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Preparation of Cationic Membrane of Polyethylene Film by γ-Irradiation

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ABSTRACT

Grafting of acrylic acid onto PE film by a pre-irradiation method was studied. In order to prevent formation of homopolymer, Mohr salt $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ was used, and the reaction was carried out in the presence of a swelling agent, such as methanol. The influence of different factors, such as dose, dose rate, and temperature, on the kinetics of the reaction was studied. The infrared spectrum of the grafted acrylic acid onto PE shows bands characteristic of carboxylic acids, which demonstrates that grafting has occurred. The grafting sites were shown to be of a semi-spongy shape and irregular structure which is thought to be due to the copolymerization of acrylic acid onto PE film.

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INTRODUCTION

In recent years the formation of graft copolymers has received considerable attention. Much of this activity can be traced to the speculation that unique properties can be built into a material by grafting techniques. Ionizing radiation has provided a convenient and clean method of activating a substrate polymer and undoubtedly has added impetus to this field of research [1].

When crystalline or vitreous polymers are subjected to radiation, a number of polymer radicals remain trapped in the rigid polymer matrix and may survive for a considerable length of time [2]. These radicals can be used to initiate grafting. For this purpose a monomer is allowed to diffuse into the irradiated polymer. Grafting takes place during the diffusion process and is brought to an end as soon as the polymer is swollen, upon which the radicals acquire enough mobility to combine.

This report presents a study of kinetic reaction of the radiation induced grafting of acrylic acid to low density PE pre-irradiated at different doses (0.25 - 4 Mrad) and dose rates (112 - 570 rad/min).

Acrylic acid was chosen because it is potentially a strong hydrogen bonder. It is obvious that the chemical reactivity could also be increased by grafting of acrylic acid onto PE.

The physical properties of the grafted film in polar solvents such as H_2O, methanol, and ethanol were studied. This should enhance the possibility of industrial application of radiation-induced grafting to PE as a semipermeable membrane.

EXPERIMENTAL

Irradiation Procedure

Samples of PE film (80 μm thick) were placed in small test tubes and irradiated to doses ranging from 0.25 to 4 Mrad at different dose rates (112 - 570 rad/min).

A Panoramic Co-60 gamma source with 3400 Ci activity (Gamma Beam/150-B) at the Nuclear Research Center (N. R. C. T.) was used.

Irradiation dose and absorption measurements were made with a Farmer-Baldwin ionization chamber and Fricke dosimeter, assuming [3] $G_{Fe^{3+}} = 15.5$.

Graft Polymerization Technique

The stabilized acrylic acid, as obtained from Merck Co., was purified by low-pressure distillation in a nitrogen atmosphere.

Ferrous ammonium sulfate (Mohr salt) was also obtained from Merck in pure grade. The irradiated PE films were immersed in a solution containing the monomer (50% acrylic acid), 25% methanol and 25% Mohr salt (3 g/liter), and then degassed by several freeze-thaw cycles using liquid nitrogen. Then they were sealed and kept at constant temperature (40 - 96°C) for various periods of time. The graft yield was obtained from the weight increase of the films as shown in the relationship:

$$\% \text{ grafting} = [(W_2 - W_1)/W_1] \times 100$$

where W_1 is the initial weight of PE film and W_2 is the weight of grafted film.

RESULTS AND DISCUSSION

Effect of Fe^{2+} Ions on the Grafting Reaction

It was found convenient to limit homopolymerization by addition of scavengers [4]. For example, the aqueous solution of monomer used generally contained up to 3 g/liter of ferrous ammonium sulfate.

The effect of Fe^{2+} which results in formation of graft copolymer and prevention of homopolymer can be shown in Eq. (1).

$$\sim\sim\!-CH_2-\underset{\displaystyle\underset{\displaystyle\underset{\displaystyle H}{|}}{\overset{|}{O}}}{\overset{}{\underset{|}{\underset{O}{CH}}}}\!\!-CH_2-CH_2-\sim\sim \xrightarrow{Fe^{2+}} -CH_2-\underset{\displaystyle O^{\bullet}}{\underset{|}{CH}}-CH_2\ldots$$

$$\text{or } (R^{\bullet}) + OH + Fe^{3+} \qquad (1)$$

The initiation of the grafting reaction presumably occurs at radical sites on the polyethylene [Eq. (2)].

$$R^{\bullet} + CH_2{=}\underset{\displaystyle COOH}{\underset{|}{CH}} \longrightarrow R{-}CH_2{-}\underset{\displaystyle COOH}{\underset{|}{CH^{\bullet}}} \xrightarrow{+AA} \text{propagation} \qquad (2)$$

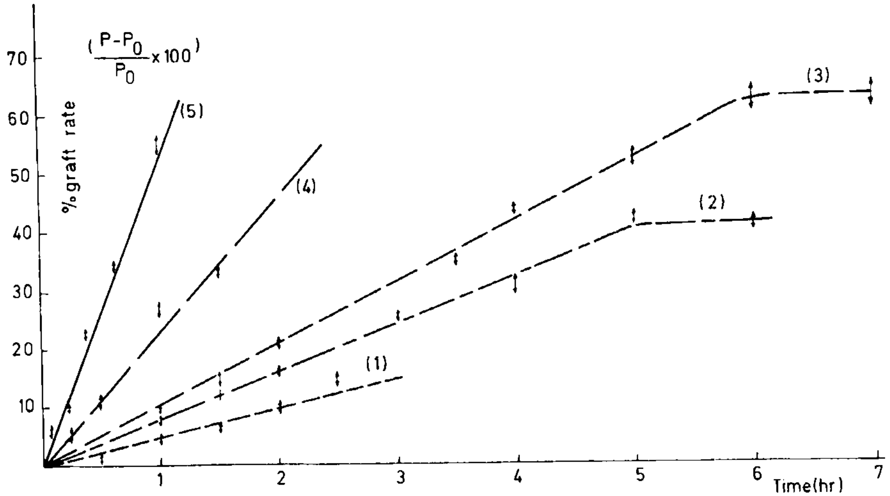

FIG. 1. Effect of dose on grafting rate.

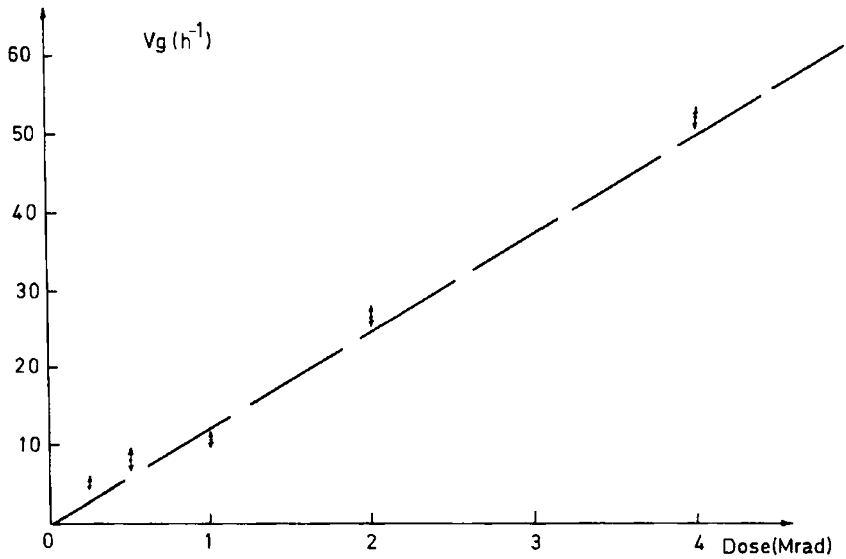

FIG. 2. Variation of pre-irradiation dose vs. initial grafting rate.

Effect of Dose

The effect of dose on the graft rate of acrylic acid onto PE film was studied. The variation of pre-irradiation dose in the range of 0.25 to 4 Mrad versus initial grafting rate (determined from linear portion of the conversion curves, Fig. 1) is shown in Fig. 2.

It was observed that initial velocity varied linearly as a function of the pre-irradiation dose up to a dose of approximately 4 Mrad, but deviations from linearity occurred as the result of recombination of radicals.

The experiments could not be carried out above 4 Mrad, due to the fact that some small cracks were observed on the grafted PE film. Therefore the optimum dose for carrying on the pre-irradiation dose was determined to be 1 Mrad in view of the physical state of the grafted film.

Effect of Dose Rate and Temperature

The effect of dose rate in the range of 112-570 rad/min was studied (Fig. 3). The intensity exponent was found to be [5]

$$V = KI^{\alpha}$$

with

$$\alpha = -0.3$$

The effect of temperature in the range of 40-96°C was also studied (Fig. 4). It was observed that with increasing temperature, the initial rate of grating of PE increases. Because of the physical change of the grafted PE at about 96°C, the experiments could not be carried out further.

From the Arrhenius plot (Fig. 4), the activation energy for the reaction was found to be 20 kcal/mole. In this study 70°C was found to be the optimum temperature for grafting process.

Infrared Spectroscopy

It is well known that acrylic acid easily forms cyclic dimers bridged by hydrogen bonds, especially in nonpolar solvents. This behavior is similar to that of other carboxylic acids [6].

The hydrogen-bonded acid dimer is the principal form of the AA

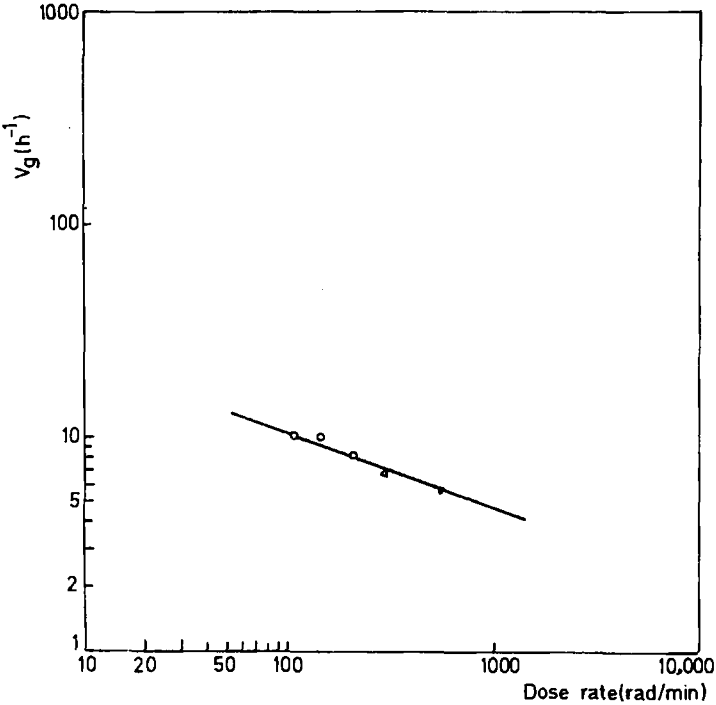

FIG. 3. Influence of dose rate on rate of grafting.

in the grafted PE film. The carboxylic dimer has a center of symmetry; only the asymmetrical C=O stretching mode absorbs in the infrared [7]. Hydrogen bonding and resonance weaken the C=O bond, resulting in absorption at a lower frequency than in the monomer (near 1705 cm^{-1}). Therefore in the resulting graft copolymer (7% graft), in addition to the usual PE bands at 2900, 1450, and 725 cm^{-1} a broad OH band underlying the OH peak at 2900 cm^{-1} was observed which indicates the presence of a strong intermolecular hydrogen bonding [8], and a peak at 1705 cm^{-1} due to asymmetric C=O stretching of carboxylic acids was also observed (Fig. 5).

Scanning Electron Microscope (SEM)

SEM studies were carried on the surface of the grafted and ungrafted films. The ungrafted PE film (Fig. 6) showed almost a

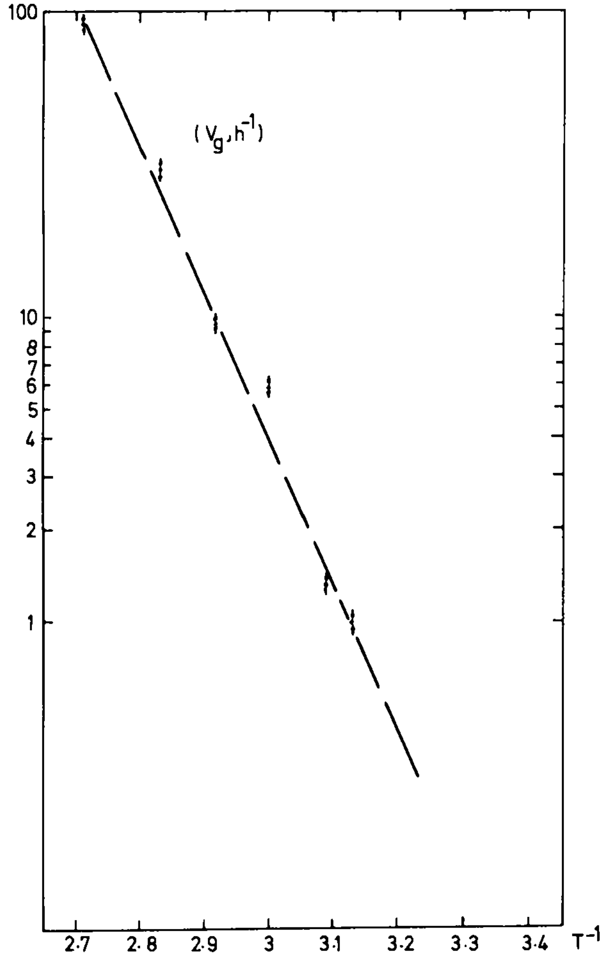

FIG. 4. Arrhenius plot of the effect of temperature on initial rate of grafting.

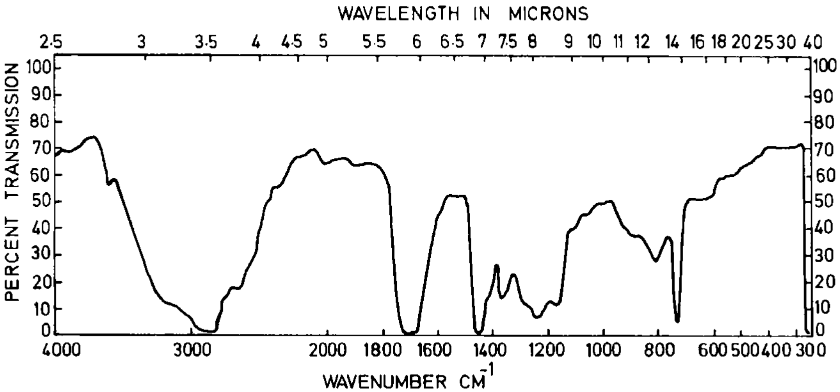

FIG. 5. IR spectrum of the grafted PE film (7%).

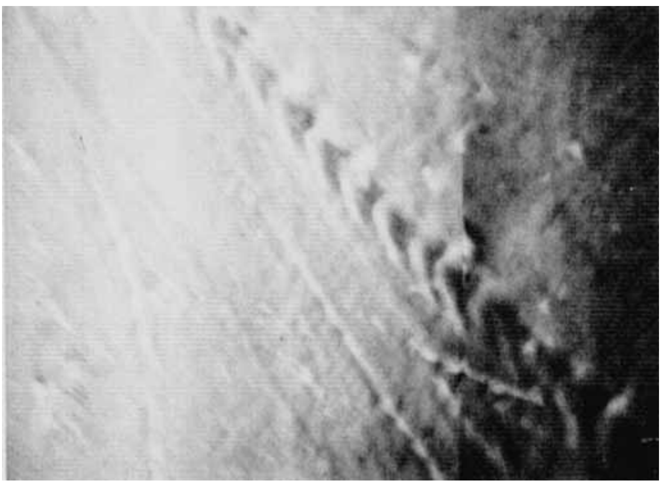

FIG. 6. Electron micrograph of PE film.

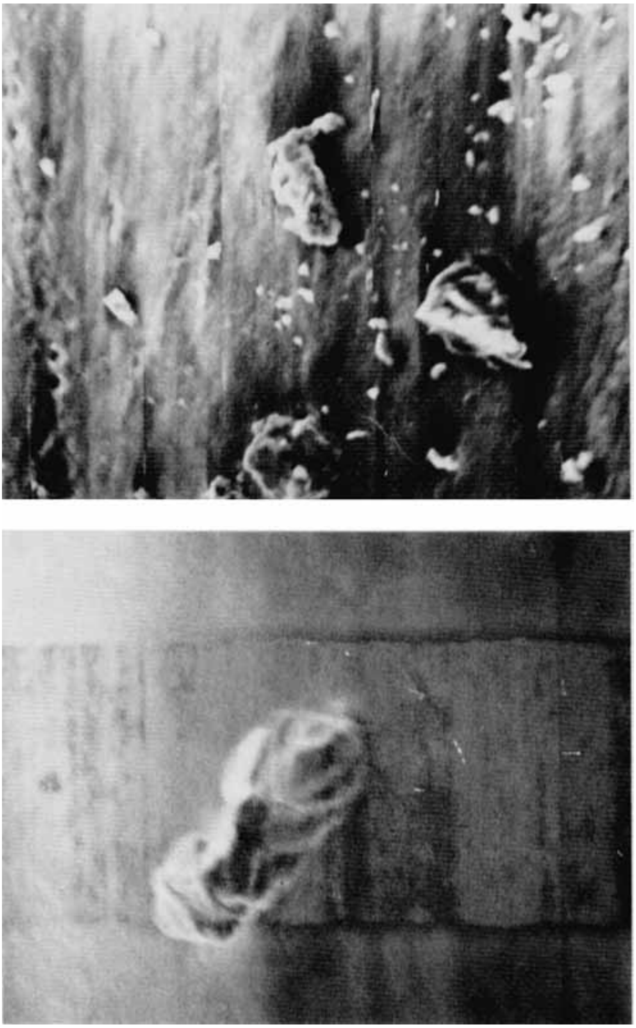

FIG. 7. Electron micrographs of grafted PE film (7%).

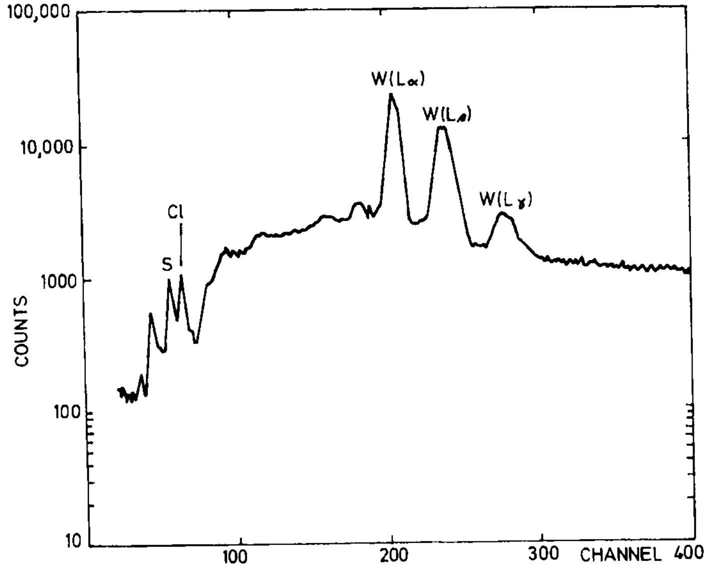

FIG. 8. X-ray fluorescence of the ungrafted PE film.

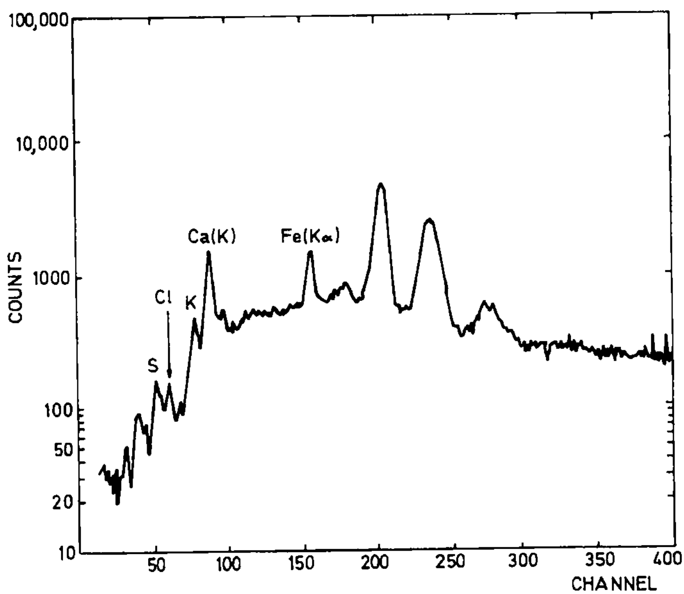

FIG. 9. X-ray fluorescence of the grafted PE film.

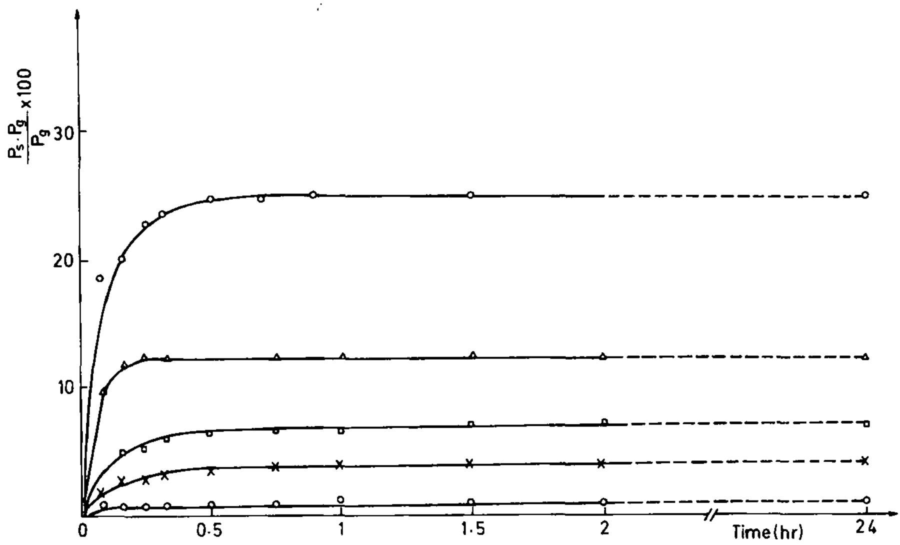

FIG. 10. Swelling of PE film and grafted PE films in water at 25°C: (●) 65%; (▲) 47%; (■) 25%; (×) 13%; (○) ungrafted film.

uniform surface, whereas in the case of grafted PE film large, irregular spongy shapes were observed, as well as small spots scattered all over surface (Fig. 7). These spongy shapes probably show areas of grafting of the acrylic acid onto the PE film. This nonuniformity of the species is due to the some impurities on the surface of the PE film at which the grafting starts and is propagated.

Since in the grafting process a reasonable amount of Mohr salt was used, it was expected that iron ion could either interfere with the crystalline lattice or be adsorbed on the surface of the polymer. This case was demonstrated by use of an x-ray fluorescence technique on the grafted film (Figs. 8 and 9). The spectrum of the grafted film showed a peak in the region of 6.4/keV belonging to the iron ion, indicating the presence of Fe^{2+} ion in the grafted film.

Swelling Properties

Crystalline polymers do not dissolve and are barely swollen unless the temperature is raised to a point at which some crystalline regions start to melt. Polyethylene, for example, can be readily dissolved in benzene or toluene only at temperatures above about 60-80°C, although irradiated PE will then only swell [9]. Therefore the degree of swelling of PE and grafted PE film in water and other polar solvents such as methanol and ethanol were studied.

Figure 10 shows the swelling rate of films with different percentages of grafting (13, 25, 47, 65%) in water at 25°C. In the case of PE film, swelling measurement appeared as a straight line, whereas in higher grafting percentage of the PE, the degree of swelling increased considerably. The rates of swelling of the grafted PE in methanol and ethanol were lower with respect to water, whereas in the case of the two alcohols, the results were almost the same.

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