Kinetics of waterborne fluoropolymers prepared by one-step semi-continuous emulsion polymerization of chlorotrifluoroethylene, vinyl acetate, butyl acrylate and Veova 10

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Abstract. Due to using gaseous fluorine monomer with toxicity, waterborne fluoropolymers are synthesized by semi-continuous high-pressure emulsion polymerization method which differs from free-pressure emulsion polymerization. To dates, the research on preparing process and kinetics for high-pressure emulsion polymerization is reported relatively less, which hinders researchers from understanding of mechanisms for monomer-fluorinated emulsion polymerization. The paper also provides a new method by element auxiliary analysis to calculate kinetics parameters of high-pressure emulsion polymerization. Based on aforementioned consideration, waterborne fluoropolymers were prepared by copolymerization of chlorotrifluoroethylene (CTFE), vinyl acetate (VAc), butyl acrylate (BA) and vinyl ester of versatic acid (Veova 10) using potassium persulfate as initiator and mixed surfactants. The kinetics of emulsion polymerization of waterborne fluoropolymers was then investigated. Effects of emulsifier concentration, initiator concentration, and polymerization temperature on polymerization rate (Rp) were evaluated, and relationship was described as $Rp \propto [I]^{0.10}$ and $Rp \propto [E]^{0.12}$. The apparent activation energy was determined to be 33.61 kJ·mol$^{-1}$. Moreover, the relative conversion rate of CTFE with the other monomers was observed, and results indicated that CTFE monomer more uniformly copolymerized with the other monomers. The resulting emulsion properties and pressure change in an autoclave were evaluated at different stirring rates. The initial reaction time, defined as the beginning time of dropwise addition, was determined by the change in solid content and particle size of emulsion.

1. Introduction

Fluoropolymers have been among the most important materials used in various fields because of their chemical structure and unique properties [1]. Recently, studies on environment-friendly waterborne fluoropolymers have gained increasing interest [2, 3]. Numerous studies have been conducted on different types of waterborne fluoropolymers [4-8], including the preparation [9-15] and performance evaluation of fluoropolymers [4, 16-19].

In the past decades, studies on the kinetics and mechanism of CTFE (chlorotrifluoroethylene)-based copolymer have also been undertaken. These studies include topics on radical copolymerization...
of CTFE with 1-fluoromethyl vinyl benzene [20], emulsion copolymerization of CTFE with VAc (vinyl acetate) and vinyl propionate [21], thermal degradation of homopolymers and copolymers of CTFE with MMA (methyl methyly acrylate) [22] and thermal degradation of copolymers for VDF (vinylidenefluoride)-CTFE [23, 24]. Thomas et al. [25] provided a survey on the kinetics of polymerization of CTFE with several monomers such as VAc in bulk and in solution. However, the kinetics of emulsion polymerization was not further investigated. Synthesis and characterization of waterborne fluoropolymer by semi-continuous emulsion polymerization of CTFE with VAc, BA (butyl acrylate), and Veova 10(a vinyl ester of a highly branched decanoic acid) was completed in our previous study [26]. To the best of our knowledge, no studies on the kinetics of semi-continuous emulsion polymerization of CTFE with VAc, BA, and Veova10 have been reported. This inadequacy hinders the understanding of the mechanism of emulsion polymerization, which affects production control and polymerization engineering design.

In this paper, we will report the kinetics of the quadric-copolymerization system of CTFE-VAc-Veova10-BA implemented by semi-continuous emulsion polymerization. Thus, CTFE was directly added into the autoclave, and the other monomers were dropwise-added into the autoclave within 3 h according to 173ml/h, 138ml/h and 115ml/h, sequentially. The relationships of the initiator concentration, emulsifier concentration, and reaction temperature with the polymerization rate were evaluated. The activation free energy (Ea) of the polymerization system was calculated. The copolymerization rates between the CTFE monomer and the other monomers were investigated. In addition, the effects of stirring rate on the properties of waterborne fluoropolymers were evaluated.

2. Experimental

2.1. Materials
CTFE, VAc, BA and Veova 10 were supplied from Dalian Zhenbang Fluorocarbon Paint Stock Co., Ltd. (Dalian, China) as polymerization grade monomers and were used as received. NP-10 (octylphenolpolyoxyethylene ether), 600#A (styrylphenolpolyoxyethylene ether), SDS (sodium dodecyl sulfate) were obtained from Liaoning OxiranChemstry Co., Ltd (Liaoyang, China). Potassium persulfate (KPS) and sodium bicarbonate (NaHCO₃) were purchased and used as initiator and bafferting agent, respectively. The deionized water was obtained by ion exchange and used in polymerization. AMP-95(2-amino-2-methyl-1-propanol) was purchased from Dow Chemicals (Midmland, MI, USA) and used as pH adjusting agent.

2.2. Emulsion polymerization
A specific amount of deionized water, which was 20% of the amount of the emulsifier and sodium bicarbonate, was added directly into the autoclave and dissolved evenly by stirring. After the autoclave were vacuumed and filled with nitrogen three times, all of the CTFE and a certain amount of the mixed monomers were added into the reactor and emulsified for 30 min. Under required stirring, the temperature of the reactant reached 60°C. Feeding with 20% of potassium persulphate solution, polymerization began, causing the temperature of the reactor to gradually increase because of exothermic reaction. After maintaining the polymerization for 30 min, the remaining emulsified monomers and the initiator solution were added dropwise into the reactor within 3 hours. Polymerization was maintained for another 3 hours. The experimental formulation was presented in table 1. 2-5 grams of the samples were removed from the reactor every 30 min for detection.

| Table 1. Experimental formulation of the waterborne fluoropolymer. |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Charge(g)      | 80.00          | 8.74           | 2.91           | 2.91           | 3.34-6.23      | 0.35-1.05      |
| Feed(g)        | 0              | 141.24         | 47.09          | 47.09          | 9.34-17.46     | 1.15-4.52      |
| Total(g)       | 80.00          | 149.98         | 50.00          | 50.00          | 12.68-23.69    | 1.86-5.57      |
| KPS            | 0.90           | 0.90           | 0.90           | 0.90           | 0.90           | 0.90           |
| NaHCO₃         | 212.19         | 181.97         | 212.19         | 181.97         | 212.19         | 181.97         |
| H₂O            | 394.16         | 394.16         | 394.16         | 394.16         | 394.16         | 394.16         |

*Emulsifier mixture includes NP-10, 600#A, and SDS (weight ratio of 5:4:1).
2.3. Nonvolatile and fluoride content
About 0.5000-1.000 g of emulsion samples was placed in a tin foil box and then dried for 24 hours at room temperature. Nonvolatile content \( (N.V.\%) \) was calculated by formula 1:

\[
N.V.\% = \frac{W_1 - W_2}{W_3} \times 100\%
\]

(1)

Where \( W_1 \) is the weight of the tin foil box, \( W_2 \) is the weight of emulsion, \( W_3 \) is the total weight of the dried emulsion and the tin foil box.

Fluorine content was detected by the lanthanum nitrate method[27]. Sample weighing 10-25 mg was wrapped in a filter paper flag and then clipped to a platinum wire. As much as 8 ml of water was added to 250 ml of Molotov cocktails. Oxygen was passed for about 20 s, light filtered, and inserted rapidly for the sample to burn and decompose completely. Molotov cocktails were shaken to facilitate the complete absorption of smoke into the solution. The stopper was rinsed using platinum with 10 ml of acetone. A drip of perchlorate solution \( (\text{HClO}_4 = 2 \text{ mol/L}) \) was dropped into the water bath at 70 °C for 5 min. Subsequently, 1 g of hexamethylenetetramine, 20 ml of acetone, and four drops of hematoxylin indicator \( (2.5 \text{ g/L}) \) were added into the Molotov cocktails. Under shaking condition, the titrate lanthanum nitrate standard solution \( (\text{C}_{\frac{1}{3}\text{La(NO}_3)_3} = 0.1\text{mol/L}) \) and when the color of the solution in the Molotov cocktails changes from yellow to pale blue, the consumption volume \( V \) was recorded and blank experiment \( (V_0) \) were conducted. The fluorine content of the samples was calculated by formula 2.

\[
F\% = \frac{C_L \times (V - V_0) \times 19.00 \times 100}{m \times 1000}
\]

(2)

Where \( F\% \) is the fluorine content of the samples; \( C_L \) is the \( 1/3\text{La(NO}_3)_3 \) molar concentration of the standard solution, mol/L; \( m \) is the sample quality, g; 19.00 is the molar quality of fluorine atoms, g/mol.

2.4. Conversion
The emulsion was removed from the autoclave (2-5 g). The nonvolatile and fluorine contents of each phase were evaluated as described in section 2.3.

First, the conversion of CTFE was determined by formula 3.

\[
W_{\text{CTFE}} = \frac{W_L}{48.92\% \times N.V.\% \times F\%}
\]

(3)

Where \( W_L \) denotes the instant liquid materials of the system in the autoclave, which is equivalent to the sum of the polymerization reactor base and the dropwise-added material; \( W_{\text{CTFE}} \) is the quality of CTFE that has been converted into a fluoropolymer; 48.92% is the fluoride content of CTFE.

Conversion of monomers other than CTFE was determined by formula 4.

\[
W_m = (W_L + W_{\text{CTFE}}) \times N.V.\% \times W_{\text{CTFE}}
\]

(4)

Where \( W_m \) is the quality of the other monomers that have been converted to polymers.

Finally, the conversion rate \( C \) of the system at each phase was calculated by formula 5.

\[
C = \frac{W_{\text{CTFE}} + W_m}{W_{\text{CTFE}} + W_m} \times 100\%
\]

(5)

Where \( W_{\text{CTFE}} \) is the total quality of CTFE, \( W_m \) is the total quality of the monomers except for CTFE.

2.5. Calculation of the polymerization rate (Rp)
Emulsion polymerization is generally divided into three stages: acceleration stage, constant speed stage, and slowdown stage [28]. The constant speed stage begins when micelles disappear, the number
of latex grains becomes constant, and the polymerization rate remains constant. In accordance with this theory and by applying linear regression, the curve slope \( \frac{dc}{dt} \) at different reaction stages \( t \) and monomer conversion \( C \) during polymerization were calculated. The polymerization reaction rate \( R_p \) (mol/L·s) was calculated by formula 6:

\[
R_p = \frac{dc}{dt} \times [M_0]
\]  

(6)

Where, \([M_0]\) is the amount of monomer (mol)/water volume in the system (L).

3. Results and Discussion

3.1. Effects of the initiator dosage on polymerization rate

Figure 1 shows the relationship of the monomer conversion with reaction time at different initiator concentrations. As the initiator dosage is increased, the polymerization reaction rate also increases. This effect is attributed to the increased rate of free radical generation in the polymerization system. The nucleation rate simultaneously increases, and so polymerization is accelerated. Figure 2 presents the relation curve between the pressure of CTFE steam and reaction time at different initiator concentrations inside the autoclave. As the initiator concentration increases, the autoclave pressure decreases faster, this further demonstrates markedly faster polymerization with increasing initiator dosage.

![Figure 1. Influence of initiator dosage on polymerization rate.](image1)

![Figure 2. The change of autoclave pressure with reaction time.](image2)

By using linear regression of the slash part in figure 1, the relationship between \(-\ln R_p\) and \(-\ln[I]\) is determined. As shown in figure 3, the slope of the straight line is 0.10, so \( R_p \propto [I]^{0.10} \) is obtained, which differs from the classic emulsion polymerization index \( R_p \propto [I]^{0.4} \). The experimental result indicates that the polymerization rate is affected relatively less by the initiator concentration. As we know, the initiator concentration is controlled by dropwise addition technology, and is relatively low in reaction system, and thereby affect and reduce the reactive center.

![Figure 3. Relationship between \(-\ln R_p\) and \(-\ln[I]\).](image3)
3.2. Effects of emulsifier concentration on polymerization rate

The effects of emulsifier dosage on polymerization rate are shown in figure 4. A higher emulsifier concentration results in faster polymerization. Increasing the emulsifier concentration leads to more micelles, thereby generates more emulsion grains. This occurrence indicates the presence of more reaction centers, and so the polymerization rate increases. This effect conforms to the basic principle of emulsion polymerization.

Figure 4. Influence of emulsifier dosage on reaction rate.

By using linear regression of the slash part in figure 4, the relationship between -lnRp and ln[E] was obtained, as shown in figure 5. The linear slope is 0.12, and the result is Rp ∝ [E]^{0.12}, which differs from the classic emulsion polymerization index(Rp ∝ [E]^{0.6}). This outcome indicates that the emulsifier concentration only slightly influences polymerization. This result also relates the polymerization process. The emulsifier is fed into the autoclave through two parts: one part is entirely added into the reactor to produce micelles and an active reactive site, which significantly affects the polymerization rate. The other part is dropwise added to the reactor, whose key function is to maintain the emulsion particles stably.

3.3. Relationship between the conversion rates of CTFE and other monomers with reaction time

In this study, CTFE is added into the polymerization autoclave by disposable feeding way, whereas other monomers are fed dropwise. At different stages of reaction, the sample is removed from the autoclave, and the conversion rates of the CTFE and other monomers are calculated. The results are shown in figure 6.

Figure 6. Change in the curve of charge and reaction of monomer with time.

As shown in figure 6, although CTFE involves one-step loading, it tends to copolymerize with other monomers and not self-polymerize. The dropwise addition of the monomer is faster than the

Figure 7. Change in fluoride content at different reaction stages with time.
speed of polymerization, CTFE and the other monomers are filled excessively in the system, which shows the macro-polymerization rate is controlled by the polymerization reaction rate. Figure 6 shows that the conversion of CTFE is relatively faster and in accordance with the copolymerization reaction rate of the other monomers. Thus, water-based fluoropolymers exhibit a relatively uniform copolymer structure. Fluorine contents at different stages of reaction are shown in figure 7. Fluorine content at the dropwise stage is relatively high. With a longer reaction time, the fluoride change becomes gradually stable, reaching a state of relatively homogeneous and synchronized copolymerization. Therefore, water-based fluoropolymer with an almost uniform structure can be prepared by adding CTFE via a disposable feeding syringe and other monomer mixtures by continuous dropping. If the CTFE monomer is fed by dropwise feeding, polymerization process will becomes complex. Whereas this technique can simplify polymerization process and facilitate industrialization.

In addition, polymerization reaction could remain inadequate by decreasing the feeding speed and increasing the dropping time, which is favorable for removing the heat of polymerization heat and controlling the reaction rate.

3.4. Relationship between the initial reaction time and monomer conversion
About 80 g of CTFE, 14.56 g of the other mixed monomers and 216.78 g of base (including initiator, emulsifier, pH buffer, and H₂O) are added into the autoclave (see table 1). The reactants are heated to 60 °C and time is started. A sample of about 2-5 g is removed every 8 min to detect nonvolatile and fluorine content. The conversion rate of monomers (including CTFE and the other monomers) are calculated. The results are listed in figure 8. As shown in the figure, monomer conversion is faster at 8-16 min and almost reaches 18% at 25-30 min. After this point, the monomer conversion slows down, suggesting that the base reaction of seed emulsion has been completed. It is defined as the initial reaction time, which is generally determined for about 25 min. After this period, the rest emulsified monomer can be added dropwise.

The particle size of the sample is evaluated at different stages, and the average particle size of the sample by weighted average is calculated. The results are shown in figure 9. When the reaction time is 8 min, the average particle size of the emulsion is 36 nm; when reaction time is 24 min, the average particle size of the emulsion is 73 nm. The average particle size changes slowly as the reaction time is extended. This result is in agreement with the conversion experimental data.

![Figure 8. Change in the conversion rate of initial monomer with reaction time.](image1)

![Figure 9. Change in the particle size of the emulsion at the initial reaction stage.](image2)

3.5. Effect of reaction temperature on polymerization rate
The influence of temperature on the polymerization rate is shown in figure 10. The results show that the polymerization rate increases with reaction temperature increasing, and no induction period is clearly observed during the initial stage of the reaction. It is because the initiator decomposition constant and chain growth rate constant increases with temperature increasing, which resulted in the increasing of monomer diffusion velocity to micelles, thereby increasing the polymerization rate.
Figure 10. Effect of temperature on polymerization rate.

Figure 11. Relationship of $-\ln R_p$ and $1/T$.

By using linear regression of the slash part in figure 10, the relationship between $-\ln R_p$ and $1/T$ is determined, as shown in figure 11, the linear slope is obtained, and the apparent Ea of the polymerization system is calculated by formula 7 (Arrhenius equation formula), the result is 33.61 kJ/mol.

$$\ln k = \frac{E_a}{RT} + \ln A$$  \hspace{1cm} (7)

3.6. Effect of stirring speed on polymerization rate and characteristics of emulsion

Stirring speed is an important process condition for emulsion polymerization. Six different stirring speeds are used for the CTFE-VAc-BA-Veova10 quadri-copolymerization system. The reactor pressure is monitored by the gauge of autoclave. The particle size is evaluated by laser particle size distribution (MALVERN DTS 5101). The sample is diluted 1:2000 with deionized water and dispersed for 3 min in an ultrasonic bath. Viscosity is evaluated using 2# rotor of rotational viscometer (NDJ-1 style, Shanghai Jingke, China) at 30 rpm. After polymerization is completed, the coagulum is collected from the residue of the resulting emulsion by filtering. The coagulum is calculated by formula 8. The data are presented in table 2.

$$\text{coagulum\%} = \frac{\text{coagulum dried}}{\text{discharge amount}} \times 100\%$$  \hspace{1cm} (8)
Table 2. Characteristic of water-based fluoropolymer.

| Stirring rate /rpm | Nonvolatile /% | Fluoride content /% | PSD /nm | Viscosity /mPa.s | Reactor pressurea /Mpa | Coagulum /% |
|--------------------|----------------|---------------------|---------|-----------------|------------------------|------------|
| 100                | 45.05          | 12.11               | 145     | 20.0            | 0.28                   | 0.035      |
| 150                | 46.78          | 12.20               | 153     | 20.0            | 0.14                   | 0.002      |
| 200                | 46.82          | 13.50               | 157     | 26.5            | 0.22                   | 0.062      |
| 250                | 45.58          | 11.72               | 149     | 17.5            | 0.06                   | 0.093      |
| 300                | 45.05          | 13.87               | 168     | 22.5            | 0.16                   | 0.101      |
| 400                | 44.79          | 13.88               | 181     | 17.5            | 0.09                   | a lot      |

a Reactor pressure is the residual pressure after polymerization.

The stirring speed strongly influences the change of pressure in autoclave and the amount of coagulum, as shown in table 2. These results relate to CTFE as gas monomer which can polymerize with other monomers only by entering into liquid reactants. With stirring speed increasing, gaseous CTFE is dissolved much more in the liquid phase, so polymerization reaction speeds up. This phenomenon can be observed from the pressure on reaction ending. Whereas, the stability of the reactant in autoclave declines when keeping the condition of emulsifier unchanged, and the condition of high temperature and faster stirring speed is unfavorable for the stability of emulsion polymerization. So it leads to more coagulum. Accordingly, fluoride content also increases slightly, while nonvolatile decrease slightly with more coagulum. In addition, the viscosity of emulsion becomes smaller, and the PSD of emulsion will slightly increase by micellar’s decrease used for nucleation at constant monomer amount. Thus, an appropriate stirring rate of 200-300 rpm is recommended.

4. Conclusions

Waterborne fluoropolymer emulsion based on four kinds of monomers of CTFE-VAc-BA-Veova 10 was synthesized by the semi-continuous seed emulsion polymerization with the dropwise addition technique. CTFE was fed directly in the reactor, and the other monomers were dropwise added during polymerization. The results of the fluorine content at different stage and conversion of CTFE and other monomers demonstrated that polymerization process was relatively homogeneous. The polymerization rates were accelerated when increasing concentration of initiator and emulsifier, and raising reaction temperature. The kinetics relationship was described as Rp ∝ [I]^{0.10}, Rp ∝ [E]^{0.12}, and Ea of the polymerization system was 33.61 kJ/mol. The faster stirring speed led to more coagulum amount and bigger particle diameter, and made nonvolatile and viscosity of emulsion lower.

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