The Radiation-Induced Graft Copolymerization of Methacrylic Acid with Polyethylene. Ion-Exchange Properties of the Copolymeric Composites

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Synopsis

The study involves the preparation and characterization of a series of polyethylene-*g*-co-methacrylic acid polymers in which the comonomer provides a degree of hydrophilicity to the backbone polymer. Such copolymers have been shown to possess efficient ion-exchange properties with respect to Fe(III) ions, used as a model for general exchange. As such, we have a useful extension to our work on enzyme immobilization and protein separations using this type of support. Grafting was carried out in air and under vacuum. A correlation between the carboxylic acid group content and the extent of grafting was found. Under the conditions employed in our experiments, a maximum in grafting levels was observed when water was used as a continuous medium but not when methanol was included in the solvent assembly. No significant difference was observed between grafting carried out in air and that carried out under vacuum, when aqueous solutions of methacrylic acid were used. The graft copolymers have been shown to be effective in isolating Fe(III) ions and to be amenable to recycling procedures.

INTRODUCTION

The history of grafting studies involving polyethylene as the support material is extensive. Though not the earliest study, that provided by Chapiro[1] serves as a convenient starting point. The earlier papers were largely concerned with achieving grafting, with studies of kinetic and mechanistic factors, and with attempts to provide a detailed understanding of the nature of the grafting process. More recently, the emphasis has been placed on the use of radiation processing to provide crosslinking within the pololefin.[2,3] Other areas of interest have included (i) electron spin resonance studies of oxidation processes in irradiated polyethylene,[4,5] (ii) formation of the hexagonal lattice and destruction of crystallinity in polyethylene on irradiation,[6] (iii) syntheses of ion-exchange membranes based on the polyethylene-*g*-co-acrylic acid system,[7,8] (iv) interest in the primary effects of irradiating polyethylene,[9] (v) cage effects in recombination of radicals in irradiated polyethylene,[10] (vi) irradiation at low temperatures,[11] (vii) the effect of tacticity of the termination rates during grafting to polyethylene,[12] (viii) comparisons between the pre-irradiation method of grafting and the simultaneous method,[13,14] and (ix) aspects of the radiation-induced oxidative degradation of polymers.[15-17]

Journal of Applied Polymer Science, Vol. 37, 39–54 (1989)

CCC 0021-8995/89/010039-16$04.00

Our interest in polyolefin-based copolymers concerns their value as support materials in enzyme and protein immobilization.[18-20] Related studies include the use of such copolymers in the biomedical and biophysical fields, in textile applications, and as supports in geophysical applications.

Inert, hydrophobic polyethylene provides a useful backbone for immobilization studies. It can be used in a variety of physical forms—fibers, films, membranes, and powders. It is readily amenable to grafting with a variety of vinyl and acrylic monomers to provide a range of modifications to physical and chemical properties.

Grafting with hydrophilic monomers provides a means where polyolefinic copolymers can be used in aqueous assemblies under a variety of conditions of temperature, pH, etc. It is this blend of physical attributes that makes polyethylene-*g*-co-methacrylic acid appear attractive as a support in ion-exchange separation processes.[7,8]

We are largely concerned in separations undertaken using packed column assemblies based on graft copolymers of low density polyethylene powder.

EXPERIMENTAL

Reagents

Low density polyethylene (Telcon Plastics Ltd, Orpington, Kent, U.K.) was washed several times with distilled water and methanol, filtered, and dried to constant mass under vacuum at 313 K.

The monomer used (methacrylic acid) (Imperial Chemical Industries Ltd, Mond Division, Runcorn, Cheshire, U.K.) was purified by vacuum distillation over KOH pellets. The solvent for the monomer was distilled water, although methanol and mixed solvent systems (methanol–water) were also tried. This was to ensure development of a stable suspension of polyethylene throughout the reaction medium. In this connection, the most satisfactory combination was found to be a mixture containing 62.2% (by weight) of methanol and 37.8% (by weight) of distilled water. Precautions to optimize the formulation of graft copolymer and reduce homopolymerization were taken by using $0.01M$ solution of $CuCl_2$ in all grafting experiments.

Pre-Irradiation Procedures

The graft-copolymerization reactions were initiated by γ-irradiation using the 10,000 Ci Co(60) source located in the Department of Physical Chemistry at the University of Leeds.

Radiation-Induced Graft Copolymerization in Air

Accurately weighed, purified polyethylene powder (5 g) was placed into each of six Pyrex glass test tubes (internal diameter 22 mm, height 150 mm). A solution of $0.01M$ $CuCl_2$ in distilled water, methanol, or water/methanol mixture was then prepared whereupon freshly distilled methacrylic acid was added to give a concentration of 10 or 20% as required. Thirty cubic centimeters of the above solution was poured into each tube. The tubes were subsequently sealed by means of special rubber serum caps, placed on the aluminum stand, and thermostated for 1 h at 30°C, immediately prior to irradiation (equilibrium swelling). The grafting procedure was undertaken via the simultaneous, heterogeneous route at 20°C. After thorough shaking, the six tubes containing the polymer/monomer mixtures were placed into the Co(60) γ-radiation unit and irradiated for different times at a dose rate of 1.1 rad s^{-1}. Blank samples were separately prepared, containing the same mixture but not subjected to irradiation.

Radiation-Induced Graft Copolymerization under Vacuum

Solutions were prepared as for irradiation in air, but in ampoules which were amenable to evacuation. Such evacuation, incorporating freeze–thaw cycles, was routinely followed before the ampoules were thermally sealed at 1.33×10^{-3} N m^{-2}. Prior to irradiation, the samples were allowed to thaw and subsequently "equilibrated" for 1 h at 30°C. The irradiation procedure and preparation of blank samples have been described above.

Post-Irradiation Treatment

The contents of each ampoule (bulk solutions and graft copolymer) were carefully transferred to 250 cm^3 of distilled water, stood overnight, and filtered under vacuum. They were then thoroughly washed with water, 1.0M HCl, water, and methanol. After overnight storage in air, the samples were dried under vacuum at 40°C to constant mass.

The samples were then Soxhlet-extracted with water for 24 h to ensure removal of extractable attendant homopolymer. The drying procedure was repeated, again to constant mass.

Grafting may be expressed by the degree of grafting (W) as follows:

$$W(\%) = \frac{W_f - W_{i_c}}{W_{i_c}} \times 100$$

where W_f = weight of graft copolymer and W_{i_c} = initial weight of polyethylene (corrected for the possible small weight changes in the blank samples).

Determination of the Carboxylic Group Content of the Copolymer

Accurately weighed, dry samples (0.05 g each) were placed into 25 cm^3 volumetric flasks and 10 cm^3 of 0.1M NaOH (Analar) were then added. The suspensions were allowed to stand for 48 h with occasional shaking. Then, after filtration, 5 cm^3 of the solution were backtitrated with 0.1M HCl, using methyl orange as the indicator. The concentration of —COOH groups (Q) of the copolymers was calculated as follows:

$$Q = \frac{2(V_0 - V)M_{\mathrm{HCl}}}{q} \qquad (\mathrm{meq/g})$$

where V_0 = is the number of cm^3 of 0.1M HCl for backtitration of a blank sample, $V =$ is the number of cm^3 $0.1M$ HCl used in the backtitration of the grafted sample, M_{HCl} is the concentration of HCl used (g dm^{-3}), and $q =$ is the mass of the grafted sample (g).

Ion-Exchange Experiments

The ion-exchange experimental program was designed such that the prepared polyethylene-*g*-co-methacrylic acid polymer acts as an exchanging medium for Fe(III) ions in aqueous solution. In order to assess the ion-exchange performance of each copolymer prepared, use of spectrophotometric methods of measuring Fe(III) ions in solution was favored compared to titrimetric methods due to the rapidity and accuracy of the former. A study was also made of the recycling of the substrate for further exchange, by running dilute hydrochloric acid through the exchanging column to "flush-off" the retained Fe(III) ions. The ion exchange procedure was then repeated, using even more concentrated Fe(III) solutions in order to assess the performance of the recycled substrate. Exchange was also conducted on blank samples, prepared during the grafting experiment (i.e., the nonirradiated samples in the presence of methacrylic acid solution with zero degree of grafting).

Construction of the Calibration Curve of Fe(III) Ions

Standard solutions of iron(III) sulfate [$Fe_2(SO_4)_3$] were made up in the concentration range 10^{-5} mol dm^{-3}–10^{-2} mol dm^{-3} using distilled water. Their absorbance was measured at 304 nm, using a Pye Unicam UV-VIS spectrophotometer SP8-150. A calibration curve was then constructed.

Preparation of the Ion-Exchange Column

In all cases, a uniform mass of 1 g polymer, accurately weighed, was taken in the study of Fe(III) salt uptake. A Pyrex glass ion-exchange column with an internal diameter of 5 mm and a height of 300 mm was partially filled with distilled water whereupon the 1 g of graft copolymer was carefully added. The polymer layer was compacted using a glass rod and was left overnight for preliminary swelling.

Column-Exchange of the Fe(III) Ions

Distilled water was passed through the column, and the contents were compacted using a glass rod. The necessary flow rate was adjusted to give a flow rate of 35–45 cm^3 h^{-1}. This was found to be completely satisfactory for an ion-exchange through a polymer layer having a volume of 3–3.5 cm^3, bearing in mind the column diameter (5 mm) and the commonly recommended linear velocity (3–10 cm^3 cm^{-2} of surface min^{-1}) of the solution.

Distilled water (10 cm^3) was then passed through the column. The eluant was collected and made up to 25 cm^3 with distilled water. A solution of Fe(III) ions (2×10^{-3} mol dm^{-3}), freshly prepared, was passed through the column (50 cm^3) and collected in 10 cm^3 aliquots. Each portion was then made up to

25 cm^3 in labeled volumetric flasks using distilled water. The ion-exchange experiments were conducted at 20°C.

Recycling of the Ion-Exchange Copolymer Substrate

Hydrochloric acid ($1M$) was passed through the column (10 cm^3, 35–40 cm^3 h^{-1}) and collected. A microspatula was then used to reorientate the particles constituting the column of exchange medium to prevent liquor channeling in any subsequent exchange. This procedure was found to be particularly difficult with the blank sample and samples of low grafting level because of their high level of hydrophobity. This is suspected to influence some of the results.

Distilled water (12 cm^3) was then run through the column to remove any residual acid, so that the last few drops of eluant were at pH 6.0–7.0 (Universal indicator paper). This wash-water was added to the eluted acid and made up to 25 cm^3 in a labeled volumetric flask, using distilled water.

Assessment of the Recycled Ion-Exchange Substrate

Further Fe(III) ions (concentration 4×10^{-3} mol dm^{-3}, 50 cm^3) were passed through the recycled substrate and collected in 10 cm^3 aliquots, which were subsequently made up to 25 cm^3. The column was then washed with $1M$ HCl, as previously described.

Assessment of the Ion-Exchange Performance and the Column Recycling

In order to assess the ability of the substrate to retain Fe(III) ions, a spectrophotometric method (Pye Unicam UV-VIS SP-8-150) was used. The concentration of the solutions (C) collected from the column and placed in labeled volumetric flasks was measured, in turn, by their absorbance at 304 nm at 20°C. The distilled water, collected after attaining the initial water flow rate, was used as a reference cell in the spectrophotometer. This makes an allowance for any soluble parts of the system that might be extracted during elution of the Fe(III) ions in water. Graphs, describing the dependence of c/c_0 on the number of cm^3 of Fe(III) solution passed through the column were constructed. The abscissa value, corresponding to the point $c/c_0 = 0.5$, was multiplied by the initial concentration (C_0) of the Fe(III) ions in order to provide an approximate measure for the total capacity of the column towards Fe(III) ions in milligram equivalents (meq). The amount of Fe(III) ions removed by $1M$ HCl in the cleaning procedure (regeneration) was calculated by multiplying the volume of the "cleaning" solution by its Fe(III) ion concentration as spectrophotometrically measured, with reference to the calibration curve.

RESULTS AND DISCUSSION

Radiation-Induced Graft Copolymerization in Air

For each set of conditions, grafting is assessed in terms of percent increase in weight, based on the original weight of substrate. In addition, grafting is

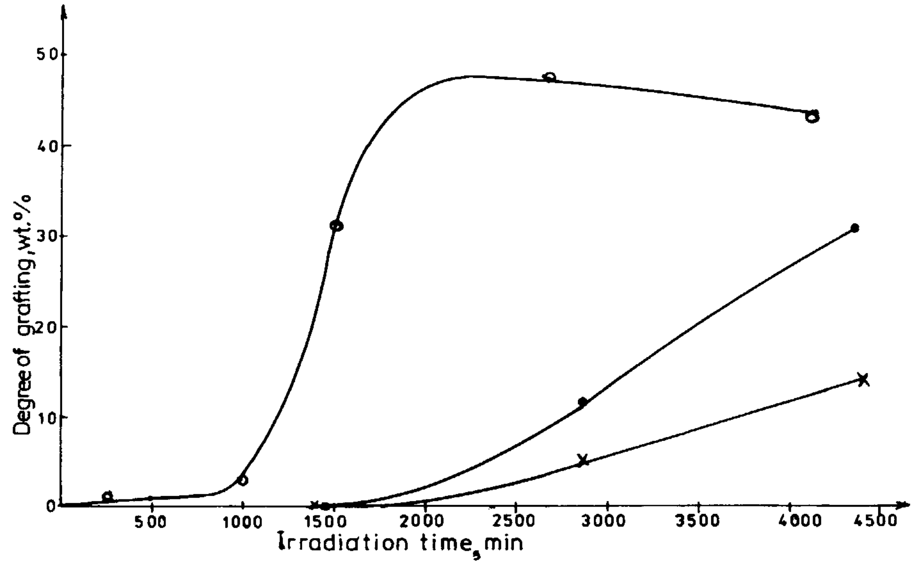

Fig. 1. Variation in degree of grafting with irradiation time (min). Monomer concentration, 10% methacrylic acid (MAA) grafting media: (●) water; (○) 62.2% methanol + 37.8% water; (×) methanol.

monitored through the carboxylic acid group content in the assembled copolymers. A summary of results obtained in different reaction media is represented in Figure 1.

It is clear that the presence of water markedly enhances the degree of grafting achieved at a particular time. A decrease in this water content leads to an increase in the apparent induction period. We should recall that the 62.2% H_2O:37.8% CH_2OH combination gave a stable suspension of the polyethylene powder. However, the maximum grafting extent, within the total dose level considered, was achieved with grafting in the absence of methanol.

In the water:methacrylic acid:polyethylene system, grafting maximizes after an irradiation time of approximately 33 h at a dose rate of 1.1 rad s^{-1}. The apparent decrease in grafting on prolonged irradiation may arise from subsequent, radiation-induced, breakdown of the grafted branches. However, it may represent the limitation of the quantitative measurements, in that grafting may level off within the period specified and that the "apparent" leveling may be merely an artefact of the system.

Figure 2 provides data related to the content of carboxylic acid groups in the polyethylene-*g*-co-methacrylic acid samples as a function of the irradiation time and the content of methanol in the grafting medium. It is clear that a maximum in the carboxylic acid group content occurs irrespective of the medium type, by increasing the water content, decreasing the time of irradiation (1.1 rad s^{-1}) needed to provide the "maximum" content of carboxylic groups. Doubling the monomer content of the aqueous system gives an increase in the speed with which the maximum value is achieved but does not increase the maximum value. This maximum value centers on 40 meq carboxylic acid groups/g copolymer.

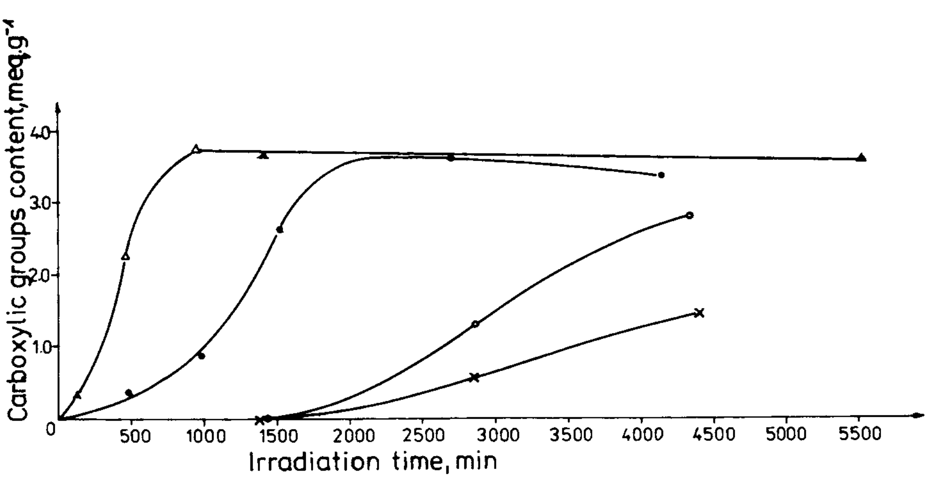

Fig. 2. Variation in the carboxylic acid group content (meq g^{-1}) with irradiation time (min) for grafted samples: (●) water/10% MAA; (○) water: methanol/10% MAA; (×) methanol, 10% MAA; (△) water, 20% MAA.

Radiation-Induced Graft Copolymerization under Vacuum

The results obtained during the irradiation of polyethylene in the presence of 10% methacrylic acid aqueous solutions are given in Figure 3, which gives the extent of grafting versus irradiation time for both vacuum and atmospheric conditions.

As can be seen from Figure 3, any induction period in the grafting reaction carried out under vacuum conditions seems to be much shorter than any induction period found in the presence of air. Possible explanations are believed to be: (i) A difference between the radiation-chemical changes of the system during the initial stages of irradiation under vacuum and in air. Low density polyethylene is likely to contain a significant proportion of oxidation sites. These are likely to be amenable to grafting by an indirect, radiation-induced mechanism. (ii) A difference in access of monomer to active sites which arises from "vacuum" treatment. Such treatment may assist diffusion of the monomer into the polyethylene. (iii) Once access has been achieved, to whatever level is possible under the prevailing experimental conditions, the grafting behavior might be expected to become somewhat standardized. Thus, we can see that the use of vacuum treatments largely modifies the occurrence of induction periods and the initial rates of copolymerization reactions. Therefore, the degree of grafting cannot exceed 47–49% in both cases, however long the irradiation time. The similarity in the mechanisms of radiation grafting under vacuum and in air, when the copolymers become more "hydrophilic," is demonstrated by Figure 4, which describes the dependence of carboxylic group content on the degree of grafting. Both relationships appear to be very close to each other, when the degree of grafting exceeds 25–30%.

The possibility of grafted-branch degradation developing on longer term irradiation must always be considered. Such events are likely to be more pronounced in the presence of oxygen. Explanations of this type can be

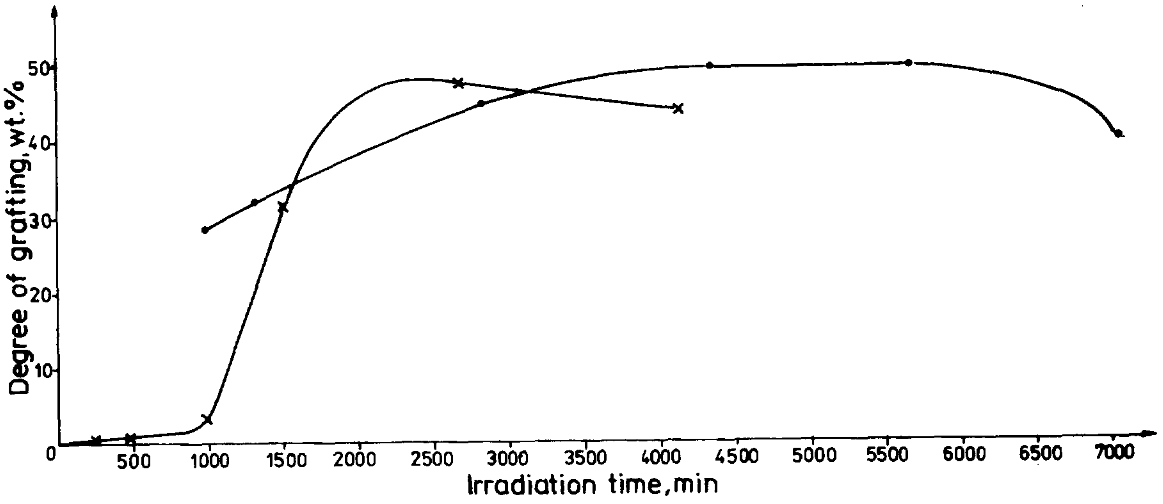

Fig. 3. Effect of vacuum degassing on grafting. Variation in grafting with irradiation time. Initial concentration, 10% MAA in water: (●) grafting under vacuum; (×) grafting in air.

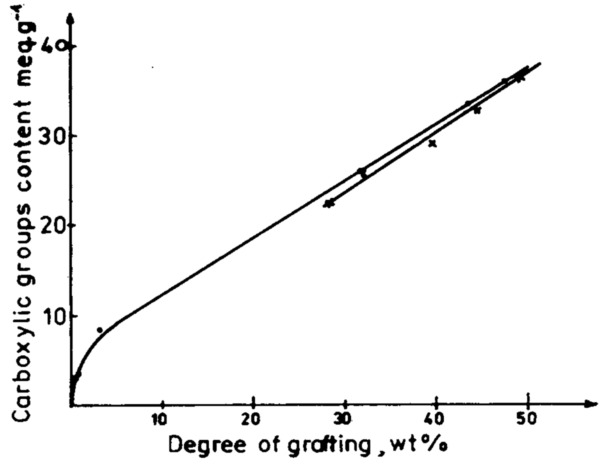

Fig. 4. Variation in the carboxylic acid group content of copolymers with variation in the degree of grafting. Initial MAA concentration, 10% in water: (×) grafting under vacuum; (●) grafting in air.

invoked to assist an understanding of the decrease in the extent of grafting which is apparent on prolonged exposure.

Effect of Water on the Grafting of Methacrylic Acid onto Polyethylene

Figure 5 shows the effect of water on the grafting of methacrylic acid on polyethylene via water/methanol continuous media, using the simultaneous method of grafting. Two irradiation times were considered namely 2.9×10^3 and 4.4×10^3 min, respectively. In both instances, the extent of grafting

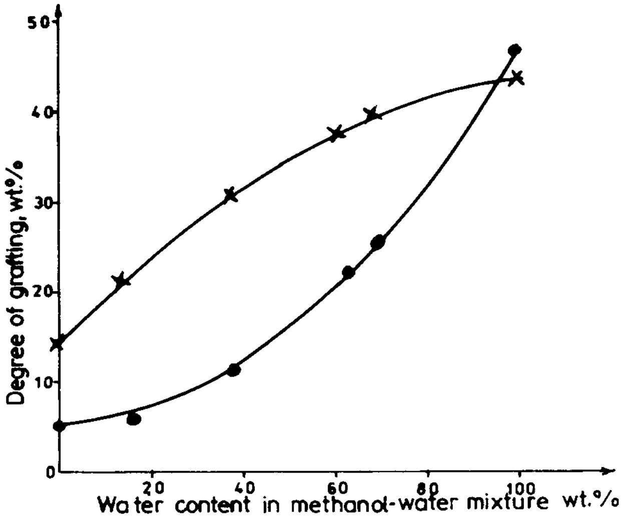

Fig. 5. Variation in the extent of grafting with water content of the water/methanol medium. Initial concentration of MAA, 10%: (●) irradiation time, 2900 min; (×) irradiation time, 4400 min.

increases as the water content in the system increases. However, the nature of the change differs depending on the irradiation time. As might be expected, higher total dose values yield higher graft levels in the majority of instances. On increasing the content of water in the solvent for the methacrylic acid, the extent of grafting is almost identical for both irradiation times, suggesting that a maximum level of grafting is achievable irrespective of the physical conditions, at a constant dose rate. It is clear that attention should be given to the nature of the continuous medium in this type of system. Thus, the optimum level of grafting is not given by the methanol/water ratio which gives stability to the dispersion of the polyethylene powder in the water/methanol/methacrylic acid system (i.e., 62.2% CH_3OH and 37.8% H_2O). Perhaps we have evidence of the development of preferential adsorption of the monomer onto the polyethylene surface as the concentration of water in the system increases. Such observations have been recorded previously for different systems.[18,19]

Induction Effects

It is clear from Figures 1, 2, and 3 that induction periods exist in the grafting profiles. We should recall that $CuCl_2$ was included in the monomer solution so that involuntary homopolymerization reactions would be suppressed. Figure 1 indicates that the inhibition of grafting depends, to some extent, on the nature of the solvent for the monomer (i.e., the water content). Thus, as the water content increases the induction period decreases. A similar proposal can be placed on subsequent retardation events. It should be noted that induction periods are much less pronounced for vacuum-irradiation systems.

The price paid for total inhibition of homopolymerization appears to be partial inhibition/retardation of grafting. One reason for the prolonged induction period (and the lower degree of grafting) in the presence of methanol is suspected to be the diminished efficiency of $CuCl_2$ as homopolymerization inhibitor in methanol or water/ methanol solutions, particularly if the organic solvent predominates.

This observation raises the significance of the various types of interaction which can arise in such complex systems of this type. Thus, we need information concerning the relationships between each of the components. Here, we are particularly concerned with (i) the manner in which the $CuCl_2$ interferes with homopolymerization, (ii) how $CuCl_2$ complexes with H_2O, and (iii) how methanol interferes with the establishment of complexing in the methacrylic acid–$CuCl_2$ and H_2O–$CuCl_2$ systems.

Another point that should be considered is the nature of the pictorial representations, corresponding to grafting arising with the 10% methacrylic acid aqueous solution (Figs. 1 and 2). The degree of grafting and the carboxylic acid group content show a complex dependence on the irradiation time (or absorbed dose). After a slow, almost linear increase at short irradiation times (low doses), a considerable rise is caused by an "autoacceleration," showing the possibility that grafting onto grafted branches also takes place to some extent, together with the more common "gel effect." The degree of grafting reaches a maximum value, and then very slightly decreases.

Since the reaction occurs in polyethylene, which is swollen to a very limited extent in methacrylic acid, the instantaneous concentration of the monomer steadily drops during the copolymerization and the grafting yield cannot exceed a limited value. After a certain irradiation time the degree of grafting becomes almost constant. This may be due to a decrease of diffusion of the monomer from the bulk solution into polyethylene, which has been covered with a thin layer of poly(methacrylic acid). This suggestion is supported by the grafting carried out in the presence of 20% methacrylic acid aqueous solution (Fig. 2).

With the 20% monomer solution, the initial rate of copolymerization is several times higher than the 10% monomer situation. Also, the increase of the grafting level seems to occur much more rapidly. However, the maximum value of the carboxylic acid group content (or degree of grafting) is almost the same as it is in the presence of a 10% solution of methacrylic acid.

The above explanations are to a great extent speculative, and a more detailed study should be considered as necessary to establish the mechanism of the phenomena observed.

Ion-Exchange Properties of Poly(ethylene-*g*-co-Methacrylic Acid)

It was thought that low molar mass hydrophilic branches attached to the hydrophobic backbone would provide optimal efficiency of the ion-exchange properties of the resultant copolymer composite. Ion-exchange could then take place at as many sites as possible, for a given percentage of grafted monomer. Having long polymer chains attached to a limited number of sites is not desirable for ion exchange. This is because they would minimize the efficient use of monomer, giving far less potential for ion exchange to occur. By introducing carboxylic acid groups via methacrylic acid, potential cation exchange properties are imparted to the substrate as well as potential chelating ligands derived from these groups. The efficiency of this system is a function of the number of stable chemical bonds formed in the grafted copolymer and their subsequent ability to exchange ions. If the copolymer contains stable chemical bonds after exchanging with metal cations [e.g., Fe(III) ions], it should be possible to recycle (i.e., regenerate) the substrate and perform numerous ion exchange cycles without subsequent loss in exchanging efficiency. Furthermore, methacrylic acid has similar behavior to acetic acid, functioning better at pH 6 or higher. It is a weak acid and the polyethylene-*g*-co-methacrylic acid system should be useful for compounds sensitive to high hydrogen-ion concentrations.

Assessment of the ion exchange efficiency towards Fe(III) ions, related to the number of active sites present in the exchange substrate, is the main purpose of this part of the work. It offers a useful transition stage towards the study of other possible areas of application of polyethylene-*g*-co-methacrylic acid systems (e.g., enzyme immobilization).

Ion-Exchange Performance of Samples Irradiated in Air and under Vacuum in the Presence of 10–20% Methacrylic Acid Aqueous Solutions

The number of milligram equivalents of Fe(III) ions passed through the ion-exchange column, corresponding to the point $c/c_0 = 0.5$ (c_0 is the initial

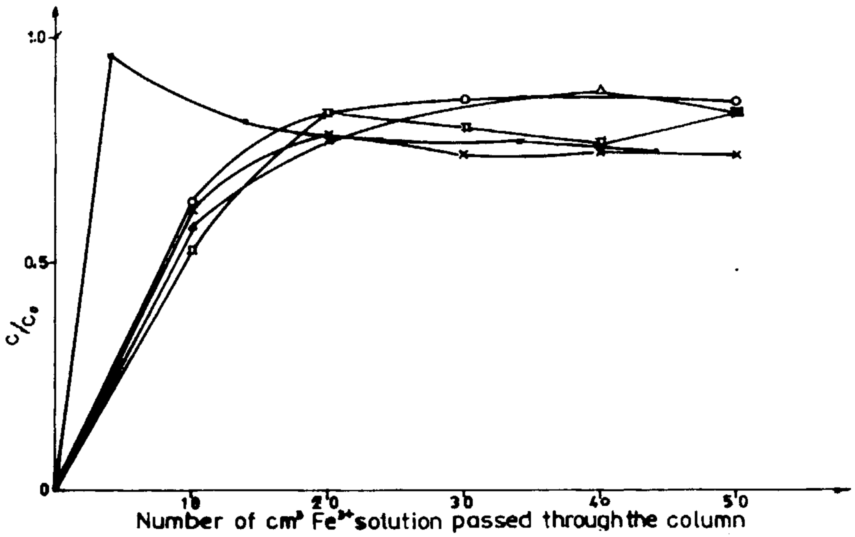

Fig. 6. Iron exchange performance. Variation in C/Co (see text) with variation in the volume of Fe(III) solution passed through a column. (●) blank, 0% grafting; (○) [—COOH] 0.84 meq g^{-1}; (×) 2.61 meq g^{-1}; (△) 3.36 meq g^{-1}; (□) 3.60 meq g^{-1}.

Fe(III) ion concentration, c is the current concentration of Fe(III) ions) in the graphs [c/c_0 vs. number of cm^3 of Fe(III) ions passed] was adopted as an approximate measure for the ion-exchange capacity of substrate towards Fe(III) ions. Polyethylene irradiated in air for 1400 min in the presence of 10% methanolic solution of methacrylic acid (0% degree of grafting) has been chosen in all cases as a blank. The amount of Fe(III) ions removed by washing with 1M HCl was easily calculated from the absorbance at 304 nm of the corresponding "acid flush" solutions. The results obtained have been summarized in Figures 6 and 7, respectively.

The ion-exchange performance of the samples, irradiated in air in the presence of a 20% aqueous solution of methacrylic acid, has been estimated in a similar manner.

Figures 8 and 9 indicate the efficiency of the cation exchange/absorption process and the column "cleaning" process respectively, both related to the carboxylic acid group content (i.e., the degree of grafting).

The results, associated with the ion-exchange performance of polyethylene-*g*-co-methacrylic acid grafted polymers, prepared by γ-irradiation in aqueous solutions may be considered, as follows:

(a) Some correlation exists between the carboxylic acid group content (i.e., degree of grafting) and the absorption/ion-exchange efficiency towards Fe(III) ions. Generally, samples with higher carboxylic acid group content indicate higher ion-exchange capacity towards Fe(III) ions (Fig. 8). The corresponding dependences seem to be complicated, since various factors contribute to the whole process (e.g., diffusion phenomena associated with the hydrodynamics of the system, uniformity of particles size, column packing, structure of the substrate at different levels of grafting, etc.).

(b) Generally, samples irradiated under vacuum seem to possess higher ion-exchange/absorption capacity. This is particularly true with grafting

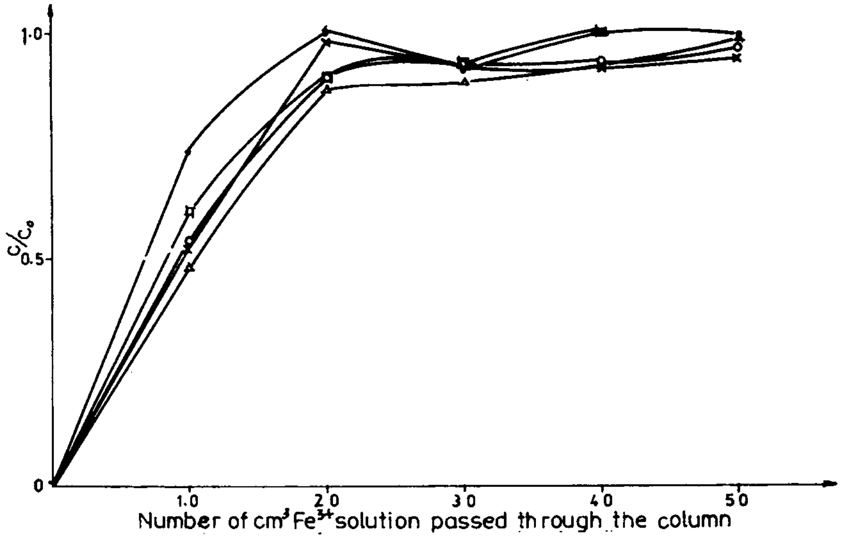

Fig. 7. Iron exchange performance of samples prepared by irradiation under vacuum. Variation in C/Co (see text) with variation in the volume of Fe(III) solution passed through a column. (●) [—COOH], 2.2 meq g^{-1}; (○) 2.61 meq g^{-1}; (□) 2.89 meq g^{-1}; (×) 3.28 meq g^{-1}; (△) 3.66 meq g^{-1}.

levels over 30% (carboxylic acid group content of more than 2.60 meq/g). The corresponding increase of the ion-exchange capacity vs. carboxylic acid group content appears to be sharper than with the samples irradiated in air.

(c) Only part of the Fe(III) ions retained by the grafted copolymers can be removed by 1*M* HCl (Fig. 9). More concentrated hydrochloric acid solutions

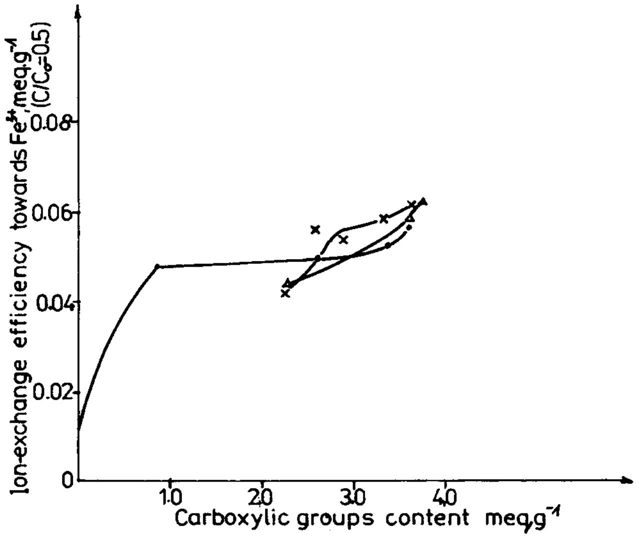

Fig. 8. Variation in the iron exchange efficiency with variation in the carboxylic acid group content for copolymer assemblies: (●) irradiation in air, 10% MAA in water; (×) irradiation under vacuum, 10% MAA in water; (△) irradiation in air, 20% MAA in water.

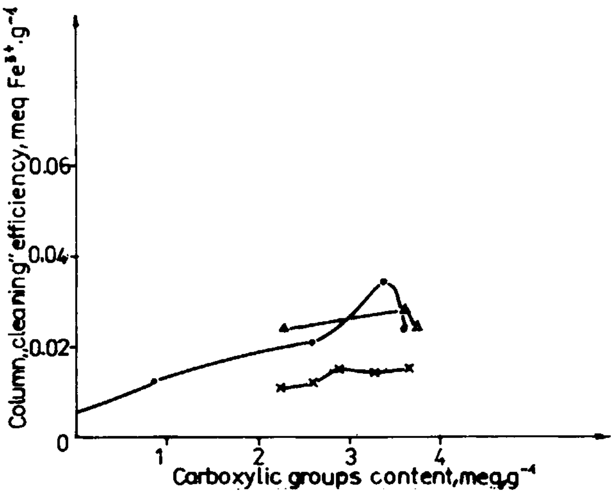

Fig. 9. Variation in the column cleaning efficiency ((removal of Fe(III) ions), meq Fe(III) g^{-1} copolymer) with variation in the carboxylic acid group content of the copolymers prepared by irradiation: (●) in air (10% MAA in water); (×) vacuum (10% MAA in water); (△) in air (20% MAA in water).

are considered to be necessary for removal of all Fe(III) ions absorbed (column "cleaning"). Samples irradiated under vacuum are less efficient in this respect than those irradiated in air. It may be assumed that polyethylene-*g*-co-methacrylic acid polymers prepared under vacuum possess a structure which is slightly different from that of samples prepared in air. Oxygen is supposed to contribute considerably to a formation of functional groups other than the carboxylic acid group (e.g., hydroperoxides, etc.), thus creating more "irregularity" in the strength of the interaction with Fe(III) ions. Any attendant carboxylic acid groups could act as chelating ligands towards Fe(III) ions with the formation of the corresponding strong chemical bonds. Therefore, Fe(III) ions retained by samples irradiated under vacuum are more difficult to "flush off" with 1*M* HCl. This assumption has been supported by the sharper increase in the ion-exchange capacity towards Fe(III) ions as the carboxylic group content increases for samples irradiated *in vacuo* as compared to those prepared in air (Fig. 8).

(d) Generally, samples prepared under longer irradiation times seem to possess better ion-exchange performance. The maximum values of the number of milligram equivalents of Fe(III) ions removed by 1*M* HCl correspond to the longest irradiation times applied (but not always to the highest —COOH content). It is difficult to find a satisfactory explanation of this phenomenon, although one possible reason is believed to involve degradation which presumably facilitates Fe(III) ion removal.

Ion-Exchange Performance of the Recycled Substrates

Although only a part of Fe(III) ions absorbed were found to be removed by 1*M* HCl, some experiments were performed with the samples previously subjected to ion-exchange/regeneration cycles. More concentrated Fe(III) solutions were applied. A summary of the results obtained which are associ-

TABLE I
Ion Exchange Performance of the Recycled Samples.
Copolymers from Samples Irradiated in Air[a]

10% Aqueous solution of MAA					20% Aqueous solution of MAA				
Irradiation time (min)	Degree of grafting (%)	—COOH content (meq/g)	Fe^{3+} ($c = 0.5$) c_0 (meq)	Fe^{3+} removed (meq)	Irradiation time (min)	Degree of grafting (%)	—COOH content (meq/g)	Fe^{3+} ($c = 0.5$) c_0 (meq)	Fe^{3+} removed (meq)
Blank	0.0	0.00	0.080	0.012	460	—	2.26	0.085	0.013
978	3.1	0.84	0.083	0.011	954	—	3.73	0.104	0.038
1511	31.6	2.60	0.084	0.028	5514	—	3.60	0.110	0.039
2684	47.5	3.60	0.086	0.032					
4140	43.7	3.36	0.087	0.043					

[a] Initial Fe^{3+} concentration 3.83×10^{-3}–4.07×10^{-3} mol dm^{-3}.

ated with the ion-exchange efficiency of the recycled substrates towards Fe(III) ions is shown in Table I.

The results are presented in tabular form only. It is difficult to judge the development of changes to the possible structure of the copolymers. The dependence between carboxylic acid group content and the exchange/absorption capacity towards Fe(III) ions was found to be much more regular, particularly with samples irradiated in air as compared to the corresponding "fresh" samples. One reason is believed to involve the complexity of the structure of copolymers prepared by irradiation in air as well as the fact that these samples contain Fe(III) ions retained during the previous cycle. Obviously, the copolymers prepared by γ-irradiation of polyethylene, in the presence of aqueous methacrylic acid solutions, contain stable chemical bonds, because no subsequent loss in exchanging capacity towards Fe(III) ions has been observed. The absorption efficiency even increases when more concentrated Fe(III) solutions are applied. Again the amount of Fe(III) ions removed by washing the copolymers, obtained under vacuum with 1*M* HCl, is less than that of "in air" irradiated samples, presumably because of the stronger —COOH/Fe(III) bonds formed in the former (Tables I and II).

TABLE II
Ion Exchange Performance of the Recycled Samples. Copolymers from Samples Irradiated under Vacuum, 10% Aqueous Solution MAA[a]

Irradiation time (min)	Degree of grafting (%)	—COOH content (meq/g)	Fe^{3+} ($c = 0.5$) c_0 (meq)	Fe^{3+} removed (meq)
990	28.3	2.26	0.081	0.013
1316	31.9	2.61	0.083	0.017
2823	44.6	3.28	0.089	0.015
4344	49.1	3.66	0.094	0.017
4140	43.7	3.36	0.087	0.013

[a] Initial Fe^{3+} concentration 3.83×10^{-3}–4.07×10^{-3} mol dm^{-3}.

Copolymeric materials of the types developed in this work have application in a variety of areas. Reasoned exploitation of these copolymeric products is dependent on the acquisition of understanding regarding their physical properties. Studies are currently being undertaken which should provide this much-needed information.

We gratefully acknowledge the support of our work provided by the following: The International Atomic Energy Agency, Vienna, Austria; The Institute of Chemical Sciences, Burgas, Bulgaria and the British Council, London, U.K.

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Received July 18, 1987
Accepted July 28, 1987