The Radiation-Induced Emulsion Copolymerization of Vinyl Chloride with Vinyl Acetate in an Engineering Flow System

J. T. TSAI,* E. P. STAHEL, and V. T. STANNETT, *Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27650*

Synopsis

A flow reactor system was used to study the radiation-induced emulsion copolymerization of vinyl chloride with vinyl acetate. The emulsion was recirculated from a stirred vessel through transfer lines to a tubular reactor located within a high-intensity Co-60 source. The effects of physical chemical variables such as soap concentration, phase ratio, reaction temperature and residence time distribution on the molecular weight properties were investigated. The rate of copolymerization was found to be proportional to the 0.17 power of the soap concentration. Variation of the monomer-water ratio produced no significant change in rate. The rate increased with an increase in temperature over the range 5–50°C, while the average molecular weights of the copolymer increased with decreasing polymerization temperature. The molecular weight distribution in this engineering system was found to be essentially similar to those produced in a batch system.

INTRODUCTION

The copolymerization of vinyl chloride and vinyl acetate is usually initiated by a free radical mechanism[1] and the reaction may be carried out in mass, solution, suspension or emulsion systems. Bulk polymerizations although capable of providing high purity resin, present difficult engineering problems due to the high exothermic nature of the reaction (30,000 BTU/lb. mole of monomer).

The kinetics of emulsion copolymerization of a number of olefin monomers has been investigated by numerous authors.[2-9] Compared to other free radical initiated systems, the emulsion process offers high molecular weights with simultaneous high reaction rates. In some cases, emulsion system can provide a good control of copolymer composition which is sometimes difficult to control in bulk or solution. The capability of tailoring a homogenous copolymer composition by manipulating the relevant physical chemical parameters is regarded as a useful means of quality production.

Conventional emulsion systems are not widely employed with vinyl chloride and its copolymers because there are a number of inherent disadvantages some of which are peculiar to the use of chemical initiators. For example, the presence of buffering salts to keep the pH under control can result in a marked effect on the color and clarity of the end products. Recently, research of radiation induced polymerization has brought back the potential of emulsion systems because many of the disadvantages associated with chemical initiators are eliminated.

The advantages in the use of high energy radiation to initiate emulsion poly-

---

* Present address: General Tire & Rubber Co., Research Division, Akron, Ohio 44305.

0021-8995/79/0023-2701$01.00

merization have been discussed by Stannett et al.[10] The comparatively high yield of free radicals from the radiolysis of water (4–7 per 100 eV) plus the large kinetic chain lengths found in emulsion polymerization ensures 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 does not diminish exponentially as in the case of chemical initiation. The temperature independence of radical flux enables polymerizations to be carried out at any desirable temperature. 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 with the initiating system on changing emulsifiers, for example, to a cationic system.

In connection with the development of radiation induced emulsion polymerization into a possible industrial process, an engineering recirculating flow reactor was designed. The aim of this study was to investigate the feasibility of this type of reaction system. The effects of physical chemical variables and engineering variables on reaction rate and molecular weights were investigated.

EXPERIMENTAL

A schematic diagram of the polymerization equipment is shown in Figure 1. The emulsion handling system provided a single location where charging, sampling, oxygen desorption, and recirculating the emulsion were performed. A diaphragm type pump was provided to recirculate the emulsion from the stirred vessel through the reactor loop and back. The stirred vessel was a one gallon unit and jacketed for temperature control. Agitation was provided by a 3 in. impeller connected to a variable speed drive.

A transfer line was used to connect the stirred vessel and the tubular reactor. The emulsion flowed through the 1/4 in. line, exchanging heat with the temperature control fluid passing through the annular space. The emulsion was then passed through the tubular reactor contained in a 4 × 14 in. canister, around which eight Co-60 strips were located. The radiation intensity in the reaction zone was about 0.25 Mrad/hr. The outlet of the helical tube reactor was connected by another section of the transfer line back to the stirred vessel. Thermocouples sensed the reactant temperature at the entrance, midpoint, and exit of the reactor. All the transfer lines were insulated.

A typical recipe of the emulsion mixture is as follows:

deionized water	1800 ml
sodium lauryl sulfate	3% by weight (based on water)
vinyl chloride	367 g
vinyl acetate	139 g

In preparation for a polymerization run, the vinyl acetate monomer was purified. The inhibitor was removed by vacuum distillation through a four foot packed fractional distillation unit, using a high reflux ratio. Sodium lauryl sulfate, U.S.P. grade, was used as an emulsifying agent without any further purification.

With the agitator on, the monomer and soap solution metering pumps were turned on and set for the desired phase ratio. As the mixing tank was allowed to fill up the desired charge volume, the feed pump was turned on and the emulsion recycled through the bypass loop, which bypassed the reactor to stabilize the temperature and to ensure a uniform mixing.
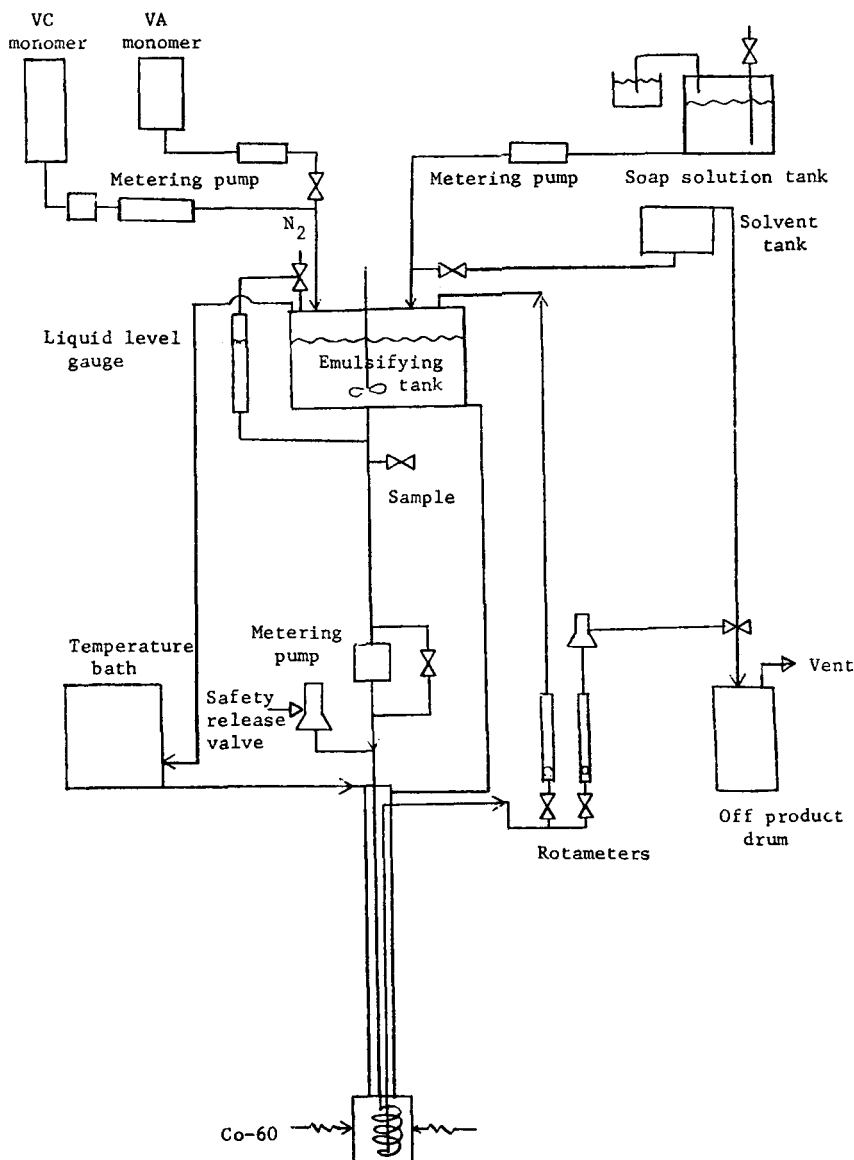
Fig. 1. Schematic diagram of radiation-induced copolymerization pilot plant.

To start the polymerization reaction the valve to the reactor was opened and the valve to the bypass was shut off.   For the total recycle runs, a high flow rate of approximately 500 ml/min was used.

Samples were taken at various time intervals from the outlet of the emulsifying tank.   By pressing the truck tire valve of the tared weighing cylinder into the air chuck, a 50 ml sample was collected.   The sample was washed into a beaker with 150 ml methanol which quickly precipitated the copolymer.   The precipitated copolymer was recovered by centrifuging and then placed in a 40°C oven for 12 to 18 hr until dry.   The dried copolymers were then cooled and reweighted to determine the yield of polymer.

Molecular weights of the samples were determined from intrinsic viscosity measured at 25°C using a modified Ubbelohde viscometer. The molecular weights were calculated from the expression developed by Chen and Blanchard[11]:

$$[\eta] = 1.87 \times 10^{-4} M_v^{0.746} \tag{1}$$

Molecular weight distributions were analyzed with a Model 200 Waters gel permeation chromatograph using THF as a solvent.

RESULTS AND DISCUSSIONS

Four typical conversion curves for this engineering system are shown in Figure 2. The conversion histories were found to be linear with time after a comparatively brief initial period. The average reaction rates in the reactor were calculated from the slopes of the linear portion of the curve

$$\bar{\gamma}_c = (\text{slope}) \, (V_T/V_P)$$

where $\bar{\gamma}_c$ is the average reaction rate, V_T is the total volume of reaction mixture in the system, and V_p is the volume of the tubular reactor.

The copolymers obtained were examined with a number of solution property tests[12] and showed that no homopolymer was produced. A typical infrared spectra of the copolymer produced from this system is shown in Figure 3. By comparing the absorbance at 5.47 and 7.01 μm the copolymer composition could be calculated.[13]
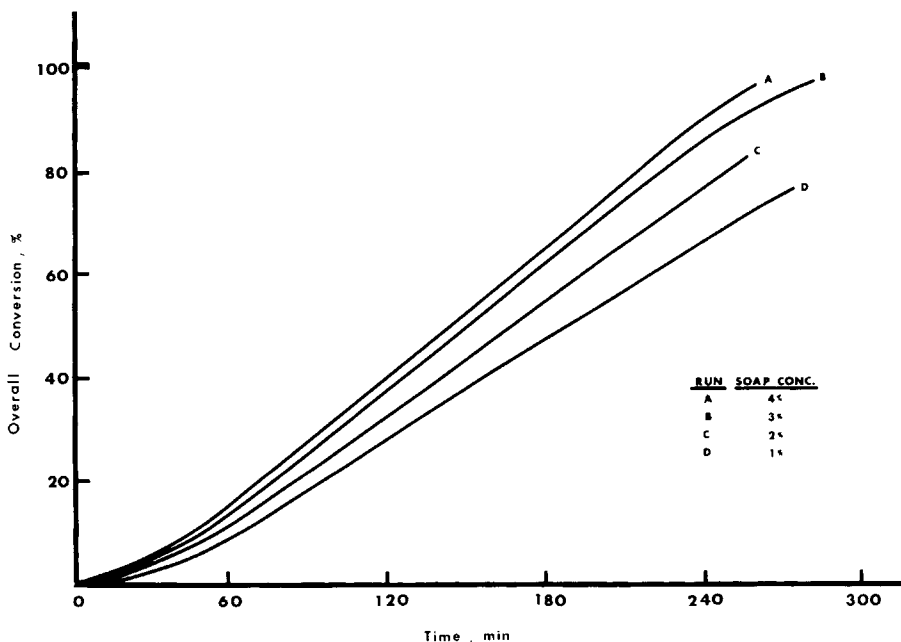

Fig. 2. Time-conversion curves of VCl-VAc emulsion copolymerization in the pilot plant system. Polymerization conditions: isothermal 30°C, residence time: 28 min, tubular reactor volume 100 cm^3, total reaction volume 1800 cm^3, radiation dose rate 0.135 Mrad/hr, VCl/VAc weight ratio 3.08, water/comonomer phase ratio 5:1.
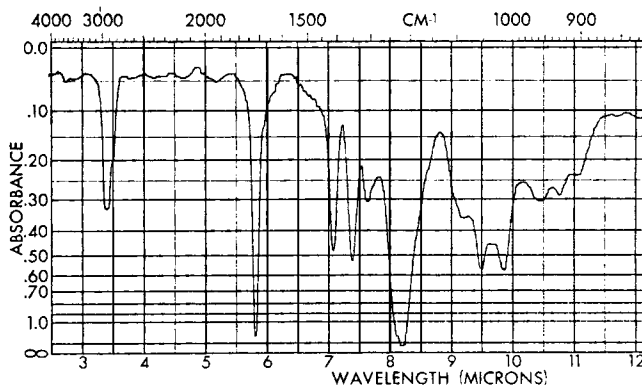
Fig. 3. Infrared spectra of the copolymer produced from the radiation-induced system with feed charge VCl/VAc weight ratio 1.03 and water/comonomer phase ratio 2.0.

The dependency of the copolymerization rate on the soap concentration is shown in Figure 4. The following relationship is derived from the log-log plot:

$$\text{rate of polymerization} \propto (\text{soap concentration})^{0.17}$$

In a somewhat similar vinyl chloride homopolymerization study, Prehoda[14] found a 0.26 power rate dependency for a comparable range of sodium lauryl sulfate concentrations. This value which is somewhat lower than the classical
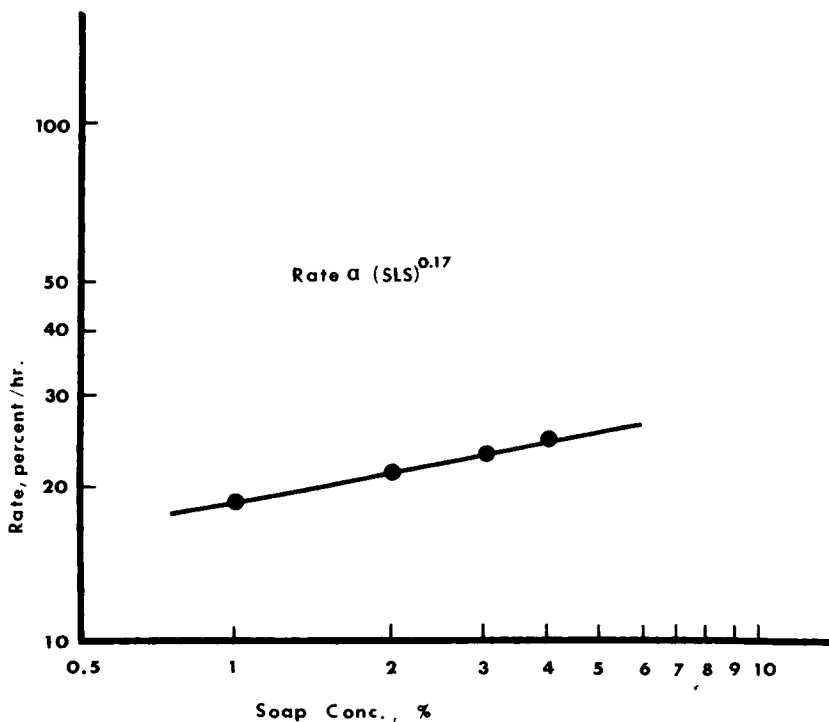

Fig. 4. Variations of copolymerization rate with soap concentration, polymerization conditions were same as in the Figure 2 caption.
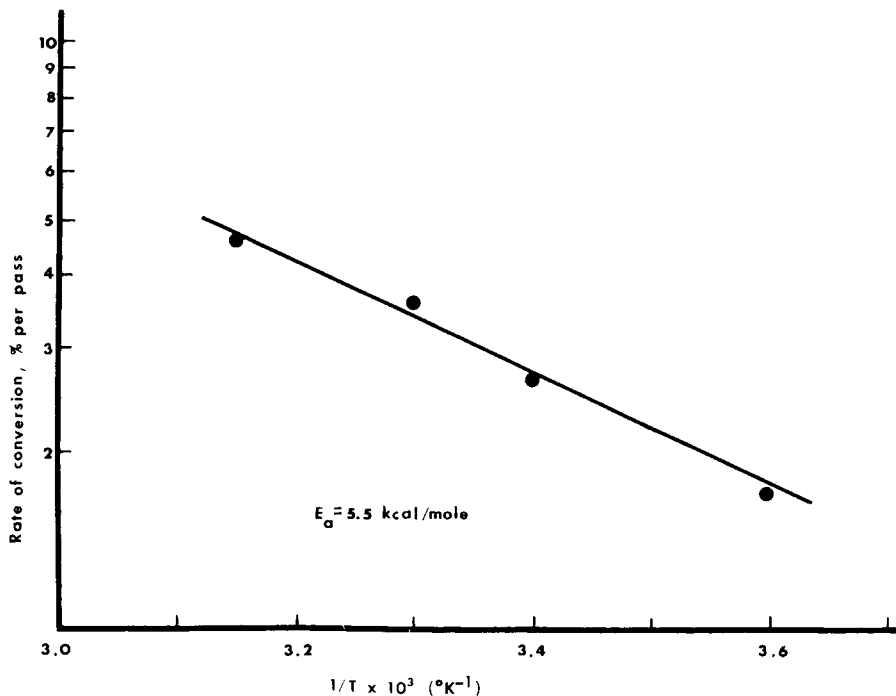
Fig. 5. Copolymerization rate as a function of temperature: Radiation dose rate 0.135 Mrad/hr, VCl/VAc weight ratio 4.33, H_2O/comonomer ratio 3.0, residence time: 28 min, tubular reactor volume 100 cm^3.

Smith-Ewart[6] value of 0.6 and considerably lower than a value of 1.0 obtained in the radiation initiated batch emulsion polymerization of vinyl acetate[10] was attributed to a unique soap exchange mechanism.[14] O'Neill et al.,[15] using a somewhat similar flow system, found a value of 0.3 with the radiation initiated emulsion polymerization of vinyl acetate.

The complexity of soap dependency in the case of the copolymerization of butadiene and acrylonitrile has been reported by Stannett and Stahel[16] and by Ishigure and Stannett.[17] At high concentrations of acrylonitrile in the mixture, both the initial and the 50% conversion polymerization rates were found to be proportional to about the 0.3 power of the soap concentration. At low concentrations of acrylonitrile, on the other hand, the initial rate is proportional to about the 0.4 power of soap concentration compared with the 0.3 power dependency at high conversion. (The soap dependency for homopolymerizations are 0.68 power for butadiene and 0.1 power for acrylonitrile.) In the present work it was also found that the soap dependency of VCl − VAc copolymerization is only slightly affected by the variation of comonomer concentration. However, there is not enough data for multiple regression analysis to determine the exact relationship between reaction rate, feed composition and soap concentration.

A few measurements were made of the rate of polymerization as a function of the water-monomer ratio at a constant monomer feed composition at 30°C. The results are presented in Table I. Very little change in the reaction rate or copolymer composition was observed.

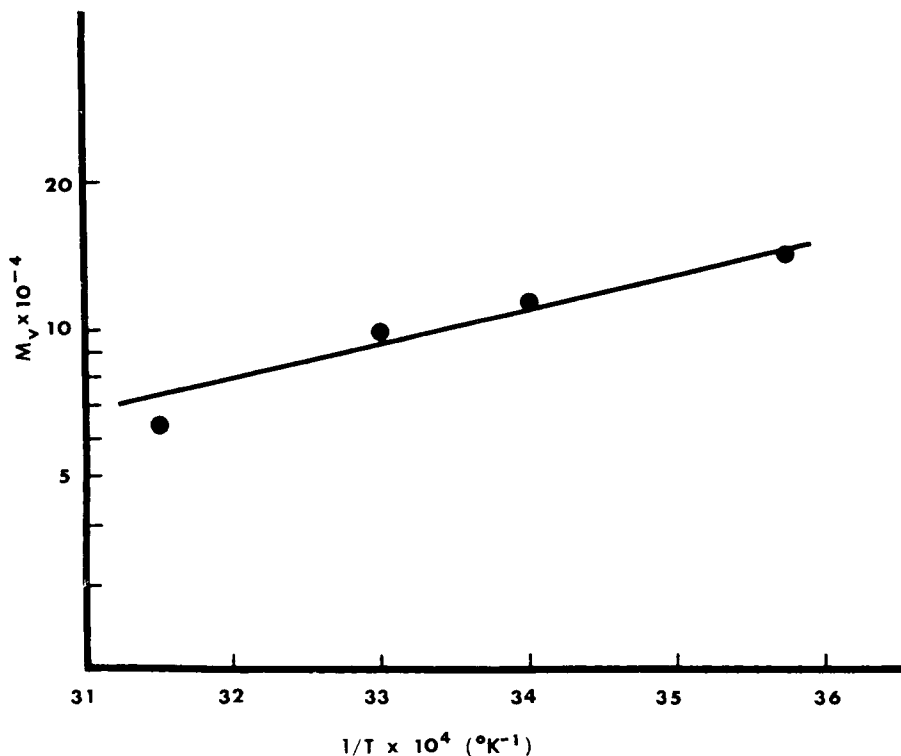The experimental results obtained with varying temperatures showed an in-

Fig. 6. Intrinsic molecular weights as a function of the reciprocal absolute reaction temperature.

TABLE I
Effects of Water-Monomer on Rate and Copolymer Composition

H_2O/M	R_p (% conversion/min)	VCl/VAc ratio	Conversion (%)	Chloride (%)
5/1	4.8	3.05	21.8	48.6
3/1	4.0	2.89	24.0	47.4
2/1	4.5	2.89	23.3	45.2

crease in reaction rate with increasing temperature. The Arrhenius plot is shown in Figure 5. An overall activation energy of 5.5 kcal/mole is calculated from the plot.

Copolymers were prepared at 7, 21, 30, and 45°C to about 24% conversion, and the viscosity-average molecular weights were determined (as shown in Table II). An Arrhenius plot (Fig. 6) of these data gave $E_p - E_{tr} = -2.0$ kcal/mole. The negative value indicates that the chains are mainly terminated by chain transfer to monomer as is also found with both homopolymers. Since E_p was found to be 5.5 kcal/mole E_{tr} is 7.5 kcal/mole.

The GPC elution curves for different polymerization temperature are shown in Figure 7. The number average and weight-average molecular weights are presented in Table III. The DP values calculated from the gel permeation chromatography (GPC) measurement were plotted as a function of $1/T$. An activation energy of -2.0 kcal/mole was obtained, in agreement with the intrinsic viscosity measurements.
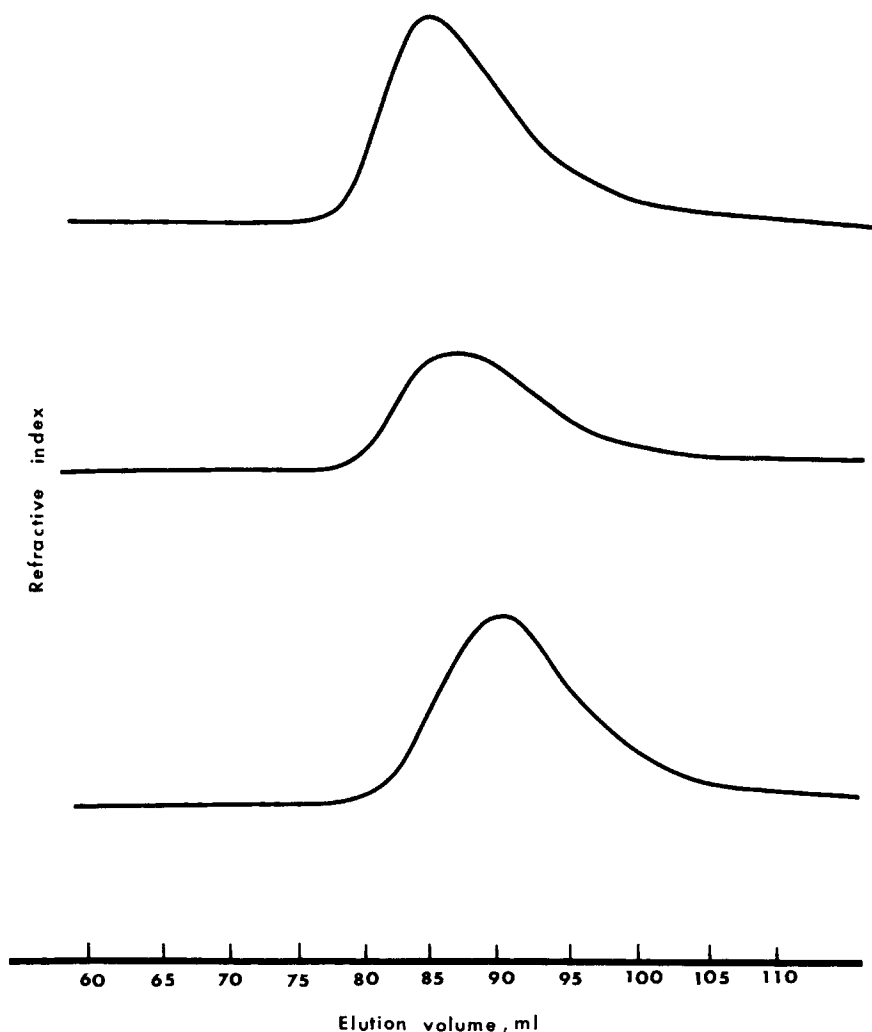
Fig. 7. Comparison of GPC chromatogram with different polymerization temperatures: from top to bottom: 7, 30, and 45°C, respectively.

TABLE II
Viscosity Average Molecular Weights

Run number	Temperature °C	$[\eta]$	M_v (10^5)
8	7	1.20	1.31
10	21	1.13	1.22
7	30	1.03	1.05
3	30	0.96	0.96
2	30	0.95	0.95
9	45	0.72	0.64

The experimental values of the dispersity factor, M_w/M_n, averaged 1.85 for 10 runs.   This value is within the range of the calculation reported by Katz et al.[18] who predicted that M_w/M_n varied from 2.0 for small particle (Smith-Ewart Case II polymerization) to 1.5 for large particles (bulk polymerization).   The
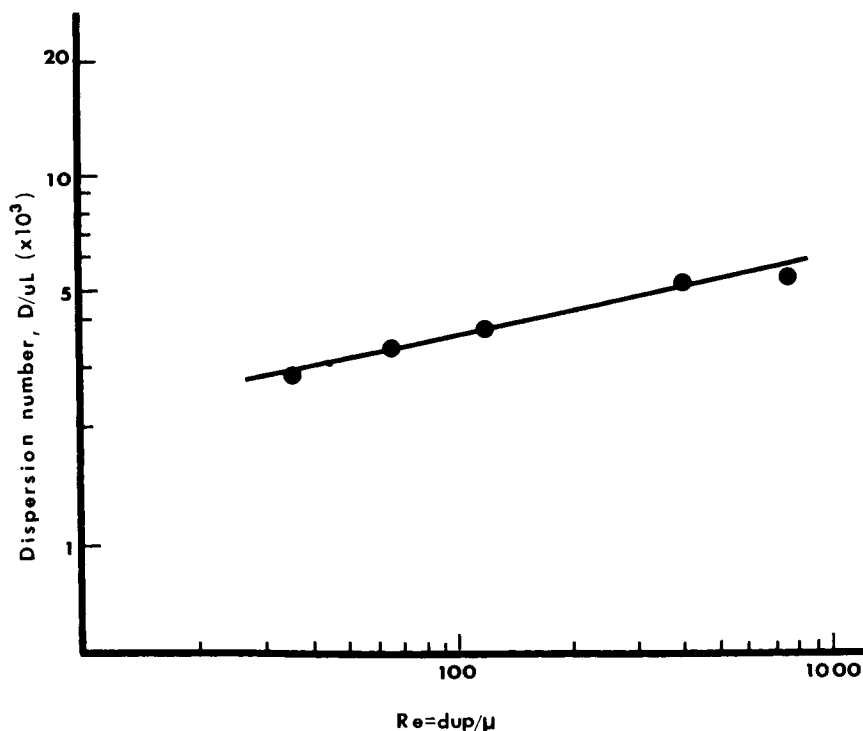
Fig. 8. Variation of dispersion number in laminar flow region in tubular reactor during emulsion copolymerization of VCl/VAc at 80% conversion.

TABLE III
GPC Molecular Weight Distribution Results

Run number	Temperature °C	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
8	7	88,700	158,400	1.79
7	30	64,500	125,500	1.94
9	45	49,850	89,700	1.80

residence time distribution of the tubular reactor has been measured. Dispersion numbers calculated from these responses are shown in Figure 8. The low dispersion number indicates that a plug flow assumption is reasonable. In emulsion polymerization the monomer concentration in the polymer particle is about constant and each particle behaves as a batch reactor. From the results of residence time distribution, it is clear that the recycle system approaches a batch reactor for a long run regardless of whether or not the fluid elements are partially segregated and subsequently remixed.

CONCLUSIONS

The radiation induced emulsion copolymerization of vinyl chloride with vinyl acetate has been carried out in an engineering flow system. Radiation offers a unique route to accomplishing radical generation at consistent intensity whenever needed without being coupled with reaction temperature, provides

a simplified model for copolymerization kinetics. The dependency of the co-polymerization rate on the emulsifier was found to be only slightly affected by the comonomer concentrations. Copolymerization at different temperatures showed that the activation energy based on the degree of polymerization is negative, i.e., the molecular weight of the copolymer increases with decreasing reaction temperature. This is characteristic of systems where chain transfer to monomer is predominant. The results demonstrate that gamma radiation can be used to produce stable latices of high solids with exceptionally high re-action rates. In addition the initiating system makes polymerization at low temperatures very simple and leads to much higher molecular weights.

References

1. G. E. Ham, *Copolymerization, High Polymer Series,* Vol. 18, Wiley-Interscience, New York, 1964, pp. 587–600.

2. R. G. Fordyce and E. C. Chapin, *J. Am. Chem. Soc.,* **69,** 581 (1947); **69,** 1903 (1947).

3. R. G. Fordyce and G. E. Ham, *J. Polym. Sci.,* **3,** 891 (1948).

4. R. G. Fordyce and G. E. Ham, *J. Am. Chem. Soc.,* **73,** 1186 (1951).

5. W. F. Fowler, Jr., *Vinyl Polymerization II,* Marcel Dekker, New York, 1969, pp. 139–174.

6. W. V. Smith, *J. Am. Chem. Soc.,* **70,** 2177 (1948); and *J. Chem. Phys., 16,* 592 (1948).

7. G. C. Vegter, *Adv. Chem. Ser.,* **91,** 178 (1969).

8. F. T. Wall, R. E. Florin, and C. J. Delbecq, *J. Am. Chem. Soc.,* **72,** 4769 (1950).

9. F. T. Wall, R. W. Powers, G. D. Sands, and G. S. Stent, *J. Am. Chem. Soc.,* **70,** 1031 (1948).

10. V. Stannett, J. A. Gervasi, J. Kearney, and K. Araki, *J. Appl. Polym. Sci.,* **13,** 1175 (1969).

11. H. R. Chen and L. P. Blanchard, *J. Appl. Polym. Sci.,* **16,** 603 (1972).

12. C. S. Marvel, G. D. Jones, T. W. Mastin, and G. L. Schertz, *J. Am. Chem. Soc.,* **64,** 2356–2362 (1942).

13. M. H. Swann, in *Chemical Analysis of Resin-Based Coating Material,* C. P. Kappelmeier, Ed., Interscience, New York, 1959, pp. 337–342.

14. G. S. Prehoda, Ph.D. Thesis, Department of Chemical Engineering, North Carolina State University at Raleigh, North Carolina, 1971; University Microfilms Inc., Ann Arbor, Mich.

15. T. O'Neill, J. Pinkava, and J. Hoigne', *Proc. Third Tihany Conf. Radiat. Chem., 1,* 413 (Budapest) (1971).

16. V. Stannett and E. P. Stahel, *Research and development studies into the basic technology of radiation induced emulsion polymerization,* Final Report, U. S. Atomic Energy Commission, Washington, D. C., 1971, pp. 27–65.

17. K. Ishigure and V. T. Stannett, *J. Macromol. Sci. Chem.,* **A8**(2), 337 (1974).

18. S. Katz, R. Shinnar, and G. M. Saidel, *Adv. Chem. Ser., 91,* 145 (1968).