteristic bands of both PE and PDMAEMA. This leads to the conclusion that both components exist in the grafted layer.

<u>Swelling behavior</u>. Maximum swelling was obtained in less than 15 minutes and then leveled off. Swelling percentage increased with grafting yield, preirradiation dose and reaction temperature.

Maximum swelling was 200% in samples with more than 86% grafted, a good condition for chemical reactions and salt formation.

<u>Thermal measurements</u>. The endothermic peak in the DSC thermogram corresponding to the melting point of the grafted films decreased with the increase in grafting percent from 115 °C (PE) to 112 °C in the grafted samples.

CONCLUSIONS

Reaction conditions to obtain maximum grafting percentage were: preirradiation dose of 250 kGy, reaction temperature of 55 °C, concentration DMAEMA/benzene 60/40, and reaction time of about 14 hours. Under these conditions, a maximum of about 110% graft was obtained.

If higher grafting percentages are needed to form salts with liquid crystal compounds, a different radiation method must be studied. The direct joint irradiation of monomer solution and PE films is not very efficient because it results in gel and homopolymer, and the separation of the entrapped film from the gel is difficult.

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