

Radiation-Initiated Inverse Emulsion Polymerization of Vinylpyrrolidone

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SYNOPSIS

The radiation-induced inverse emulsion polymerization of vinylpyrrolidone using an isoparaffinic hydrocarbon and nonionic emulsifier blend is described. High molecular weight polyvinylpyrrolidone (PVP) (1 million to 2 million M_v) was readily obtained at rapid polymerization rates ($R_p \sim 10\text{--}35 \text{ mol l}^{-1} \text{ s}^{-1}$) to high conversions (90–95%). The polydispersity of the polymer varied from 2.6 to 4.4, suggesting that chain transfer to the polymer had occurred. Adding a polymeric surfactant to the nonionic blend modified the polymerization rate and particle-size distribution. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Inverse emulsion polymerization of water-soluble monomers to obtain high molecular weight polymers and copolymers is a well-known and established technique. The commercial preparation of ultrahigh molecular weight polyacrylamide is widely practiced. Vanderhoff et al.¹ studied the kinetics of inverse emulsion polymerization using *p*-sodium styrene sulfonate as the monomer. Since then, there have been numerous publications particularly relating to the polymerization of acrylamide (e.g., Refs. 2–4). More recently, microemulsions have been employed.⁵

In these studies, both water-soluble and oil-soluble initiators were used. The use of high-energy radiation to initiate conventional emulsion polymerizations of a number of vinyl monomers is well known and has been reviewed,^{6,7} but there are no reports involving the initiation of inverse emulsion polymerizations. Likewise, there is only one report of the inverse emulsion polymerization of *N*-vinylpyrrolidone.⁸ Typical free-radical initiators were employed. Here, we describe the X-ray-initiated inverse emulsion polymerization of *n*-vinylpyrrolidone.

EXPERIMENTAL

Reagent-grade *n*-vinylpyrrolidone (Aldrich Chemical) was kept refrigerated and aliquots were vacuum-distilled as needed. Isopar M (petroleum naphtha) was obtained from Exxon Chemical and Soltrol 220 (isoparaffinic solvent) from Phillips Petroleum. All surfactants were obtained from the ICI Corp. and were used as supplied; any that phase-separated were homogenized by sonication before use. Water was distilled from dilute alkaline permanganate and then redistilled. GPC solvents were obtained from Burdick/Jackson Co.

A high-vacuum system was employed to distill the monomer and to introduce it into ampules and for degassing, etc. A Model 7637 Roto Torque Rotator (Cole Parmer Instruments) was used to provide end-over-end mixing (6 rpm) of the polymerization ampules in the 60CO source. A 6000 Curie 60CO source, Gamma beam 150-A, Atomic Energy of Canada, was used for irradiation at 0.45 Mrad/h, 4.18 cm from the source center. Sample doses were evaluated by radiachromic films (film calibration by NBS and rated at a relative sensitivity of 95%). Optical density readings were made with a radiachromic reader from Far West Technology Corp.

After polymerization, three film samples attached to the front and back at the top, middle, and bottom of selected ampules were read. The change in optical density over thickness was calculated, and by com-

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parison to an NBS calibration curve, the dose was obtained. Then, from the exposure time, the dose rate was determined.

Vinylpyrrolidone (VP) was polymerized in different formulations having varying percentages of monomer, oil water, emulsifier, and emulsifier types. The emulsifier was added to the oil phase. The monomer in water, or the monomer alone, was slowly added to the emulsifier-oil phase with vigorous stirring, and then the mixture was homogenized in the sonicator.

The emulsions (5–8 mL) were introduced into ampules (typically, each experimental run included 13–16 different samples) connected to the high-vacuum system, the contents frozen by liquid N₂ and then freeze-thawed five times (pressure at the manifold was typically 1–2 mTorr), the contents again frozen and the ampules sealed and placed in an ice bath, and after thawing, the contents sonicated before transferring to the ⁶⁰Co source.

Larger-scale polymerizations were conducted in vials (2 oz) with plastic screw caps and self-sealing silicone rubber/Teflon gaskets. The monomer-emulsifier-water mixture was homogenized (5000 rpm for 45 s) and an aliquot (15–20 mL) pipetted into the vial, the vial capped, and it and the contents flushed with N₂, and after cooling in an ice bath, transferred to the ⁶⁰Co source.

At various time intervals, the ampules or vials were opened and quenched with oxygen. A sample

(1–2 mL) was taken with a syringe (3 mL), the sample and syringe weighed, the sample discharged into acetone (10 mL) in an Al pan, and the empty syringe reweighed. Residual oil was decanted from the coagulum, which was washed with an acetone/isopropanol mixture (10 mL); the pan and coagulum dried in a vacuum oven overnight at 55°C, then for 24 h at RT; and the dried residue weighed and the percent solids calculated. The percent conversion was calculated as follows:

$$\text{Conversion (\%)} = 100 \left[\frac{\text{solids (\%)} - \text{nonvolatile components (\%)}}{\text{original monomer (\%)}} \right]$$

The polymer intrinsic viscosity in water at 25°C ($\pm 0.05^\circ\text{C}$) was determined using a Cannon-Ubbelohde four-bulb viscometer (International Research Glassware, Kenilworth, N.J.), $t_s = 105$ s.

Gel permeation chromatograms were obtained with a Waters 150-C ALC/GPK chromatogram using a Waters 440 UV and a differential refractive index detectors in series and *N,N*-dimethylformamide with LiBr (0.05 molar) as the eluent at 0.8 mL/min. Two Ultrastyrigel columns (Waters Associates, 2K–4M range) were used in series. The column oven and detectors were thermostated at 80°C. Narrow molecular weight distribution poly(2-vinylpyridine) samples (Scientific Products, On-

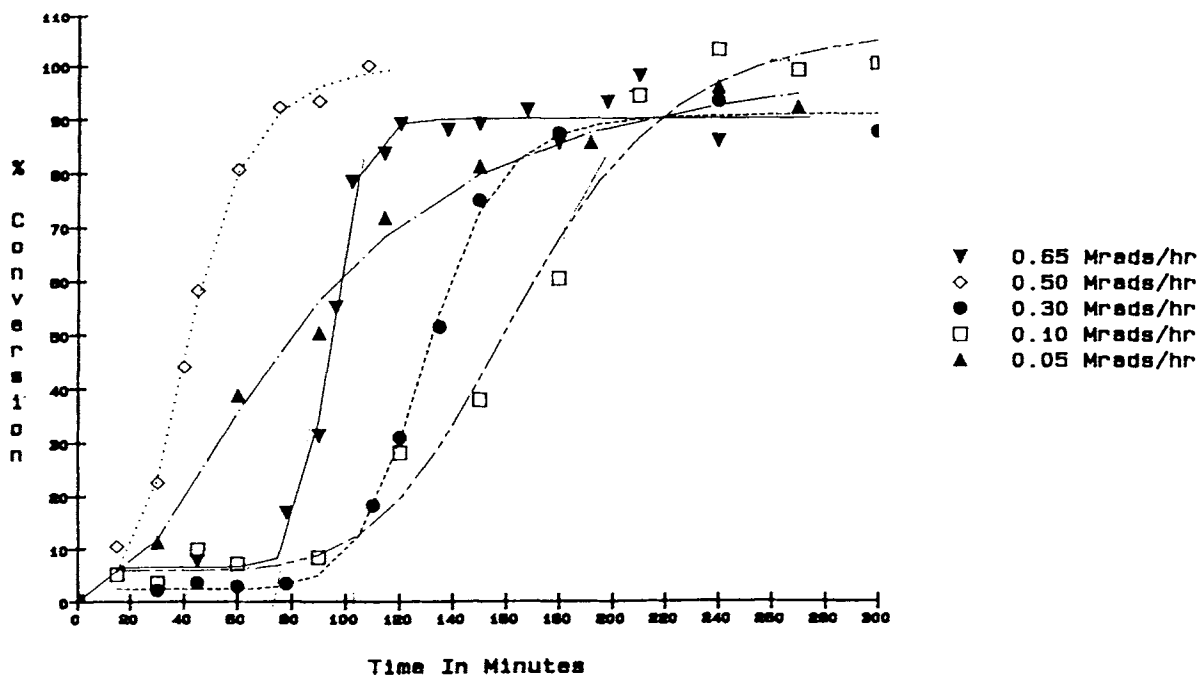


Figure 1 Conversion as a function of dose rate.

Table I Effect of Radiation Dose Rate on Polymerization Rate and Molecular Weight

Dose Rate (Mrad/h)	Conversion Curve Slope	$R_p \times 10^5$ (Mol/L s)	$\overline{M}_v \times 10^{-6}$	$\overline{M}_w \times 10^6$
0.65	2.41	35.3	1.25	1.40
0.50	1.97	28.9	1.40	1.70
0.30	1.41	20.7	1.80	—
0.10	0.82	12.1	1.95	—
0.05	0.67	9.8	2.08	—

tario, NY) were used to construct a calibration curve. Known broad molecular weight samples of commercial polyvinylpyrrolidone (PVP) were obtained for comparison purposes. An agreement of $\pm 3\%$ up to 400,000 molecular weight was obtained using the calibration curve. All PVP solutions were filtered through Teflon Millipore filters (0.45 M) prior to injection (100 μ L) onto the columns.

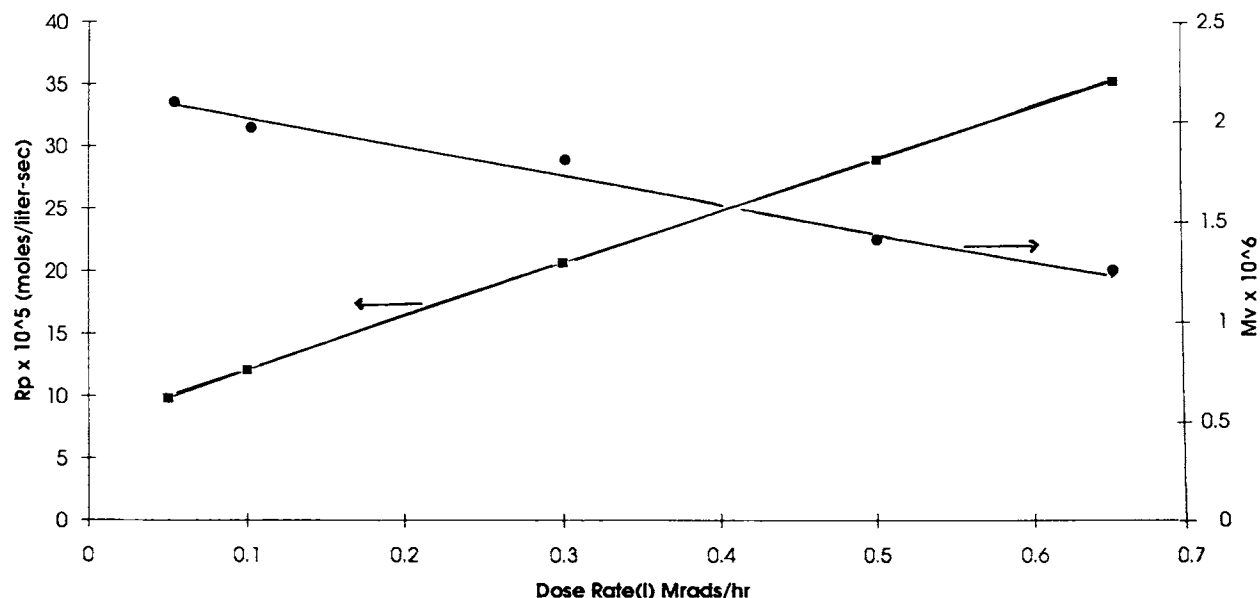
Particle sizes and particle-size distributions were determined by laser-light scattering using photon-correlation spectroscopy. The apparatus was constructed using an Argon ion laser (Spectra Physics, Series 2000), an air-cushion table (Technical Mfg. Corp.), and a beam steerer, goniometer, scattering cell, and photomultiplier tube (BrookHaven Instruments). Agitated latex (1-2 drops) was diluted with isoparaffinic oil (2-3 mL) in glass vials and the vials and contents suspended in the toluene scattering well of the goniometer.

^{13}C -NMR spectra were obtained with a 200 MHz Bruker WP 200 SY FT spectrometer, using a

switchable carbon and proton probe. CD_3OD was used as an internal reference and as a solvent for PVP. VP was dissolved in D_2O . ^{13}C -NMR spectra were obtained at 50.3 MHz using quadrature detection, a 11.1 spectral window, 16,000 data points, and inverse-gated decoupling.

RESULTS AND DISCUSSION

Prior to the actual polymerizations, the solubility of VP in heptane and Isopar M was examined by filling a capillary tube with a 50 : 50 mixture of VP and oil, sealing the tube, and observing the phase volumes for 6 weeks. On this basis, Isopar M was selected as the oil phase. Similarly, emulsions of water, surfactants of various HLB values, Isopar M, and VP were prepared. The level of surfactant(s) (2.5-12.5%), the HLB value (by mixing different surfactants), and the aqueous/oil ratio were varied. The surfactant(s) were first added to the oil phase

**Figure 2** Rate of polymerization and molecular weight vs. dose rate.

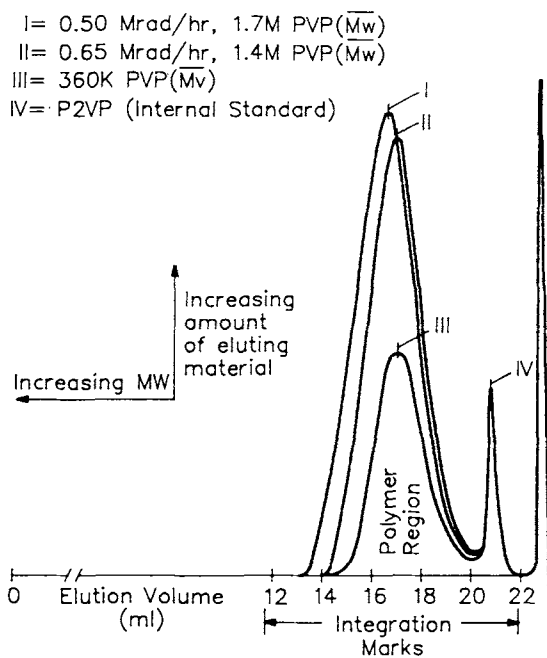


Figure 3 HPGPC molecular weight and molecular weight distribution data.

and then the aqueous phase added and the mixture sonicated. After 2 weeks storage, the emulsion stability was evaluated by observing the direction of creaming after the emulsion separated and by dye solubility and fluorescence dye techniques.

Based on these results, the following formulation was selected for the initial polymerization studies:

	Wt %
Monomer	10.6
H ₂ O	21.2
Isopar M	63.4
Emulsifier ^a	4.8

^a Span 80 (HLB 4.38)/Tween 85 (HLB 11.0) 90/10.

Various dose rates (0.5, 0.10, 0.30, 0.50, 0.65 Mrads/h) were used. The conversion vs. time data are plotted in Figure 1. Rapid polymerization rates to high conversions (90–95%) were obtained. However, in spite of extensive purging with N₂ or Ar,

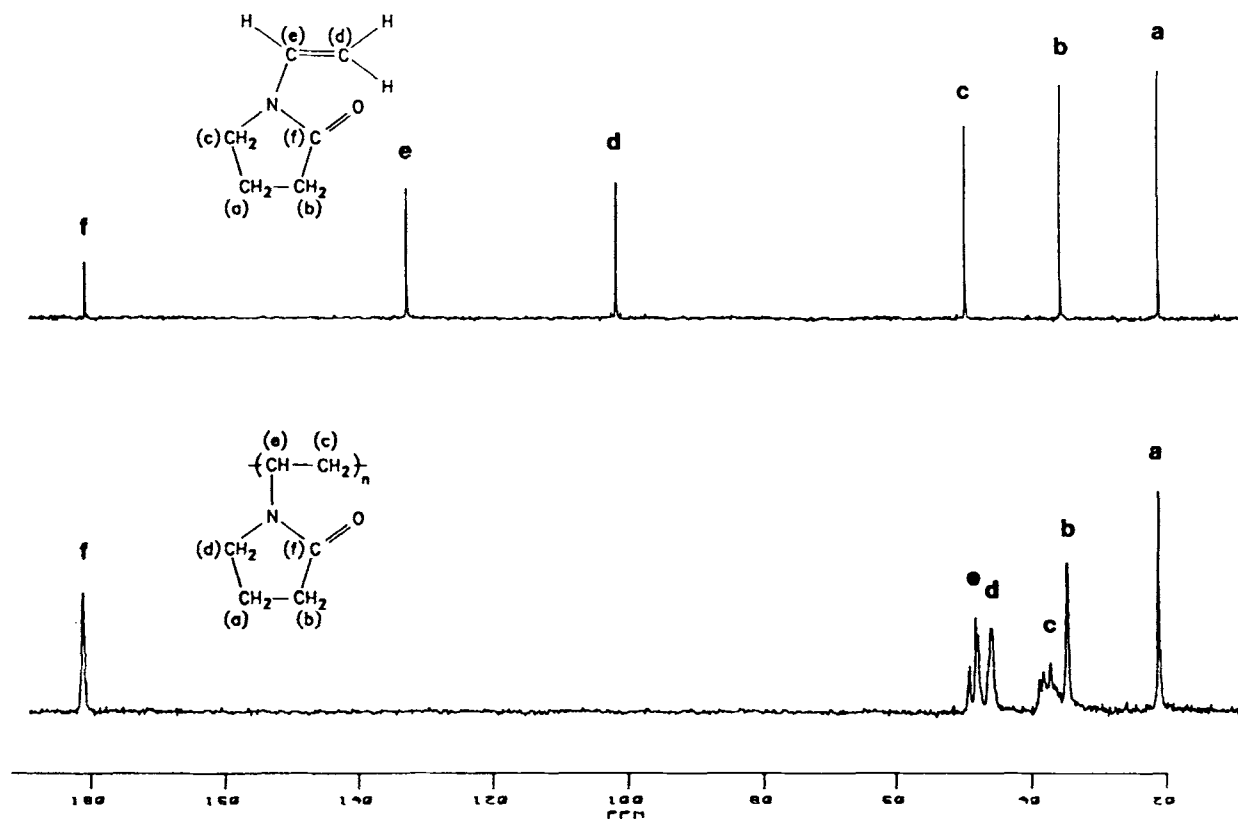


Figure 4 ¹³C-NMR spectra of VP and PVP.

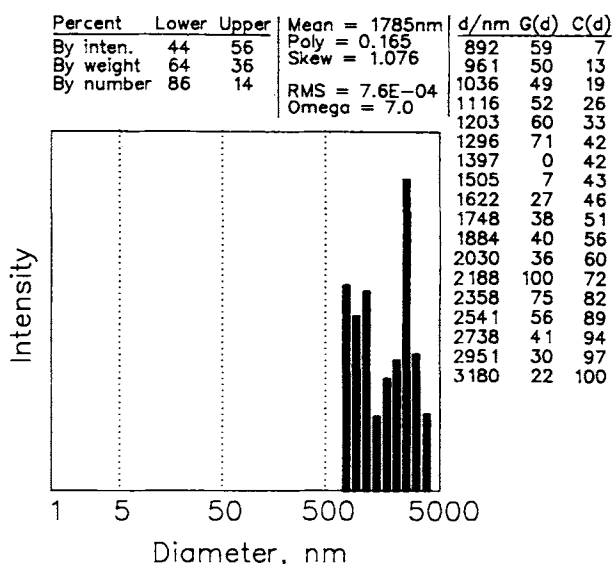


Figure 5 Particle size and particle-size distribution for 0.1 Mrad/h polymerization.

there was still a significant induction period due to residual O_2 .

The conversion data were fitted with a four-parameter logistic equation of the form

$$F(x) = \frac{A - D}{1 + (K/X)^N} + D$$

which represents a sigmodal growth curve and affords a "best-fit" to the data. The fitted curves are shown in Figure 1. Each data point in Figure 1 is the average for three polymerizations. However, the samples for a particular dose rate were all prepared and degassed at the same time so that each polymerization was not totally independent. Otherwise, the induction period of the individual runs would vary.

The rates of polymerization and corresponding molecular weight at the different dose rates are in Table I and plotted in Figure 2. The rate of polymerization is very nearly a linear fit to the first order

of the dose rate. The plot does not extrapolate to zero, indicating that some thermal polymerization had occurred. The molecular weights are the average of three separate samples at each dose rate as determined by intrinsic viscosity and the \bar{M}_v calculated using the following equation: $[\eta] = KM_v^a(K, 14 \times 10^3; a, 0.70)$. The molecular weights of PVP prepared at dose rates of 0.50 and 065 Mrad/h were also determined by GPC. The data are in Figure 3.

As can be seen, molecular weights as high as 2×10^6 were obtained. As expected, the molecular weight is inversely proportional to the dose rate (Fig. 1). The GPC data indicate that the heterogeneity indexes for the PVP prepared by an inverse emulsion polymerization range from 2.6 to 4.4, suggesting that chain transfer to the monomer or to polymer structural units occurred during the polymerization. Transfer to polymer would lead to branching, accounting for the high heterogeneity indexes.

The ^{13}C -NMR spectra of VP and PVP are shown in Figure 4. Each spectra has the expected number of carbon resonances. In the case of PVP, there are some additional signals at ca.35 and 50 ppm that could be due to the presence of grafted side chains resulting from the branching reaction.

Particle size and particle-size distribution for the latex prepared at 0.1 Mrad/h were determined by laser-light scattering and are shown in Figure 5. The average particle size was calculated to be 1785 nm from a sample population of 1.27×10^6 particles. The bimodal distribution suggests that particle agglomeration and coalescence occurred during the polymerization. However, this is not obvious from the conversion vs. time plot (Fig. 1). It is possible that the bimodal distribution may, in part, be due to particle aggregation during manipulation prior to the light-scattering measurement.

Several polymerizations were made using the following formulas to examine the effect of emulsifier type on the polymerization rate and average particle size (all formulas expressed in wt %):

	Run No.					
	1	2	3	4	5	6
Monomer	10.6	10.6	10.6	10.6	10.6	10.6
H ₂ O	21.2	21.2	21.2	21.2	21.2	21.2
Isopar M	63.4	63.4	63.4	63.4	63.4	63.4
SPAN 80 (HLB 4.33)	4.5	4.05	3.375	2.25	1.125	—
TWEEN 85 (HLB 11.0)	0.5	0.45	0.375	0.25	0.125	—
Hypermer B246 (HLB 6.0)	0	0.5	1.25	2.5	3.75	5.0
Dose rates (Mrad/h)	0.10					
Temp	23°C					

Table II The Effect of Emulsifier Type on the Rate of Polymerization, Molecular Weight, and Average Particle Size

Run No.	Hypermer B-246 ^a	$R_p \times 10^5$ (Mol/L s)	$\bar{M}_v \times 10^6$	Average Particle Size (nm)
1	0	12.1	1.95	1785
2	10	19.4	2.18	1264
3	25	32.2	2.75	320
4	50	19.9	1.30	509
5	75	18.4	1.08	745
6	100	14.3	0.99	1518

^a Percent of emulsifier concentration.

The data are in Table II. It was anticipated that the Hypermer B-246 would provide additional steric stabilization.

The rate of polymerization vs. the average particle size relationship were typical for an emulsion polymerization up to 25% of Hypermer B-246, i.e., the number of particles initiated increased as the level of Hypermer B-246 increased (up to 25%) at a constant dose rate (or initiator level) and, consequently, the average particle size decreased and the molecular weight increased:

$$DP_n = \frac{R_p[M][N]}{\rho} \quad (1)$$

At higher levels of Hypmer B-246, the rate decreases as does the average particle size and the polymer molecular weight. These data suggest that the B-246 influences monomer partitioning and diffusion rates between the water and oil phases.

Hypermer B-246 alone does give faster polymerizations than does the combination of SPAN 80 and TWEEN 85 (90 : 10 ratio), but the polymer molecular weight is significantly lower—contrary to eq. (1). It is possible that the Hypmer B-246 also functions as a chain-transfer agent.

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