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Radiation-induced grafting of functional acrylic monomers onto polyethylene and polypropylene films using acryloyl chloride

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Summary

Radiation-induced graft polymerization of acryloyl chloride onto films of polyolefins (polyethylene and polypropylene) using gamma radiation was investigated in order to establish a convenient method to obtain polymer films grafted with polyacrylic esters. Grafting was carried out by three different methods; (i) direct irradiation of film in monomer solution (ii) vapor phase irradiation method, and (iii) pre-irradiation in air. The effects of monomer concentration, radiation dose and methods of grafting, on the formation of grafted polyolefins are reported in this paper.

Introduction

There are many polyacrylates, which contain liquid crystal (LC) groups in their side chains (1,2). They are usually prepared by the synthesis and polymerization of the corresponding acrylic monomers. The present authors are interested in grafting such polymers onto films of other polymers to obtain free standing LC films. Radiation grafting is an important tool for the modification of polymers in general, and is used mainly for the introduction of polymers with special functions. Radiation-induced grafting of LC forming acrylate monomers onto polyolefin films can be done by the conventional method, however, the synthesis of such acrylate monomers with functional groups is commonly accompanied by the problem that the monomers are very active and polymerize prematurely during synthesis and purification. Furthermore, the functional groups might be destroyed by the radiation. The present authors have previously studied the grafting of some tolane-containing acrylates onto polyethylene film (3), but the yield was very low for the above reason, and therefore acryloyl chloride (AC) had to be first grafted first, followed by the esterification. Mesophases were observed on the grafted polyethylene films (3). Therefore, grafting of AC onto the polymer films can be made more efficiently, followed by esterification or amidation with desired functional compound with OH or NH groups. The grafting of functionalized polymers onto thin films of host polymers is a promising tool for obtaining novel film materials with specific functionality. The radiation-induced graft polymerization of AC has not been reported previously. In this work, therefore, in order to establish a specific methodology for preparation of polymer films grafted with polyacrylates, the grafting of AC onto polyolefins (polypropylene and polyethylene) was carried out by three different methods; (i) direct, (ii) direct in vapor phase and (iii) pre-irradiation in air. Details on radiation-induced grafting have been thoroughly described in the literature

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(4,5,6). The grafted polyacryloylchloride was converted to the corresponding esters with different alcohol. The main objective of this work was to provide an optimum methodology for obtaining polyolefin films grafted with polyacrylates containing functional groups.

Experimental

Polyethylene (PE) films from PEMEX, with a density of 0.926 gml^{-1}, crystallinity of 62% , and thickness of 0.07 mm, and polypropylene (PP) films with a density of 0.902 g ml^{-1} crystallinity of 71% and thickness of 0.07 mm, were used without preliminary treatment. Pieces of 1 X 5 cm unoriented films were cut and their exact weights were recorded. AC supplied by Aldrich Chemicals was purified by distillation under reduced pressures before use. A C0^{60} Gamma-Beam 651-PT with an activity of 55,000 Curies, was used for irradiation of the samples.

Direct method. The films were placed in Pyrex ampoules, and the monomer solutions of AC in toluene, at different concentrations, were added. The ampoules were sealed off after degassing by repeated freeze- and thaw process. The grafting of PE was performed with a dose rate of 5.4 kGy/h varying radiation doses from 0.7 to 5.4 kGy, and that of the PP film with two dose rates of 3.1 and 7.1 kGy/h, and radiation doses from 2 to 70 kGy.

Vapor phase direct method. The films and AC were placed in a Pyrex tube with two chambers as shown in Fig. 1 and after degassing the system the ampoules were sealed off under vacuum. The PE films were then irradiated with a dose rate of 5.4 kGy/h varying the dose from 8 to 13 kGy, and PP films with a dose rate of 2.4 kGy/h. During this process the acryloyl chloride was shielded from radiation by a lead capsule.

Pre irradiation oxidative method. The films were irradiated in air at room temperature at radiation doses of 50 to 250 kGy, and dose rate of 10 kGy/h, in order to form peroxides and hydroperoxides in the system. The films were then introduced into ampoules containing monomer solution in toluene with a monomer concentration of 60%. After degassing and sealing the system they were heated at 65° C for different reaction periods ranging from 1 to 24 hours.

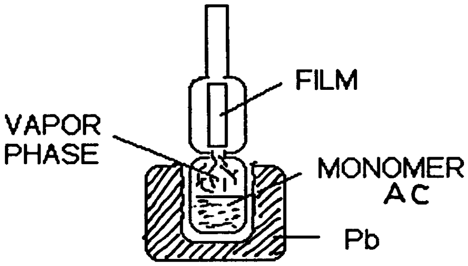

Fig. 1. Vapor phase method ampoule

Polyacrylates are polymers which suffer crosslinking by radiation. The radiation-induced bulk polymerization of acryloyl chloride was carried out in a sealed tube, and it was found that the crosslinking occurred only when the radiation dose exceeded 30 kGy. Duplicate samples were used in all of the experiments. After graft polymerization, the ampoules were opened and the homopolymer was immediately reacted with alcohol using triethylamine as an acid acceptor of the reaction. Esterification with methanol was carried out in order to evaluate the percentage of grafting. The films were placed in methanol containing triethylamine and stirred with a magnetic stirrer for 24 hours, washed with methanol and dried in vacuum. The grafting yields were calculated from the difference in weights of the films before and after grafting. They were converted to percentage in mole with respect to moles of the polyolefin films.

In the case of esterification with different alcohols, the films were placed in dry chloroform containing an excess of a selected alcohol, and a stoichiometric amount of triethylamine or pyridine as the acid acceptor, and the system was stirred for 24 hours at room temperature. After the esterification, the films were washed with chloroform and dried in vacuum. The grafting yield were determined from the weight differences before and after grafting, and then converted to mole percentage with respect to the film polymers.

Swelling determination. PE or PP films were immersed in different solvents (toluene, dichloroethane, chloroform, dimethylformamide and methanol) at room temperature until equilibrium swelling was reached. Then the samples were taken out and the excess solution deposited on the film surface was removed quickly with blotting paper, and the samples were weighed. The swelling degree was calculated from the difference in weight before and after swelling.

FTIR spectra of the films were recorded with attenuated total reflection (ATR-FTIR) technique using a Perkin Elmer Model 1600 spectrophotometer. Elemental analysis was made by Desert Analytics of Tucson, AZ,

Results and discussion

The swelling of the films due to the penetration of the solvents employed for grafting is an important factor in controlling the degree and the form of grafting. After testing various solvents, toluene was found to be the most suitable solvent for the grafting of acryloyl chloride onto PE, the swelling degree being 18%. The swelling of PE in other solvents was found to be 16% in chloroform, 8% in dichloroethane and 5% in DMF.

1. Grafting onto polyethylene

Direct method. Fig. 2 shows the relationship between the AC concentration in toluene and the grafting yield using the direct method and a radiation dose of 5.4 kGy at room temperature. The plot shows that the grafting percentage increased with concentration.

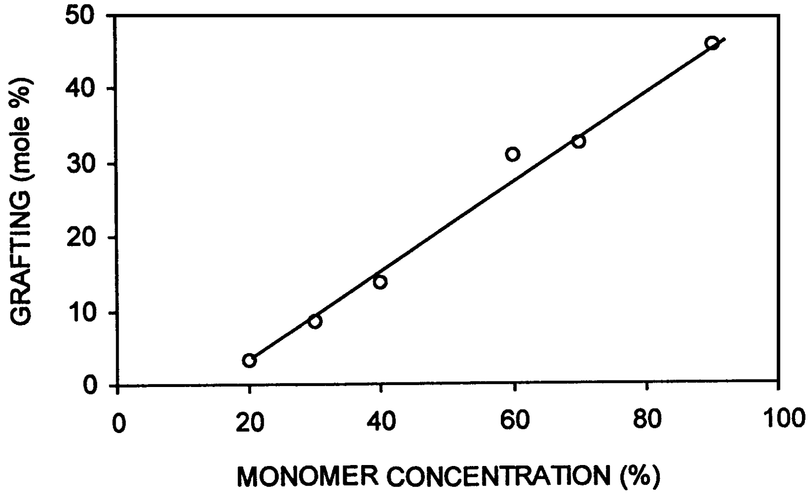

Fig. 2. Graft (%) as a function of concentration; direct method, room temperature, dose rate 5.4 kGy/h

When the AC concentration exceeded 90%, and at doses above 5.4 kGy the amount of homopolymerization of AC increased, and the separation of the grafted film became difficult. However, if the AC concentration was decreased, higher doses could be applied.

When the esterification was carried out with different alcohols, the grafting yields based on weight, increased with the size of the alcohols, but remained more or less constant in terms of concentration (moles). Figure 3 shows the esterification results based on mole percentage with four alcohols of different alkyl chain lengths for the films grafted with AC. It can be seen that there is no appreciable difference in the esterification among the alcohols employed. The reactivity of these alcohols with the grafted polyAC may be different, but the under the conditions of this work, they reacted similarly to each other indicating that the esterification was completed.

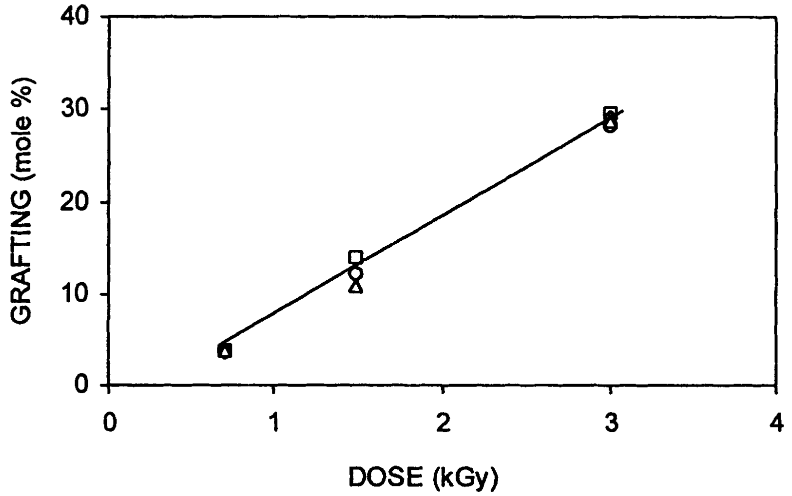

Fig. 3. Graft (%) as a function of dose, room temperature, direct method, dose rate 5.4 kGy/h, monomer concentration 90%, with different alcohols; (◇) methanol, (O) propanol, (Δ) hexanol, (□) octanol

Vapor phase direct method Figure 4 shows the plot of percentage grafting against the radiation dose for the samples prepared by the vapor phase method. The grafting yields were somewhat lower than in the case of the direct method. When the radiation dose exceeded 4 kGy the films increased in size and became wave-shaped, and fragile. It seems that grafting takes place not only on the films' surface but also inside the films. This was not observed in the direct method.

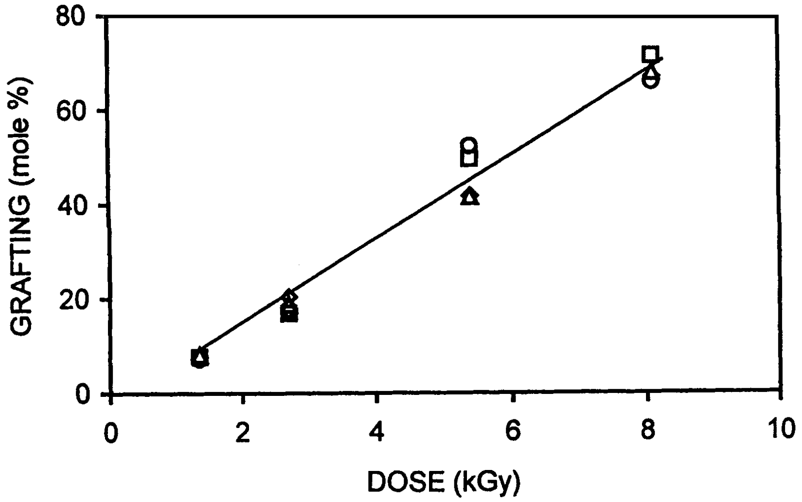

Fig. 4. Graft (%) as a function of dose, room temperature, vapor phase direct method, dose rate 5.4 kGy/h, monomer concentration 100%, with different alcohols; (◇)) methanol, (O) propanol, (Δ) heptanol, (□) decanol

Preirradiation oxidative method The initial studies showed the grafting yields to be negligeable, and so far detailed studies were not made.

2. Grafting onto polypropylene

Direct method Figure 5 shows the relationships between percentage grafting and radiation dose for the films irradiated in two AC concentrations of 30 and 70% in toluene and esterified with methanol. Similarly to the case of PE, the grafting percentage increased with the monomer concentration, but the grafting yields were much higher than those in the cases of PE. Because of the high grafting percentages obtained with PP in comparison with PE and because the formation of homopolymer increased with the AC concentration, the monomer concentration was limited to a maximum of 70%. As can be seen from the figure, more than 500 mole percent of grafting was attained with a dose of 20 kGy, and more than 100 mole percent with a dose of only 5 kGy. It is worth mentioning that the grafted polymers (after esterification with methanol) with a monomer concentration of 70% were homogeneous and transparent with doses up to 20 kGy, and the films became opaque with higher doses.

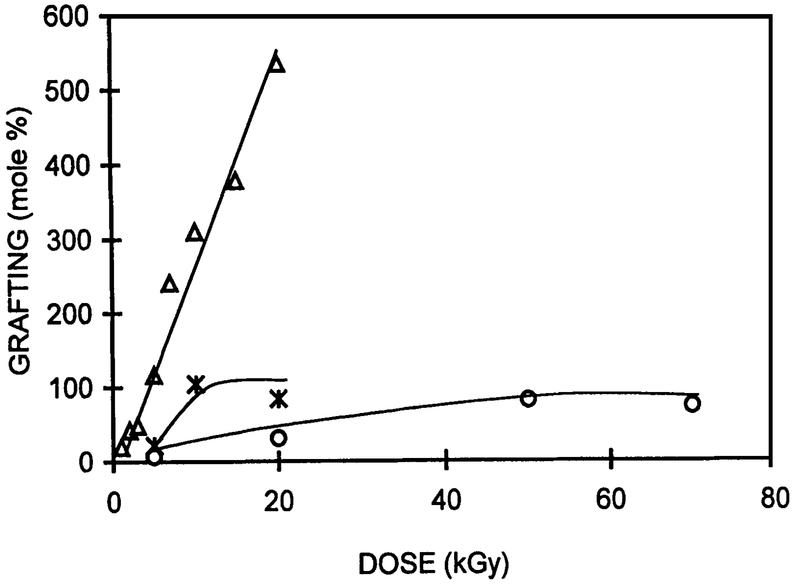

Fig. 5. Graft (%) as a function of dose, room temperature, direct method; (Δ) monomer concentration 70% in toluene, dose rate 3.1 kGy/h, (*) monomer concentration 30% in toluene, dose rate 3.0 kGy/h, (O) monomer concentration 30% in toluene, dose rate 7.1 kGy/h

Those obtained with monomer concentration of 30%, were also homogeneous and transparent, but when the grafting percentage exceeded about 100 mole percent the films became opaque and white. When the grafting yield increases excessively the surface is covered with polymethylacrylate (polyacryloylchloride esterified with methanol) and due to the difference in refractive indexes of the PP layer and the grafted layer, light scattering takes place. In the cases of the AC concentration of 30%, the intensity seems to be less important the same results being obtained at all the intensities used. The concentration is more influential for the grafting as expected.

Vapor phase direct method. By this method, homogeneous films with grafting percentage of 185 mole percent were obtained with a radiation dose of only 6 kGy as shown in Fig. 6. The yield was not much different from that of the direct method, but no homopolymer was formed by this method. Figure 7 shows the results of the grafting of AC and methacryloyl chloride (MAC) onto PP under the same conditions for the two monomers. The percent of grafting with AC was much higher than that of MAC, because the former polymerizes more rapidly than the latter.

Preirradiation oxidative method The grafting yields with this method were also very low compared with the other two methods. The films were not homogeneous, and some round spots were formed on the surface.

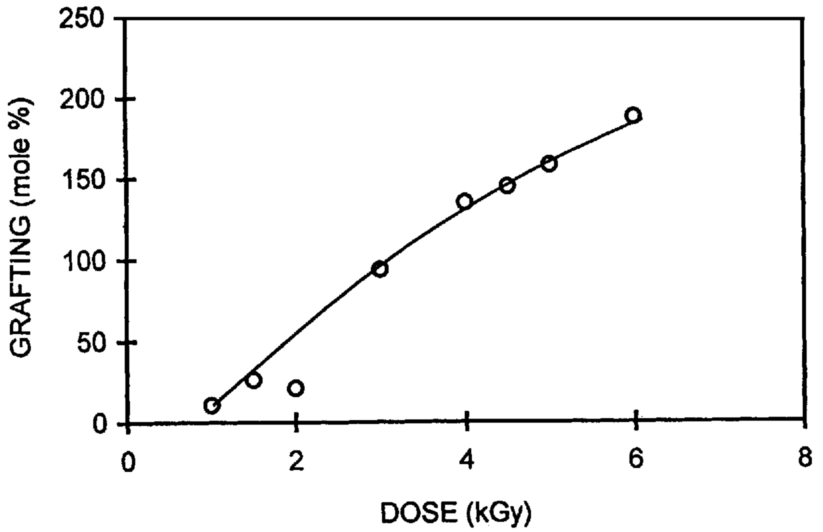

Fig. 6. Graft (%) as a function of dose, room temperature, vapor phase direct method, dose rate 2.4 kGy/h, monomer concentration 100%.

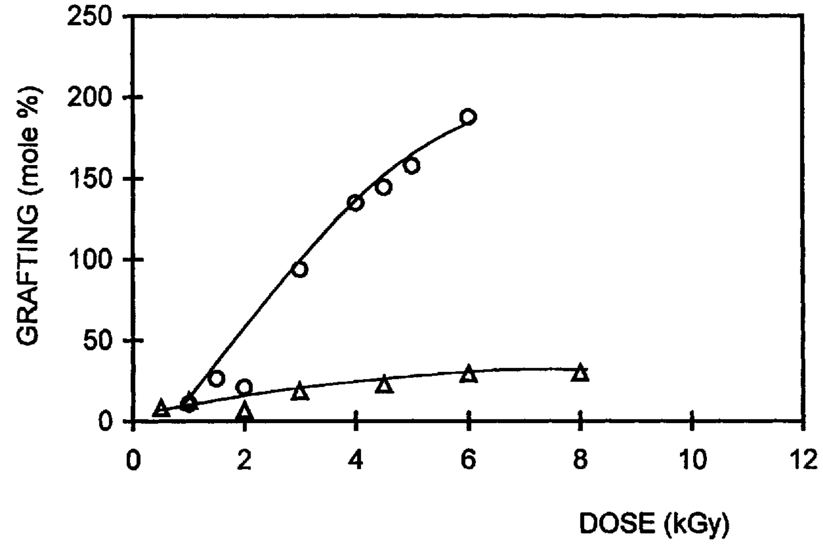

Fig. 7. Graft (%) as a function of dose, room temperature, vapor phase direct method, dose rate 2.4 kGy/h, monomer concentration 100%; (O) acryloyl chloride, (Δ) methacryloyl chloride

Characterization. The grafting of AC and its esterification were confirmed by infrared spectroscopy; the characteristic bands of –CO at 1735-1737 cm^{-1}, the -COO of the esther group at 1373-1374, OCH_3 at 1373 cm^{-1}, and those bands at 1164 and 1260 cm^{-1} due to C-O bonds were found in all the cases studied.

Conclusion

From the above study it can be concluded that polyolefin films grafted with polyacrylic esters can be readily obtained either by the direct method or the vapor phase direct method. The pre-irradiation method was found to be unsatisfactory, probably because the alkyl or hydroxyl peroxides formed require higher temperatures to be effective initiators, where the PE (65°C) and PP (85°C) become soluble in toluene which was used as a solvent. By these methods, it is easy to obtain acrylates derivates grafted in PP or PE films grafted with polyacrylates or polymethacrylates having various functional groups.

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