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Radiation-Induced Graft Copolymerization of Styrene to Poly(vinyl Chloride) Latex in a Pilot Plant System

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ABSTRACT

A pilot plant study of the radiation grafting of styrene to poly(vinyl chloride) (PVC) latex is described. When correct extraction conditions are used less than 3% grafting took place. This is shown to be due to the low total radiation doses needed to polymerize the styrene in an emulsion system. A parallel study with PVC film did, however, lead to substantial true grafting. The G (radical) value for PVC film as determined by ESR was found to be 4.6.

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INTRODUCTION

Styrene–poly(vinyl chloride) (PVC) graft copolymers are of considerable industrial interest, in that they have improved processability and higher tensile strength, elongation, and flexural strength compared with pure poly(vinyl chloride) or polystyrene [1, 2]. Furthermore, the styrene–poly(vinyl chloride) system is, in principle, ideal for direct radiation grafting, since the yield of free radicals is much greater for poly(vinyl chloride) than for styrene. Studies of grafting of styrene to PVC films and powder have been reported [3-6], but only one report on grafting to PVC latex was found [7].

In the present paper the pilot plant grafting of styrene to PVC latex and a brief parallel study to PVC film are discussed.

The reported G_R values for PVC, measured by ESR absorption methods, range from 1.6 to 17 in vacuo at room temperature [8-10]. These values could be rather unreliable, since the use of an internal standard is not mentioned [8, 9] or is unsuitable for this work, since the irradiation of the PVC was accomplished with fast electrons [10]. In view of this, a more accurate G value for the free-radical production in γ-ray irradiated PVC was determined.

EXPERIMENTAL

Emulsion polymerization experiments were conducted in a flow system where the emulsion is recirculated from a stirred vessel through transfer lines to a helical flow reactor positioned within a Co-60 source [11]. Figure 1 shows a schematic diagram of this system.

The system is all stainless steel, except for Teflon for some moving surfaces, and was made up of typical industrial components. Ultra-high-purity nitrogen was used for oxygen desorption as well as for maintaining a nitrogen pressure blanket of about 100 psi during the polymerizations. γ-Rays from a Co-60 source were utilized to prepare the vinyl chloride polymer latex as well as to "copolymerize" the styrene with the latex.

The polymerizations were conducted in the total recirculation mode at conditions approaching batch reactor behavior, at 24° C and at a dose rate of 0.16 mrad/hr. Sodium lauryl sulfate was the emulsifier used, and the experiments covered a wide range of emulsifier to monomer ratio.

The conversion of styrene in the presence of PVC was followed by gravimetric analysis. Soxhlet extraction for 4 days in 100%

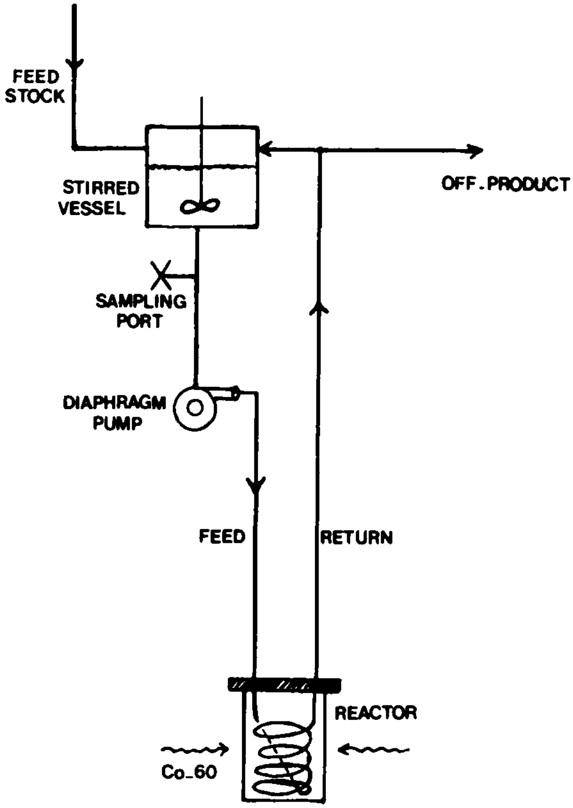

FIG. 1. Schematic diagram of pilot-plant system.

benzene was found to be necessary in order to ascertain the removal of all the homopolymer. Infrared spectra of the purified polymer samples were also obtained. The intrinsic viscosity of the polystyrene homopolymer was measured with an Ubbelohde viscometer in benzene at 25.0° C.

Monomer purification, pilot plant polymerization procedure, and analyses are discussed in more detail elsewhere [11].

A transmission electron microscope (JEM-120, Japan Electron Optics) was utilized to obtain particle size data on the PVC and PS/PVC emulsions. Particle size data from different batches and dilutions of the same emulsion and for different magnifications on the electron microscope were reproducible to within 6%. Particle counts ranged between 130 and 280 for a given sample and for any given particle size distribution.

The weight-average particle size diameter $\bar{d}_w$ is defined as

$$\bar{d}_w^3 = \sum n_i d_i^6 / \sum n_i d_i^3$$

The average densities, weighted according to the relative amounts of polystyrene and poly(vinyl chloride) in the final copolymer as determined gravimetrically, were utilized for the calculation of N (the number of polymer particles per milliliter of emulsion).

Bulk graft copolymerization experiments were conducted by utilizing Genotherm, unplasticized PVC film (American Hoechst Corporation) of 0.035 mm thickness, which was swollen with styrene for 24 hr, thus insuring equilibrium swelling.

The styrene monomer was purified by washing with 5% NaOH solution, washing with water, drying on $CaCl_2$, and distilling at reduced pressure over CaH_2. The films were irradiated in vacuo in a Gamma cell 220 Co-60 source (Atomic Energy of Canada, Ltd.) at a total dose of 3.6 Mrad and a dose rate of 0.41 Mrad/hr. After irradiation, the films were exhaustively extracted with benzene in order to remove the homopolymer. The true percent grafting was thus calculated relative to 100 g of original PVC polymer.

The unplasticized PVC film was degassed at 10^{-4} Torr, while contained in ESR tubes, then sealed under vacuum and irradiated in the Co-60 source at a dose rate of 0.41 Mrad/hr. ESR spectra were recorded with an X-band spectrometer with 100 kHz field modulation (Japan Electron Optics Laboratory Co., Model JES-ME-1X) with double-mode cavity.

The number of free radicals was estimated by double integration of the first derivative spectrum and comparison with a sample with known number of spins. This sample was α,α'-diphenyl-β-picrylhydrazyl uniformly dispersed in a polymer so as to provide the same dielectric losses as the PVC samples. The reference sample was MgO powder containing Mn^{2+} ions thermally dispersed.

RESULTS

Table 1 shows a summary of all the data from the successful pilot-plant polymerizations of styrene in the presence of PVC latex (runs B through E) together with results of a styrene/polystyrene run (run A) of a previous study [11, 12] and calculated from the original raw data.

TABLE 1. Complete Data from All Successful Pilot-Plant Experiments[a]

Run	Description	SLS on monomer (initial) (%)	Monomer-water ratio (initial)	Conversion (%)	Total dose (Mrad)	[M] in particles (mole/liter)	Actual rates (initial) (mole/liter-hr)	$N \times 10^{-17}$ per liter water	$\overline{D_w}/\overline{D_n}$	$\overline{DP_n}$	$\bar{n}^{*}$[b]
A	PVC	0.5	0.26	23.3	0.051	–	–	4.5	1.3	–	–
B	styrene on polystyrene	0.25	0.0050	68.1	0.20	3.6	0.073	3.3	–	6,600	0.38
C	styrene on PVC	0.5	0.020	31.0	0.045	3.1	0.040	–	–	–	–
D	styrene on PVC	0.25	0.061	45.1	0.061	8.5	4.3	–	–	–	–
E	styrene on PVC	0.25	0.11	44.0	0.023	7.5	2.0	3.0	1.3	22,200	0.50
F	styrene on PVC	0.25	0.037	64.6	0.085	5.7	4.6	3.3	1.2	6,400	0.45

[a] Dose rate, 0.16 Mrad/hr (0.35 Mrad/hr for B).

[b] Calculated from the relationship $R_p = k_p[M]_p N\bar{n}$. A value of 27 m^{-1} sec^{-1} was chosen for k_p [13].

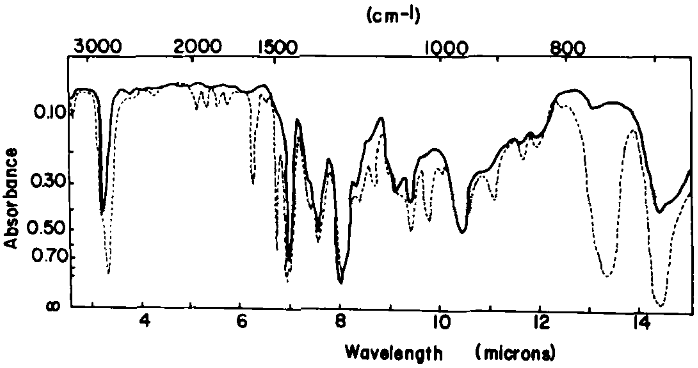

FIG. 2. Infrared spectra of copolymer from run D. (- -) after Soxhlet extraction with a 70:30 by volume cyclohexane-benzene mixture for 30 hr [7]; (—) after Soxhlet extraction with pure benzene for 4 days.

The styrene/PVC emulsion polymerization runs conducted over a wide range of emulsifier to monomer ratios and various monomer to polymer ratios showed a very low (or negligible) true grafting yield of less than 3%. The apparent grafting yield was found to be highly dependent on the extraction condtions.

Figure 2 shows the infrared spectrum for run D copolymer extracted with a cyclohexane–benzene solvent mixture (70:30 by volume) for 30 hr in the same manner as employed by Wang [7] and the infrared spectrum for the same copolymer extracted in 100% benzene for 4 days. It can be seen that essentially all the characteristic lines of polystyrene, for example 13.2 μm, have disappeared with the more severe extraction procedure. In fact, extraction according to Wang's procedure led to an erroneous conclusion of 93% grafting yield.

The grafting experiments on the PVC film, on the other hand, led to a grafting yield of 33 ± 1% when a total dose of 3.6 Mrad was used at 24° C and a dose rate of 0.41 Mrad/hr. This value was checked by dissolving in dimethyl sulfoxide and precipitating in cold benzene. No further polystyrene homopolymer could be extracted.

Table 1 includes the particle size data for the initial poly(vinyl chloride) latex for runs D and E. It can be seen that there was only a small decrease in the number of particles, presumably due to some coagulation. In any case, there was no evidence for new particle formation from the total number or from the appearance of the electron micrographs of the two copolymer runs.

The polymerization rates for all the experiments conducted are included in Table 1. The rates of polymerization of the styrene can be seen to be much higher, as expected, at the higher styrene contents of the particles. The values of $\bar{n}$, the average number of radicals per particle, were calculated according to Smith-Ewart theory, from the equation

$$R_p = k_p[M]_p N\bar{n}\cdot$$

the literature value of 27 m^{-1} sec^{-1} being used for k_p, the propagation rate constant for styrene at 24° C. The ideal value for $\bar{n}$ is 0.5 for Case I Smith-Ewart kinetics. The actual values obtained are included in Table 1 and vary between 0.43 and 0.64, in good agreement within the experimental error.

The accumulation of free radical in PVC film as a function of dose at a dose rate of 0.41 Mrad/hr is shown in Fig. 3. A value of 4.6 radicals/100 eV was obtained at room temperature.

DISCUSSION

The radiation-induced polymerization of styrene sorbed into poly(vinyl chloride) latex proceeded smoothly in the semicontinuous pilot-plant system used. The latices produced were of low solids content (15-20%) to avoid any possible coagulation in the circulating system. No evidence of the production of new particles was obtained, and the calculated values of $\bar{n}$ were 0.50 and 0.45, showing that normal Case I Smith-Ewart kinetics were operating. However, no measurable amounts of grafting took place when a rigorous extraction procedure was used. A parallel experiment on irradiating PVC film in which styrene was absorbed did show a good grafting yield, in agreement with literature work.

It is believed that the differences in the grafting yields between the latex and the film experiments is mainly due to the total doses used. It can be seen from Table 1 that the maximum total dose used in the pilot plant latex grafting experiments was only 0.085 Mrad. This was due to the highly favorable emulsion polymerization kinetics compared with bulk systems. On taking the data of Harmer as the most relevant, since styrene swollen powder of pure PVC was used, it can be seen that the rate of grafting was about 25%/Mrad at comparable dose rates. Thus, even in our highest dose experiment, the grafting yield would only be 2.1%, within the limits of the results actually obtained.

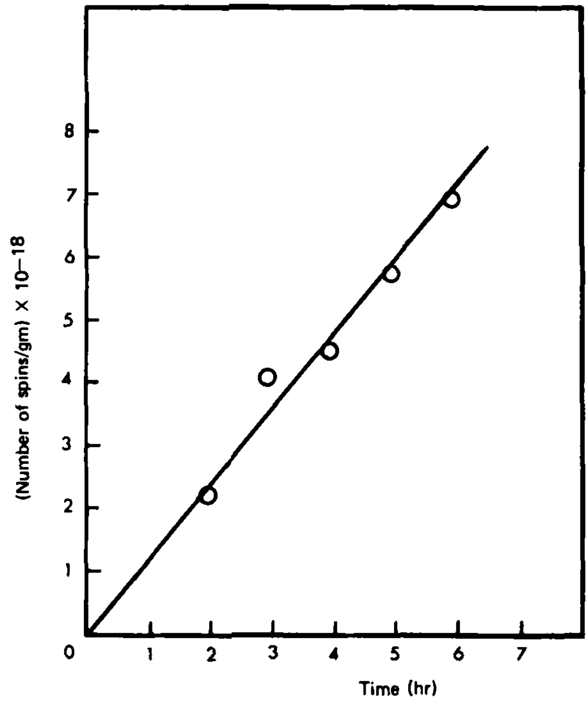

FIG. 3. Accumulation of free radicals in PVC in vacuo as a function of dose; dose rate 0.41 Mrad/hr.

In conclusion, it can be said that the PVC-styrene system is ideal, in principle, for mutual radiation grafting because of the G (radical values of 4.6 and 0.7 for the PVC and styrene [14], respectively. However, in a latex system, the high rates of polymerization of the styrene lead to very low total doses, even for high conversions. Consequently only minor amounts of grafting are achieved.

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