

Photo-Induced Emulsion Polymerization of Vinyl Acetate in the Presence of Poly(Oxyethylene) Nonyl Phenyl Ether, A Nonionic Emulsifier (II)

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Received 5 June 2001; accepted 7 February 2002

ABSTRACT: Synthesis of high molecular weight poly(vinyl acetate) having less branched structure via photo-induced emulsion polymerization of vinyl acetate in the presence of poly(oxyethylene)₂₀ nonyl phenyl ether, a nonionic emulsifier, was attempted at 0°C or even below 0°C in the presence of methanol. It was found that 100% conversion is always achieved in all runs and poly(vinyl acetate) having the number-average degree of polymerization of 9000 with

less branched structure (degree of branch < 0.5) can be obtained from this photo-induced emulsion polymerization system. Mechanisms of the polymerization were also discussed on the basis of the kinetic results. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2153–2158, 2002

Key words: nonionic; photo-induced; emulsion polymerization; branch; degree of polymerization

INTRODUCTION

Synthesis of high molecular weight poly(vinyl acetate) (PVAc) having less branch structure has been the subject of extensive study for manufacturing of high-strength, high-modulus poly(vinyl alcohol) (PVA) fiber because PVA is obtained industrially by the saponification of PVAc. However, no satisfactory result was obtained in any attempt because of the operation of frequent chain transfer to solvent, monomer, and initiator.¹ A remarkable decrease in the molecular weight of PVA occurred in the saponification of PVAc by the hydrolysis of the ester linkage between branched and main chain formed in the later stage of the polymerization by chain transfer to polymer and the oxidative cleavage of 1,2-glycol structure in the main chain, which is formed by the head-to-head propagation of PVAc polymerization.² Tremendous efforts have been made to develop the polymerization of VAc at low temperature to depress the chain transfer processes by using redox initiators^{3–7} and photo-induced and radiation-induced polymerizations.⁸ However, the highest number-average degree of polymerization value of PVA, obtained from VAc radical polymerization, carried out at 0°C in methanol using various redox-initiating systems, showed a value

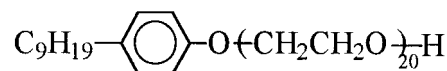
< 3000, and the rates of polymerizations were too low for practical application.⁹

In this article, we report photo-induced emulsion polymerization of VAc in the presence of poly(oxyethylene)₂₀ nonyl phenyl ether, a nonionic emulsifier, carried out at 0°C or even below 0°C.

Experimental

Chemicals

VAc (Aldrich) was purified by fractional distillation under reduced pressure (12.69 cmHg at 27.3°C) after successive washing with 2% NaOH aqueous solution and distilled water and then dried over a molecular sieve.¹⁰ Methanol (Oriental Chemical), sodium hydroxide (NaOH, Duksan Chemical), *n*-hexane (Duksan Pharmaceutical), acetone (Oriental Chemical), pyridine (Oriental Chemical), acetic acid (Shinyo Pure Chemical), acetic anhydride (Tedia), and ammonium persulfate (APS) (Aldrich) of reagent grade were used without further purification. Purified poly(oxyethylene)₂₀ nonyl phenyl ether (POENPE), a nonionic emulsifier, was kindly donated by Dongnam Chemical Co. (Incheon, Korea):



Polymerization procedures

An ampoule containing proper amounts of VAc, distilled water, POENPE, and APS was degassed on a

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Contract grant sponsor: Korea Institute of Industrial Technology Evaluation and Planning; contract grant number: A00-981-5401-02-1-2.

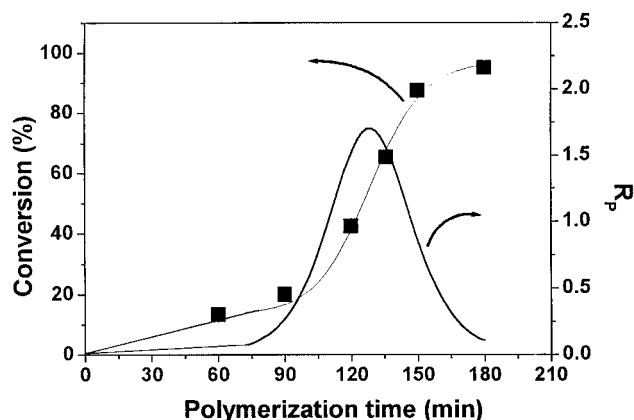


Figure 1 Time-% conversion and time rate of polymerization curves of photo-induced emulsion polymerization of VAc. Temp.: 0°C, [APS] = $1.8 \times 10^{-3}M$, [POENPE] = $3 \times 10^{-3}M$, composition (in volume ratio of VAc/water): 1/2.

vacuum line by repeated freeze-thaw operation and then sealed off. Then, the ampoule was irradiated by UV rays by using a 500-W high-pressure Hg lamp (Ushio) at predetermined temperatures ranging from -15 to 0°C for a certain period of time. After the completion of the reaction, polymer was precipitated by aqueous sodium sulfate solution, followed by washing with distilled water. The polymer was dried at room temperature under reduced pressure. % Conversion was determined by gravimetry.

Saponification of PVAc

To a flask where 1 g PVAc is dissolved in methanol, 5% NaOH solution of methanol was added slowly and let to stand for 5 h at room temperature for the completion of the reaction. PVA was washed with methanol and dried under reduced pressure for 48 h at room temperature.¹¹

Determination of DP of PVAc

Intrinsic viscosity of the polymer was measured by using a Ubbelohde viscometer in acetone at 30°C and the number-average degree of polymerization (DP) was determined by using the Mark-Houwink equation shown below.¹² DP of PVA was determined by same viscometer after PVA is converted to PVAc by reacylation:

$$[\eta] = 4.10 \times 10^{-1} \overline{P}_n^{0.72}$$

where \overline{P}_n is the number-average DP of PVAc and $[\eta]$ is the intrinsic viscosity in the unit of ml/g.

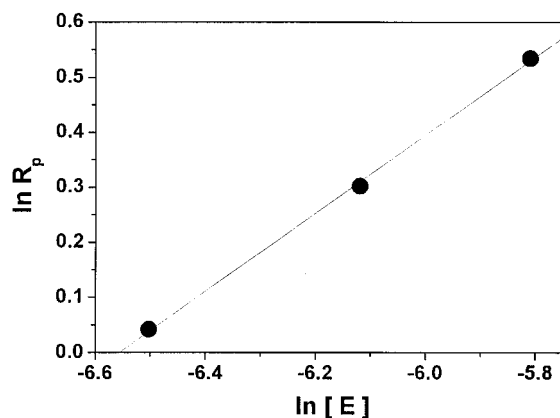


Figure 2 Dependence of the rate of polymerization on the emulsifier concentration. Temp.: 0°C , [APS] = $1.8 \times 10^{-3}M$, composition (in volume ratio of VAc/water): 1/2.

Reacylation of PVA

Mixtures of 1 g PVA, 20 mL acetic anhydride, 20 mL acetic acid, and 2 mL pyridine in a 100-mL round-bottom flask were heated to 100°C for 48 h under nitrogen atmosphere, and then, the polymer was purified by repeated dissolution and precipitation in methanol and distilled water. The polymer was dried under reduced pressure at room temperature.⁸

The degree of branch of PVAc was determined by the ratio of the DP value of the original PVAc and reacylated PVAc, reacylated from PVA, which was the product of the saponification of the original PVAc as follows:

Degree of branch

$$= \frac{\text{Number-average DP of original PVAc}}{\text{Number-average DP of reacylated PVAc}} - 1$$

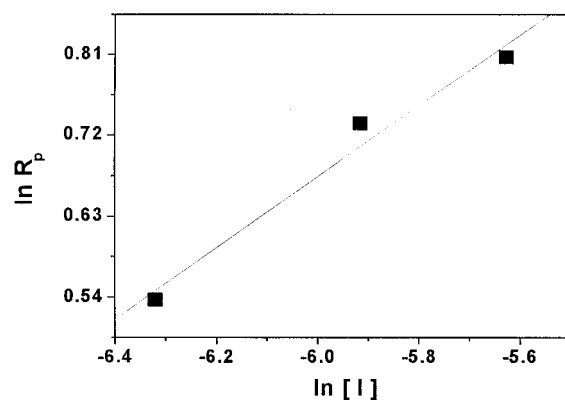


Figure 3 Dependence of the rate of polymerization on the initiator concentration. Temp.: 0°C , [POENPE] = $1.8 \times 10^{-3}M$, composition (in the volume ratio of VAc/water): 1/2.

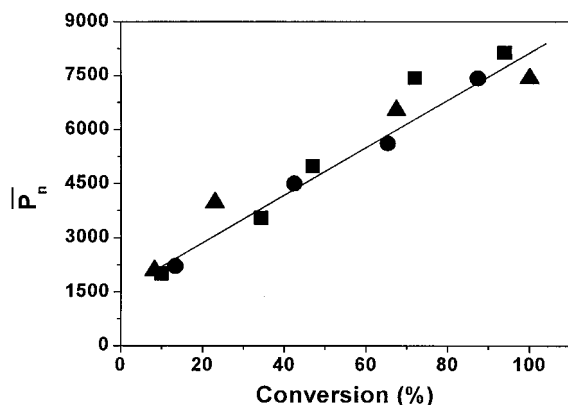


Figure 4 Relationship between % conversion and the number average degree of polymerization. Temp.: 0°C, [APS] = $1.8 \times 10^{-3}M$, composition (in volume ratio of VAc/water): 1/2.

Melting-temperature determination of methanol-added emulsion polymerization systems

Melting temperature of the emulsion polymerization systems, consisting of VAc, water, emulsifier, and methanol, was determined by using a differential scanning calorimeter (Shimadzu DSC-50). The rate of temperature raising was 10°C/min.

RESULTS AND DISCUSSION

Emulsion polymerization

A typical time–conversion curve of photo-induced emulsion polymerization of VAc, in the presence of the emulsifier, is shown in Figure 1, together with its corresponding time–rate curve. POENPE was used as a nonionic emulsifier and the reaction was carried out at 0°C. The % conversion increases almost linearly with time until % conversion reaches around 80% and the reaction continues until the full consumption of the monomer. It becomes evident that no flat portion of the curve is observed which appears in the emulsion polymerization of styrene because of the presence of stage II, where the polymerization proceeds in a constant number of polymer particles containing constant concentration of radical species.¹³ The rate increases rapidly in the early stage of polymerization but decreases in the later stage after showing a maximum. The short duration of stage I suggests the simultaneous operation of homogeneous and micellar nucleation¹⁴ and the late transition of stage II to III implies that the concentration of the monomer to the polymer particle is high due to the high solubility of the monomer, which results in the slower decrease in the monomer concentration in the polymer particle, as reported earlier.^{15,16} The increase in the conversion is not observed after the irradiation is cut off. It is thought that the hydrophilic oligomeric radicals are

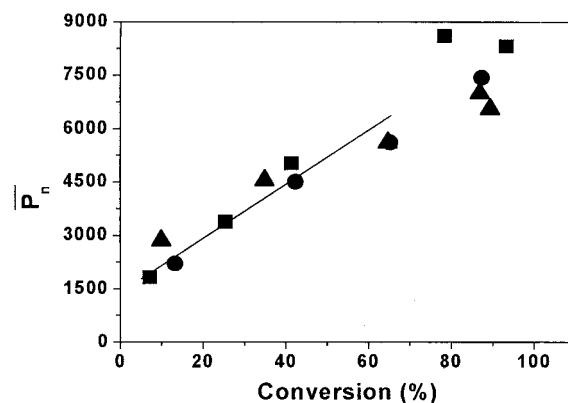


Figure 5 Relationship between % conversion and number average degree of polymerization. Temp.: 0°C, [POENPE] = $3 \times 10^{-3}M$, composition (in the volume ratio of VAc/water): 1/2.

frequently desorbed from the particle to aqueous phase in this emulsion polymerization system, as was reported previously.¹⁷ The existence of the maximum rate in the course of the polymerization also suggests the presence of high-transient particle numbers or a high proportion of radical-containing particles in the early stage of the polymerization.^{15,16}

Figure 2 shows the dependence of the rate of polymerization on emulsifier concentration. The order of the dependence, obtained from the slope of the curve, gives a value of 0.7, which is not far from the value of 0.6, predicted by the Smith–Ewart theory for the emulsion polymerization of water-insoluble monomer.¹³

Figure 3 shows the dependence of the rate of polymerization on initiator concentration, revealing that the order of dependence is 0.4, which also agrees well with the results of 0.4 order dependence, predicted by the Smith–Ewart theory for the emulsion polymerization of styrene.

These kinetic results are strikingly different from the results of our previous article concerning the photo-induced emulsion polymerization of VAc in the presence of poly(oxyethylene)₁₀ nonyl phenyl ether

TABLE I
The Degree of Branch of PVAc, Determined by the Number-Average Degree of Polymerization of PVAc and Recetylated PVA, Prepared from the Polymerization Systems Having Composition of H₂O/VAc (v/v) = 2/1 in the Presence of 3 mM Emulsifier

[APS] (mM)	Conversion (%)	\bar{P}_n of original PVAc	\bar{P}_n of recetylated PVA	Degree of branch
0.9	25.5	3370	2600	0.3
0.9	41.5	5010	3500	0.43
0.9	78.4	8600	5640	0.52
1.8	87.4	7430	4930	0.51
3.6	87	6980	4300	0.62

TABLE II
Melting Temperature of the Methanol-Added
Emulsion Systems

No.	Compositions (v/v/v)			T_m (°C)
	Water	VAc	MeOH	
1	3	1.5	0	0.3
2	3	1.5	0.15	-2
3	3	1.5	0.3	-5.5
4	3	1.5	1.5	-15
5	3	1.5	3	-37
6	3	1.3	0.5	-10.3
7	3	1.7	0.1	-1
8	3.3	1.8	0.3	-6
9	2.7	1.2	0.3	-6

ammonium sulfate (POENPES), an anionic emulsifier¹⁸ that has similar chemical structure with the current emulsifier except for the polarity. The first-order dependence of rate on initiator concentration in the POENPES system was explained in terms of the charged surface of the polymer particle.¹⁸

The relationship between the % conversion and the number-average DP of resulting PVAc, from the polymerizations carried out in the presence of various concentrations of the emulsifier and of the initiator, are shown in Figures 4 and 5, respectively. Both figures clearly show that DP of the resulting PVAc increases as % conversion increases, and all experimental data form a smooth curve, irrespective to the concentrations of the initiator and the emulsifier. This implies that DP of the resulting PVAc is not significantly affected by the concentrations of the initiator and the emulsifier. The insensitiveness of the DP to the concentrations of the initiator and the emulsifier was ascribed to the frequent operation of chain transfer to

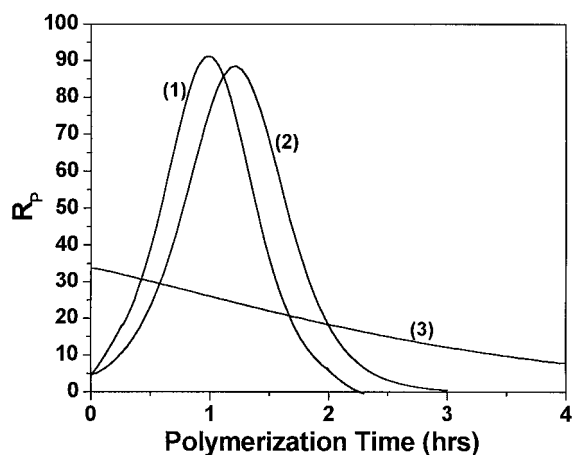


Figure 6 Time-rate of polymerization curves of photo-induced polymerization of VAc in the presence of MeOH. Temp.: 0°C, [APS] = $1.46 \times 10^{-3}M$, [POENPE] = $3.78 \times 10^{-3}M$, composition (in volume ratio of VAc/water/MeOH): (1) 1/2/0, (2) 1/1/1, (3) 1/0.1/1.9.

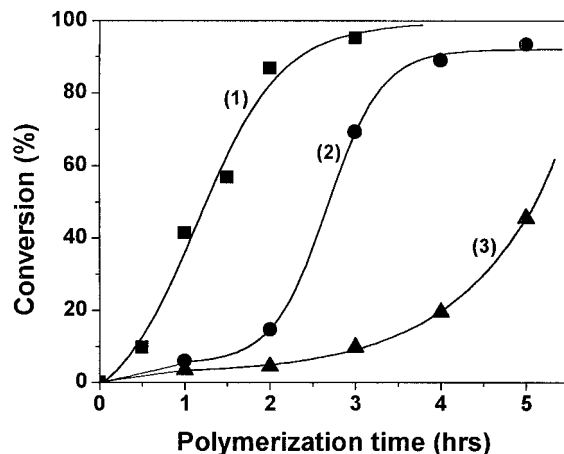


Figure 7 Time-% conversion curves of photo-induced emulsion polymerization of VAc in aqueous MeOH solution. Composition (in volume ratio of VAc/water/MeOH): 1/2/1, [APS] = $1.8 \times 10^{-3}M$, [POENPE] = $3 \times 10^{-3}M$, temp.: (1) 0°C, (2) -5°C, (3) -10°C.

monomer¹⁷⁻¹⁸; therefore, the DP of resulting polymer is mainly determined by the ratio of propagation and chain transfer constant in the polymer particles because the oligomeric radical species produced by chain transfer is not able to play any role in the propagation due to the desorption to aqueous phase from the polymer particle.¹⁹

The degree of branch of the resulting PVAc was estimated by the comparison of the DP of original PVAc and that of reacetylated PVAc from PVA. The degree of branch values, scattered around 0.5, strongly suggest that less-branched PVAc is obtained from this photo-induced emulsion polymerization system, as summarized in Table I.

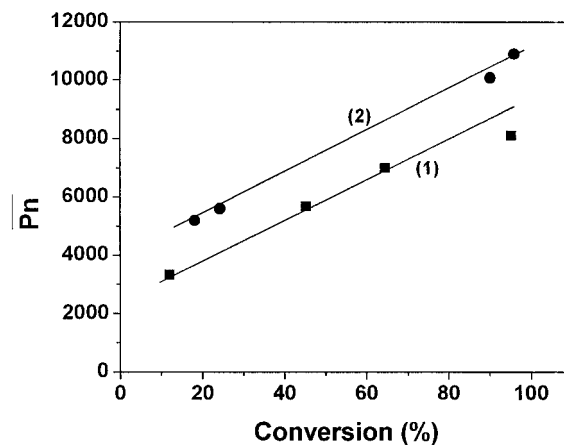


Figure 8 Relationship between % conversion and number-average degree of polymerization in photo-induced emulsion polymerization of VAc in the presence of MeOH. Composition (in volume ratio of VAc/water/MeOH): 1/2/0.2, [APS] = $1.8 \times 10^{-3}M$, [POENPE] = $3 \times 10^{-3}M$, temp.: (1) 0°C, (2) -5°C.

TABLE III
Degree of Branch of PVAc

Temp. (°C)	Conversion (%)	Methanol (ml)	\bar{P}_n of PVAc	P_n of Reacetylated PVA	Degree of branch
0	95.14	1.5	5530	3780	0.46
0	95.26	0.3	8100	4560	0.78
-5	93.33	1.5	8800	4660	0.89
-5	95.97	0.3	10900	5350	1.03

Emulsion polymerization in the presence of methanol

To carry the polymerization at lower temperatures below 0°C, methanol was added to lower the melting temperature of the emulsion polymerization systems. As summarized in Table II, the mole fraction of methanol increases, and the melting temperature of the emulsion system decreases. However, there is a restriction in the increase in the mole fraction of methanol because the emulsion system loses its heterogeneity with increasing mole fraction of methanol.

A typical plot of typical time versus rate of polymerization carried out in the presence of methanol is shown in the Figure 6, revealing that the rate of polymerization decreases²⁰ and the polymerization loses its characteristic behaviors of emulsion polymerization as the system becomes homogeneous because of the addition of methanol. The rate of polymerization decreases monotonically with time in a methanol-rich homogeneous system; on the other hand, the rate of polymerization increases with time in the early stage of reaction until it reaches its maximum in a heterogeneous emulsion system. This characteristic phenomenon (i.e., the appearance of the maximum rate in the course of polymerization) is maintained as far the system keeps its heterogeneity, irrespective to the presence of methanol.

Figure 7 shows some time-conversion curves of photo-induced methanol containing emulsion polymerization carried out at various temperatures ranging from 0 to -10°C. It is evident that the induction period becomes longer as temperature is lowered; however, the effect of temperature on the maximum rate of polymerization is not so significant. The induction period at -5°C becomes shorter with increasing methanol content in the system. The shorter induction period in methanol-rich systems at -5°C seems to be related to the diffusion of the aqueous radical to the emulsifier micelle. It is thought that the diffusion of the radical to the micelle is greatly retarded because the melting temperature of the emulsion system is just above the reaction temperature by 0.5°C.

The plot of the number-average DP versus % conversion of the photo-induced polymerizations carried out at 0 and -5°C are compared in Figure 8. It clearly shows

that the PVAc, obtained from -5°C polymerization, has a DP value higher by 2000 than that of the corresponding PVAc, obtained from 0°C polymerization.

The degree of branch of the polymer was investigated by the ratio of DP of original PVAc and that of reacetylated PVA based on an assumption that the ester linkage between main chain and the branched chain is cleaved during the saponification of PVAc to PVA. The results are summarized in Table III. The low values of the degree of branch indicate that higher molecular weight PVAc having linear and less-branched structure was successfully obtained from the photo-induced emulsion polymerization by using POENPE, a nonionic emulsifier, and the reaction temperature of the emulsion polymerization can be lowered below 0°C by the addition of methanol to the emulsion without loss of the characteristics of the emulsion polymerization system.

CONCLUSION

High molecular weight PVAc having less-branched structure was successfully obtained from the photo-induced emulsion polymerization of VAc at 0°C or even below 0°C by using POENPE, a nonionic emulsifier. Photo-induced polymerization, carried out at low temperature, results in not only an increase in molecular weight of PVA but also in a decrease in the degree of branch by depression of the various chain-transfer processes. However, the addition of methanol also results in the loss of the characteristics of emulsion polymerization due to the loss of the heterogeneity of the system. Kinetic results reveal that the order of dependence of the rate of polymerization on the concentrations of the emulsifier and the initiator are 0.7 and 0.4 power, respectively.

The authors express gratitude to Korea Institute of Industrial Technology Evaluation and Planning for financial support for this research (Grant A00-981-5401-02-1-2).

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