

Electron Beam Irradiation Induced Grafting of Acrylonitrile to Polyethylene Powder

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Synopsis

This study focuses on the influence of various parameters on the post-irradiation grafting of acrylonitrile monomer to a low density polyethylene powder having an average particle size of 20 μm diameter. The type of radiation used was 0.8 MeV electrons with a dose rate of either 0.1 Mrad/min or 4.0 Mrad/min. Irradiations were carried out in vacuum, air, and dry oxygen environments at room temperature to total doses ranging from 1 Mrad to 15 Mrad. Several experimental techniques were used to investigate various interrelated aspects of both the graft copolymer product and the graft process, including infrared spectroscopy to measure percent graft, electron spin resonance to measure radical concentrations, scanning electron microscopy to investigate surface morphology, and differential scanning calorimetry to measure crystalline content. Comparisons of the percent graft determined from different probes were found to be consistent. The dose dependence of grafting exhibited a linear relationship below 8 Mrad. Initiation by both alkyl and peroxy radicals at 77°C was supported by results of decreased grafting with decreased temperature, increased dose rate, or vacuum irradiation. Decreased grafting after oxygen irradiation suggested a unique change in grafting mechanism. Higher grafting yields were found for quenched relative to annealed samples. The amount of extractable homopolymer formed was found to be $\sim 10\%$ at a dose of 10 Mrad and a dose rate of 4 Mrad/min.

INTRODUCTION

In order to modify the properties of polymeric materials or create new materials with specific properties various techniques have been used including polymer blending, copolymerization, and composite forming. Of these methods copolymerization is unique because the monomer units of two or more different polymers are chemically bonded together. Various types of copolymers with unique properties may be formed depending on the methods used and the specific monomers involved. Random copolymers usually exhibit properties which are intermediate between those of the specific homopolymers. The fact that graft copolymers contain long sequences of two different monomer units indicates that it should be possible to select polymer combinations to give highly specific properties which are characteristic of the homopolymers involved.

A number of methods have been used to prepare graft copolymers in the past three decades including both conventional chemical and radiation-chemical methods.¹⁻³ In either case graft copolymerization is usually initiated by creating active radical sites on existing polymer chains. The advantages of radiation-chemical methods are: (1) the ease of preparation as compared to conventional chemical methods, (2) the general applicability to a wide range of polymer combinations (due to the relatively unselective absorption of radiation in matter), and (3) the more efficient (and, thus, more economical), energy transfer provided by radiation compared to chemical methods requiring heat.

Of the various forms of ionizing radiation available (X-rays, beta rays, gamma rays, etc.), beta ray or electron beam radiation has several advantages. First, the development of high power, dependable, electron beam accelerators has made a wide range of dose rates on the order of 100–100,000 rad/s easily attainable, and the depth of electron penetration has been increased with accelerating voltages of up to 10 MeV. Second, the high dose rate and increased penetration depth, coupled with the energy efficiency of radiation use has made electron beam processing economically competitive and commercially appealing. Examples of the efficiency of electron beam processing include the vulcanization of rubber and the curing of acrylic coatings which, by conventional methods, require about 100 times the energy of the equivalent radiation process.⁴ The third advantage of electron beam radiation is the clean, simple, safe operating conditions, with no residual radioactivity. The use of electron beam radiation in industrial processes has become a rapidly expanding field. Important radiation processes currently in industrial use include: crosslinking of plastics for wire and cable insulation; curing of rubber for use in tires, sheets, and hoses; sterilization of medical disposable products, i.e., sutures, syringes, bandages; preparation of composites based on plastic and wood; degradation of polytetrafluoroethylene to a very fine powder for use in inks and lubrication; and lithography to produce electronic resists of high spatial resolution ($<0.2 \mu\text{m}$) for use in very large scale integrated (VLSI) circuits.^{5–7}

Over the past 25 years radiation grafting has been used to combine a variety of polymer systems by different groups of researchers, but, by far, the greatest amount of work done has been on grafting to polyethylene (PE) chains.^{3,8–10} Both high- and low-density PE samples have been studied, usually in the form of films, but, occasionally, PE pellets have been used. To date, only a small amount of work has been reported on grafting to PE powder, presumably due to the difficulties involved in handling powdered polymers.¹¹ Irradiated powders are highly electrostatic and accurate weight determinations of the amount of graft cannot be made easily.

Interest in powders stems from two areas. First, the high surface-to-volume ratio of small particles should have a strong influence on the radiation grafting process where diffusion has been reported to play a major role.^{3,12,13} Second, graft copolymers have been shown to play an important part in the improved properties of polymer blends.¹⁴ Small grafted particles could provide the compatibility required for improved blend properties from otherwise highly incompatible polymers.

The methods of achieving graft copolymerization using radiation include:

1. Simultaneous irradiation of the backbone polymer in the presence of the monomer.
2. Prior irradiation of the backbone polymer in the presence of oxygen and subsequent monomer grafting by polymeric peroxides.
3. Prior irradiation of the backbone polymer in vacuum and subsequent monomer grafting by trapped radicals.
4. Simultaneous irradiation of two polymers to cause intercrosslinking.

Although each method has its advantages and disadvantages, grafting on polymeric peroxides has several advantages of specific appeal to industrial production. In particular, the long lifetime of the peroxides and peroxy radicals (relative to the trapped polymeric radicals produced in vacuum irradiation) provides a long

shelf-life (~1 month) for irradiated materials. Also, the amount of homopolymer byproduct formed during peroxide grafting is very low compared to the amount formed in grafting method 1. The porous structure of PE which enhances the diffusion of oxygen throughout the polymer makes it particularly attractive for grafting based on radiation peroxidation.

Of the wide range of monomers grafted, styrene, acrylonitrile (AN), and methyl methacrylate have been the ones most often chosen, depending on the method of grafting employed and the specific monomer-polymer combination used. Other factors which have influenced the types of monomer-polymer combinations joined by grafting include the relative reactivities and radical formation during irradiation as measured by the G values (see next section) and the properties desired for the grafted polymer. The most extensive results are available for styrene grafting,^{3,9,14-20} and AN grafting^{3,9,21-26} by grafting methods 1 and 2 described above.

In this paper we report on the handling techniques and mechanism of radiation grafting AN onto fine powdered low-density PE to characterize the amount of graft in the copolymer and its structure as formed under various irradiation conditions. A variety of experimental probes were used to gain information about the grafted samples including infrared spectroscopy, electron spin resonance, scanning electron microscopy, and differential scanning calorimetry.

BACKGROUND THEORY OF RADIATION-INDUCED GRAFTING

The theory of radiation-induced grafting has received extensive treatment.^{1,3,9,27,28} The direct effect of ionizing radiation in materials is to produce active radical sites. A material's sensitivity to radiation ionization is reflected in its G value, which represents the number of radicals of a specific type (e.g., peroxy or allyl) produced in the material per 100 eV of energy absorbed. The G values of some selected polymers and monomer used in radiation grafting are given in Table I.

During the vacuum irradiation of polymers some of the radicals become trapped and can be used to initiate the free radical polymerization of a second monomer to produce a graft copolymer. In PE these trapped radicals have been identified as, mainly, alkyl and allyl radicals with the structures ($-\text{CH}_2\dot{\text{C}}\text{HCH}_2-$) and ($-\dot{\text{C}}\text{HCH}=\text{CH}-$).^{29,30} In the presence of oxygen the polymeric radicals will react to form diperoxides and hydroperoxides, as well

TABLE I
Expected Free Radical Yields of Selected Monomers and Polymers³

Material	G value
Styrene	0.69
Ethylene	~4
Acrylonitrile	5.6
Methyl methacrylate	11.5
Polystyrene	1.5-3
Polyethylene	6-8
Poly(methyl methacrylate)	6 or 12
Poly(vinyl chloride)	10-15

as certain amounts of less stable peroxy radicals ($-\text{CH}_2\text{OO}\cdot$). To initiate graft polymerization, these polymeric peroxides are thermally decomposed at temperatures in the range 90–140°C to produce active radical sites.

The mechanism of grafting in a polymer–monomer system involves a complicated combination of effects in which diffusion plays an important role. In both trapped radical and peroxidized polymer grafting, diffusion of the monomer to the radical sites appears to be the rate limiting step. For PE–AN grafting the low equilibrium concentration and slow diffusion of AN in both PE and polyacrylonitrile (PAN) should limit the grafting to a very thin layer near the surface of the particles. Furthermore, during radiation peroxidation of PE at high dose rates, the diffusion of oxygen into the polymer is rate-determining and should produce a decreasing concentration of peroxide towards the interior of the spherical PE particles.

The typical steps involved in free radical polymerizations are also applicable to graft polymerization including initiation, propagation, and chain transfer.³¹ However, the complicating role of diffusion prevents any simple correlation of individual rate constants to the overall reaction rate. Changes in temperature, for example, increase the rate of monomer diffusion and monomer reaction, but, also, increase the rate of radical decay by crosslinking and various other competing reactions. Termination of the growing chains occurs by the recombination of radicals in most free radical systems. In the case of AN polymerization, however, termination has been proposed to occur by occlusion of the growing chain ends because the polymer is insoluble in the monomer. As a result, once the graft polymerization at the surface has proceeded to a significant extent, an impermeable layer may form, and no further grafting occurs interior to this layer. The chains on the surface could continue to grow until their active radicals become buried and inaccessible to more monomer.

In addition to the polymerization initiated at graft sites, a competing reaction involving the homopolymerization of the monomer is found to occur. The hydroxyl radicals produced during grafting on peroxidized PE are probably the most significant initiators for homopolymerization in this method. Other sources of radicals which could initiate homopolymer formation include radical products of chain transfers and thermal initiation of the monomer. Thus, the product of the graft reaction will contain a mixture of PAN homopolymer and graft copolymer, the relative amounts of which will be highly dependent on the method of radiation-induced grafting employed. Separation of the two components is achieved by selective dissolution of the homopolymer in a solvent which does not dissolve the backbone polymer. For the PE–AN system, dimethylformamide is a suitable solvent for PAN.

An important result of the irradiation and radical production in polymers is the intercrosslinking, chain scission, or enhanced oxidation that can occur subsequently. While chain scission and enhanced oxidation³² are not significant in PE, it has been found that PE readily undergoes crosslinking reactions during both irradiation and grafting.³³ Crosslinking can occur either by the combination of radicals on adjacent PE chains, or by the termination of a growing graft chain on another polyethylene backbone. The degree of crosslinking is dependent on the total radiation dose received, and, while some crosslinking may be desirable in polymer blending and other applications, the network polymer which results from a high degree of interlinking is usually undesirable because of poorer

processability. The total radiation dose allowed (and, thus, the amount of grafting) will be limited by the amount of crosslinking allowable for a specific application.

EXPERIMENTAL METHODS, MATERIALS, AND PROCEDURES

Polyethylene and Acrylonitrile Properties and Other Chemicals

The material used for these experiments was a low-density, virgin resin PE containing no antioxidants,³⁴ and is commercially produced by U.S. Industrial Chemicals Corporation (USIC), trade named FN510. It was used as supplied in the form of a fine powder with a nominal particle size specified as 20 μm . The manufacturer's specifications are

density	0.924 g/cm ³
Vicat softening point	97°C
melt index	5 g/10 min
\bar{M}_n	20,600
\bar{M}_w	264,000
D_p	12.8

where \bar{M}_n and \bar{M}_w are the number-average and weight-average molecular weights, respectively, and D_p is the polydispersity.

Reagent grade AN was vacuum distilled to remove inhibitors prior to use in grafting. Solvents used include reagent grade dimethylformamide (DMF) for extracting polyacrylonitrile (PAN) homopolymer and benzene, ethanol, and methanol for rinsing and precipitating the grafted material.

Instruments Used in Measurements and Irradiations

The infrared spectra were measured using a Perkin-Elmer Model 621 Double-Beam, Grating Spectrophotometer. The Model 621 is capable of covering the wavelength region from 2.5 μm to 50 μm (4000–200 cm^{-1}). Additional details are published elsewhere.³⁵

In order to determine the type and relative amounts of radicals present in PE irradiated and stored under various conditions, electron spin resonance (ESR) measurements were made using a Varian E-9, X-Band Spectrometer. All samples were carefully weighed and inserted into quartz tubes for use in the standard X-band cavity of the ESR spectrometer.

The scanning electron microscope (SEM) studies of grafted and ungrafted materials were made using a JEOL JSM-2, 5–45 kV microscope. All samples were sputter-coated with gold to an approximate thickness of 200 Å to act as an electrical ground to eliminate charge buildup. The picture resulting from SEM provides a view of the sample with much higher definition, clarity, and depth of view than an optical light microscope.

Measurements of the heat of fusion, to determine changes in the degree of PE crystallinity in the grafted and ungrafted samples, were made using a DuPont Model 910 Differential Scanning Calorimeter (DSC) and a Model 990 Thermal Analyzer. This combination is capable of scanning from room temperature to

600°C at various rates from 0.5°C/min to 100°C/min and with sensitivities ranging from 0.05 mcal/s-min to 50 mcal/s-min. The area under the DSC curve, which provides a direct measure of the crystalline heat of fusion,³⁶ is used to measure the relative amounts of crystalline PE in various grafted and ungrafted samples.

The source of radiation for all experiments was a 0.5–0.8 MeV cathode ray accelerator built by the General Electric Company in 1939. The accelerating principle is based on the resonant transformer concept, which is described in detail elsewhere.³⁷ The details of equipment positioning, irradiation geometry, and dosimetry are given in a previous paper.³⁵

Procedures for Irradiation, Grafting, and Extraction

Most PE samples were used directly as supplied by USIC, but in some experiments samples were heated and quenched or annealed prior to irradiation in order to alter their degree of crystallinity.³⁸ The samples to be annealed were placed in a vacuum desiccator which was evacuated and then filled with dry nitrogen gas. The desiccator was placed in an oven at either 85 or 100 ± 2°C for 24 h. The sample heated to 85°C was gradually cooled to room temperature at a rate of 5°C/h. The sample heated to 100°C was annealed in a similar manner at a cooling rate of 2.5°C/h. The PE samples to be quenched were first heated to 95 ± 2°C for 1 h in air and quickly dumped into a beaker of rapidly stirred distilled water and ice at 0°C.

The ambient air irradiations were carried out by centering the petri dish containing the sample material on the water-cooled platform located 13 cm below the beam exit window. For the irradiations in oxygen and in vacuum the petri dish and sample were placed in an evacuable aluminum chamber.

Three days prior to the oxygen irradiation, the chamber with the sample in place was evacuated to less than 5×10^{-4} torr and this vacuum was maintained for 24 h. The chamber was then filled with dry oxygen to a pressure of 5 psig and remained under oxygen for 48 h before irradiating. Immediately after irradiation, the chamber was opened, and the sample was exposed to air.

For the vacuum irradiations the chamber was evacuated to less than 5×10^{-4} torr and stored under this vacuum for 1 day prior to irradiation. Immediately after irradiation the chamber was filled with dry nitrogen, and the sample was transferred to a vacuum desiccator and again evacuated.

All samples were irradiated at room temperature (~23°C). The dose rate used for the majority of the samples was 4 ± 1 Mrad/min and was adjusted by changing the beam current while maintaining the electron energy at 0.8 MeV. For the low dose rate experiment the beam current was decreased by a factor of 40 while the electron energy was again kept at 0.8 MeV. Within 1 h after irradiation all samples were either used for grafting or stored at -10°C for a maximum of 10 days. Samples irradiated in air or oxygen were stored in air, while the sample irradiated in vacuum was stored under vacuum.

All AN monomer was vacuum distilled before use to remove inhibitors and any traces of water. Before reacting with AN, about 2.0–3.0 g of irradiated PE were placed into the glass reaction flask of the grafting apparatus. The system was evacuated and then backfilled with nitrogen to a pressure of about 0.5 atm. AN was added to the irradiated PE in a mass ratio of 20:1. After all of the

monomer had been added the system was repressurized to 1 atm with nitrogen. To initiate reaction, a preheated, heating mantle was placed around the bottom of the flask. Grafting was allowed to take place in the boiling AN medium (at 77°C), for various lengths of time from 2 h to 24 h. In order to stop the reaction after the specified time, the heater was removed and the reaction medium was rapidly cooled in the acetone-dry-ice bath. The grafting products were washed with either benzene or ethanol to remove the excess monomer. In the case of the quenched and annealed samples, ethanol was used to prevent swelling and to preserve the crystallinity of the samples. The product was then dried under vacuum for 24 h at room temperature ($\sim 23^\circ\text{C}$), and stored in an air atmosphere at -10°C until extracted.

Polyacrylonitrile homopolymer was extracted from the desired product with DMF. For exhaustive extractions a Soxhlet-type, continuous extractor can normally be used. However, since the nitrile groups of PAN are known to undergo a cyclization reaction when heated above approximately 80–90°C for extended periods of time, a modification of the normal Soxhlet extractor was necessary. With the apparatus shown in Figure 1, extractions can be carried out at temperatures down to room temperature. If necessary, heat can be supplied to the extraction cup via a thin film heater jacket. It was found that the most significant extraction occurs within the first 2–5 h, and no further improvements in separation occur even after several days. For convenience an extraction time of 24 h was adopted for all experiments in this study.

Extractions were carried out at 25°C, 45°C, and 90°C under nitrogen atmosphere; 40–45°C was used as a suitable intermediate temperature. After ex-

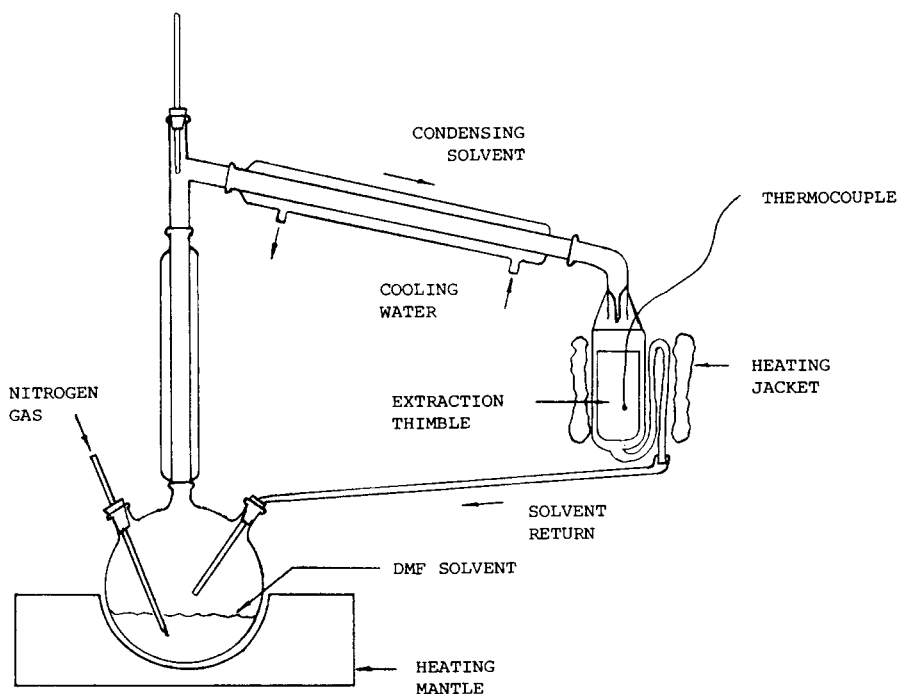


Fig. 1. Continuous extraction apparatus.

tracting for 24 h, the material was removed from the thimble, and one of two procedures was used to prepare the sample for infrared analysis. The samples extracted at room temperature tended to retain their powdery nature and were dried under vacuum at $\sim 45^\circ\text{C}$ for 24 h immediately after extraction. Subsequently, the material was cooled in liquid nitrogen and crushed to a fine powder by hand with a mortar and pestle. The samples that were extracted at 45°C and, especially those at 90°C , tended to coalesce into a gelatinous mass. On drying they hardened into a hard, tough solid that could not be crushed sufficiently even at liquid nitrogen temperatures. These samples were dispersed with rapid stirring in DMF solvent and continued heating at $\sim 45^\circ\text{C}$. When the sample appeared to be well dispersed (i.e., anywhere from 4 h to 24 h), an equal volume of cold methanol was added to precipitate the graft as a fine powder. After filtering and rinsing the material with methanol, it was dried at $45 \pm 2^\circ\text{C}$ under vacuum for 24 h. The resulting grafted sample could be easily crushed in a mortar at room temperature.

The KBr technique has been used quantitatively on powders of AN grafted to polypropylene,²⁵ and this method was adopted for quantitative analysis of percent graft by infrared absorbance. A standardized sample was produced in the form of a 13-mm disk containing 5 mg of sample and 300 mg of IR-grade KBr powder and placed in a stainless steel ball and shaker mill. Finally, the material was pressed for 15 min at 10 tons force in a steel die under vacuum.

The amount of AN grafting was determined from the infrared absorbance of the nitrile group at 2240 cm^{-1} after extraction of homopolymer. In order to minimize the effects of weighing errors, an internal reference method utilizing the methylene absorbance of PE at 730 cm^{-1} was adopted. Infrared analysis of PE film showed a change in the absorbance of the 730 cm^{-1} peak of only 5% over a range of 0–15 Mrad in dose. Thus, the mass of PAN in a sample was correlated to the ratio of the absorbance A_{2240}/A_{730} , and the weight percent graft, defined by eq. (1) below, was computed from the mass of PAN by eq. (2):

$$\% \text{ graft} = \frac{W - W_0}{W_0} \times 100 \quad (1)$$

$$\% \text{ graft} = \frac{W_p}{5.0 - W_p} \times 100 \quad (2)$$

where W_p , W , W_0 are the weights (mg) of PAN, grafted PE, and ungrafted PE, respectively. A calibration curve was constructed by measuring the absorbance of samples of a mixture containing various known weights of PE and PAN. The PAN was produced by irradiating AN monomer to 15 Mrad.

RESULTS

Infrared Results

The infrared spectra of both PE and PAN in the $2400\text{--}2000\text{ cm}^{-1}$ and $800\text{--}600\text{ cm}^{-1}$ regions, where there are no overlapping absorption bands, are shown in Figure 2. Spectra of a thin PE film, irradiated to an accumulated dose of 15 Mrad, showed a relative change in the methylene absorbance at 730 cm^{-1} of only 5% when compared to the unirradiated sample.

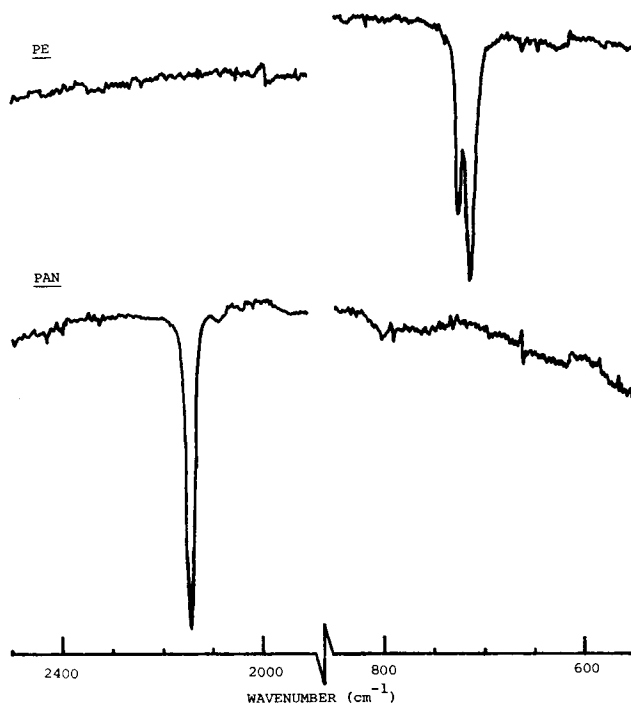


Fig. 2. Infrared spectra of PE and PAN in the 2400–2000 cm^{-1} and 800–600 cm^{-1} regions.

Figure 3 shows the infrared spectrum of PAN produced by irradiation of distilled AN monomer to a dose of 15 Mrad. Comparison of this spectrum with that of conventionally polymerized PAN shows that there are additional absorption bands at 1665 cm^{-1} and 2030 cm^{-1} in the radiation-polymerized sample. The band at 1665 cm^{-1} has been observed both in radiation-polymerized PAN and on thermal treatment of conventionally polymerized PAN. The structure responsible for the 1665 cm^{-1} band is formed by the cyclization of the nitrile groups to give a conjugated $\text{C}=\text{N}$ linkage.^{39–42} Various researchers have attributed

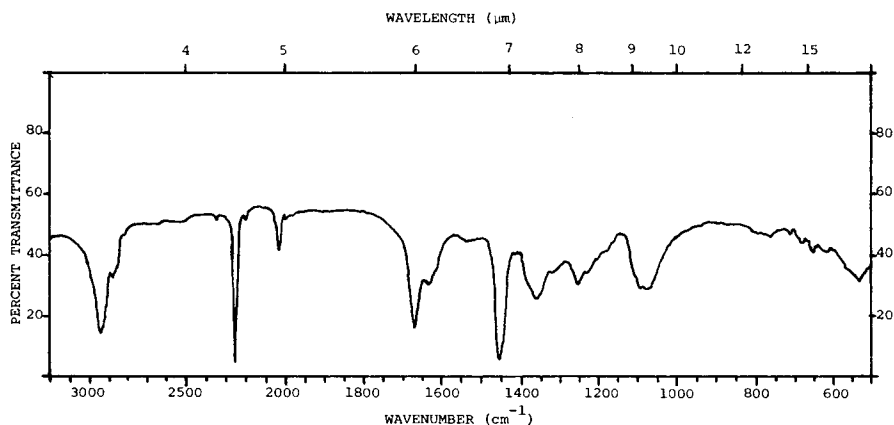


Fig. 3. Infrared spectrum of radiation polymerized PAN.

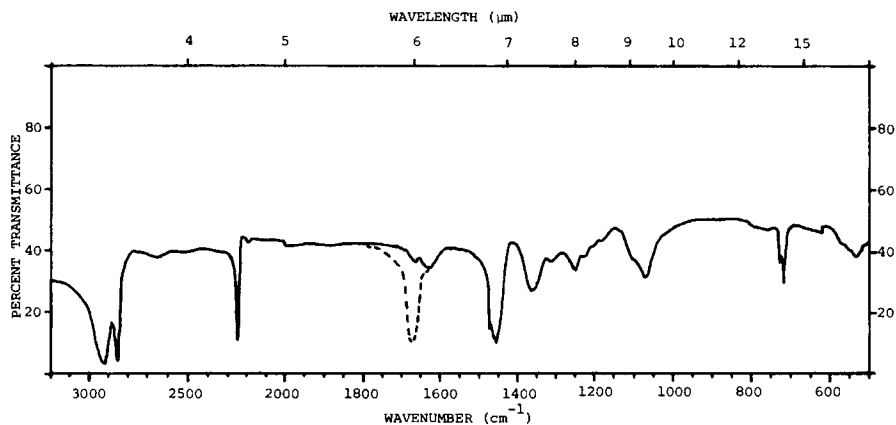


Fig. 4. Infrared spectrum of PE-PAN-grafted material.

the 2030 cm^{-1} absorption band in radiation-polymerized PAN to the keteneimine group ($\text{C}=\text{C}=\text{N}$) formed during polymerization.^{41,42} In the reported literature, however, this structure was only observed after radiation polymerization at low temperature (-78.5°C). Our similar results at room temperature may be due to the much higher dose rate used in our experiments.

A typical spectrum of graft material is given in Figure 4. The characteristic nitrile absorption band of PAN and methylene absorption band of PE are visible at 2249 cm^{-1} and 730 cm^{-1} , respectively. The various other absorption bands are the result of overlapping peaks from both the PAN and PE segments of the graft. The enhanced absorption at 1680 cm^{-1} present in some samples (shown by the dashed line) was caused by residual solvent remaining in the graft after extraction and could be greatly reduced by further drying of the sample material under vacuum at a higher temperature ($\sim 60^\circ\text{C}$).

No new absorption peaks exclusively attributed to the graft structure were

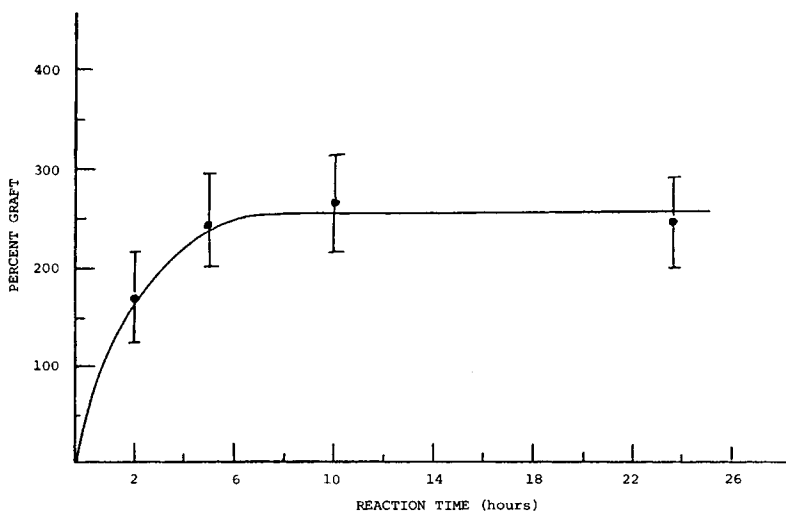


Fig. 5. Percent graft vs. reaction time graph.

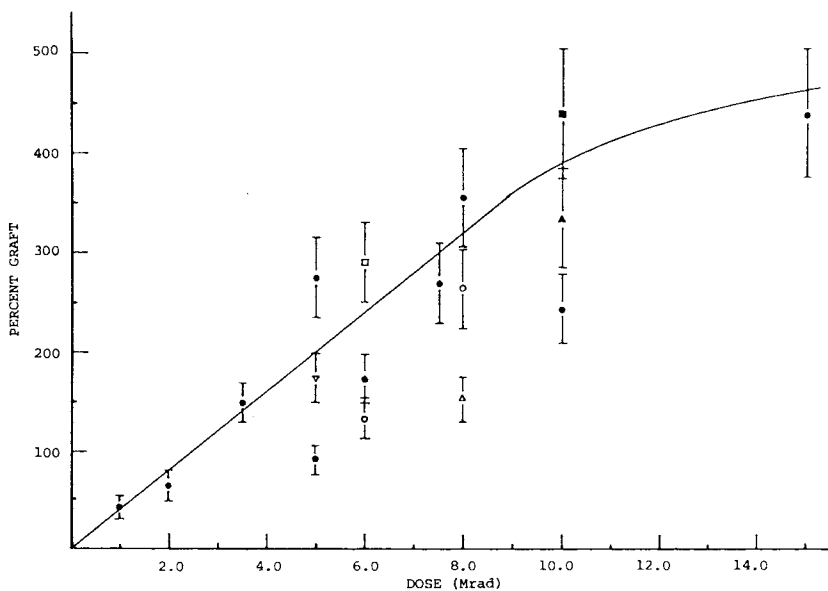


Fig. 6. Percent graft vs. radiation dose graph: (●) air irradiation; (○) oxygen irradiation; (Δ) vacuum irradiation; (□) low dose rate irradiation; (▽) high temperature grafting; (■) quenched, grafted PE; (▲) annealed, grafted PE.

observed in any of the spectra. However, this does not rule out their existence. Expected structures which would be unique to peroxide grafted material include either (C—O—C) and residual diperoxide linkages (C—O—O—C). The absorption bands that would result from these structures are either obscured by other peaks or are too weak to be detected. In some samples an absorption peak at 1710 cm^{-1} due to carbonyl (C=O), oxidation products was found.

Figure 5 shows a plot of the percent AN grafting, as measured from the infrared spectra, at a dose of 10 Mrad for reaction times of 2 h, 5 h, 10.5 h, and 24 h. The error bars represent the maximum accumulation of errors involved in the measurement of the percent graft (including weighing errors, infrared spectrum measurements, and calibration). From the overall trend of these results it is obvious that after 5 h at 77°C the graft polymerization rate is very small and the reaction has essentially ended.

The influence of the dose of irradiation in air on the percent graft is shown by the results in Figure 6. The graft curve shows a fairly constant increase in grafting with increasing dose from $\sim 40\%$ at 1 Mrad up to $\sim 350\%$ at 8 Mrad. Results at higher doses indicate a slight saturation, and the sample irradiated to 15 Mrad showed $\sim 440\%$ grafting. Each point of the curve is the result of one experiment but is the average of several infrared measurements. The two points representing grafting results on PE irradiated to 5 Mrad in ambient air and reacted for 24 h at 77°C represent the first and last experiments performed. The large difference in percent graft between these two samples suggests that there may be an important parameter that has not been recognized or controlled during the grafting process and is the cause of the poor reproducibility of this sample (see Discussion).

In Figure 6 the results of grafting under a variety of different conditions are

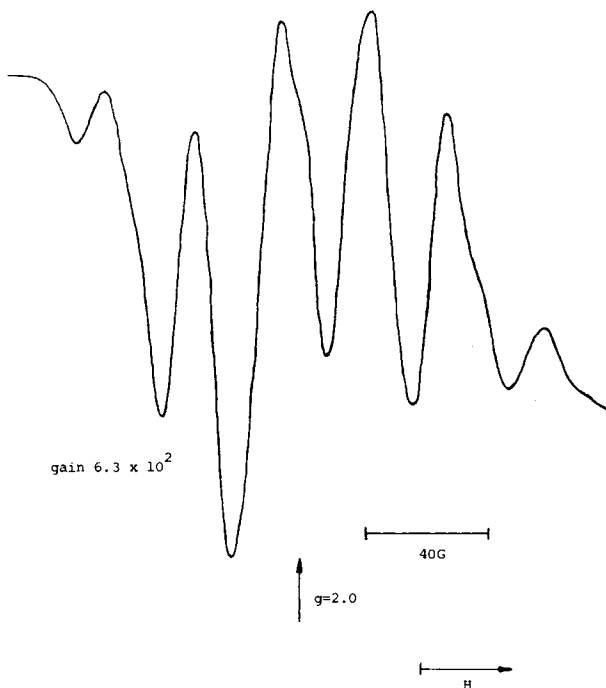


Fig. 7. ESR spectrum of 10 Mrad, air-irradiated PE, 2 h at 21°C.

also presented. The percent graft of PE samples irradiated in vacuum or in pure oxygen environments is found to be lower than that of samples irradiated in air. The oxygen-irradiated samples contain 50% to 100% less graft, and the vacuum-irradiated sample contains over 150% less graft than those samples irradiated in air. The sample irradiated at a lowered dose rate, 0.1 Mrad/min as compared to 4.0 Mrad/min, shows an increase in the percent graft of 50%. Grafting at a temperature of 100°C in a stainless steel pressure vessel for only 2 h using air-irradiated PE produced a graft material with 25% less AN than that expected for a grafting reaction at 77°C lasting 24 h. These results indicate that increased temperature, and decreased dose rate, increase the rate of grafting.

Electron Spin Resonance Results

Figures 7–9 show some of the ESR spectra of the radicals typically produced in PE powder by irradiation at room temperature. The spectrum in Figure 7 was taken within 2 h after irradiation and clearly shows the sextet spectrum attributed to the alkyl radical.²⁹ The apparent hyperfine splitting value of $\sim 30G$ is also in good agreement with results reported elsewhere.⁴³

Comparison of our various ESR spectra show little difference in the type of radicals produced after irradiation in vacuum and air environments. However, comparison of Figures 8 and 9 from samples irradiated in oxygen and vacuum environments, respectively, shows a distortion due to the superimposed signal from peroxy radicals, which are present in higher concentration in the oxygenated sample than in those exposed to air during irradiation. The differences in the total signal strength between the vacuum and air-irradiated samples show a 49%

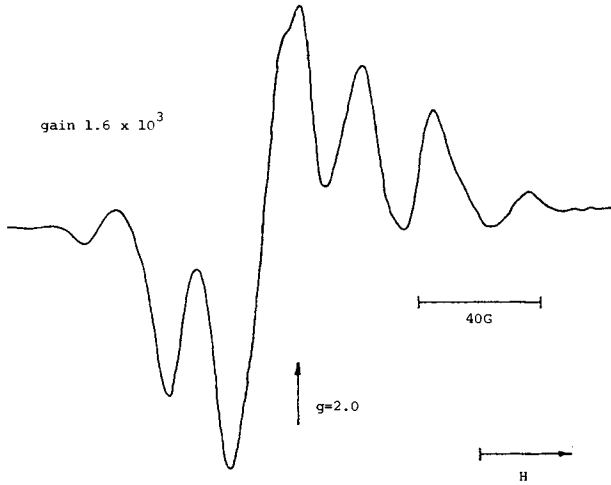


Fig. 8. ESR spectrum of 8 Mrad, oxygen-irradiated PE, 2 h at 21°C.

and 28% decrease in radical concentrations for doses of 5 Mrad and 10 Mrad, respectively. The differences in the portion of the signal due to alkyl radicals (as measured by the area of the outermost peak) show a 48% and 28% decrease in alkyl radical concentrations for the same samples. In contrast, the difference in the alkyl radical signal between the vacuum and oxygen irradiated samples at a dose of 8 Mrad shows an 88% decrease in the alkyl radical concentration while the total signal shows only a 78% decrease in the total radical concentration. While these results are not sufficiently quantitative to be conclusive, they do indicate a consumption of alkyl radicals in the formation of hydro- and diperoxides in the presence of oxygen. A higher rate of consumption in the pure

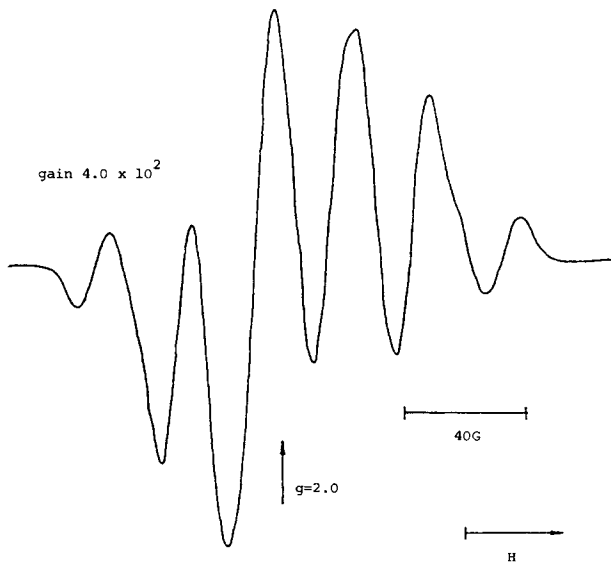


Fig. 9. ESR spectrum of 8 Mrad, vacuum-irradiated PE, 1 h at 21°C.

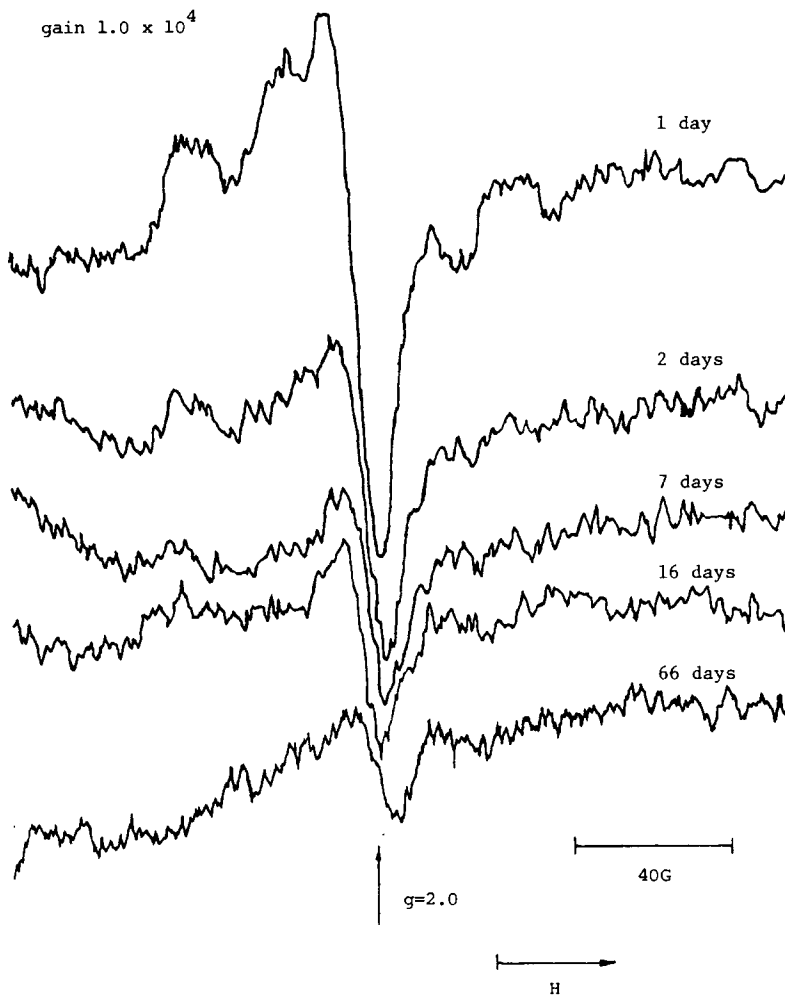


Fig. 10. ESR spectrum of 5 Mrad, vacuum-irradiated PE, 1-66 days at 21°C.

oxygen environment leads to a buildup of incompletely reacted peroxy radicals.

Figures 10 and 11 show several spectra taken over a period of 66 days; note that both samples show a complete disappearance of the alkyl sextet radical signal (Fig. 9) after the first 24 h of storage of the sample at room temperature in air, followed by the gradual decay of the asymmetric peak near $g = 2.0$, which is attributed to peroxy radicals in both the vacuum and air-irradiated samples. In contrast, Figure 12 shows the much slower rate of radical disappearance if after irradiation the sample is stored at -10°C in air for the same sample shown in Figure 7. After 117 days storage at -10°C , the alkyl radical signal has decreased by 84% while the total signal from all radicals present has decreased by only 54%. Finally, after heating at 90°C for 15 min, none of the samples showed any detectable free radical signals.

The ESR spectrum of grafting product (including PAN homopolymer as well as graft material) taken immediately after removing excess AN monomer and

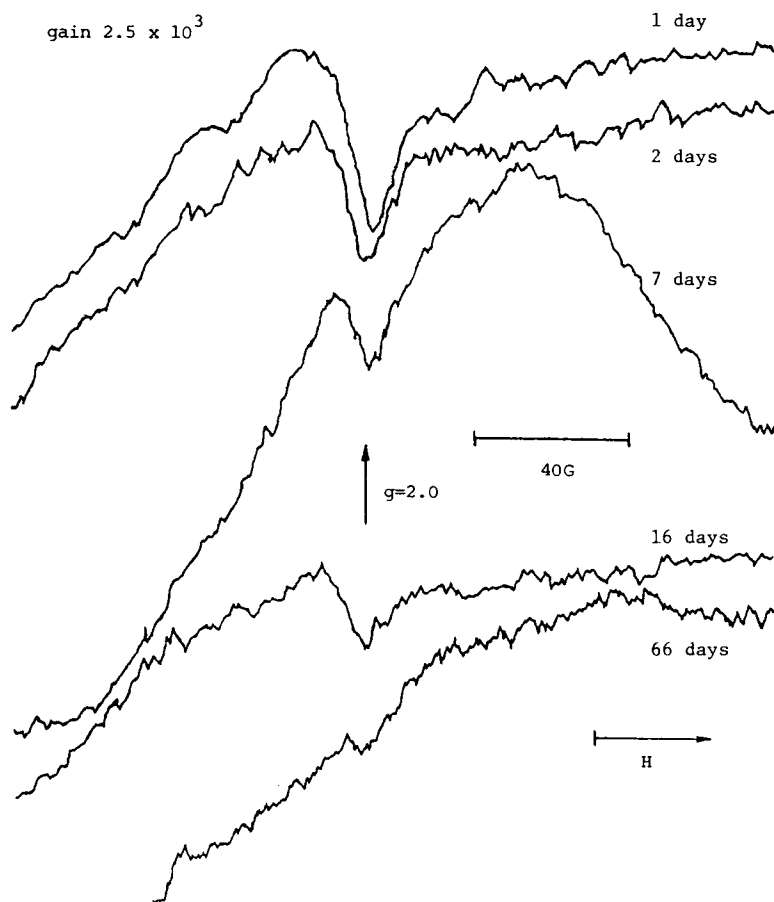


Fig. 11. ESR spectrum of 5 Mrad, air-irradiated PE, 1-66 days at 21°C.

within 45 min of stopping the reaction by quenching shows no signal due to free radicals. Though termination of polymerization in the heterogenous AN system has been attributed to radical occlusion in the solid phase, there is no verifiable radical signal apparent in this sample. The PE used had been irradiated to 10 Mrad in air and reacted with AN for 10 h under nitrogen. Our inability to detect any radicals in grafted material may be caused by a low concentration and increased signal noise at the higher amplification required, or the occluded radicals may, also, undergo a rapid reaction when exposed to oxygen for even short periods of time and disappear.

Scanning Electron Microscopy Results

Figures 13-23 show the photomicrographs of several grafted and ungrafted PE samples taken with the SEM at magnifications from 400 \times to 13,000 \times . Figures 13-15 show the unirradiated starting material and graft material produced by 1 Mrad and 10 Mrad irradiations in air and 24-h reactions with AN. Coverage of the PE surface by grafted PAN is visible in Figure 14 and especially in Figure 15. The graft does not appear to form a uniform coating on the PE

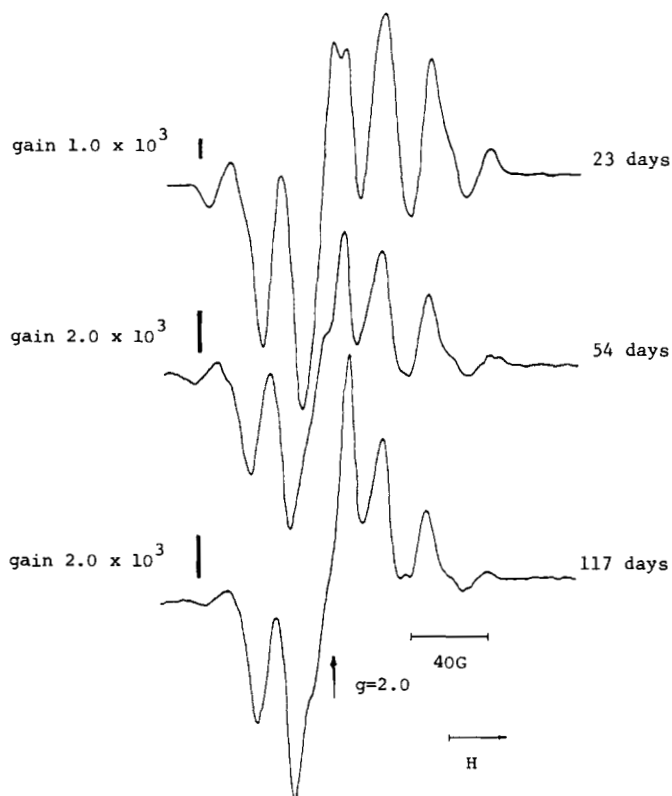


Fig. 12. ESR spectrum of 10 Mrad, air-irradiated PE, 23–117 days at -10°C .

particles in either sample, though. In both samples the graft appears to grow to a considerable distance away from the particle surface before termination occurs. Figure 16 shows a sample of the material shown in Figure 15 taken before extraction of the PAN homopolymer. The material which is apparently un-

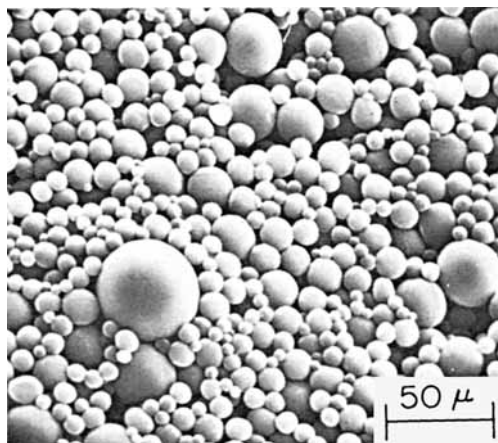


Fig. 13. Unirradiated PE (260 \times).

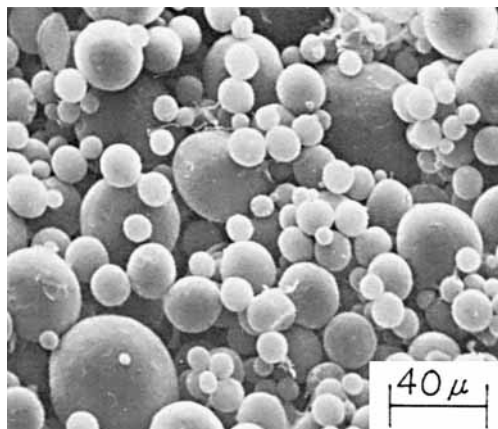


Fig. 14. 1 Mrad, grafted PE (338 \times).

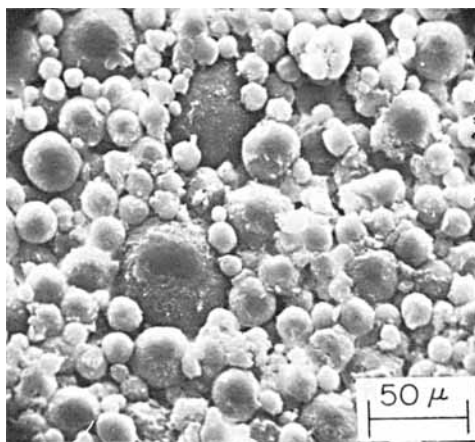


Fig. 15. 10 Mrad, grafted PE (260 \times).

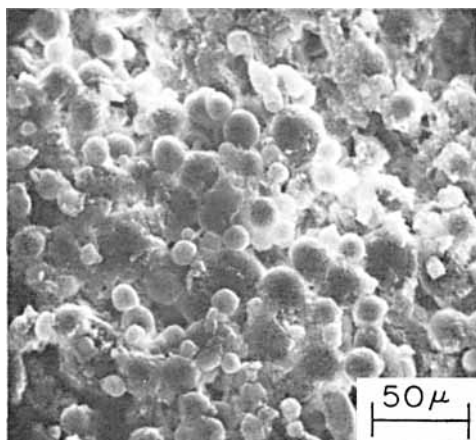


Fig. 16. 10 Mrad, grafted PE and PAN homopolymer before extraction (260 \times).

grafted PAN is evident in the interstices between and around the spherical particles, especially in the upper-right portion of the photomicrograph in Figure 16.

Closer views of the samples using higher magnifications shown in Figures 17–22 reveal the highly nonuniform coverage of the graft polymer. The flattened surfaces apparent in the 10-Mrad grafted sample are due to abrasion during sample preparation. The relatively smooth surface of the unirradiated PE is shown by the portion of a particle in Figure 19 with a smaller, approximately 1 μm diameter, particle on it. Comparison of Figures 20 and 22 shows little difference in the morphology of the graft coating before and after extraction. The differences in the appearance of the graft coating between the 1-Mrad sample, Figures 17 and 21, and the 10-Mrad sample, Figures 18 and 22, is striking, however. In the 1 Mrad sample the graft appears to be a thin, filmy layer, while in the 10-Mrad sample the graft is coarse and bushy. A closer view of the filmy graft (1 Mrad dose) which extends away from the particle surface is shown in Figure 23.

The average particle sizes of ungrafted and grafted PE were determined by measuring the particle sizes in enlarged photomicrographs of Figures 13 and 15, respectively. The result of the determination was 20- μm and 30- μm average particle sizes for the ungrafted and grafted PE, respectively. While the irregular particle shapes of the grafted material make the size measurements and average particle size only approximations, these results are sufficient for comparison with the results from infrared measurements on the percent graft.

From the percent graft computed using the infrared analysis of 10 Mrad grafted PE, the average particle size after grafting can be calculated from the densities of PE and PAN and the average particle size before grafting. If the grafted PAN can be assumed to form a uniform surface layer on the PE substrate, then the diameter of the grafted particle can be found by solving for d_2 from

$$\% G \times \left(\frac{4}{3} \pi \frac{d_1^3}{8} \right) \times \rho_{\text{PE}} = \frac{4}{3} \pi \left(\frac{d_2^3 - d_1^3}{8} \right) \times \rho_{\text{PAN}} \quad (3)$$

where % G = percent graft of 10 Mrad, grafted PE = 233%, ρ_{PE} = density of PE

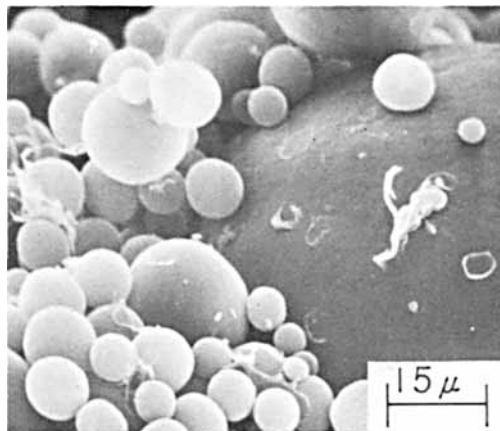


Fig. 17. 1 Mrad, grafted PE (845 \times).

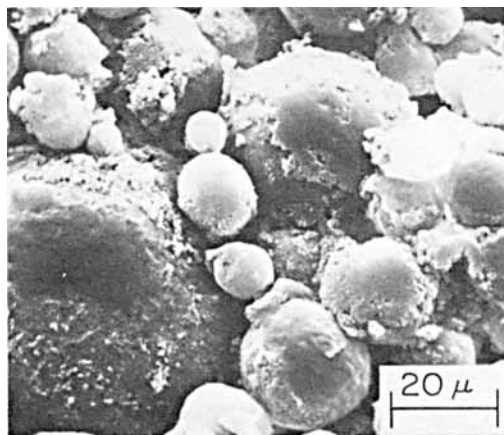


Fig. 18. 10 Mrad, grafted PE (650X).

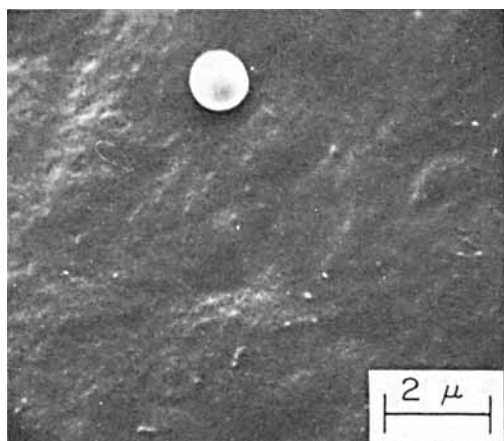


Fig. 19. Unirradiated PE (6500X).

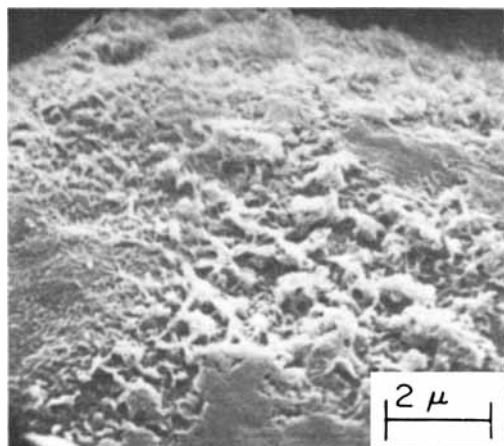


Fig. 20. 10 Mrad, grafted PE before extraction of PAN homopolymer (6500X).

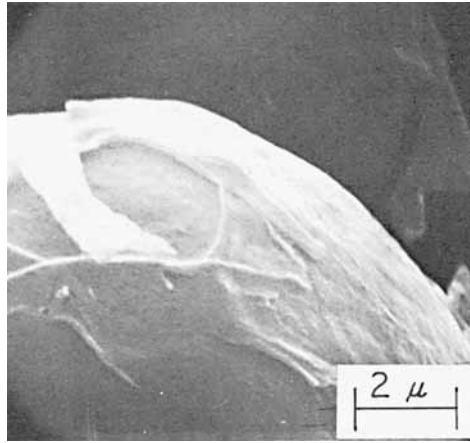


Fig. 21. 1 Mrad, grafted PE (6500X).

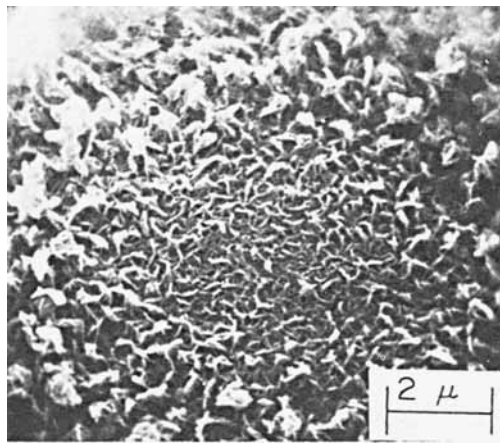


Fig. 22. 10 Mrad, grafted PE (6500X).

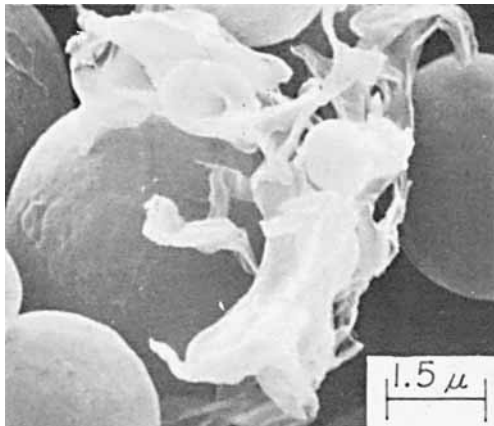


Fig. 23. 1 Mrad, grafted PE (8450X).

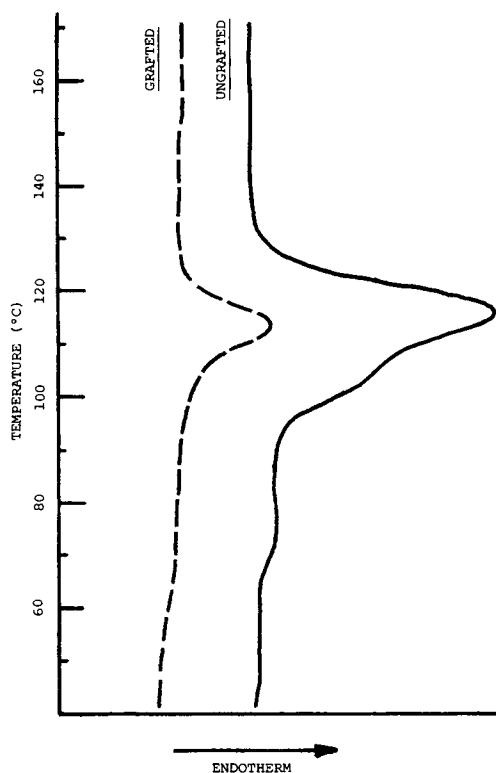


Fig. 24. Melting endotherms of ungrafted (—) and grafted (---) PE.

$= 0.924 \text{ g/cm}^3$, $\rho_{\text{PAN}} = \text{density of PAN} = 1.15 \text{ g/cm}^3$, $d_1 = \text{average diameter of unirradiated PE} = 2.0 \times 10^{-3} \text{ cm}$, and $d_2 = \text{average diameter of grafted PE}$. Equation (3) expresses the mass of PAN in the graft on the left-hand side in terms of the mass of PE and the percent graft and on the right-hand side in terms of the density of PAN and the volume of PAN in the surface layer model. The grafted particle diameter of $28 \mu\text{m}$ determined in this way coincides with the result (obtained from the SEM photomicrograph) within the experimental limits of error ($\pm 10\%$).

Differential Scanning Calorimetry Results

Figure 24 shows the typical crystalline melting endotherms of ungrafted and grafted PE. The crystalline melting temperatures of various low density PE samples are reported in the range from 105°C to 132°C .⁴⁴ The glass transition of PAN occurs nearby in the range $87.5\text{--}98.8^\circ\text{C}$ for molecular weights of 1.35×10^4 to 66.4×10^4 .⁴⁵ There appear to be no effects due to the glass transition of PAN ($87.5 \leq T_g \leq 98.8$), observed even with the signal gain increased 10 times larger than that shown in Figure 24. In order to reduce the effects of thermal treatments of PE incurred during grafting, the ungrafted PE was subjected to the same conditions which occur during grafting and extraction but without irradiation or AN monomer. This material was then used as the starting material for grafting.

The changes in the crystallinity of PE found after grafting include a small 2.5°C drop in the location of the maximum in the melting curve from ~115.5°C to ~113.0°C and a significant decrease in the area under the melting peak. While the decrease in the melting temperature, represented by the shift in the melting curve, indicates there is some change in the PE crystallinity caused by the presence of the grafted PAN, comparison of the areas before and after grafting indicate this may be a small effect. By assuming the difference in areas is due only to a difference in the amount of PE present (i.e., no difference in the degree of crystallinity), the percent graft can be calculated from eq. (4) for comparison with the results of infrared analysis:

$$\% G = \frac{(A_1 - A_2)}{A_2} \times \frac{\rho_{\text{PAN}}}{\rho_{\text{PE}}} \times 100 \quad (4)$$

where A_1 = area before grafting and A_2 = area after grafting. The percent graft calculated in this way from Figure 24 (which takes into account adjustments for amplifier gain and sample mass) is 235%. The percent graft of the same sample determined by infrared analysis is 245%.

The effect of the degree of crystallinity of PE on the graft yield was also investigated, and the crystalline content of quenched and annealed PE, before and after grafting, as well as untreated PE are presented in Table II. These values represent averages with different samples taken from the same material varying by as much as 10% from each other for the quenched PE. The percent graft found by infrared analysis of the quenched and annealed samples was 440% and 335%, respectively. The difference in the melting temperatures and the similarity in the areas of the endotherms in spite of the difference in the percent graft indicate that the degree of crystallinity of the PE is different in the quenched and annealed grafted samples. For these reasons comparable values for the percent graft could not be calculated from the endotherm areas for these samples.

DISCUSSION

The stated objectives of this research were to investigate the process of grafting AN to fine powders of PE and the characterization of the graft copolymer formed. In the pursuit of these objectives a variety of different experimental techniques and probes were used to gain information, and the foregoing results will be in-

TABLE II
DSC Results of Grafted and Ungrafted PE

Sample	Area (arbitrary units/mg)	T_m (°C)
Untreated PE	0.114	115.5
Quenched PE	0.122	115.5
Annealed PE	0.155	116.0
Quenched PE, 10 Mrad grafted	0.0214	112.5
Annealed PE, 10 Mrad grafted	0.0200	115.0

tegrated in the following discussion in order to present a more complete and overall description of the major aspects of grafting investigated, which include: radiation dose dependence, graft saturation with time, dose rate effect, surface grafting, effect of PE crystallinity, and effect of irradiation environment.

The results of AN grafting at different radiation doses, which are shown in Figure 6, indicate that the percent graft increases monotonically with increasing dose for air-irradiated samples. Note that there are also data for six different irradiation conditions on Figure 6 which complicate the plot. The grafting dose dependence for the air-irradiated sample follows the increase in radical concentration observed by ESR measurements and the increase in peroxide concentration described in the literature⁴⁶ with increasing radiation dose. From the method of procedure and ESR results it must be assumed that both alkyl and peroxy radicals contribute to the initiation of AN grafting at 77°C as was also found by Shinohara and Tomioka⁴⁷ for styrene grafting onto polyethylene at 80°C. Their conclusions were based on the results of grafting reactions carried out at 80°C immediately after air irradiation, which is a procedure similar to ours, as well as results of grafting at 40°C, which is well below the activation temperature for hydroperoxides (~75–95°C), and results at 80°C with irradiated PE which had been stored at room temperature for 2 days to allow the alkyl radicals to decay.

The relative contribution of the alkyl and peroxy radicals to graft initiation at any given dose and time during reaction is difficult to determine since not all of the radicals present will initiate grafting as was found by Yasukawa et al.¹⁶ However, the change in alkyl radical concentration along with the change in total radical concentration with dose was determined by ESR measurements for vacuum and ambient air irradiations. The results show that the total and alkyl radical concentrations increase in going from vacuum to air-irradiated samples. The radical concentration appears to increase linearly with doses from 0 Mrad to 10 Mrad in air, while over the same range of dose the radical concentration in vacuum-irradiated PE has begun to show some saturation effects. These results suggest that, since the rate of alkyl radical production remains constant in air while the rate of production in vacuum decreases with increasing radiation dose (which, it should be noted, also represents increasing irradiation time at a fixed dose rate), the rate of radical consumption by oxygen must decrease over the range of doses shown. The difference between the curves should also give, at least, a relative and qualitative measure of the number of radicals consumed by oxygen to form peroxides during air irradiation.

The curve shown in Figure 6 represents the trend in the AN grafting results and is supported by the ESR results on radical yields. The increase of 100% in grafting between 5 and 10 Mrad doses, and the corresponding increase of 100% in alkyl radical concentrations must be considered coincidental, however, since not all radicals contribute to grafting as mentioned earlier, and this does not account for initiation by peroxy radicals which are activated at elevated temperatures. While the overall trend of the data can be represented by this curve, the scatter of some points and other results indicate that the specific details of the grafting process may be complicated by factors that have not been recognized or controlled in these experiments. Of the various parameters affecting the postirradiation grafting process, those that have been recognized to have significant influence on the percent graft yield are:

1. Radiation dose and dose rate
2. Irradiation temperature
3. Irradiation environment
4. Sample thickness
5. Degree of crystallinity
6. Storage time and temperature
7. Degree of swelling prior to grafting
8. Grafting temperature
9. Reaction time

Five of these parameters have remained fixed throughout these experiments including irradiation temperature [constant at room temperature ($\sim 23^{\circ}\text{C}$)], sample thickness—(20 μm particles in a 2-mm layer during irradiation), storage time and temperature (24 h or less at -10°C), and degree of swelling (no time for any swelling of PE in AN to occur was allowed prior to grafting), while the effects of various changes in the other parameters were observed.

The results of grafting onto PE irradiated under vacuum supports the assumption that graft initiation occurs from both alkyl and peroxy radicals at 77°C . The much lower percent graft produced by vacuum-irradiated PE as compared to air-irradiated PE implies either a much lower rate of initiation or a much higher rate of termination during grafting to the vacuum-irradiated sample. From the relatively short (<15 min) lifetime found for alkyl radicals at elevated temperatures, it appears that a lower rate of initiation is the more reasonable explanation. The conclusion that a lower rate of initiation occurs in the vacuum-irradiated PE in spite of the much higher radical concentration found in this sample by ESR measurements supports the view that not all radicals present contribute to graft initiation. However, the large difference in grafting yields suggests a very low efficiency of graft initiation, much lower than that indicated by the results of previous work,⁴⁶ and we would therefore further conclude that additional radicals available for graft initiation are present in the air-irradiated sample resulting from the dissociation of polymeric peroxides.

Further indication of the initiation by both radical types is given by the results of irradiating PE at a much lower dose rate. The longer time required to achieve a given dose at a lowered dose rate allows more time for the reaction of oxygen to produce peroxides. If oxygen diffusion is a limiting factor in the peroxide formation during irradiation, the predicted peroxide yield should increase with decreasing radiation dose rate, thus providing more radicals for grafting and increasing the percent graft relative to the high dose rate sample as was observed experimentally. Even the lowered dose rate used here is much higher than that used by other researchers, including Chapiro,⁴⁸ who reports a much higher graft yield on thin films. For this reason it is concluded that oxygen diffusion is still a limiting factor during peroxidation at the dose rates used here and is the cause of the relatively small, 25%, increase in the percent graft relative to the dose dependence curve, resulting from a dose rate 40 times smaller.

A similar increase in the number of radicals present for grafting also accounts for the increase in the percent graft produced by reacting irradiated PE with AN at a higher temperature of $\sim 100^{\circ}\text{C}$. The increase in the reaction temperature should affect the overall grafting process by increasing the rates of both the peroxide dissociation reaction and the propagation reaction during polymerization. However, if we assume that termination occurs primarily by occlusion

of the active radicals when the local polymer concentration near the radical reaches a certain fixed amount, then the increased propagation rate will lead to an increased rate of termination and not have a significant effect on the amount of grafted AN. The predominant effect of an increase in the reaction temperature will be an increase in the rate of peroxide dissociation and a corresponding increase in the rate of graft initiation, resulting in the larger percent graft observed.

Irradiation of PE in a pure oxygen environment leads to grafting results which appear, at first, to be inconsistent with other results and the foregoing discussion. The apparent decrease in grafting of AN to PE for oxygen-irradiated samples may well be within the experimental limits of error from the results of the corresponding air-irradiated samples at the same dose (see Fig. 6). This explanation would imply that the increase in oxygen concentration used did not increase the rate of diffusion sufficiently to overcome the high radiation dose rate and radical production, and therefore the peroxide yield was effectively the same as in the air-irradiated samples. From the consistently lower values found for oxygen-irradiated samples at two different doses and the significant decrease in the alkyl radical concentration, shown by ESR measurements of the oxygen-irradiated sample relative to the air-irradiated sample, a different interpretation of these results is preferred.

As a result of the large amount of surface area provided by the small-sized particles used, the increase in oxygen concentration may have produced a large increase in the oxidation and peroxide formation of PE during irradiation. Several factors support this interpretation, including the large decrease in alkyl radicals found by ESR measurements mentioned earlier. The carbonyl absorption (1710 cm^{-1}) found in the infrared spectra of oxygen-irradiated grafted PE, but not detected in samples produced by air irradiation, and the reported results of increased grafting of styrene on oxygen irradiated PE at $\sim 120^\circ\text{C}$ relative to air-irradiated PE⁴⁹ also support the proposed large increase in peroxide formation under oxygen irradiation. This description of the irradiation process in an oxygen environment leads to two opposing interpretations of the cause of the reduction in grafting, one of which will be favored in the remainder of this discussion.

If the increased oxidation and decreased number of alkyl radicals is sufficient to cause a decrease in the total number of radicals available for grafting, then there will be a corresponding decrease in the number of initiating graft chains resulting in the lower percent graft observed. However, irradiation at a lower dose rate also decreases the number of alkyl radicals produced by enhancing the peroxidation process. The higher graft results produced at a lower dose rate and the relatively small amount of carbonyl oxidation observed in oxygen-irradiated samples strongly suggest that the decrease in alkyl radicals is not a significant factor affecting these results.

On the other hand, if the increased oxygen concentration produced a drastic increase in the number of peroxides formed during irradiation, then there would be a corresponding increase in the number of radicals available to initiate grafting. The result of a large number of initiating graft branches within close proximity of each other may lead to rapid occlusion of the active radical sites and, thus, an increase in the rate of termination. Since the rate of thermal dissociation of peroxides is constant at a given temperature, the rapid initiation of grafting in

the oxygen-irradiated sample may lead to the occlusion of peroxide radicals also, resulting in a decrease in the rate of initiation after a relatively short reaction time. The combined effect of these two results, increased termination and decreased initiation, could yield the lowered percent graft observed.

The product of this grafting process should show characteristics which are a direct consequence of the rapid initiation and termination involved, including a very high concentration of relatively short graft chains. While measurements of the molecular weights of the graft branches have not been made, the high concentration of graft chains predicted by the increase in initiating sites follows the trend of increased surface coverage of the PE particles observed in the SEM results with increased dose for air-irradiated samples. The process which results in an increased grafting at higher doses in air-irradiated PE is also due to an increased number of radicals present to initiate grafting at higher doses. The increase in the number of radicals produced by the oxygen-irradiated PE must be much higher even than the number produced by irradiating at lowered dose rate in air, though in order to affect the rates of termination and initiation such that an overall lower percent graft results. A drastic increase in the peroxidation of PE during oxygen irradiation is possible, especially at the surface of the particles because of the large surface area provided by small particle sizes.

Another characteristic result of the grafting mechanism described for oxygen-irradiated PE is a possible change in the grafting process from a heterogeneous reaction occurring throughout the particle volume to an interfacial reaction occurring primarily on the particle surface. If this change in reaction were to occur equivalently in samples irradiated to high doses, it should appear as a change in the shape of the percent graft vs. dose plot. However, the required concentration of peroxides may not be reached during air irradiation even at high doses due to the simultaneous radiolysis of the existing peroxides. From the present results it is not possible to determine conclusively whether grafting occurs predominantly at the surface of the particles or throughout the volume. The results of Chapiro,⁴⁸ however, with 0.05 mm thick grafted films, suggest that grafting must occur throughout the PE particles, especially when considering the greatly increased surface to volume ratio of the small particles used here, compared to film samples, which would favor rapid diffusion of both oxygen and AN monomer. Some question arises from this description as to the reasons for the favorable percent graft calculated from the change in particle size distribution after grafting. The correlation of the particle size before and after grafting to the percent graft may be an accurate measure of the percent graft in spite of the simplified surface layer model used.

The degree of crystallinity of PE has been described to show a major influence in radiation grafting by affecting the rate of diffusion of oxygen and the monomer.⁵⁰ Experimental results have shown that trapped radicals are formed predominantly in the crystalline regions while peroxidation is found to play a more important role in the amorphous phase.^{15,51} Although these conclusions are drawn from the results of irradiating both high and low density PE samples, increased grafting found on quenched, low density PE compared to annealed low density PE supports a similar argument. The higher peroxide concentration predicted in the more amorphous PE due to more rapid oxygen diffusion and enhanced monomer diffusion lead to a higher percent graft, although it is difficult to determine which factor plays a more important role. Differences in the crystallinity of various regions of PE that had not been thermally treated may

be the reason for the nonuniform coverage of the grafted particle surface observed in the SEM photomicrographs of 1 Mrad and 10 Mrad samples. The results of 1 Mrad grafted PE clearly show the isolated surface areas containing graft which may correspond to the less crystalline areas of the surface.

Somewhat anomalous results were also found in conjunction with the thermally treated PE samples. The crystalline content of the quenched PE was found to be about 7% higher than that of the untreated material. This is very likely a result of the relatively lower thermal treatment temperature used in order to maintain the sample as a fine powder. At this temperature, rearrangement of some of the disordered regions of the material was possible, resulting in the increased degree of crystallinity. However, the results of grafting onto both of the thermally treated samples indicate a significant increase in the percent graft over the untreated PE. While the increase may be related to the thermal treatment and inadequate precautions to prevent thermal oxidation of the sample, it is believed that the result found for the grafted, untreated sample is abnormally low and the actual result should lie somewhere in the region near that for the quenched sample. This problem will be discussed further, subsequently.

The effects of the grafting process on the crystallinity of the PE substrate appear to be relatively small. The low-temperature tail of the broad melting endotherm found for both treated and untreated PE samples indicate that this material contains a wide range of crystalline sizes, presumably due to chain branching, and the broad molecular weight distribution indicated by the high polydispersity (12.8). Therefore, even the annealed sample is not a highly crystalline material with uniform crystal sizes. The lower percent graft and comparable heat of fusion given by DSC area measurements of the annealed, grafted PE compared to the other grafted and ungrafted samples indicate there is a decrease in the crystalline content after grafting. That this is a result of a decrease in the number of smaller crystallites which are molten at the temperature of grafting is evidenced by the relatively slight change in melting temperature of this sample ($\Delta T = 1^\circ\text{C}$). The lower melting temperature ($\Delta T = 3^\circ\text{C}$), measured by DSC in the quenched, grafted sample, also indicates a decrease in the degree of crystallinity, the larger change possibly being due to the larger amount of grafting present. It is interesting that the presence of AN grafts, which are relatively stiff and rigid, do not significantly affect the packing of PE chains into crystallites. This is understandable, however, in view of the fact that low density PE is already a highly branched polymer.

Grafting reactions carried out for varying lengths of time from 2 h to 24 h show that the average lifetime of the active, growing radicals is on the order of several hours. The decrease in the reaction rate to approximately zero after 5 h indicates that either all of the peroxides produced by irradiation have been thermally dissociated or that the grafting has proceeded to such an extent that the initiating sites are occluded by PAN polymer, preventing further initiation as well as preventing further chain growth. The sparse grafting observed by SEM in 1 Mrad grafted PE indicates that at least at the lower doses, the decrease in rate is due to the depletion of radical initiating sites. At higher doses, where there is more complete coverage of the PE particles, it is questionable just which mechanism is controlling. The slight decrease in the percent graft between 10.5 h and 24 h, although well within the experimental error, may be a result of a chain transfer reaction occurring at a very slow rate.

Several independent measurements of the proportions of PE and PAN in the

graft copolymer samples, utilizing SEM, DSC, and infrared techniques, have given percent graft values agreeing within 15% of each other. Results of extraction-time experiments shown that very little ($\sim 10\%$) extractable PAN homopolymer is formed in the grafting process, and the characterization of the percent graft is not believed to be a source of experimental errors. The scatter and disagreement of some results, however, suggest that there are parameters affecting the grafting process other than those investigated and described previously that have not been controlled. The lowered graft results of the 5-Mrad and 10-Mrad air-irradiated samples, in particular, which were the first experiments performed, are considered to be the result of an, as yet, unidentified change in the grafting procedure. The factors subsequently identified as possibly affecting the grafting results include the density of PE packing for irradiation, lack of mixing during grafting, change in rate of heating to initiate polymerization, and variable quantity of dissolved oxygen in AN monomer. The degree of variation of all of these factors was not carefully controlled between experiments and the extent to which they may have affected the percent graft is not known.

CONCLUSIONS

Based on the foregoing discussion, several conclusions are drawn with respect to the major aspects of the grafting process investigated. The grafting efficiency is found to be very high with only 15% of the PAN present as extractable homopolymer. The previously observed relation of increasing graft with increasing radiation dose is found as a linear relation at lower doses (< 8 Mrad) and reaches a saturation at higher doses. The rate of grafting, initially quite high, decreases rapidly to zero after 5 h of reaction, as a direct result of the depletion of initiating radicals at lower doses. Initiation of grafting of both alkyl and peroxy radicals at 77°C is concluded directly from the influence of several factors which showed increased grafting at lower dose rate and higher temperature and decreased grafting from vacuum irradiation. Decreased grafting on oxygen irradiation suggests a change in grafting mechanisms unique to this system in which the large particle surface area, providing a high peroxide concentration, leads to rapid initiation and rapid termination via radical occlusion. The degree of crystallinity can affect the percent graft with more grafting occurring in the amorphous regions, but the effect of grafting on the degree of crystallinity is relatively small. The results presented do not provide conclusive evidence of whether or not grafting occurs only near the particle surface.

Further conclusions, with regard to an industrial radiation process involving AN grafting to PE powder are:

1. Irradiation in ambient air is sufficient to produce high graft yields.
2. The lowest economical dose rate is preferable for highest grafting.
3. Reaction under slight pressure at elevated temperature to reduce processing time is preferable.
4. Percent graft yield may be sensitive to the thermal history of the substrate.

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