

Grafting to Irradiated Polyethylene and Polypropylene by Means of Redox Polymerization

Chapiro¹ found that polyethylene is peroxidized by high energy irradiation in the presence of air. These peroxide centers may initiate a graft polymerization. This type of polymerization proceeds at a reasonable rate at a temperature of about 70°C. with such monomers as styrene, methyl methacrylate, and acrylonitrile.

We have now found that grafting takes place rapidly at room temperature if a redox system, viz., ferrous acetylacetonate (FeA_2), ferric acetylacetonate (FeA_3), plus benzoin or cobaltous acetylacetonate (CoA_2), is applied.

The system FeA_3 -benzoin has been used earlier by Kern² in bulk polymerizations of various monomers initiated by benzoylperoxide and, after our work was finished, we found that the use of similar accelerating systems was also cited in a recent patent³ (grafting of monomers on polystyrene hydroperoxide).

The above accelerators dissolve in monomers, such as styrene and methyl methacrylate, and the procedure simply consists of immersing irradiated polyethylene or polypropylene film in such a solution and allowing it to stand at room temperature for some time.

Apparently the accelerator diffuses into the film together with the monomer, thus making possible redox initiation. The reaction is not general, and quite a number of potential accelerators proved to be inactive: dimethylaniline, phenylhydrazine, toluenesulfonic acid, benzoin, methyl ethyl ketone, cobaltous naphthenate, cupric acetylacetonate, ferrous and cobaltous compounds of salicylaldehyde, of 8-hydroxyquinoline, and of glycine, and the cupric compound of glycine. Mild acceleration has, however, been observed with tetraethylenepentamine.

Experimental Details

Irradiation. Polyethylene and polypropylene films were exposed to 2 m.e.v. electrons from a Van der Graaf accelerator, under conditions allowing free access of atmospheric oxygen. The radiation dose was accumulated at 1 Mrad per pass, intervals between passes being in the range of 4-30 min.

Grafting. Weighed pieces of irradiated film were immersed in a measured volume of monomer or a solution of accelerator in monomer. Oxygen was removed by degassing on a high vacuum line by the freeze-thaw method. Other experiments were carried out under nitrogen (sealed tubes) or in air (open tubes). With CoA_2 , extremely dry conditions had to be employed to avoid transformation to $\text{CoA}_2 \cdot 2\text{H}_2\text{O}$. The extent of grafting* was determined gravimetrically, after washing off any adhering homopolymer with cold styrene (Tables I and II) or ethyl acetate (Fig. 1). For polypropylene, homopolymer extraction values, obtained by extraction of the film with chloroform, can be derived from Table II. For polyethylene these ex-

* In principle, an additional polymerization during the procedure of drying is possible. Actually, in the beginning of the period of drying the film still contains initiator, accelerator, and some absorbed monomer. However, in view of the rapid evaporation of monomer from a thin film, the additional polymerization is considered to be slight as compared with the total grafting.

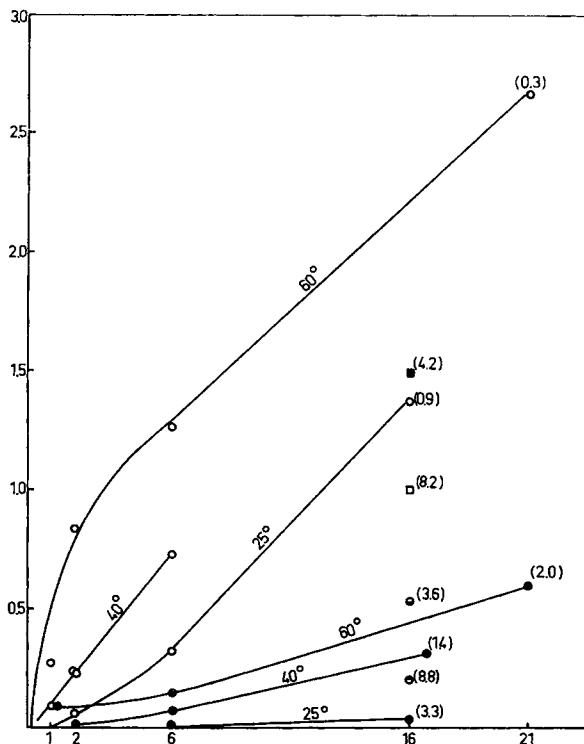


Fig. 1. Grafting of styrene to irradiated polyethylene film (15 Mr): (○) in presence of 0.2% FeA_2 in vacuo; (●) control (no FeA_2) in vacuo; (■) in nitrogen at 60°C., 0.2% FeA_2 ; (□) in air at 60°C., 0.2% FeA_2 ; (⊖) in nitrogen at 60°C. (control); (⊖) in air at 60°C. (control). Figures in parenthesis give the ratio: g. homopolymer/g. deposited polystyrene. Abscissa: reaction time, hr. Ordinate: grafting yield, g. polystyrene deposited/g. polyethylene.

traction values are about 20% of the total amount of polymer grafted. Homopolymer (in the solution) was determined by precipitation of the liquid phase with methanol, centrifugation, and drying to constant weight.

Ferric acetylacetonate was prepared according to Hantzsch and Desch.⁴ Ferrous acetylacetonate was prepared according to Emmert and Jarczyński,⁵ and was purified by sublimation at 145-150°C. in vacuo. The melting point (evacuated tube) of the red-brown crystals was 201°C. Cobaltous acetylacetonate was prepared from $\text{Co}(\text{NO}_3)_2$, acetylacetone, and piperidine in an analogous manner. The hydrate was recrystallized from ethanol and dehydrated *in vacuo* at 45°C.

Results

The results of exploratory tests have been assembled in Tables I and II, from which it is seen that facile grafting to electron-irradiated polyethylene occurs at normal temperatures with styrene, methyl methacrylate, and butyl methacrylate. Despite very careful purification of the monomers, we have not succeeded in grafting acrylonitrile or vinyl carbazole under these conditions. Unexpectedly, the extent of grafting was rather less with polypropylene than with polyethylene film. The exploratory work also showed that the redox grafting reaction is not inhibited

TABLE I
 Grafting on Irradiated Polyethylene

Ra- dia- tion dose, Mrad	Accelerator system	Monomer	Poly- meriza- tion temp., °C.	Weight in- crease, % ^a
4	0.2% FeA ₃ + 0.4% benzoin	Styrene	~20	130
2	0.2% FeA ₃ + 0.4% benzoin	Styrene	~20	120
4	0.1% FeA ₂	Styrene	~20	150
2	0.1% FeA ₂	Styrene	~20	40
4	0.2% FeA ₂	Styrene ^b	~20	200
2	0.2% FeA ₂	Styrene ^b	~20	140
3	0.2% FeA ₃ + 0.4% benzoin	Methyl methacrylate	40	420
3	0.2% FeA ₃ + 0.4% benzoin	Butyl methacrylate	40	410
4	0.2% CoA ₂	Styrene	~20	100
3	0.2% CoA ₂	Methyl methacrylate	40	640
3	0.2% CoA ₂	Butyl methacrylate	40	390

^a After 6 hr.

^b In open tubes; all other tests done in vacuum.

but only retarded by the presence of air, hydroquinone, or 1,4-diaminoanthraquinone and that the reaction was greatly accelerated by a small rise in temperature.

In studying the time dependence of the reaction, the grafting of redistilled styrene to polyethylene (Alkathene grade 7, 0.005 in., 15 Mrad) was compared in the presence and absence of ferrous acetylacetonate (0.2% on styrene) at various temperatures. The results are shown in Figure 1, from which it is seen that the rate of grafting is considerably increased by the presence of FeA₂, the enhancement being most marked at the lower temperature. Lower yields occurred in both cases, when the experiments were carried out in the presence of nitrogen or in air. The principal effect of the presence of air, however, was the increase in polymer formation in the liquid phase. Thus the homopolymer yield, expressed as grams of homopolymer/grams deposited polystyrene, rises from 0.3 *in vacuo* at 60°C. to 4.2 in nitrogen and to 8.2 in air at the same temperature.

The grafted polyethylene films were examined by means

 TABLE II
 Grafting on Irradiated Polypropylene

Ra- dia- tion dose, Mrad	Accelerator system	Monomer	Poly- meriza- tion temp., °C.	Weight increase, %	
				Be- fore ex- trac- tion	After ex- trac- tion
3	0.2% FeA ₃ + 0.4% benzoin	Styrene	40	60	50
3	0.2% FeA ₃ + 0.4% benzoin	Methyl methacrylate	40	40	—
3	0.2% CoA ₂	Styrene	~20	130 ^a	100
3	0.2% CoA ₂	Methyl methacrylate	40	40	20
3	0.2% CoA ₂	Butyl methacrylate	~20	50	—

^a After 72 hr. *in vacuo*; all other tests after 6 hr. *in vacuo*.

of phase contrast microscopy and found to be substantially homogeneous.

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