

Synthesis of High-Molecular Weight Poly(vinyl alcohol) by Low-Temperature Emulsifier-Free Emulsion Polymerization of Vinyl Acetate and Saponification

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ABSTRACT: High-molecular weight (HMW) poly(vinyl alcohol) (PVA) was prepared via an emulsifier-free emulsion polymerization of vinyl acetate (VAc) using a redox initiation system in low temperatures, and the subsequent saponification with potassium hydroxide in methanol. The effect of the polymerization conditions on the conversion, molecular weight, and branching degree was investigated. PVA with maximum viscosity-average degree of polymerization (DP) of 8270 could be prepared by saponification of poly(vinyl acetate) (PVAc), with DP of 10,660 obtained at temperature of 10°C, monomer concentration of 30%, potas-

sium persulfate molar ratio to monomer of 1/2000, agitation speed of 160 rpm. The conversion was above 90%. From the emulsifier-free emulsion polymerization of VAc in low temperature, PVAc with HMW and high linearity was effectively prepared, which might be useful for the preparation of high-strength and high-modulus PVA fiber. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2771–2778, 2012

Key words: poly(vinyl acetate); poly(vinyl alcohol); emulsion polymerization; emulsifier-free; degree of polymerization; kinetics

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a linear flexible chain polymer that has a very high potential for preparation of high-strength and high-modulus fibers because of its superior qualities of tensile strength, crystalline modulus, weather durability, good abrasion resistance, and so on.¹ Ultradrawing is an effective means to prepare high-strength and high-modulus fiber for flexible chain polymer. It requires the raw material polymer with high-molecular weight (HMW). Commercially, PVA is a product by saponification of poly(vinyl acetate) (PVAc), which is prepared by solution radical polymerization of vinyl acetate (VAc).^{2–4} The VAc radical is so active that it tends to transfer to monomer, macromolecule, and even solvent during the polymerizing process. The chain transfer to macromolecule will lead to branching of polymer. The chain transfer to macromolecule is shown in Scheme 1. On one hand, chain transfer on main chain leads to linearity decline of PVAc and PVA. On the other hand, chain transfer on side chain results in chain rupture during saponification, causing the decrease in molecular weight of PVA. The activation energy of chain transfer is higher

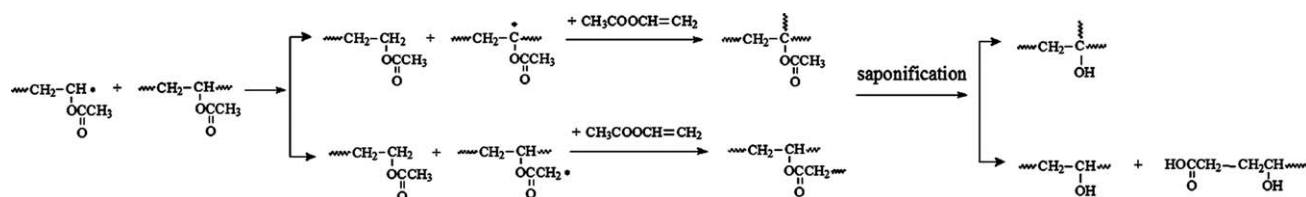
than that of chain growth, so polymerization of VAc in low temperature is beneficial to prepare linear HMW PVAc. However, conventional polymerizing process of VAc mostly occurs in relatively high temperature (50–80°C). Even though the HMW product of PVAc could be synthesized, its branching degree (BD) is inevitably very high and the HMW of subsequent PVA is difficult to obtain.

Some researchers have developed interest in the living radical polymerization and low-temperature radiation initiation polymerization of VAc in attempts to produce linear HMW PVAc.^{5–7} However, these polymerization methods require a harsh reaction condition or special polymerization initiators, preventing commercialization.

Emulsifier-free emulsion polymerization is of both industrial and academic interest as the resulting polymer latex is free from adsorbed surfactant and has highly monodisperse polymer particles.^{8–10} The redox initiation system could initiate polymerization in low temperature for its low activation energy.^{11,12} Some researchers have made great efforts on emulsifier-free emulsion polymerization of VAc with redox initiation system.^{13,14} However, their polymerization was carried out in a relatively high temperature and the influence of polymerization conditions on both the BD of PVAc and molecular weight was not investigated.

In this article, the emulsifier-free emulsion polymerization of VAc with potassium persulfate (KPS)–

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Scheme 1 PVAc chain transfer reaction to macromolecules.

sodium bisulfite (NaHSO_3) as a redox initiation system was conducted in temperatures of below 20°C to obtain linear HMW PVAc with high conversion. The HMW PVA was prepared by saponification of PVAc with potassium hydroxide (KOH). The structure of PVAc and PVA was characterized and the effect of polymerization variables on the conversion, molecular weight, and BD for acetyl group of PVAc was investigated. The study provides a novel approach to prepare the raw material of high-strength and high-modulus PVA fiber.

EXPERIMENTAL

Materials

VAc provided by Sinopec Sichuan Vinylon Works was vacuum distilled at 33°C and stored at -18°C in the dark. KPS was recrystallized from methanol, vacuum dried, and stored at -18°C . NaHSO_3 , KOH, pyridine, acetic anhydride, and acetic acid were all analytical reagents from Kelong Reagent Company (Chengdu, China), used without any further purification. The water used in experiment was purified with double distillation.

Polymerization of VAc

A 500-mL round-bottomed three-necked flask equipped with a mechanical stirrer and a condenser was immersed in a thermostatic water bath. The polymer temperatures were controlled to be 10°C , 14°C , 16°C , and 20°C . A prescribed amount of double distilled water was charged to the vessel and stirred for 30 min under nitrogen. Freshly distilled VAc was then added to the reaction vessel and stirring was continued for 15 min prior to the addition of NaHSO_3 and KPS. The molar ratio of NaHSO_3 to KPS was 2 : 1. A slow nitrogen purge was maintained throughout the polymerization. An induction period of 25–30 min was observed for polymerization reactions to start. Samples of the reaction mixture were taken at various intervals to calculate conversion and the polymerization of the sample was stopped by adding hydroquinone solution (0.5 g L^{-1}). The temperature of the polymerization system was increased by 3°C – 5°C at the later time of polymerization process and lasted for 10–20 min. The la-

tex was frozen for 8 h after the polymerization. After thawed out, the product was vacuum filtered and dried in air at room temperature and then under vacuum at 40°C to a constant weight.

Saponification

HMW PVAc (20 g) was dissolved in 200 mL methanol at 60°C . After PVAc was completely dissolved, 25 mL of 40 wt % KOH solution was dropwise added into the mixture while stirring. After KOH was added, white precipitation appeared in the reaction system. The saponification reaction continued for another 3 h. The product was washed and filtered several times with water and methanol. Then it was vacuum dried at 40°C .

Acetylation of PVA

To estimate the molecular weight of resulting PVA, acetylation of PVA was conducted. A mixture of 1 g of PVA, 2 mL of pyridine, 20 mL of acetic anhydride, and 20 mL of acetic acid were stirred in a conical flask at 100°C for 24 h. Then the mixture was poured into cold water to precipitate PVAc, which was filtered and purified by repeating the reprecipitation from ethanol and water.¹⁵

Characterizations

The conversion of monomer is calculated by using eq. (1)

$$\text{Conversion (\%)} = \frac{\text{the weight of polymer}}{\text{the weight of monomer} + \text{the weight of initiator}} \times 100 \quad (1)$$

The intrinsic viscosity of PVAc was determined with an Ubbelohde viscometer. The product was dissolved in benzene with the concentration of 0.2 g dL^{-1} . The temperature was kept at 30°C by a thermostatic water bath.

The degree of polymerization (DP) of PVAc is calculated by using eq. (2),⁷

$$[\eta] = 8.91 \times 10^{-3} [P_n]^{0.62} \quad (2)$$

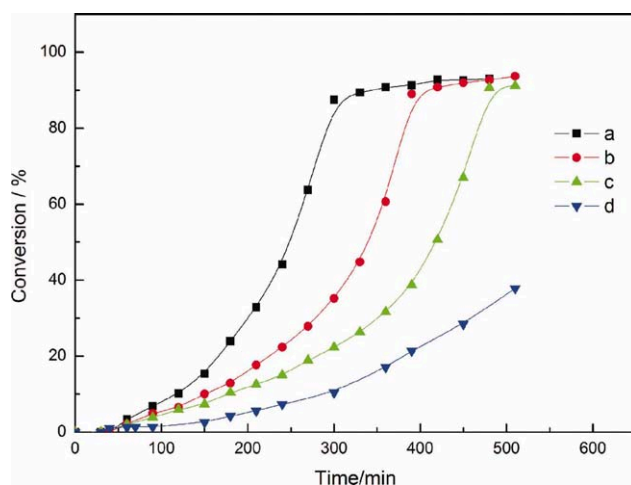


Figure 1 Relationship between conversion and polymerization time under different initiator concentrations: (a) 1/1200, (b) 1/1600, (c) 1/2000, and (d) 1/2400 (molar ratio of KPS to monomer). The polymerization temperature is 10°C; monomer concentration is 30 wt % and agitation speed is 160 rpm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where P_n is the viscosity-average DP of PVAc and $[\eta]$ is the intrinsic viscosity of PVAc.

The relationship between DP and molecular weight is shown in eq. (3).

$$\begin{aligned} &\text{molecular weight of polymer} \\ &= \text{DP} \times \text{molecular weight of monomer} \quad (3) \end{aligned}$$

The molecular weight of PVAc is proportional to its DP.

The DP of PVA is determined from that of PVAc produced by acetylating PVA also using eq. (2).

The BD for acetyl group of PVAc is calculated by using eq. (4),⁷

$$\text{BD} = (\text{DP}_1/\text{DP}_2) - 1 \quad (4)$$

where DP_1 is the P_n of PVAc and DP_2 is the P_n of PVA saponified of PVAc.

The IR spectra were recorded with a Fourier transform infrared spectrophotometer (MAGNAIR560,

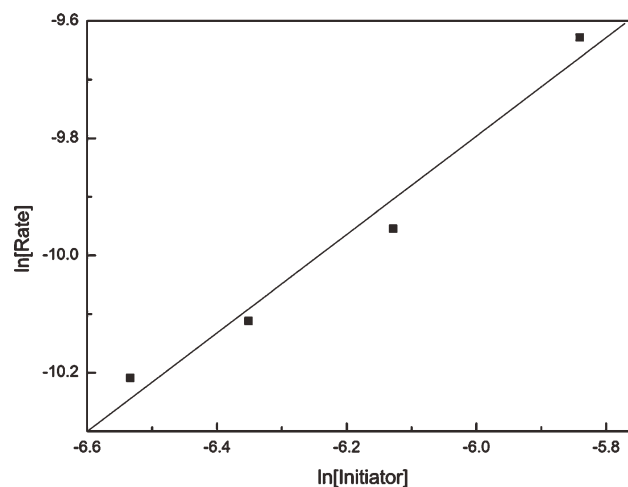


Figure 2 Logarithmic plot of reaction rate versus initiator concentration.

Nicolet, Madison, USA). The samples of PVAc and PVA were prepared by dissolving the polymers into methanol and water, respectively, then coating and drying the film with an oven.

¹H-NMR spectra were recorded on a Bruker 600 MHz NMR spectrometer (AVANCE AV II-600, Bruker, Fällanden, Switzerland) using dimethyl sulfoxide ($\text{DMSO}-d_6$) as the solvent and tetramethylsilane as an internal standard.

The morphology and size of the PVAc particles were observed with transmission electron microscope (TEM) (H-600, Hitachi, Tokyo, Japan) under an accelerating voltage of 75 kV. A drop of emulsion was negatively stained by a drop of 1 wt % phosphotungstic acid to prepare the TEM sample.

RESULTS AND DISCUSSION

Influencing factors of emulsifier-free emulsion polymerization of VAc

Figure 1 shows the conversion-time curves of emulsifier-free emulsion polymerization of VAc. The reactions are carried out at 10°C and monomer concentrations are all 30 wt %. The polymerization rate is increased with increasing the initiator concentration. The redox system initiators (KPS and NaHSO_3) are

TABLE I
Final Conversions, DP, and BD Values Under Different Initiator Concentrations^a

Initiator concentration ^b	Polymerization time (min)	Final conversion (%)	DP of PVAc	DP of PVA	BD
1/1200	510	93.0	9700	6690	0.45
1/1600	510	93.7	10,205	7395	0.38
1/2000	510	91.1	10,668	8270	0.29
1/2400	510	37.8	11,403	9830	0.16

^a The polymerization temperature is 10°C; monomer concentration is 30%, and agitation speed is 160 rpm.

^b Molar ratio of KPS to monomer.

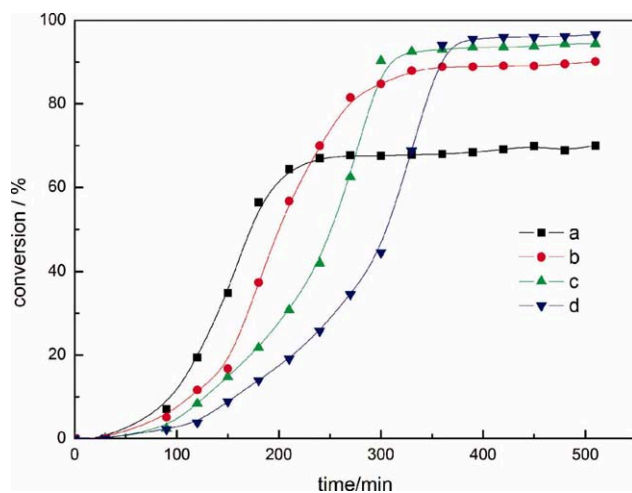


Figure 3 Relationship between conversion and polymerization time under different monomer concentration: (a) 20 wt %, (b) 25 wt %, (c) 30 wt %, and (d) 35 wt %. The polymerization temperature is 10°C; molar ratio of KPS to monomer is 1/2000 and agitation speed is 80 rpm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

very soluble in water. Moreover, the solubility of monomer VAc in water is 2.5%, which is relatively high for most monomers in emulsion polymerization. The mechanism of homogenous nucleation is applicable here. The polymerization first takes place in water phase. The radicals generated in water phase by initiator addition polymerize with monomer dissolved in water to propagate the polymer chain. If the oligomer chain grows long enough, they will become surface active and can be called as surface active oligomer (SAO). Some SAO is terminated in water phase, which plays an emulsifier in the subsequent polymerizing process. The rest continue to grow by propagation until they reach a critical size at which they precipitate as precursor particles. The precursor particles continue to propagate or coagulate with other precursor particles to form stable latex particles.¹⁶ With more initiator added, the generating rate of free radicals in water phase is increased. Both the concentration of free radicals and the polymerization rate of VAc in water phase increases. As a result, more SAOs exceed their criti-

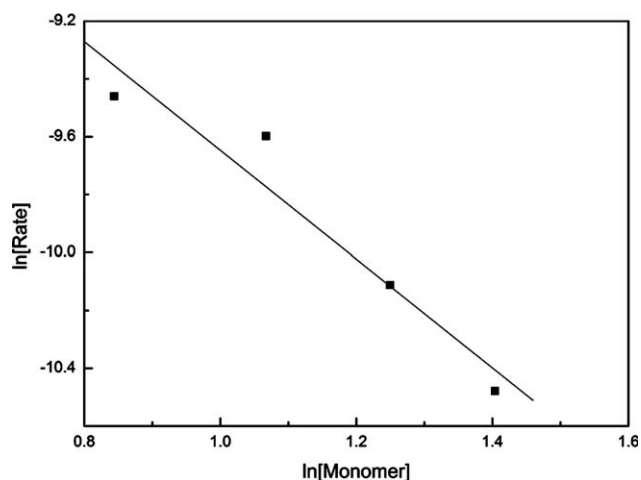


Figure 4 Logarithmic plot of reaction rate versus monomer concentration.

cal size and precipitate from water phase, so the nucleation and polymerization rate increases.

Figure 2 shows the logarithmic plot of polymerization rate versus initiator concentration. The rate of polymerization is calculated from the slope of the monomer conversion-time plot shown in Figure 1. The order of the reaction with respect to the initiator concentration was obtained by the slope in Figure 2 and was found to be 0.840. According to the classical emulsion polymerization, the rate of polymerization (R_p) is proportional to the concentration of initiator's 0.4th power and that of emulsifier's 0.6th power, as shown in eq. (5),^{17,18}

$$R_p \propto [I]^{0.4}[S]^{0.6} \quad (5)$$

where $[S]$ is the emulsifier concentration, mol L⁻¹. This is different from our result of VAc emulsifier-free emulsion polymerization. The initial polymerization takes place in water phase by radicals' addition polymerizing with monomer. Moreover, SAO acts as an emulsifier in emulsifier-free emulsion polymerization and the concentration of SAO is directly related with the initiator concentration. There is a distinctive relationship between the generation of latex particle and the concentration of initiator. The effect of initiator concentration is greater in

TABLE II
Final Conversions, DP, and BD Values Under Different Monomer Concentrations^a

Monomer concentration (%)	Polymerization time (min)	Final conversion (%)	DP of PVAc	DP of PVA	BD
20	510	70.0	5219	2965	0.76
25	510	90.1	7634	4957	0.54
30	510	94.4	9026	6356	0.42
35	510	96.6	9832	7283	0.35

^a The polymerization temperature is 10°C; molar ratio of KPS to monomer is 1/2000 and agitation speed is 80 rpm.

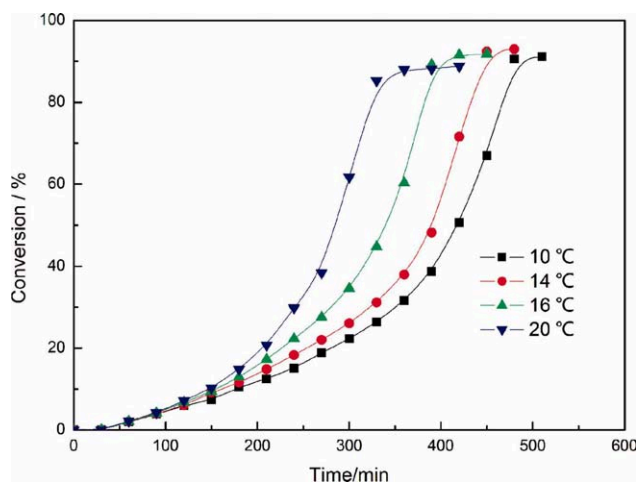


Figure 5 Relationship between conversion and time under different polymerization temperatures. The molar ratio of KPS to monomer is 1/2000; monomer concentration is 30 wt % and agitation speed is 160 rpm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

emulsifier-free emulsion polymerization than in classical emulsion polymerization.

The dependence of final conversions, DP and BD values on initiator concentration is shown in Table I. The result turns out to be consistent with the traditional radical polymerization, which is DP decreases with the increase in initiator concentration. As the concentration of initiator decreases, the initiation and polymerization rate decreases, which minimizes the exotherm and viscosity enhancement generated in the latex particles during the polymerization. Therefore, the Trommsdorff effect¹⁹ is not likely to occur. As a result, the probability of chain transfer of radicals to macromolecule become lower, the BD for acetyl group of PVAc decreases, and the DP of corresponding PVA increases. The DP of PVA is up to 9830 and BD of PVAc is low to 0.16 when KPS amount is 1/2400 (molar ratio) of monomer. However, the final conversion is only 37.8% at this kind of circumstance. Low initiator amount will lead to the decrease of production efficiency.

Figure 3 shows the conversion-time plots of emulsifier-free emulsion polymerization of VAc in various

monomer concentrations. The polymerization temperature is 10°C and the molar ratio of KPS to monomer is 1/2000. The agitation speed is 80 rpm. The final conversion increases with the increase in monomer concentration, but the lower initial polymerization rate is observed. The rate of polymerization decreases as the concentration of monomer increases. This is because increasing monomer concentration decreases the molar ratio of radical to monomer, which has a similar effect to decreasing the initiator concentration.

Figure 4 shows the logarithmic plot of polymerization rate versus monomer concentration. The order of the reaction with respect to the monomer concentration was found to be -1.87 . In classical radical polymerization, the higher the concentration of monomer is, the higher the polymerization rate gets. In VAc emulsifier-free emulsion polymerization, particle nucleation takes place in water phase. In the case of constant total amount of reaction mixture (400 g), as the added amount of monomer increases, the weight of water reduces. Therefore, less monomer is dissolved in water, and fewer oligomer radicals are generated in water phase. Thus, the nucleation and polymerization rate goes down.

As is shown in Table II, with the increasing of monomer concentration, the DPs of PVAc and PVA are raised. The polymerization rate decreases, so heat of polymerization will be generated steadily and released soon. As is mentioned above, temperature of reaction system will not rise sharply. As a result, the probability of chain transfers become lower, the BD of PVAc decreases, and the DP of PVA increases.

As shown in Figure 5, the final monomer conversions of the polymerizations in the temperature range from 10 to 20°C, all reach up to 90%. With the rise of reaction temperature, the polymerization rate increases and the molecular weight of product PVAc decreases, which is consistent with classical polymerization. The DP of PVAc polymerized at 10°C is almost twice of that at 20°C, whereas the BD of PVAc polymerized at 10°C is only half of that of at 20°C, which is shown in Table III. Therefore, the

TABLE III
Final Conversions, DP, and BD Values Under Different Temperatures^a

Polymerization temperature (°C)	Polymerization time (min)	Final conversion (%)	DP of PVAc	DP of PVA	BD
10	510	91.1	10,668	8270	0.29
14	480	93.0	9821	7329	0.34
16	450	91.8	8720	5972	0.46
20	420	88.8	5952	3545	0.68

^a The molar ratio of KPS to monomer is 1/2000; monomer concentration is 30% and agitation speed is 160 rpm.

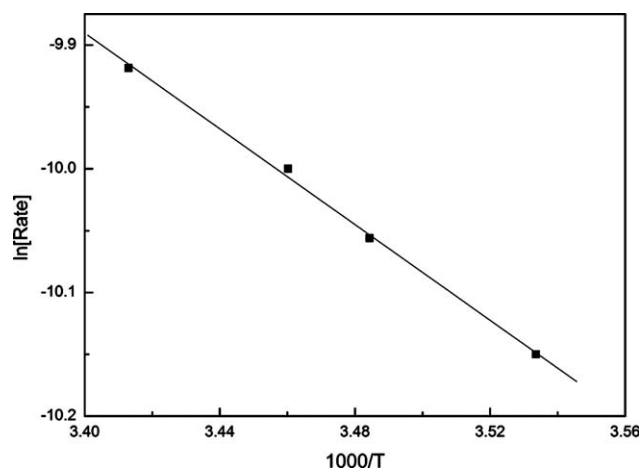


Figure 6 Logarithmic plot of reaction rate versus $1000/T$.

PVA corresponding to the PVAc polymerized at 10°C has a higher molecular weight, which is beneficial to the preparation of high-strength and high-modulus fiber. The apparent activation energy (E_a) was calculated and found to be 16.1 kJ mol^{-1} from Figure 6 by using Arrhenius plotting of the polymerization rate against $1000/T$. The value agrees well with that reported in other similar polymerization systems.¹³

Figure 7 shows the initial conversion-time curves under different agitation speeds. The initial polymerization rates are very slow under all agitation speeds. The conversion-time curves almost coincide in the first 30 min, which is consistent with the experimental phenomenon that the transparent reaction system changes into white after the reaction starts 30 min. From Figure 7, we can conclude that the polymerization rate decreases as the agitation speed rises from 80 to 200 rpm. The polymerization rate does not change much with a further rising of agitation speed to 300 rpm. After the nucleation stage, the polymerization proceeds in the polymer particles. To these polymerization loci, monomer is transferred from monomer droplets through the aqueous phase. A reduction in agitation speed gives rise to a reduction of the mass transfer coefficient of monomer, which causes the decrease in monomer concentration in the polymer particles. The viscosity in the latex particles

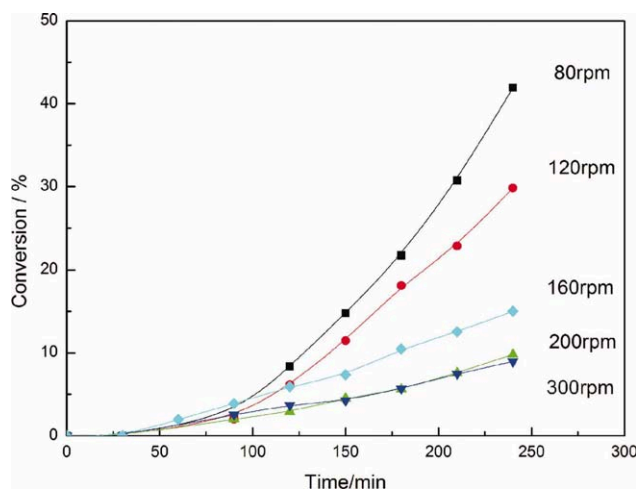


Figure 7 Relationship between conversion and time under different agitation speeds. The molar ratio of KPS to monomer is 1/2000; monomer concentration is 30 wt % and polymerization temperature is 10°C . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

is therefore increased and Trommsdorff effect may be promoted. This effect may possibly be responsible for the experimental results in which a decrease in agitation speed shortened the reaction time needed to attain high conversion. When the agitation speed rises to 200 rpm, the mass transfer rate is large enough to keep the monomer concentrations in polymer phase, water phase and monomer droplet remain unchanged. The agitation speed almost has no influence on polymerization rate when it reaches to over 200 rpm. The conclusion is similar to what is reported in other literature.²⁰

Table IV illustrates the effect of agitation speed on final conversions, DP and BD values of the product. As the agitation speed gets larger, DPs of PVAc and PVA show a trend of increasing, while the value of BD is getting small. As mentioned before, with the agitation speed rising, mass transfer rate of VAc increases and the possibility of Trommsdorff effect is decreased. The DP of PVAc is increased and BD is decreased with rapid agitation. However, when agitation speed is too high, the latex particles gain more kinetic energy. As a result, the latex particles

TABLE IV
Final Conversions, DP, and BD Values Under Different Agitation Speeds^a

Agitation speed (rpm)	Polymerization time (min)	Final conversion (%)	DP of PVAc	DP of PVA	BD
80	510	94.4	9026	6356	0.42
120	510	94.8	8637	6351	0.36
160	510	91.1	10,668	8270	0.29
200	510	38.4	11,583	9494	0.22

^a The molar ratio of KPS to monomer is 1/2000; monomer concentration is 30% and polymerization temperature is 10°C .

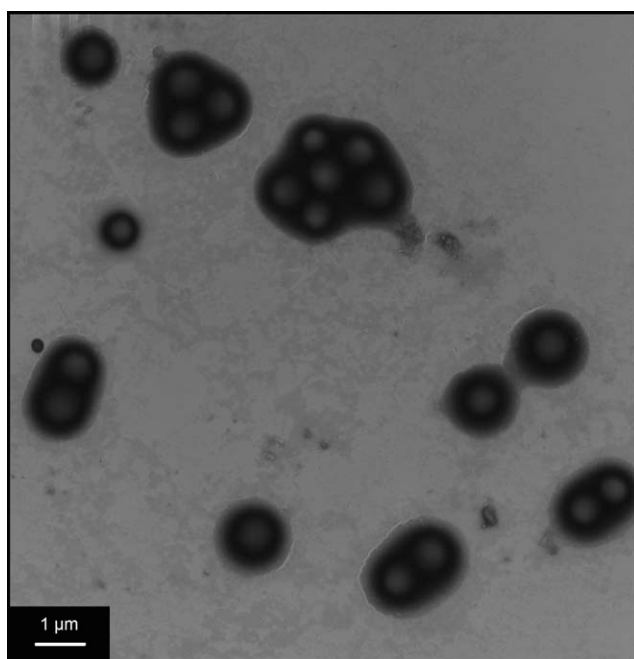


Figure 8 TEM photograph of PVAc microspheres. The KPS molar ratio to monomer is 1/2000; monomer concentration is 30 wt %; polymerization temperature is 10°C and agitation speed is 160 rpm.

would agglomerate, leading to the reduction of emulsion stability.

Particle size and distribution

In this study, PVAc microspheres and nanospheres were obtained via emulsifier-free emulsion polymerization. Figure 8 shows the TEM photograph of PVAc microspheres. The particle diameters of the sample were measured directly from TEM. The histogram of the particle sizes is shown in Figure 9.

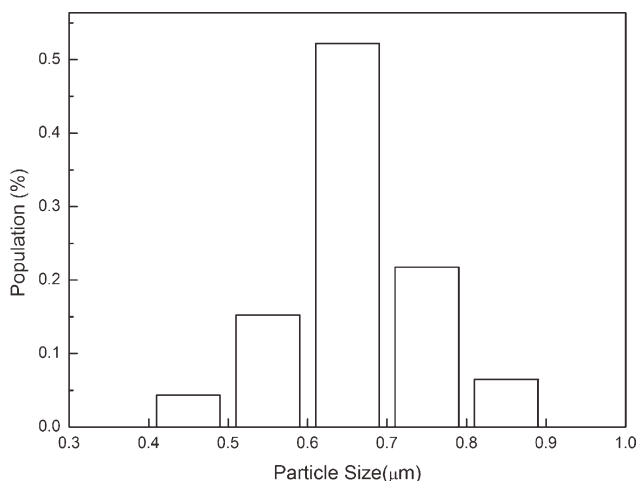


Figure 9 Size distributions of latex particles of PVAc. The KPS molar ratio to monomer is 1/2000; monomer concentration is 30 wt %; polymerization temperature is 10°C and agitation speed is 160 rpm.

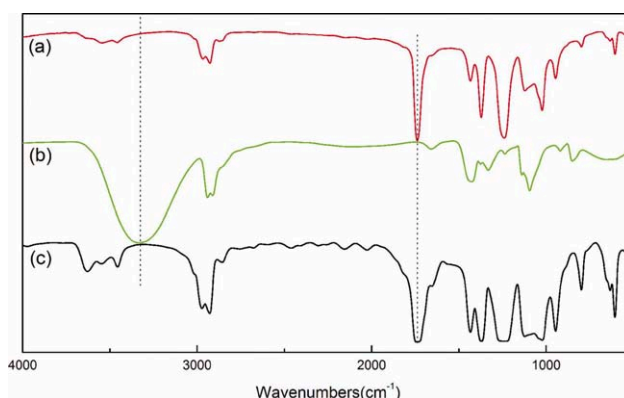


Figure 10 FTIR spectra of (a) PVAc, (b) PVA, and (c) PVAc after acetylation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The average diameter of the particles is 660 nm. The number-average diameter (D_n) and weight-average diameter (D_w) are calculated from the following equations.^{21,22}

$$D_n = \frac{\sum N_i D_i}{\sum N_i} \quad (6)$$

$$D_w = \frac{\sum N_i D_i^4}{\sum N_i D_i^3} \quad (7)$$

The polydispersity index (PI) of the particle size is expressed as D_w/D_n . The PI of the PVAc particles is 1.05, which demonstrates that the spheres are monodispersed.

Characterization of polymers

The structures of PVAc and PVA were characterized by FTIR (Fig. 10). The absorption peaks at 1738 cm^{-1} (C=O), 1240 cm^{-1} (C–O), 2963 cm^{-1} (CH₃), and 2927 cm^{-1} (CH₂) can be observed in Figure 10(a,c), which indicates successful polymerization of VAc. The disappearance of peak at 1738 cm^{-1} (C=O) and

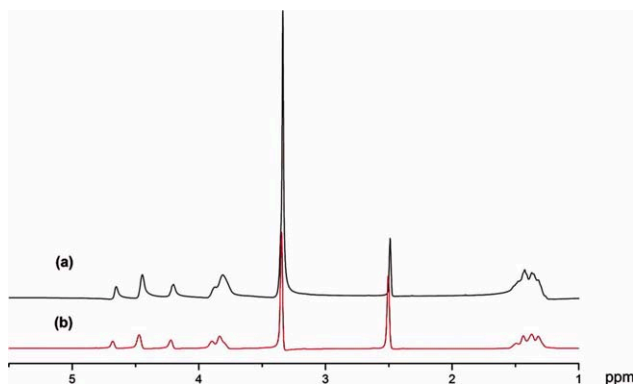


Figure 11 ¹H-NMR spectra of (a) HMW PVA and (b) normal PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

emergence of peak at 3330 cm^{-1} (OH) observed in Figure 10(b) is an evidence of generation of PVA. The spectrum of PVAc polymerized is almost identical with that of the PVAc after acetylation. The disappearance of peak at 3330 cm^{-1} (OH) demonstrates complete acetylation of PVA. $^1\text{H-NMR}$ was used to determine the stereoregularity of PVA. Figure 11 shows the $^1\text{H-NMR}$ spectra of (a) HMW PVA prepared from emulsifier-free emulsion polymerization and (b) PVA commercially produced with DP of 1700. Signals at 4.1–4.7 ppm correspond to the hydroxyl groups of PVA. The three hydroxyl lines are assigned to isotactic (*mm*), heterotactic (*mr*), and syndiotactic (*rr*) triad configurations with increasing field strength. The percentages of triad tacticities of PVA are determined from the area ratio of the —OH triplet. The syndiotactic dyad contents *r* of HMW PVA and normal PVA are calculated according to the Equation of $r = rr + 0.5 mr^{23,24}$ and are found to be 61% and 52%, respectively. The high syndiotactic dyad content PVA is effectively prepared by low-temperature emulsifier-free emulsion polymerization.

CONCLUSIONS

In this work, high yield PVAc is successfully synthesized via low-temperature emulsifier-free emulsion polymerization. The polymerization rate is greatly dependent on the initiator concentration, monomer concentration, reaction temperature, and agitation speed. The order of the reaction with respect to the initiator concentration and monomer concentration was found to be 0.84 and -1.87 , respectively. The apparent activation energy was calculated and found to be 16.1 kJ mol^{-1} . The DPs of PVAc and PVA decrease with an increase of the initiator concentration and polymerization temperature, whereas increase as the monomer concentration increases. PVAc and PVA with DP of 10,660 and 8270 were prepared with the conversion of above 90%. The syndiotactic dyad content of aforementioned PVA determined with $^1\text{H-NMR}$ is 61%. The process is simple and practicable in industrial field. Such

HMW and syndiotactic dyad is very beneficial to the preparation of high-strength and high-modulus PVA fiber, which is the future work we are committed to.

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