

## Radiation-Induced Emulsion Polymerization of Vinyl Acetate and Styrene

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### Synopsis

Studies have been made of the  $\gamma$ -induced emulsion polymerization of styrene and comparisons made with chemically initiated emulsion polymerization. The polymerization proceeded smoothly to high conversions at 0 and 60°C, the reaction showing a high  $G$  (monomer) value. Complete conversions were obtained with total doses of less than 0.05 Mrad. In accordance with the behavior expected of systems having a constant rate of initiation, the molecular weight was found to decrease with decreasing temperature. The molecular weight and particle size distributions were narrower than those obtained in chemically initiated emulsion polymerizations at the same temperature. The radiation-induced emulsion polymerization of vinyl acetate proceeded smoothly at temperatures in the range 0–50°C to give polymers of much higher molecular weight than those obtained from chemically initiated polymerizations at the same temperature. Complete conversion was attained after a dose of 0.02 Mrad for latices approaching 50% solids. The elimination of ionic endgroups in the poly(vinyl acetate) radicals tends to drive the polymerization from the aqueous phase, resulting in faster rates and higher molecular weights than are obtained from chemically initiated systems. Rates of polymerization were found to be independent of temperature and the molecular weight of the polymer to be independent of dose rate. Latices of poly(vinyl acetate) of high solids content were evaluated for latex and film properties and found to have improvements over commercially available samples in both areas, especially in clarity of film and scrub resistance. A number of acrylate and maleate esters were copolymerized with vinyl acetate in a radiation-initiated emulsion system. High molecular weight copolymers were produced after low dose.

The use of high energy radiation to initiate emulsion polymerization systems has obvious advantages. The comparatively high yield of free radical from the radiolysis of water (4–7 per 100 eV) plus the large kinetic chain lengths found in emulsion polymerization ensure the efficient use of the radiation. In addition there are a number of other potential advantages over chemical initiation. The flux of radicals is constant throughout the reaction and not diminishing exponentially as in the case of chemical initiation. This leads to greater ease of removal of residual monomer

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without the disadvantage of leaving residual catalyst in the system. Furthermore there is no loss of catalyst during any induction period which might occur, leading to different polymer and latex properties or premature exhaustion of the catalyst. The temperature dependence of the radical flux with radiation is essentially zero. This enables polymerization to be carried out at low temperatures without the necessity of devising elaborate and often unreliable redox systems which are particularly vulnerable to induction period losses. Other possible advantages are the ease of control, less pH change than often found with catalysts, no combined or free catalyst fragments such as sulfate ions, and lack of interference on changing emulsifiers such as, for example, to a cationic system. Possible disadvantages, on the other hand, are the direct interaction of the radiation with the polymer, leading to increased branching or even, eventually, to some gelation. The literature on radiation-induced emulsion polymerization is surprisingly meager compared with bulk or solution polymerization. Some early work was described by Ballantine<sup>1</sup> in 1954 but never published. Okamura and co-workers<sup>2-5</sup> carried out extensive work which was published also in 1954 continuing through 1960. A number of different groups of workers have investigated the radiation-initiated polymerization of styrene in some detail.<sup>6-8</sup> More recently, extensive work has been reported by Hummel and his co-workers.<sup>9-11</sup> Other references will be quoted in the discussion section. The work to be described in this paper will be mainly concerned with the radiation-induced emulsion polymerization of vinyl acetate, although a few experiments were also conducted with styrene as the monomer.

## EXPERIMENTAL

The  $\gamma$ -radiation was provided by a 1500-Ci <sup>60</sup>Co source contained in a shielded room. Dosimetry measurements were made by means of the Fricke dosimeter a value of  $G(\text{Fe}^{+++})$  as 15.6 eV being assumed. Potassium persulfate was used for all the chemically initiated polymerizations. Sodium lauryl sulfate was used as the emulsifier in most cases. Later a number of polymerizations were conducted with the use of an ethylene oxide-nonyl phenol product. The monomers were freed from inhibitors by distillation and stored over calcium sulfate before use.

The polymerizations were carried out in two ways. A 200-ml round-bottomed flask was used with dented sides and the opening necked down to about 12 mm. The soap solutions were frozen in the vessel, the monomer added, and the whole degassed with at least three freeze-thaw cycles. The vessels were then sealed off under a high vacuum of  $10^{-5}$  torr at a previously formed constriction. Agitation during the polymerization was carried out by rotating on an angle with an electric stirrer. The latices were freed from small amounts of coagulum, if present, by passing through a 50-mesh screen. The polymers were isolated by coagulation of the latex with Dry Ice and filtered.

For the rate studies a simplified dilatometer was constructed and is illustrated in Figure 1. The dilatometer consisted of a reaction vessel A of 75 ml capacity sealed off at the upper part by a Delmar-Urry O-ring stopcock B. A side arm D connected the reaction vessel to a small reservoir C, into the top of which was sealed a graduated 1-ml pipet E whose end extended to within 5 mm of the bottom of the reservoir. The upper part of the pipet could be sealed off from the reservoir by a 2-mm stopcock F, and it could be attached to a high vacuum line through an O-ring joint H sealed to the upper end of the pipet. A second side-arm G extended from just above the seat of the stopcock B to a right-angle bend 4 cm from the seal and contained an O-ring joint H at the upper end for attachment to a vacuum system. Agitation was provided by a magnetic stirring bar I.

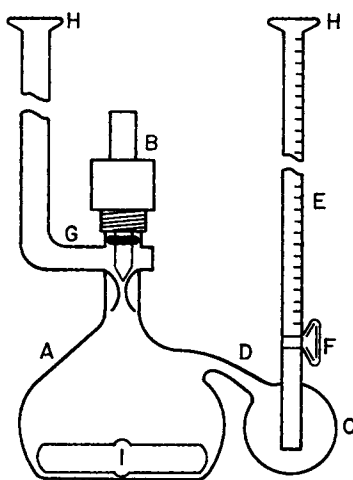


Fig. 1. Dilatometer.

The dilatometer could be loaded either under a nitrogen atmosphere or under high vacuum conditions. In the former procedure, the nitrogen was admitted through the side arm G with the stopcock B in place and released through the pipet E. The dilatometer was flushed for 30 min, after which mercury was added to the reservoir C through the pipet E until it covered the end of the pipet. Then the stopcock F was closed, sealing the reservoir from the atmosphere. The stopcock B was removed maintaining the nitrogen flow, and the water, soap, and vinyl acetate added through the opening. Mercury was added to fill the pipet to the zero graduation mark, the stopcock B replaced but not seated, and the stopcock F opened slowly so that the liquid was forced above the seat of stopcock B. The stopcock B was then tightened until it seated so that the dilatometer was ready for irradiation. Temperature control was maintained by placing the dilatometer in a constant temperature water bath which was placed on a magnetic stirrer to provide the agitation in the dilatometer. The dilatom-

eter was allowed to come to temperature equilibrium, the mercury column adjusted to the zero mark, and the system exposed to radiation.

In order to load the dilatometer under high vacuum conditions, the side-arm G was attached to a vacuum manifold. Two loading flasks sealed by vacuum stopcocks and containing the previously degassed vinyl acetate and soap solutions were attached to the manifold. A quantity of mercury, sufficient to cover the end of the pipet when the mercury is tipped into the reservoir, was placed in A. The assemblage was then evacuated to as high a vacuum as could be attained ( $10^{-5}$  mm) and the stopcock F closed. The whole assemblage was tipped to allow the mercury to pass into the reservoir and the stopcocks to the water and vinyl acetate flasks were opened to allow the reactor to fill. Mercury was added to the pipet, E. The stopcock F opened, forcing the liquid in the reactor to rise above the seat of stopcock, B, and this stopcock was then tightened, sealing the dilatometer. The manifold was then removed and the dilatometer was ready for irradiation.

As in most polymerization reactions, there is a decrease in volume on going from a monomer to a polymer system. This decrease is linear with conversion, and therefore the progress of the polymerization can be followed by the change in volume of the system as a function of time. This change in volume of the system is reflected by the decrease in the length of the mercury column as the mercury enters the dilatometer to compensate for the decreasing volume of the polymerizing systems. Readings of the mercury column were made by interrupting the irradiation periodically and reading the mercury level visually. The water used in this system was degassed by refluxing for 48 hr and was stored under a nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Styrene

A few experiments were conducted with styrene in which chemical (potassium persulfate) initiation and radiation were used at  $60^{\circ}\text{C}$ ; in

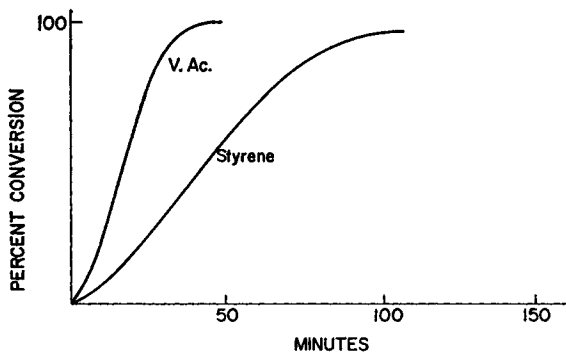


Fig. 2. Conversion as a function of time. Dose rate 0.02 Mrad/hr.

TABLE I  
Chemical and Radiation Polymerization of Styrene in Emulsion

Property	Preparation		
	$K_2S_2O_8$ at 60°C <sup>a</sup>	$\gamma$ -Radiation	
		60°C	0°C
pH	3.8	9.2	7.9
Surface tension, dyne/cm	61.1	68.9	69.0
Particle size, $\mu$	0.13	0.10	0.07
Molecular weight (viscosity)	2,700,000	1,664,000	413,000

<sup>a</sup> Recipe used: styrene, 25 g; water, 75 g; sodium lauryl sulfate, 0.5 g; potassium persulfate, 0.2 g.

addition radiation polymerizations were carried out at 0 and 30°C. A typical conversion curve is included in Figure 2. The polymerizations proceeded smoothly to more than 99% conversion. The recipe used and some of the properties of the latices and polymers are given in Table I. As can be seen from Figure 2, complete conversion was achieved at 30°C in less than 2 hr at 0.02 Mrad/hr. Since the kinetics of this system have been reported<sup>6-10</sup> in some detail, no special effort was made to continue the rate studies. The activation energy of the rate was determined, however, and found to be 3.6 kcal/mole in excellent agreement with the value of 3.7 kcal/mole reported by Ballantine.<sup>1</sup> Other values have been reported, however, including zero<sup>6-11</sup> and 7.2 kcal/mole.<sup>7</sup> Since the values contain the temperature dependence also of particle formation it is not

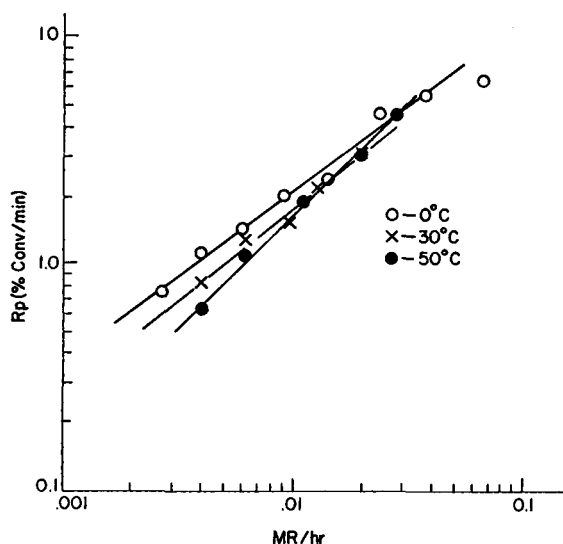


Fig. 3. Dependence of rate on intensity at various temperatures: (O) 0°C; (X) 30°C; (●) 50°C.

surprising that different values have been found. The figure of 7.2 kcal/mole reported by Vanderhoff was calculated from molecular weight data, however, and did not include the contribution from the particle formation. It is therefore in good agreement with the normal value for propagation of 7.8 kcal/mole. The molecular weight of the polystyrene decreases with decreasing temperature consistent with a constant rate of initiation and a decreasing rate of propagation. The pH of the chemically produced latex was quite low due to acid produced from the decomposition of the potassium persulfate but slightly alkaline in the radiation-produced latices. The surface tension of the chemical latex was also somewhat lower, due possibly to a contribution from the sulfate endgroups of the polystyrene.

The particle sizes were all found to be in the range of 1000 Å. The distributions however were quite different and are shown in Figure 3. Those produced by radiation were somewhat narrower especially the latex prepared at 60°C. Attempts to measure the molecular weight distribution by the column elution technique were hampered by poor resolution at the very high molecular weight end, i.e., above 4 million. It was clear however, that somewhat narrower distributions were obtained with the radiation polymers. Details of these measurements have been presented elsewhere.<sup>12</sup>

### Vinyl Acetate

The study of radiation-induced emulsion polymerization of vinyl acetate consisted of (a) an in-depth study of the reaction variables in the case of vinyl acetate homopolymerization including possible post effects, (b) a study of the properties of the resulting vinyl acetate homopolymer and copolymer latices themselves, including some properties of the films.

**Reaction Variables.** The effect of a number of reaction variables on the radiation-induced polymerization of vinyl acetate was studied in some detail in a standard system of 60 g water, 15 ml vinyl acetate, and 0.75–1.6 g sodium lauryl sulfate. This recipe was irradiated in the dilatometer described in the experimental section and illustrated in Figure 1 to yield at complete conversion a latex of 20% solids. A typical plot is included in Figure 2, it can be seen that complete conversion was achieved with less than 0.02 Mrad.

The use of the dilatometer described in Figure 1 made it imperative that the post-irradiation behavior of the system be known, since the method of operation involved interrupting the irradiation at periodic intervals to read the drop of the mercury column.

A number of experiments were therefore conducted with the use of an automatic recording dilatometer and the standard 20% solids recipe. The polymerizations were interrupted by lowering the radiation source at various conversions up to 50%. A 30-min waiting period failed to produce any additional polymerization, and the rates were identical before and after the interruption. It was clear therefore that at least up to 50% conversion no significant post-effects were involved.

It is interesting, however, that the work of Allen et al.<sup>13</sup> showed that some further polymerization was obtained after stopping the radiation at 70% conversion. The lack of post-effect during most of the polymerization of vinyl acetate compared with styrene is probably due to the ease of chain transfer to monomer with vinyl acetate plus the high propagation rate constant. It has been calculated<sup>14,15</sup> that in the emulsion polymerization system vinyl acetate transfers many times during the kinetic chain length compared with styrene. The resulting radicals can easily diffuse out of the particles and eventually lead to termination. However, as the conversion increases, more and more macro-radicals are produced and these remain in the particles. Thus, the post-effects so common with most monomers are absent with vinyl acetate, except at higher conversions.

A prior study on the chemically initiated emulsion polymerization of vinyl acetate<sup>14</sup> had shown a first-order dependence of the rate of polymerization on initiator concentration. A determination of the exponential dependence of the rate on the intensity of radiation was made at 0°C, 30°C, and 50°C for comparison with the cited work and with the 0.4 power dependence required by the Smith-Ewart theory. Figure 3 shows the exponential dependence to be 0.71, 0.79 and 0.90 at the respective temperatures. The scatter observed in the upper portion at higher dose rates at 0°C is a consequence of the high intensity rates which are obtained by approaching closely to the cobalt source and the attendant increasing critical nature of the geometrical positioning of the reaction flask in relation to the source. The very small temperature effect shows the compensating effect of other changes negating the normal 7.3 kcal/mole associated with the propagation rate constant.

The deviation of the observed exponential dependence from that expected from the Smith-Ewart theory<sup>16</sup> is commonly noted in the chemically initiated emulsion polymerization of vinyl acetate and has been partly attributed to the solubility of vinyl acetate in water. The observed increase with increasing temperature would follow the increase of solubility with temperature. In addition, the failure to show first-order dependence as was realized with chemical initiators may be a consequence of the absence of such ionic stabilizing groups as are found in the persulfate-initiated polymerization by reaction of a sulfate radical with a vinyl acetate monomer in the water phase. A theoretical and experimental treatment of the chemically initiated system has recently been presented elsewhere.<sup>14</sup>

The molecular weights of these polymer latices were determined by viscosity measurements in acetone solutions. The latices were broken by freezing. The polymer was then washed thoroughly with water to remove the soap residue, dissolved in benzene, reprecipitated in heptane, and vacuum-dried. A 0.5% solution in acetone was prepared for viscosity measurements. Table II shows that the molecular weight is independent of the intensity of radiation at each of the temperatures of polymerization. The data also indicate that the molecular weight is an inverse function of temperature, this relationship will be further discussed in a later section.

TABLE II  
Effect of Dose Rate and Temperature on Rate and Molecular Weight

Temp, °C	Dose rate, Mrad/hr	$R_p$ , % conversion/ min	Molecular weight $\times 10^{-6}$	
			Original	After hydrolysis and reacetylation
0	0.066	6.55	2.75	1.15
	0.037	5.72	—	—
	0.023	4.33	2.3	0.853
	0.014	2.43	2.96	—
	0.009	2.04	2.5	1.15
	0.006	1.45	—	—
	0.004	1.12	—	—
	0.0027	0.77	2.4	1.39
	0.0195	3.20	2.27	—
30	0.0127	2.19	2.09	1.0
	0.0096	1.53	—	—
	0.0062	1.27	2.15	—
	0.004	0.84	2.25	—
	0.0275	4.64	1.82	—
50	0.0195	3.14	1.66	—
	0.011	1.93	1.4	0.7
	0.0062	1.10	1.33	—
	0.004	0.65	1.28	—

The dependence of the rate of polymerization and the molecular weight on the emulsifier content was determined at 0°C. The results are shown in Table III and in Figure 4 for two soaps of different chemical structure, dioctyl sodium sulfosuccinate and sodium lauryl sulfate. The slopes indicate a dependence of rate on emulsifier content of about first order (0.9 and 1.0, respectively). This high order of dependence contrasts sharply with the almost zero order found with initiation by potassium persulfate. It would appear that the stabilizing effect of the sulfate endgroups tends to drive the reaction into the aqueous phase, leading to comparative independence of the soap concentration in the case of persulfate initiation.

The molecular weights of the polymers made in the study of emulsifier concentration were found to be independent of the rate and emulsifier concentration (Table III). This is to be expected if the main termination

TABLE III  
Effects of Soap Concentration on Rate and Molecular Weight at 0°C

Soap concn., mole/l. <sup>a</sup>	$R_p$ , conversion/min	Molecular weight $\times 10^{-6}$
0.096	4.20	2.3
0.076	3.25	2.47
0.064	3.10	2.01

<sup>a</sup> Sodium lauryl sulfate.



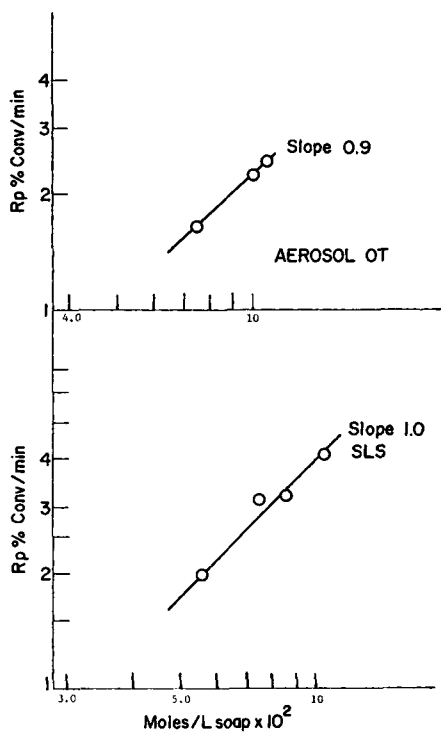


Fig. 4. Dependence of rate on soap concentration.

mechanism found in this polymerization is chain transfer, as has been reported by various authors.

A few measurements were made of the rate of polymerization as a function of the water-monomer ratio at 0°C and at a constant rate of initiation and concentration of soap. The results presented in Table IV indicate that an increase in rate might be expected as the water monomer ratio approaches 1:1. This might be a consequence of the reduced efficiency of heat transfer of the system as the relative amount of the water phase is reduced. The decrease in rate at 2:1 ratio is coincident with a destabilization of the system, the stirring in the dilatometer being not efficient enough to maintain a homogeneous system at the high monomer to water ratios.

TABLE IV  
Effect of Water-Monomer Ratio on Rate and Molecular Weight

H <sub>2</sub> O/VA	$R_p$ , % conversion/min	Molecular weight $\times 10^{-6}$
6/1	1.31	2.02
4/1	1.48	1.89
3/1	2.60	3.33
2/1	0.98 <sup>a</sup>	2.86

<sup>a</sup> Latex broke before completion.

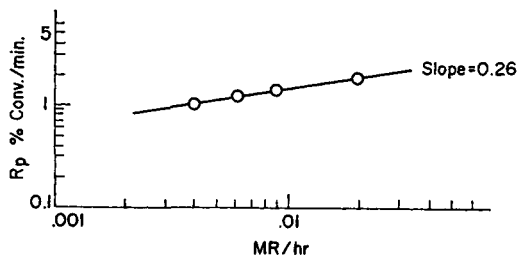


Fig. 5. Dependence of rate on intensity at a constant number of particles.

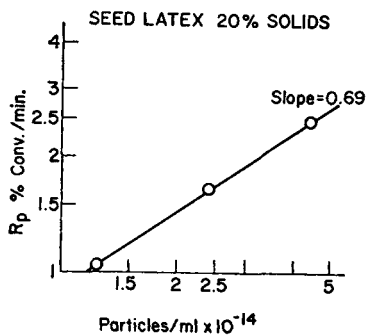


Fig. 6. Dependence of rate on the number of particles at a constant intensity.

The rate of polymerization in a system containing a constant number of particles should be independent of the intensity, provided the system follows classical Smith-Ewart case II emulsion-polymerization kinetics.<sup>16</sup> In order to evaluate the relation in the vinyl acetate system, a standard latex of 20% solids was prepared from vinyl acetate, water, and 2.5% sodium lauryl sulfate (based on weight of water) and irradiated at 40°C at 0.0062 Mrad/hr for 5 hr. The particle size of this latex was measured by light scattering and found to be 1640 Å. Different amounts of this standard latex was added to the dilatometer after being flushed with nitrogen and enough degassed water and monomer added to bring the total per cent solids to 20%. A small additional amount of soap (0.15–0.2 g), insufficient to cause new particle formation, was also added to stabilize the charge and the dilatometer sealed off and irradiated at the desired temperature. Two series of experiments were run the first in which the number of particles (amount of seed latex) was held constant and the intensity varied, and the second in which the intensity was held constant and the number of particles initially present varied.

Figure 5 shows the rate-intensity relationship found at 50°C at a constant number of particles. The slope of the log-log plot is found to be 0.26, which shows that this system approaches Smith-Ewart kinetics even at 50°C compared to the chemically initiated polymerization in which the exponential dependence was found to be 0.8.<sup>14,15</sup>

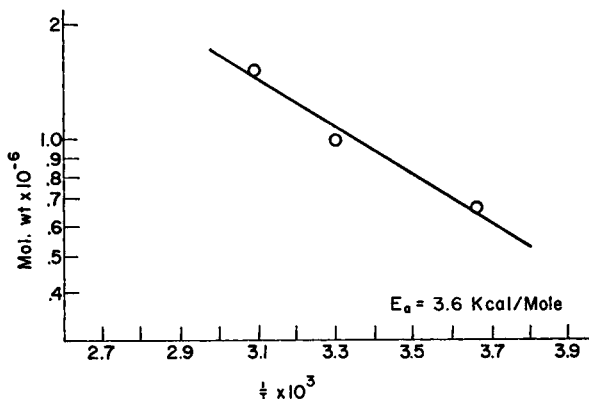


Fig. 7. Arrhenius plot of the molecular weights of low-conversion polymers from radiation-induced vinyl acetate polymerization. *Note added in proof:* Points 1 and 3 were inadvertently reversed, i.e.,  $E_a = -3.6$  K cal/Mole.

The relationship between rate and number of particles is shown in Figure 6. The log-log plot indicates an exponential relation of 0.7 compared to 0.2 for the chemically initiated system and the 1.0 dependence predicted from Smith-Ewart kinetics. This again indicates that the radiation-induced emulsion polymerization of vinyl acetate is beginning to approach "classical" behavior, even at 50°C.

The molecular weights of the polymers made in the radiation-induced emulsion system, e.g., styrene, have been very high, and while they diminished with decreasing temperature of polymerization the decrease was not nearly as marked as that observed with chemically initiated bulk or suspension polymerization systems. Since the molecular weight would be expected to increase with increasing temperature at a constant rate of initiation because of the temperature dependence of the propagation reaction this suggests a termination mechanism which is also temperature dependent. The chain-transfer termination mechanism has been accepted for vinyl acetate and the quantity  $E_{tr} - E_p = 3.1$  kcal/mole calculated from the variation of the molecular weight with temperature.<sup>17</sup> Polymers were prepared at 0, 30, and 50°C at very low conversions, where branching would be minimal, and their viscosity-average molecular weights were determined. An Arrhenius plot (Fig. 7) of these data gave  $E_{tr} - E_p = 3.6$  kcal/mole, in good agreement with the value found for bulk and suspension systems, for these polymers which are presumably more linear than those carried to high conversion.

A series of polymers was made in the standard emulsion system at a constant intensity in which the conversions varied from 10–99%. Viscosity-average molecular weights were evaluated (Table V) and found to remain fairly constant from 0°C up to 35–50% conversion where this increased. The data at 30 and 50°C, although somewhat sketchy, show the same trend.

TABLE V  
Effect of Conversion on Molecular Weight

Temperature, °C	Conversion, %	Molecular weight $\times 10^{-5}$
0	10.9	1.5
	21.2	15.8
	35.3	16.8 <sup>a</sup>
	57.2	24.6
	99.8	26.6
30	18.4	10.1
	39.2	9.32
50	16.6	8.3
	47.2	9.4

<sup>a</sup> Hydrolyzed and reacetylated  $1.5 \times 10^6$ .

Generally, the reduction in molecular weight upon hydrolysis and reacylation was found to be approximately 50% at each of the temperatures of polymerization (see Table II). This suggests that the degree of branching is much the same at each temperature and the number of hydrolyzable branches is relatively small.

The main kinetic features of the rates of polymerization with  $\gamma$ -radiation initiation compared with potassium persulfate and standard Smith-Ewart, case II, kinetics<sup>16</sup> are summarized in Table VI. It can be seen that the polymerization tends to approach the standard Smith-Ewart kinetics<sup>16</sup> with radiation initiation. It is suggested that this may be due to less polymerization in the aqueous phase in the absence of ionic endgroups. The small decrease in monomer solubility in the aqueous phase with the reduction in temperature from 60°C to 0°C also would contribute to a minor degree to this trend. The kinetics of radiation-initiated polymerization of vinyl acetate in emulsion are being studied in further detail.

TABLE VI  
Orders of Reaction for the Rates of Emulsion Polymerization of Vinyl Acetate Compared with Smith-Ewart Case II Kinetics

	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> - initiated (60°C) <sup>a</sup>	Radiation (0°C)	Smith- Ewart
Initiator (or Intensity)	1.0	0.7-0.9	0.4
Emulsifier concentration	0.2	0.9-1.0	0.6
Number of particles	0.2	0.7	1.0
Monomer-water ratio	0.35	Increase somewhat	0
Initiator (or intensity) with fixed no. of particles	0.8	0.26	0

<sup>a</sup> Data of Patsiga et al.<sup>14</sup>

**Some Properties of Vinyl Acetate Polymer and Copolymer Latices.**  
The results discussed above reveal two facts of considerable practical interest.

The yields of polymer per radiation dose was extremely high as shown, for example, by the conversion curve shown in Figure 2. Complete conversions were obtained in some cases with a total dose of only 20,000 rads.

The molecular weights were extremely high, being greater than one million compared with about 200,000 or less for most commercial poly(vinyl acetate) latices.

During informal discussions with industrial manufacturers of poly(vinyl acetate) latices, it became clear that the high molecular weights might be advantageous for certain film applications. Evaluations of some of the latices were therefore carried out, the results of these preliminary studies are shown in Table VII for three samples, one prepared at 60°C with the

TABLE VII  
Comparison of Poly(vinyl Acetate) Latices  
(Solids Content 25%)

Initiator	Temp, °C	Conversion, %	pH	Surface tension, dyne/cm	Molecular weight × 10 <sup>-5</sup>
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	60	98.5	3.1	43.9	4.9
γ-Radiation	60	99.3	3.5	43.2	10.6
γ-Radiation	0	100.0	3.8	44.7	19.0

use of potassium persulfate, and one prepared with γ-radiation as the initiator at 60°C, and one prepared at 0°C by use of radiation. Except for the molecular weights, little differences were noted. It was disappointing that the pH value was only slightly higher for the radiation-produced sample, as undoubtedly acetic acid had been produced by the radiolysis. However, these samples were made at an excessively high dose (about 1 Mrad), and later samples were lower in their acidity (see Table VIII for example).

TABLE VIII  
Properties of Two Radiation-Initiated Poly(vinyl Acetate) Latices

	Latex A	Latex B
Solids content, %	22.2	23.2
pH	4.1	5.0
Residual monomer, %	0.16	0.46
Molecular weight (viscosity-average)	1,020,000	1,060,000
$\bar{M}_w/\bar{M}_n$ Ratio	2.6	1.9
Latex viscosity, cps.	8.0	8.0
Film properties		
Appearance	Brilliantly clear	Brilliantly clear
Scrub resistance, cycles to fail	900	1,100
Tensile strength, psi	2522	1418
Elongation, %	656	372

Somewhat more complete evaluations were carried out on two additional samples also prepared at 0°C with radiation as the initiator, and the results are summarized in Table VIII. The residual monomer contents were within the acceptable range, and the pH values were higher, 5.0 being regarded as acceptable commercially. Although the tensile strength values of the films were lower than normal the scrub resistance when made into a standard paint formulation was significantly greater (about 50%) than normal commercial homopolymer latices. The scrub resistances were lower, however, than for the best commercial vinyl acetate copolymer latices. The molecular weights were lower than was usually obtained with radiation initiation at 0°C, and it is believed that some temperature increase occurred during their preparation.

A comprehensive evaluation of the performance of the latices was greatly handicapped by the small size samples available from laboratory scale experiments and by their low solids content. It is difficult on a laboratory scale to obtain the high solids contents achieved industrially. However, a number of stable polymer and copolymer latices were successfully prepared by using a nonyl phenol poly(ethylene oxide) type emulsifier with 50% solids contents. The details of these preparations are given in Table IX.

TABLE IX  
High Solids Content Vinyl Acetate Polymer and Copolymer Latices<sup>a</sup>

	Dose, Mrad	Dose rate, rad/hr	Con- version, %	Molecular weight × 10 <sup>-6</sup>
100% Vinyl acetate	0.033	6200	97.8	4.5
80/20 VAC-dibutyl maleate	0.014	6200	100	0.9
80/20 VAC-2-ethylhexyl acrylate	0.033	6200	64	—
80/20 VAC- <i>n</i> -butyl acrylate	0.031	12500	74	3.9
80/20 VAC-methyl acrylate	0.019	12500	74	3.2

<sup>a</sup> 5% emulsifier on monomer 50:50 monomer-water ratio by volume; temperature, 0°C.

Unfortunately, the conversions were far too low in most cases, however, it was clear that stable high solids content latices could be obtained. There is no doubt that high conversions could have been obtained by longer exposures in fact two samples were essentially completely polymerized. Three of the samples were obtained in large enough amounts to be evaluated after stripping of excess monomer with a stream of nitrogen. The results of the evaluations are given in Table X.

The molecular weights of all three latices were particularly high, and this was reflected in very good scrub resistance. The tensile strengths of two of the polymers, including the homopolymer, were also higher than those of the previous samples and comparable to those of commercial films.

The evaluation of the latex properties *per se* and those of the films, both pure and in paint formulations, is the least satisfactory part of this research.

TABLE X  
Evaluation of "High Solids" Vinyl Acetate Polymer and Copolymer Latices

	100% PVAC	80/20 VAC-Bu acrylate	80/20 VAC-Me acrylate
Solids Content, %	42.8	30.8	36.2
pH	4.2	3.4	4.3
Molecular weight (viscosity)	$4.5 \times 10^6$	$3.9 \times 10^6$	$3.2 \times 10^6$
Latex viscosity, cP	25	25	50
Film properties			
Appearance	V. slightly hazy	Cloudy	Cloudy
Scrub resistance (approx.), cycles	1450	1400	1050
Tensile strength, psi	3,350	1,460	3,120
Elongation, %	762	770	754

This was mainly due, however, as stated earlier to the need for larger samples at high solids content. The results obtained, however, clearly demonstrated that  $\gamma$ -radiation can be used to produce stable latices of high solids and with exceptionally high molecular weights. These latices can easily be compounded into paints with improved scrub resistance. However, larger samples are needed with the optimum formulations before a complete evaluation of their performance and commercial value can be made.

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