

# Grafting of Acrylic Acid with Diethyleneglycol-Dimethacrylate onto Radioperoxided Polyethylene

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## SYNOPSIS

Acrylic acid and diethyleneglycol-dimethacrylate are grafted onto 25  $\mu\text{m}$  low-density and 130  $\mu\text{m}$  high-density polyethylene previously peroxidized by irradiation in air under the electron beams of an accelerator. Mohr's salt and methylene blue are used to prevent monomer homopolymerization. It is shown that sulfuric acid and Mohr's salt, respectively, enhance acrylic acid and diethylene glycol-dimethacrylate grafting. When they are combined, the influence of the monomer content on grafting kinetics is studied. Monomer content is determined by exchange capacity measurements. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

In recent years, graft copolymerization has received considerable attention, to produce synthetic polymeric membranes that play an important role today for practical application in various separation processes.<sup>1</sup>

It is difficult to optimize the properties of ion-exchange membranes because the parameters determining the different properties are often acting contrarily. For instance, a high degree of cross-linking improves the mechanical properties of the membrane but it also increases its electrical resistance. A high concentration of fixed ionic charges in the membrane matrix leads to a low electrical resistance but, in general, causes a high degree of swelling.

Divinylbenzene is the most used polyfunctional monomer in cation-exchange membranes synthesis; the preparation method of this membrane is the graft polymerization of styrene and divinylbenzene onto polyethylene and subsequent sulfonation and amination.

Garnett et al.<sup>2,3</sup> showed that in copolymerization of styrene onto polyethylene films the presence of divinylbenzene and trimethylolpropane triacrylate as additives significantly enhanced the grafting yield at certain monomer concentrations, particularly in

the regions where the Trommsdorff peak is observed. They noted a synergetic effect when sulfuric acid and divinylbenzene were combined as additives.

Grafting of acrylic acid onto radiation-peroxidized polyethylene has been studied by numerous authors.<sup>4-6</sup> It is accepted, on the one hand, that irradiation in air leads to diperoxide radicals<sup>7</sup> and, on the other hand, that metal salts can inhibit monomer homopolymerization and that the grafting step is a diffusion-controlled process.

The aim of the work was to synthesize cation-exchange membranes that have good selectivity and correct resistance by grafting acrylic acid in presence of a polyfunctional monomer (diethylene glycol-dimethacrylate). The grafting reaction of the two monomers is discussed in this paper.

## EXPERIMENTAL

### Materials

Low-density polyethylene of 25  $\mu\text{m}$  thickness (British Petroleum Co., ref. LL101AA) and high-density polyethylene of 130  $\mu\text{m}$  thickness (FINA Co., ref. D320) were employed as trunk polymer. Technical-grade acrylic acid (Prolabo Chemicals Co.) and diethylene glycol-dimethacrylate (Rhöm Chemicals Co.), containing hydroquinone monomethyl ether as stabilizer, were used without any purification or removal of hydroquinone. Fydolor<sup>8</sup> showed that hy-

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droquinone has no effect on the obtained grafting of acrylic acid.

Mohr's salt and methylene blue (Flucka Chemicals Co.) were selected as homopolymerization inhibitors and used as received.

### Irradiation

The films are irradiated in air by electron beams of an accelerator (Radiation Dynamics Inc.) under a beam of 1.5 MeV and a current of 10 mA. The selected dose was approximately 7 Mrad.

### Grafting

The preirradiated films ( $3 \times 4$  cm) and the monomers solution prepared at given concentrations of acrylic acid (AA), diethylene glycol-dimethacrylate (DEGDM), and inhibitor are introduced into a glass reactor. The used solvent is a mixture of water and methanol. Methanol is necessary to obtain a ho-

mogeneous grafting solution, DEGDM being not water-soluble. At the end of the grafting reaction, the obtained grafting solution is clear. The formed homopolymers are solubilized in the water-methanol solution. After being deaerated by nitrogen bubbling, the reactor is immersed in the thermostat during grafting time. Grafted films are then taken out from the monomer solution and washed with water and methanol. The presence of water in the washing solution improves both the membrane swelling and the homopolymer extraction. After drying under vacuum, they are weighed; the grafting yield is determined by the increase of weight based on the initial film weight.

In the case of AA + DEGDM cograftering, the measurement of the exchange capacity (i.e., the number of moles of carboxylic exchange sites per mass unit of dry film) allows determination of the proportion of the two monomers grafted in the polyethylene film. As the DEGDM monomer cannot give carboxylic exchange sites (experimentally checked),

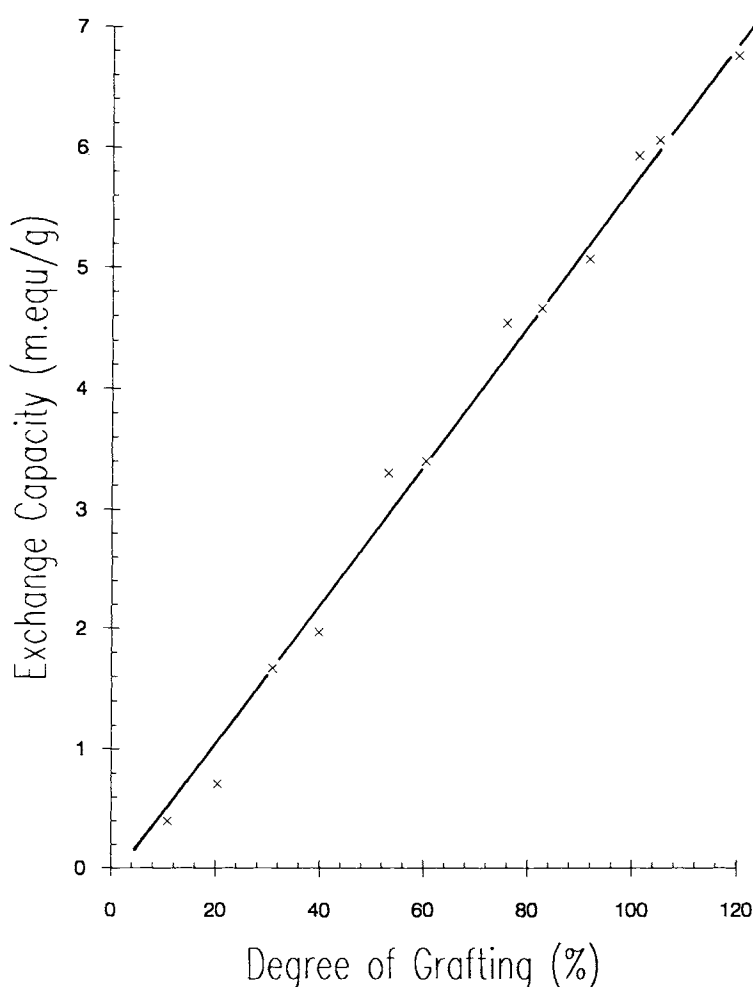
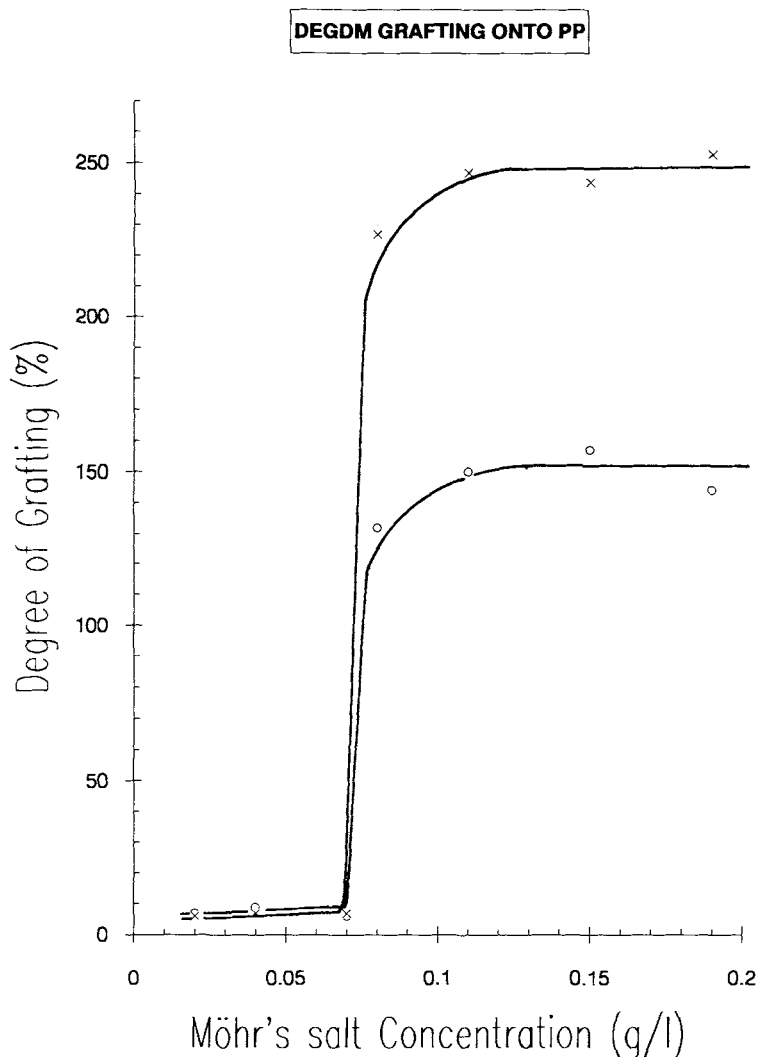


Figure 1 Exchange capacity of AA grafting LDPE.



**Figure 2** Influence of Möhr's salt concentration on DEGDM grafting onto microporous polypropylene; grafting solution: DEGDM: 22 vol %, methanol: 60 vol %, H<sub>2</sub>O: 18 vol %; grafting temperature: 65°C; dose: (x) 2 Mrad; (o) 1 Mrad.

the knowledge, on the one hand, of the exchange capacity as a function of the grafting yield in the case where only AA is grafted (Fig. 1) and, on the other hand, of the AA + DEGDM grafting yield, allow calculation of this proportion. The exchange capacity is measured following the process defined by the "Membranes Club" (E.D.F.<sup>†</sup>).

## RESULTS AND DISCUSSION

Grafting is achieved on preirradiated films before conservation at -18°C during 4 months. It is well known that during the irradiation different kinds of

radicals may be obtained (free, diperoxidic, or hydroperoxidic radicals). Taking into account the short life of free radicals, it can be supposed that these radicals react either together or with oxygen

**Table I** Influence of the Monomer Content on the Grafting Yield

DEGDM (Vol %)	AA (Vol %)	Grafting Yield (%)
2	20	6
4	18	30
6	16	180
8	14	280

<sup>†</sup> Measurements of the exchange capacity and of the conductivity of ion-exchange membranes. "Reports of Membranes Club," Electricity of France, D.E.R., 1983.

Grafting solution: Möhr's salt: 1.8 g/L; methylene blue: 0.36 g/L; methanol: 50 vol %; H<sub>2</sub>O: 28 vol %; (AA + DEGDM): 22 vol %; grafting temperature: 65°C.

held back in the macromolecular network. Consequently, one can assume that the film reactivity is only due to the peroxydic radicals.

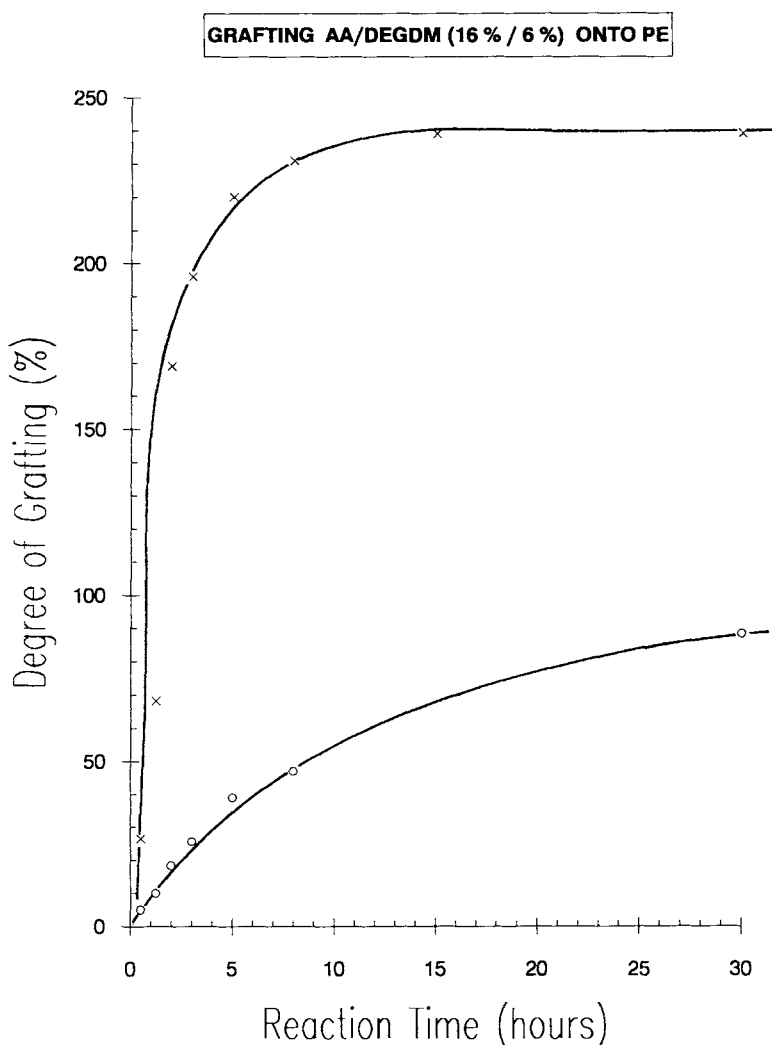
Grafting of AA or DEGDM alone has been achieved on low-density polyethylene (LDPE), of thickness 25  $\mu\text{m}$ , while grafting of AA + DEGDM has been achieved both on 25  $\mu\text{m}$  (LDPE) and on 130  $\mu\text{m}$  high-density polyethylene (HDPE).

### Acrylic Acid Grafting

First, grafting of AA onto preirradiated polyethylene films has been carried out at temperatures ranging from 50 to 70°C in the case where no sulfuric acid

is used. The films obtained are not homogeneous and the grafting yields are very low. The immersion of these grafted films in a basic solution leads to the generation of some areas more swollen than others. It is known that the presence of the crystalline zones may prevent the monomer penetration. Chapiro<sup>9</sup> showed that at temperatures lower than 80°C the grafting of acrylonitrile and of methyl methacrylate onto polyethylene films occurred mainly in amorphous regions while crystalline zones were not modified.

If sulfuric acid is introduced into the grafting solution, both the homogeneity and the grafting yields are enhanced. At the end of grafting, the solution is more viscous than without sulfuric acid.

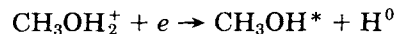


**Figure 3** (a) Grafting yield time curves: (x) 25  $\mu\text{m}$  LDPE; (o) 130  $\mu\text{m}$  HDPE. (b) Determination of monomer content of grafted LDPE films: (o) DEGDM content; (x) AA content. Grafting solution: AA: 16 vol %; DEGDM: 6 vol %; methanol: 50 vol %; H<sub>2</sub>O: 28 vol %; Mohr's salt: 0.9 g/L; methylene blue: 0.7 g/L; grafting temperature: 65°C; dose: 7 Mrad.

It is known that during the irradiation polymeric diperoxides are principally generated; their decomposition should lead to grafted copolymer. But the monomer homopolymerization is also observed, due either to hydroperoxidic radicals or to active sites formed by chain transfer of growing polymer radicals to monomers or to solvent. This phenomenon is enhanced in the presence of sulfuric acid. For this reason, the addition of metallic salts or of methylene blue is necessary to inhibit this secondary reaction.

It is quite difficult to be exactly precise about the role of sulfuric acid. According to Garnett et al.,<sup>2,3</sup> the acid effect in radiation copolymerization may be related to general acid effects observed in the radiation chemistry of simple molecules such as methanol. In the radiolysis of methanol, addition of acid increases the  $G(H_2)$  (radiolytic hydrogen yield), pre-

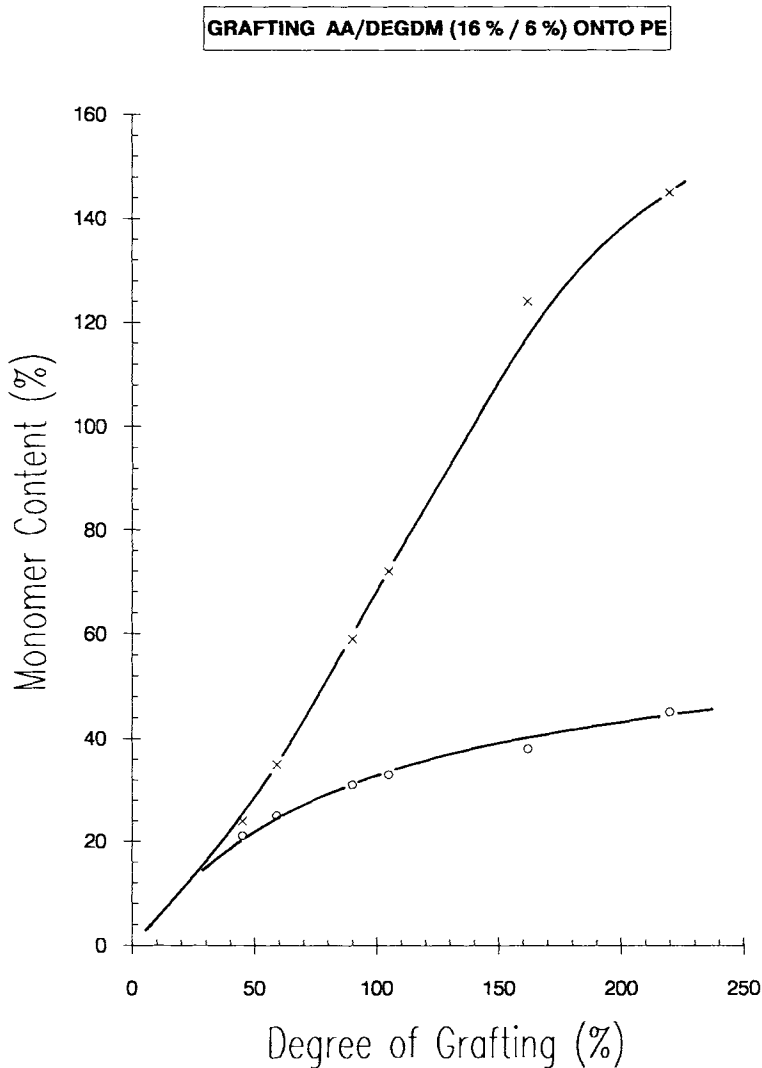
sumably by increasing  $G(H)$  through interaction of the secondary electron from the radiolysis with the mineral acid:



But in a postirradiation grafting, the solvent is never in contact with irradiation power; this explanation cannot be valid.

In fact, sulfuric acid would play a double role:

- (i) It would favor the AA polymerization in the solution as well as in the polyethylene film.
- (ii) It would favor the accessibility of the reactive sites present in the crystalline zones and, consequently, would increase the grafting homogeneity.



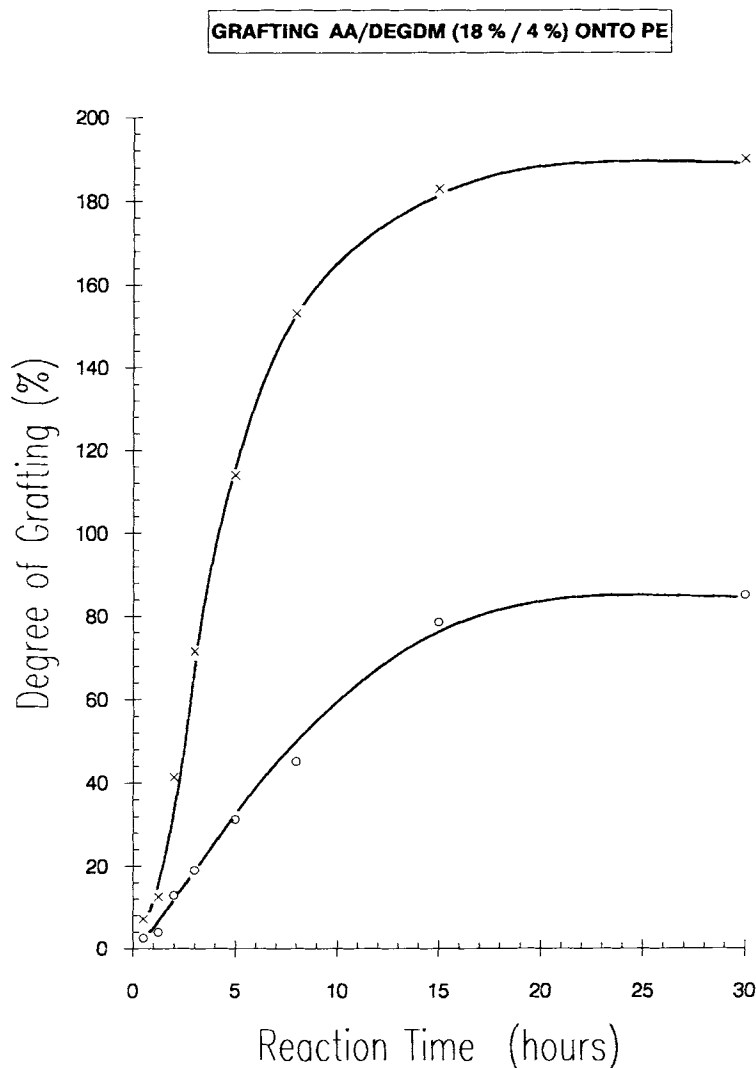
**Figure 3** (continued from the previous page)

Chapiro<sup>9</sup> showed that these crystallites melt about 115°C for the dry polymer, this melting temperature being decreased in the presence of solvent (approximately 90–95°C). The more important was the swelling, the more important was the melting temperature decrease. In our case, all this was going on as the sulfuric acid still decreased the melting temperature of the polyethylene crystallites. The increase of chain length of the grafted polyacrylic acid, which is facilitated in the presence of sulfuric acid, improves the film swelling and makes easier the accessibility of the reactive sites present in these crystalline zones.

### Diethylene Glycol–Dimethacrylate Grafting

It is very difficult to graft DEGDM alone onto polyethylene. The obtained yields never go above 25%. These yields are obtained in presence of Mohr's salt. Without this salt, the grafting is impossible even at high temperature (80–90°C) in presence of sulfuric acid where only the polymerization of monomer is observed.

For grafting yields ranging from 15 to 25%, the grafting is obtained only on the polyethylene surface. As this surface does not swell in the grafting solution, DEGDM cannot reach peroxydic sites located



**Figure 4** (a) Grafting yield time curves: (x) 25 μm LDPE; (o) 130 μm HDPE. (b) Determination of monomer content of grafted LDPE films: (o) DEGDM content; (x) AA content. Grafting solution: AA: 18 vol %; DEGDM: 4 vol %; methanol: 50 vol %; H<sub>2</sub>O: 28 vol %; Mohr's salt: 0.9 g/L; methylene blue: 0.3 g/L; grafting temperature: 65°C; dose: 7 Mrad.

more deeply within the film. To confirm the influence of Mohr's salt, DEGDM grafting has been carried out onto a microporous film (polypropylene from Cellanese Co., ref. 2502). For Mohr's salt concentration higher than 0.8 g/L, 150 and 250% grafting yields have, respectively, been obtained for 1 and 2 Mrad preirradiated films (Fig. 2). Under this Mohr's salt concentration, no significant grafting has been observed. In the same way, other metallic salts (sulfate and chloride of iron and copper) or ammonium sulfate in concentrations ranging from  $10^{-7}$  to  $10^{-1}$  g L $^{-1}$  had been used instead of Mohr' salt. With these components, no grafting was obtained on both high-density polyethylene and microporous polypropylene.

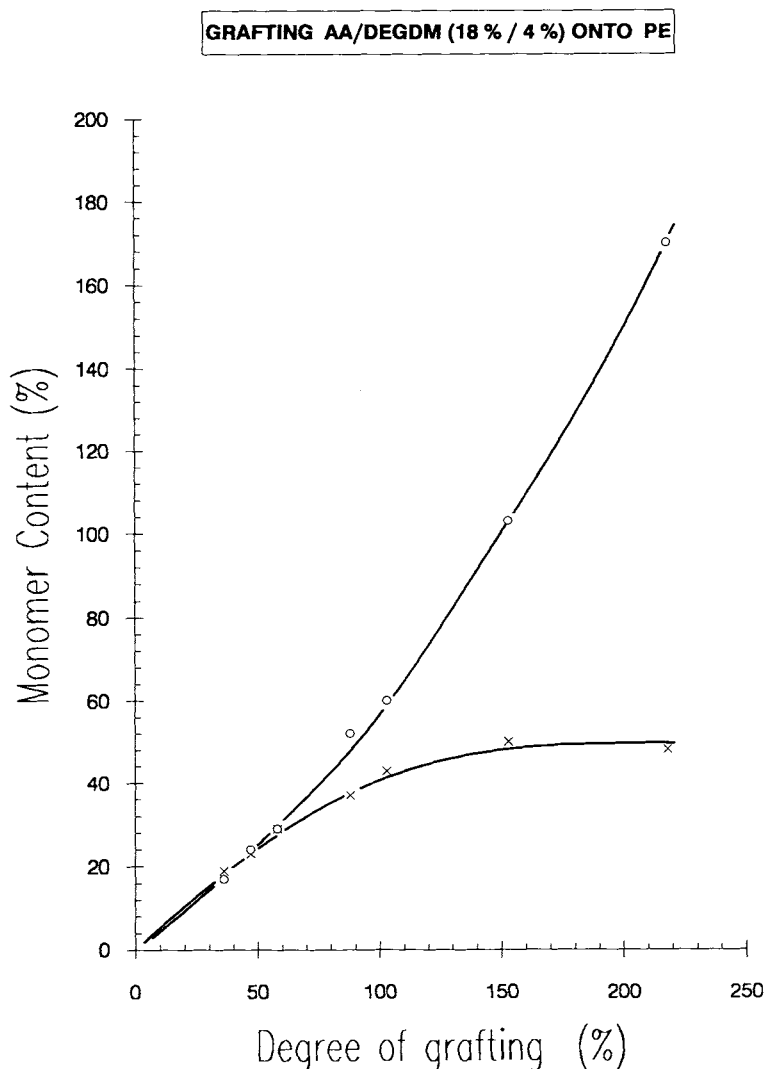
At this time, no logical explanation about the influence of Mohr's salt can be given, but the exper-

iments would lead to the assertion that its presence is necessary to the beginning of the grafting process.

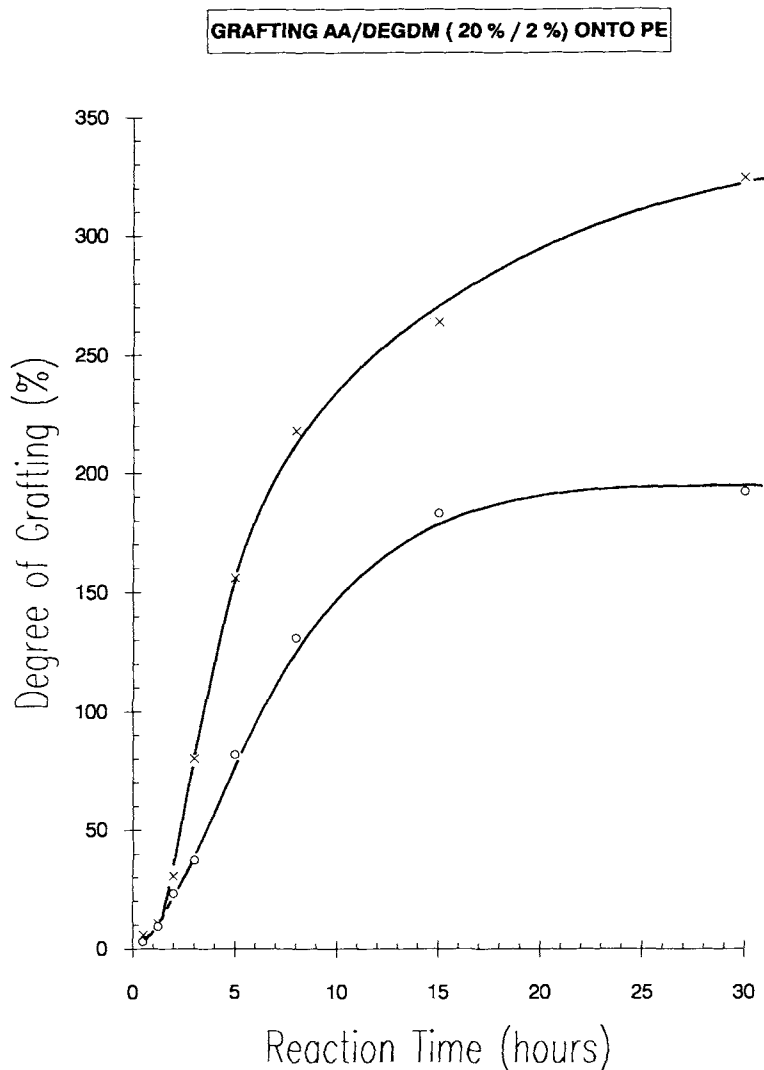
#### Acrylic Acid and Diethylene Glycol-Dimethacrylate Cograftering

In respect of the composition of the grafting solution, four compositions in monomers have been studied: (AA = 20%, DEGDM = 2%), (18%, 4%), (16%, 6%), and (14%, 8%). The amount of the monomers represents 22% volume of the grafting solution.

Table I shows that, for a same composition of the grafting solution (inhibitors, solvents), an increase of the DEGDM content increases the grafting yield. For a DEGDM content lower than 3%, the obtained grafting yields remain lower than 20%. To reach



**Figure 4** (continued from the previous page)



**Figure 5** (a) Grafting yield time curves: (x) 25  $\mu\text{m}$  LDPE; (o) 130  $\mu\text{m}$  HDPE. (b) Determination of monomer content of grafted LDPE films: (o) DEGDM content; (x) AA content. Grafting solution: AA: 20 vol %; DEGDM: 2 vol %; methanol: 50 vol %;  $\text{H}_2\text{O}$ : 28 vol %; Mohr's salt: 0.9 g/L; methylene blue: 0.4 g/L; sulfuric acid: 0.05 mol/L; grafting temperature: 65°C; dose: 7 Mrad.

higher values, the presence of sulfuric acid is necessary.

It must be pointed out that films grafted with AA + DEGDM seem more homogeneous than those grafted only with AA. An IR analysis focused on the intensity of the  $\text{C}=\text{O}$  absorption band carried out in different regions of the grafted films confirms this visual observation.

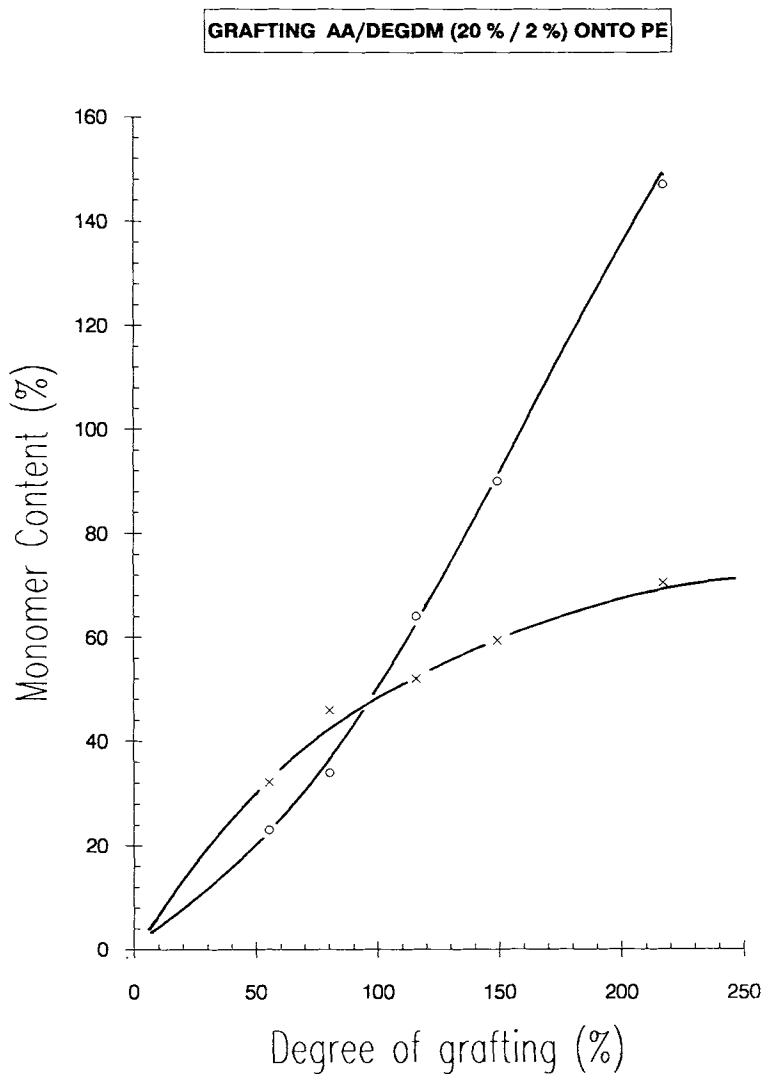
Grafting kinetics [Figs. 3(a), 4(a), and 5(a)] have been achieved on 25 and 130  $\mu\text{m}$ -thickness polyethylene films with three different monomer compositions. The results, collected in Table II,

show that, whatever is the proportion of the two monomers, both the grafting rate and the final yield are lower for the higher thickness film (130  $\mu\text{m}$ ).

The exchange capacity measurements allow the grafting of the monomers to be followed as a function of time [Figs. 3(b), 4(b), and 5(b)]. The AA content on the film does not vary after 5 h. However, the DEGDM content continues to vary until the saturation grafting yield.

An effective grafting within the polymer film is obtained only if the polymer film swells in the grafting solution. As has been seen previously, DEGDM





**Figure 5** (continued from the previous page)

grafting occurs only on the film surface without reaching peroxidic sites located more deeply. Consequently, only AA grafting is responsible for both

the film swelling and the diffusion of the two monomers. DEGDM is a polyfunctional monomer with a double reactivity. When it is grafted, it can cross-

**Table II** Grafting Rate and Final Yield for Polyethylene Films Grafted with the Association of (AA + DEGDM)

	Thickness ( $\mu\text{m}$ )					
	25		130			
Monomers content AA/DEGDM (% vol.)	20/2	18/4	16/6	20/2	18/4	16/6
Final grafting yield (% wt)	310	190	240	180	80	60
Grafting rate (% h)	32	25	91	17	7	8

link with one of its functions and reacts with one of the monomers present in the solution with its other. This possibility may explain the increasing rates observed during the increase of DEGDM content of the solution onto 25  $\mu\text{m}$ -thickness LDPE. This phenomenon is less accentuated with 130  $\mu\text{m}$  HDPE. The greater the thickness and the crystallinity yield, the lower the monomer diffusion. The grafting penetration becomes difficult when the film is weakly grafted with AA.

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