

Photo-Induced Emulsion Polymerization of Vinyl Acetate in the Presence of Poly(oxyethylene)₁₀ Nonyl Phenyl Ether Ammonium Sulfate, An Anionic Emulsifier (I)

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ABSTRACT: Poly(vinyl alcohol) (PVA) having a number-average degree of polymerization of 7000 was obtained from the poly(vinyl acetate) (PVAc) having a number-average degree of polymerization 9000, a product of photo-induced emulsion polymerization of vinyl acetate (VAc), carried out at 0°C, using poly(oxyethylene)₁₀ nonyl phenyl ether ammonium sulfate as an anionic emulsifier. It was found that 100% conversion is always attained in the whole range of the investigation and the emulsifier plays an important role in the initiation process. The applicability of the photo-induced emulsion polymerization system to a relatively large-scale production was tested by using an apparatus equipped with an internal high-pressure Hg lamp with a capacity of several hundred grams per batch under nitrogen atmosphere. It was found that both the rate of polymerization and the degree of polymerization of resulting polymers are slightly lower than those obtained from corresponding small-scale polymerizations prepared on a high vacuum system because of the presence of oxygen. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2425–2431, 2002

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

INTRODUCTION

Tremendous efforts have been made to develop a synthetic method of linear poly(vinyl acetate) (PVAc) having a high degree of polymerization (DP) to obtain poly(vinyl alcohol) (PVA), having high molecular weight for fiber manufacturing. Solution,^{1–3} bulk,^{4–6} emulsion, and suspension^{7–9} were reported for radical polymerization of vinyl acetate (VAc). Solution polymerization of VAc in methanol, initiated by conventional radical initiators, such as *N,N*-azobisisobutyronitrile and

benzoyl peroxide,^{10–12} gives a PVAc having a number-average degree of polymerization of about 2000. It has been known that the synthesis of PVA having DP larger than 2000 is very difficult because of its large chain transfer constant to monomer, solvent, and polymer.^{13–14} In the industrial process, therefore, the reaction is terminated at around 60% conversion to avoid the chain transfer to polymer, which results in the branched structure. Therefore, it is natural to attempt to lower the reaction temperature to avoid the chain transfer to polymer. Much attention has been paid to the low temperature polymerization of VAc by using redox initiators,^{1,15} photo-induced polymerization,^{5–6} and ionizing radiation-induced polymerization.⁷

In this article, we report photo-induced emulsion polymerization of VAc at low temperature by

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using poly(oxyethylene)₁₀ nonyl phenyl ether ammonium sulfate, an anionic emulsifier.

EXPERIMENTAL

Materials and Chemicals

VAc (reagent grade, Aldrich) was purified by distillation under reduced pressure¹⁶ after successive washing with 2% aqueous NaOH solution and distilled water.

Poly(oxy ethylene)₁₀ nonyl phenyl ether ammonium sulfate (purity 99%), an anionic emulsifier, kindly donated by Dongnam Chemicals (Inchon, Korea), and potassium persulfate initiator (KPS, reagent grade, Shinyo Pure Chemicals), as shown in the following equation, were used without further purification:

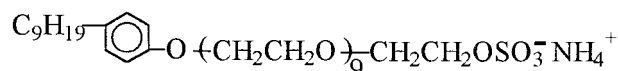


Photo-Induced Emulsion Polymerization

A Pyrex round-bottom flask, filled with a proper amount of water, emulsifier, monomer, and initiator was degassed by freeze-thaw technique on a vacuum line and sealed off for irradiation. The sample was irradiated with a high-pressure mercury lamp (500 W, Ushio) at 0°C to maintain the agitation. After the polymerization was completed, the polymer was precipitated by adding 150 mL of water containing 1 g (NH₄)₂SO₄, followed by washing with distilled water at 40°C. Then, the polymer was dried at room temperature under reduced pressure. % Conversion was determined by gravimetry.

Determination of Photolytic Dissociation of Persulfate in Emulsion

To 10 mL of emulsion system, consisting of various amounts of emulsifier and aqueous solution of KPS, 30 mM of KI (Duksan Pure Chemical Co., Korea) and 5 droplets of aqueous starch indicator solution (Aldrich) were added. The emulsion system was irradiated at the same conditions with polymerization and the concentration of the unreacted KPS was determined by titration with 4 mM aqueous sodium thiosulfate solution.

Determination of Number-Average DP of PVAc¹⁷

The number-average DP of PVAc was determined by viscometer by using a Ubbelohde viscometer in

acetone solution at 30°C. The following equation is used to convert the intrinsic viscosity to DP:

$$[\eta] = 4.1 \times 10^{-1} [\overline{Pn}]^{0.72}$$

Determination of Degree of Branch of PVAc

The degree of branch of PVAc was determined by the comparison of the DP of original PVAc and the reacetylated one from corresponding PVA, by using following equation:

$$\text{Degree of branch} = \frac{\text{Number-average degree of original PVAc}}{\text{Number-average degree of reacetylated PVA}} - 1$$

Saponification of PVAc¹⁸

PVA was obtained from PVAc by the saponification procedures described below. To the 20 mL CH₃OH containing 1 g PVAc, 5 mL CH₃OH solution containing 5 wt % NaOH was added and allowed to stand 5 h with continuous stirring and the collected precipitated PVA. PVA was dried under reduced pressure after thorough washing with CH₃OH.

Reacetylation of PVA⁸

Acetic acid (20 mL), acetic anhydride (20 mL), pyridine (2 mL) was added to a 100-mL round-bottom flask where 1 g PVA was placed and allowed to stand for 2 h under nitrogen atmosphere and then raised to 100°C for 72 h until the reacetylation was completed.

UV-Spectroscopy

UV spectra of emulsion polymerization system were measured by using a UV-Visible spectrophotometer (UV-1601PC, Shimadzu).

RESULTS AND DISCUSSION

Features of Time-Conversion Curves

A typical time-conversion curve of the emulsion polymerization is shown in Figure 1, together with the time-rate of polymerization curve. The % conversion increases almost linearly with time until the conversion reaches 80%, and 100% conversion is always achieved without exception. The

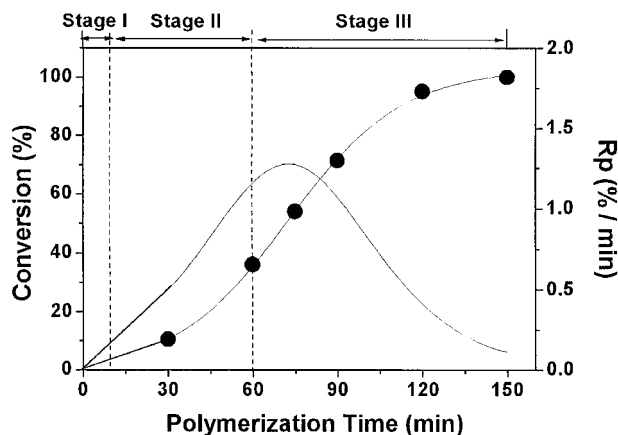


Figure 1 Time-conversion curve of photo-induced emulsion polymerization of VAc, carried out at 0°C. $[E]$, 2.2 mM; $[I]$, 0.887 mM; H_2O/VAc (v/v), 10/5.

time-rate of the polymerization curve, however, reveals that the time-conversion curve is not linear but actually sigmoidal having a maximum. Differing from the emulsion polymerization of styrene where polymerization proceeds primarily in the constant number of polymer particles with a constant rate,¹⁹ the flat portion of the curve due to the existence of stage II is not observed in this polymerization. The duration of stage I lies between 2 and 5% conversion and the shorter duration of stage I is thought to be due to the consequence of the significant extent of the homogeneous nucleation occurring simultaneously with micellar nucleation.²⁰ Stage II ends at around 15–35% conversion with the disappearance of the monomer droplet in VAc emulsion polymerization. The late transition of stage II to III can be explained in terms of the high water solubility of the monomer and the high concentration of the monomer to the polymer particle,^{21–22} which results in the slower decrease in the monomer concentration in the polymer particle.²³ The existence of the maximum rate reveals that there exists a large amount of the transient particles or the high proportion of particles containing radical in the early stage of the polymerization.^{21–22}

Dependence of Rate of Polymerization on Emulsifier and Initiator Concentration

The dependence of rate of polymerization on emulsifier concentration is shown in Figure 2. It is very interesting to note that the rate of polymerization is proportional to the 0.4th power of emulsifier concentration. However, it changes

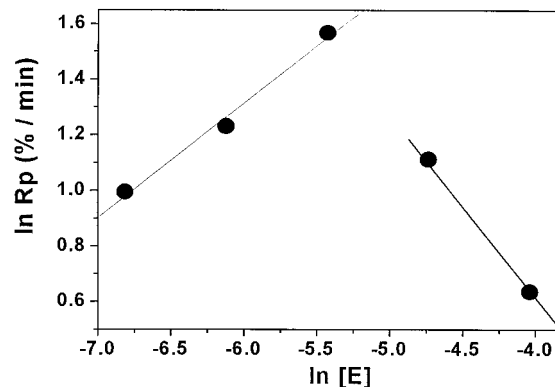


Figure 2 Dependence of rate of polymerization on the concentration of emulsifier. Temperature, 0°C; H_2O/VAc (v/v), 10/5; $[I]$, 1.8 mM.

abruptly to -0.6 th power in the region where the emulsifier concentration is higher than 4.4 mM.

The dependence of rate of polymerization on the initiator concentration is given in Figure 3. It reveals that the rate of polymerization is proportional to the initiator concentration to the first power.

It was reported that in the emulsion polymerization of water-insoluble monomer such as styrene, the rate of polymerization increases monotonically with increasing emulsifier concentration, whereas the rate of polymerization decreases as the emulsifier concentration increases after it shows a maximum²⁴ in the emulsion polymerization of water-soluble monomer, such as VAc. The maximum in the course of polymerization suggests that the decrease in the rate in the high concentration region of emulsifier is due to the enhanced desorp-

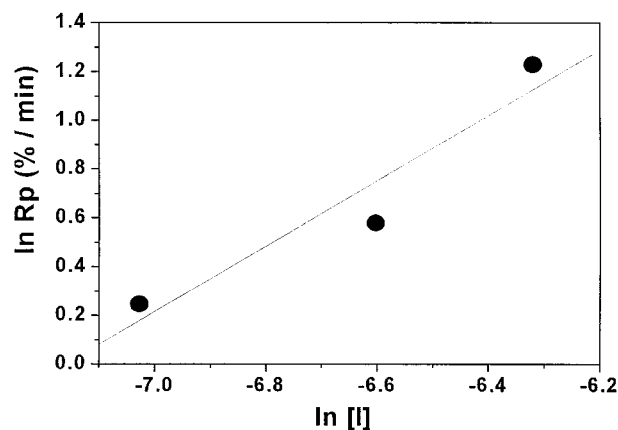


Figure 3 Dependence of rate of polymerization on the concentration of initiator. Temperature, 0°C; H_2O/VAc (v/v), 10/5; $[E]$, 2.2 mM.

tion of water-soluble oligomeric radical, a product of chain transfer to monomer, from the polymer particle whose size reduces as the emulsifier concentration increases. Therefore, it is believed that the initiation and most polymerization take place in the aqueous phase in this system. The growing polymer in the aqueous phase is partly stabilized in the aqueous phase by adsorbing the emulsifier and finally the polymer radical is adsorbed by a particle. Polymerization, then, proceeds in the particle until chain transfer to monomer occurs²⁴ and is followed by desorption of oligomeric radical to aqueous phase. This is supported by the negative dependence of the rate on emulsifier concentration where emulsifier concentration is high, as shown in Figure 2.

It is evident, however, that the kinetic data 0.4th dependence and first-order dependence of rate on the concentration of the emulsifier and the initiator, respectively, obey neither the theory proposed by Smith and Ewart,¹⁹ for water-insoluble monomers, nor the theory proposed by Nomura et al.,²⁵ for water-soluble monomer. The number of particles in the emulsion polymerization (N) is determined by

$$N \propto [E]^a [I]^{1-a}$$

where $[E]$ and $[I]$ are the concentrations of emulsifier and initiator, respectively, and a is a constant having a value $0 < a < 1$.

According to the theory, the order dependence of the number of polymer particles on emulsifier concentration is generally greater than the predicted value of 0.6 and on initiator concentration approaches to zero from 0.4 order, when extensive radical desorption occurs. A large bulk of nucleation is initiated by desorbed radical in aqueous phase, which results in the insensitiveness of a number of particles to the rate of initiation.

An explanation can be given to this contradiction (i.e., the first-order dependence of the rate on the initiator concentration is explainable by a model of polymeric radicals in the aqueous phase) onto which surfactant molecules have adsorbed such that they became stabilized as polyelectrolytes.^{21,22} The entrance to the charged aqueous polymeric radicals to existing particles, therefore, is no longer diffusion controlled as in the Smith-Ewart model. It was reported that the dependence of the rate of polymerization on ionic strength, based on the fact that the dependence of adsorption rate of the charged polymeric radicals

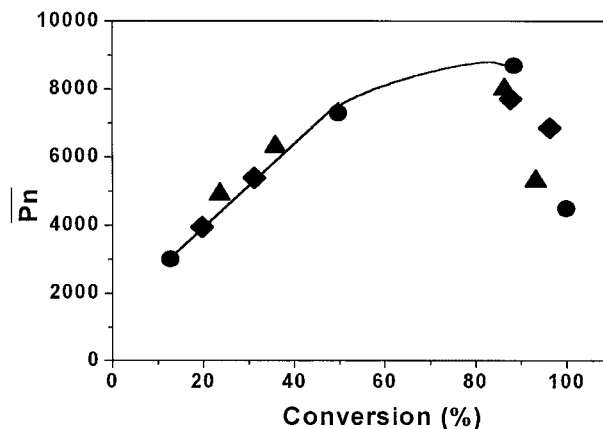


Figure 4 Relationship between conversion and the number-average degree of polymerization. Temperature, 0°C; H₂O/VAc (v/v), 10/5; $[I]$, 1.8 mM; $[E]$: ▲, 1.1 mM; ●, 2.2 mM; ◆, 4.4 mM.

to the already existing polymer particle on ionic strength, approaches first order when ionic strength is below 0.01.²⁶

Number-Average DP

Figure 4 shows the relationship between number-average DP of the resulting PVAc and the % conversion. The polymerization was carried out under the same conditions except with emulsifier concentrations. The DP of resulting PVAc increases as % conversion increases and most of the experimental data lie on a smooth curve up to 80% conversion, irrespective of the emulsifier concentration, revealing that DP of resulting PVAc is not a function of emulsifier concentration. The DP of the resulting polymer, however, decreases as % conversion increases above 80%, probably due to the main chain scission by prolonged irradiation in the presence of the initiator.

The effect of the initiator concentration on the number-average DP of the resulting PVAc is shown in Figure 5. The polymerization conditions are kept constant except for the initiator concentration. The increasing tendency of DP with % conversion is also observed in this case. The experimental DP data forms a smooth curve up to 70% conversion, irrespective of initiator concentration, implying that the DP of the resulting polymer is independent of the initiator concentration.

The effect of the volume ratio of VAc and water is shown in Figure 6. The formation of a smooth curve irrespective of the volume ratio of VAc and

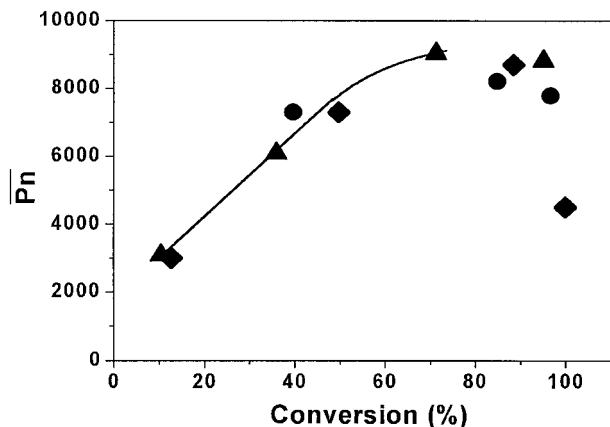


Figure 5 Relationship between conversion and the number-average degree of polymerization. Temperature, 0°C; H₂O/VAc (v/v), 10/5; [E], 2.2 mM; [I]: ▲, 0.887 mM; ●, 1.36 mM; ◆, 1.8 mM.

water means that DP of the PVAc is insensitive to the volume ratio of VAc and water.

The low power dependence DP on the concentrations of emulsifier and initiator was attributed to the frequent chain transfer to monomer, followed by the large desorption of oligomeric radical from the polymer particle due to high water solubility of the monomer.²⁶

It is thought that DP in an emulsion polymerization is synonymous with the kinetic chain length. Although termination is bimolecular coupling, one of the radicals is a primary radical, which does not significantly contribute the size of dead polymer molecules. If chain transfer occurs, the DP will be given by

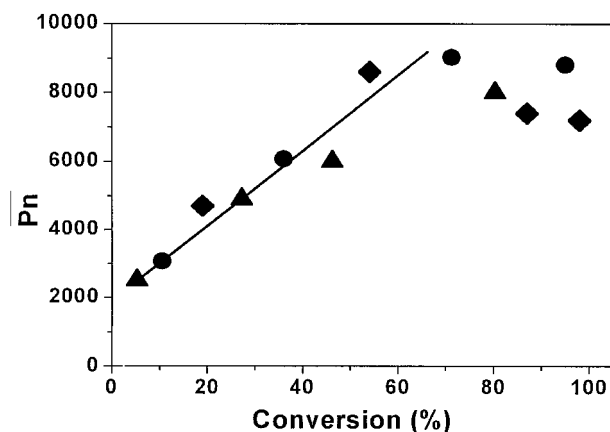


Figure 6 Relationship between conversion and the number-average degree of polymerization. Temperature, 0°C; [E], 2.2 mM; [I], 0.887 mM; H₂O/VAc (v/v): ▲, 9/6; ●, 10/5; ◆, 11/4.

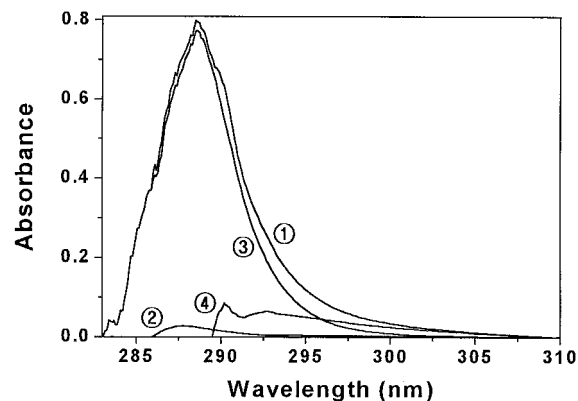


Figure 7 UV spectra of the emulsion system, consisting of initiator, emulsifier, and water. Water was used as a reference. (1) Emulsion system [II], 1.8 mM; [E], 4.4 mM; (2) aqueous initiator solution [I], 1.8 mM; (3) emulsion system without initiator; (4) difference spectrum of (1) and (3).

$$DP = \frac{r_p}{r_t + \sum r_{tr}}$$

where r_p and r_t are rate of propagation and termination processes, respectively, and $\sum r_{tr}$ is the sum of the rates of all transfer reactions.

It is postulated that chain transfer to monomer is the most important factor that determines the DP of the resulting polymer, because the reinitiation process by the product of the chain transfer is not operative in this system because of the frequent desorption of the oligomeric radical from the particle.

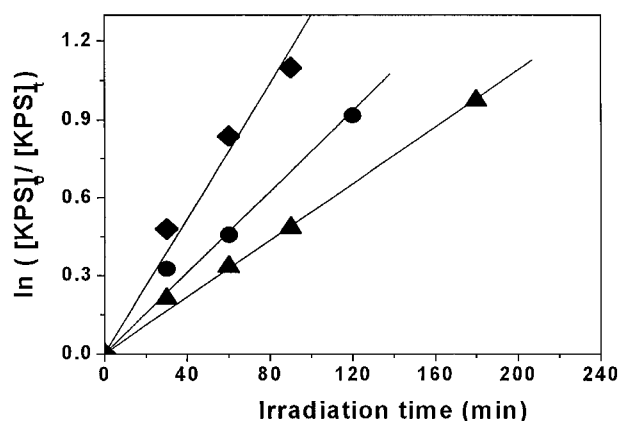


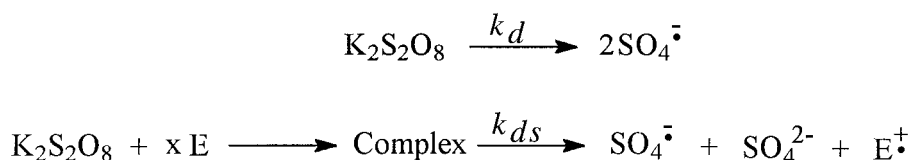
Figure 8 Photolytic dissociation of KPS in the presence of various concentrations of the emulsifier. [I], 1.8 mM; irradiation temperature, 0°C; [E]: ▲, 0 mM; ●, 2.2 mM; ◆, 4.4 mM.

It seems that the high rate of polymerization in this system is related to the participation of the emulsifier in the initiation process. An evident complex formation between the initiator and emulsifier is given in Figure 7. A very weak absorption band newly appears at around 290 nm by mixing emulsifier with initiator, probably, due to the formation of charge transfer complex.

The acceleration effect of the emulsifier on the dissociation of the initiator was followed by the method of the reduction-oxidation titration. The results are summarized in Figure 8, revealing that the dissociation rate of the initiator is greatly enhanced by the addition of the emulsifier to the aqueous initiator solution. The degree of the ac-

celeration increases as the concentration of emulsifier increases.

Therefore, it is postulated that the enhanced rate of polymerization in the presence of the emulsifier is due to the increased rate of radical production by increased UV absorption at around 300 nm or the increased rate of persulfate dissociation by the complex formation of the initiator with the emulsifier. The increase in the rate of initiation in the presence of the emulsifier is explainable when one assumes that the production of radical species by the dissociation of the initiator primarily takes place via the initiator in complexed state, namely, $k_{ds} \gg k_d$ in the following equation:



Degree of Branch

The degree of branch of PVAc was investigated by comparison of the DP of PVAc, reacetylated from PVA, with that of original PVAc.

The results are summarized in Table I, showing that degree of branch of PVAc has a value around 0.29. This means that PVAc obtained in this emulsion polymerization system has a linear structure with fewer branches because the chain transfer to polymer is remarkably depressed in this system.

Activation Energy of the Polymerization

Figure 9 shows the Arrhenius plot of the photo-induced emulsion polymerization of VAc in the presence of potassium persulfate. The activation energy, determined from the slope of the plots,

gives a value of 18 kJ/mol for $E_p - E_t/2$, which is in good agreement with the reported value,²⁷ where E_p and E_t are the activation energies of propagation and termination, respectively.

CONCLUSION

Less branched PVAc having high DP (the number-average DP, 9000; degree of branch, 0.29) was successfully obtained with high yield (% conversion, 71%) from the photo-induced emulsion polymerization of VAc, carried out at 0°C by using poly(oxyethylene)₁₀ nonyl phenyl ether ammonium sulfate as an anionic emulsifier. Kinetic results reveal that the number-average DP of the resulting polymer increases as % conversion increases and the chain transfer to polymer is

Table I Relationship Between Percentage Conversion and the Number-Average DP of PVAc, PVA, and Reacetylated PVAc

Conversion (%)	P_n of PVAc	P_n of PVA	P_n of Reacetylated PVAc	Degree of Branch
10.5	3070	2960	2000	0.535
36	6070	5900	4700	0.29
71.3	9030	8500	7000	0.29

[E], 2.2 mM; [I], 0.887 mM; H₂O/VAc (v/v), 2/1.

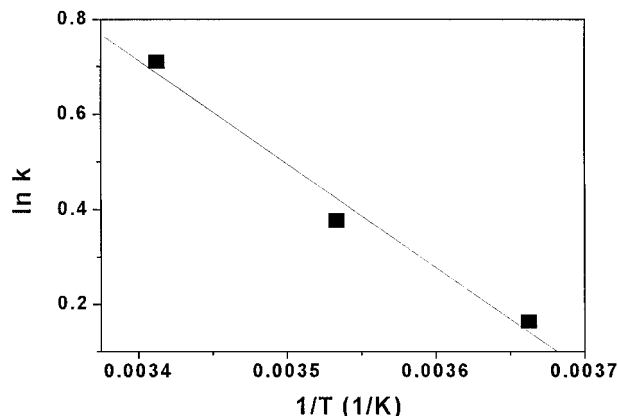


Figure 9 Temperature dependence of the rate of the photo-induced emulsion polymerization of VAc. $[I]$, 0.887 mM; $[E]$, 2.2 mM; H_2O/VAc (v/v), 10/5.

greatly depressed because polymerization was conducted at low temperature. The rate of polymerization is proportional to first order to initiator concentration and 0.4th order to emulsifier concentration and number-average DP of the resulting polymer is insensitive to the composition of the system such as concentration of initiator and emulsifier in photo-initiation process via emulsifier–initiator complex formation.

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