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Kinetic study on the ring-opening polymerization of octamethylcyclotetrasiloxane (*D*4) in miniemulsion

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ABSTRACT

A kinetic study on the ring-opening polymerization (ROP) of octamethylcyclotetrasiloxane (*D*4) in miniemulsion is presented in this work. The polymerization is initiated by dodecylbenzenesulfonic acid (DBSA) which also serves as the surfactant (inisurf). The influence of the size of monomer droplet and the concentration of DBSA on the polymerization rate were studied. Since the main place for the ROP of *D*4 was confirmed to be at the oil/water interface, a three-layer interface model was proposed to analyze the distribution of molecules at the interface and the effects of DBSA. A kinetic equation is then developed based on this model. In the equation, the polymerization rate (R_p) is related to the initial monomer concentration ($[D4]_0$), the droplet radius (r), the coverage of DBSA on monomer droplets surface (x). The polymerization rate can be predicted from the kinetic equation feeding all parameters with their experimental values. Finally, the equation gave a good accordance between the predicted polymerization rate data and the experimental results under different polymerization conditions.

1. Introduction

Since Hyde and Wehrly first report on the synthesis of α,ω-dihydroxylated polydimethylsiloxane (PDMS) latex in 1959 [1], ionic polymerization in emulsion (IPE) has attracted great attentions in recent years [2–11]. Many monomers [12–22], especially cyclosiloxanes, have been reported to generate polymer latexes by IPE method. Compared to the classical ionic polymerization of cyclosiloxanes in bulk or in solution, the final conversion of cyclosiloxanes polymerized in emulsion is sensibly higher. Meanwhile, linear polymers with higher molecular weight and narrower distribution can be obtained from emulsions with less cyclic by-products [6,15,21]. The main reactions of cyclosiloxanes in emulsion are the ring-opening polymerization (ROP) of cyclosiloxane monomers and the condensation polymerization of linear oligomers. Moreover, many subordinate reactions such as back-biting, redistribution and cross-linking of chains, all have great influence on the final conversion, molecular weight and distributions [9,15,21].

As an important part in IPE researches, the ROP in miniemulsion has been extensively studied using different kinds of cyclosiloxane monomers, such as octamethylcyclotetrasiloxane (*D*4) [6–9], 2,4,6,8-tetramethylcyclotetrasiloxane ($D4^{H}$) [12,21], 1,3,5-tris (trifluoropropylmethyl)cyclotrisiloxane (F_3) [15], etc. The ROP of cyclosiloxanes are usually initiated by H^+ or OH^- ions, then the ionized derivatives couple with surfactant ions to form active centers in ion-pair form at the oil/water interface of droplets or particles. Further propagation reactions on the active centers still carry on at the interface [21]. A reversible termination of the propagating chain has been proposed by protonation/deprotonation reactions induced by H_2O [6,15].

The miniemulsion polymerization of cyclosiloxanes is a heterogeneous reaction, whose typical kinetic and thermodynamic features significantly differ from those observed in bulk or in solution. The polymerization rate keeps constant until the conversion of monomer reaches 70% [6,23]. In addition, the polymerization rate is severely affected by the droplet size, the concentration and type of the inisurf and the possible presence of cosurfactant in the miniemulsion [7,12]. The kinetic scheme of *D*4 in anionic polymerization in miniemulsion has been established by De Gunzbourg A et al. [6], using the same formalism as that in a homogenous system. However, further kinetics analysis is still necessary taking into account the condition of oil/water interface, which is believed to be the main place for the ROP of *D*4 in miniemulsion.

In this work, a monomer miniemulsion composed simply of *D*4 and dodecylbenzenesulfonic acid (DBSA) was prepared by a high-pressure homogenizer. The size of monomer droplets can be controlled by the homogenization pressure and the DBSA

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concentration. After the monomer miniemulsion was prepared, different amounts of extra DBSA were added into the mixture and the monomer miniemulsions with same average droplet sizes but different DBSA concentrations were obtained. The influence of the droplet sizes and DBSA concentration on the polymerization rate was then studied.

Based on the experimental results, a three-layer interface model was proposed in this paper to analyze the distribution of *D*4 and DBSA molecules at the oil/water interface and the effects of DBSA molecules on the polymerization rate. A kinetic equation was then developed, in which, the polymerization rate of *D*4 was directly related to the initial monomer concentration ($[D4]_0$), the droplet radius (r), and the coverage of DBSA on monomer droplets surface (x). When all parameters are introduced in the kinetic equation, the polymerization rates under different polymerization conditions can be calculated. The kinetic equation was finally verified by comparing the experimental polymerization rates with the predicted values from the equation deduced in this work.

2. Experimental section

2.1. Materials

Octamethylclotetrasiloxane (*D*4), 99%, was purchased from Sage Chemical Co. Ltd., China; Dodecylbenzenesulfonic acid (DBSA), 99%, was purchased from Shanghai Resin Co., China. These reactants were used directly without further purification. Deionized water was prepared in our lab.

2.2. Methods

2.2.1. Preparation of monomer miniemulsion

The recipes of monomer miniemulsion tested in this work are listed in Table 1. Typically, 1.2 g DBSA was dissolved in 140 mL deionized water, then 60 g *D*4 was added. The mixture was dispersed by a mechanical stirring at 1000 r/min for 10 min, then the coarse emulsion was immediately passed through a high-pressure homogenizer (High-Pressure Homogenizer AH110D, from ATS Engineering Inc., Canada) with a flow rate of 10 L/h for four times, and the homogenizing chamber was cooled using a cooling jacket containing water at 5 °C. The size of monomer droplets was varied under different homogenization pressures (10–110 MPa). The concentration of DBSA in system can be changed by adding different amounts of extra DBSA into the monomer miniemulsions after the monomer miniemulsions have been homogenized.

Table 1
Recipes, *Z*-average droplet sizes (diameter, *d*) and droplet distribution indexes (PDI) of monomer miniemulsions.

Run	[*D*4] (mol/L)	[DBSA][a] (mol/L)	Homogenization pressure (MPa)	Extra [DBSA] (mol/L)	*d* (nm)	PDI
1	1.01	0.0184	110	0	197	0.06
2	1.01	0.0184	90	0	201	0.06
3	1.01	0.0184	30	0	220	0.09
4	1.01	0.0184	20	0	234	0.12
5	1.01	0.0184	10	0	290	0.17
6	1.01	0.0092	90	0	220	0.06
7	1.01	0.0092	90	0.0030	220	0.06
8	1.01	0.0092	90	0.0061	220	0.06
9	1.01	0.0092	90	0.0092	220	0.06
10	1.01	0.0092	90	0.0138	220	0.06
11	1.01	0.0092	90	0.0184	220	0.06
12	1.01	0.0092	90	0.0230	220	0.06
13	1.01	0.0092	90	0.0276	220	0.06
14	1.01	0.0092	90	0.0368	220	0.06
15	1.01	0.0092	90	0.0460	220	0.06
16	1.01	0.0092	90	0.0552	220	0.06
17	1.01	0.0368	110	0.0276	176	0.05
18	1.01	0.0184	110	0.0460	197	0.06
19	1.01	0.0092	20	0.0460	242	0.10
20	1.01	0.0092	10	0.0460	373	0.14
21	1.01	0.0230	90	0	197	0.07
22	1.01	0.0276	90	0	193	0.07
23	1.01	0.0368	90	0	187	0.06
24	1.01	0.0460	90	0	182	0.05
25	0.505	0.0092	90	0	208	0.06
26	0.673	0.0123	90	0	204	0.06
27	0.842	0.0153	90	0	202	0.06

[a] [DBSA]: the concentration of DBSA in the coarse emulsion.

2.2.2. Droplet sizes (*d*) and droplet distribution indexes (PDI)

The droplet sizes (*d*) and droplet distribution indexes (PDI) of monomer miniemulsion were immediately determined using a commercial dynamic light scattering (DLS, Zetasizer Nano ZS, Malvern). The samples of monomer miniemulsion were diluted 100 times and tested under 25 °C.

2.2.3. Miniemulsion polymerization

The monomer miniemulsion obtained above was immediately transferred in a four-neck flask equipped with a mechanical stirring, a nitrogen inlet and an outlet. The reaction temperature was varied from 40 to 80 °C using an external water bath. At different time intervals, 2 mL latex were withdrawn from the reacting mixture and neutralized to pH at 7–8 (tested by pH indicator strips) immediately by 5 wt% ammonia aqueous solution. The monomer conversions of each emulsion simple were immediately characterized.

2.2.4. Monomer conversion ($C(t)$) and monomer concentration ($[D4]_t$)

The monomer conversion at polymerization time t ($C(t)$) was determined by gravimetrical method. The samples were dried at 140 °C for 4 h to measure the weight of dry polymer. The conversion of *D*4 was calculated by the following equation (1):

$$C(t) = \frac{m_t - m_s}{m_0 - m_s} \times 100\% \tag{1}$$

where m_t is the mass of the residual substance, m_s is the mass of DBSA contained in the sample and m_0 is the mass of the solid substance at 100% conversion. Correspondingly, the monomer concentration at polymerization time t ($[D4]_t$) can be calculated from $C(t)$ values using equation (2):

$$[D4]_t = [D4]_0 \times [100 - C(t)]/100 \tag{2}$$

where $[D4]_0$ is the initial concentration of *D*4 in the monomer miniemulsion.

2.2.5. Surface tension

Surface tension of the monomer miniemulsion was determined by an OCA20 video-based contact angle measuring device (Dataphysics, Germany). All measurements were carried out at room temperature.

3. Results and discussion

3.1. The size of monomer droplets and average polymerization rate

Monomer miniemulsions with different *Z*-average droplet sizes (d) were prepared under different homogenization pressures. Detailed recipes are shown in Table 1 as Run 1–5. The evolutions of the monomer concentration ($[D4]_t$) are shown in Fig. 1 as a function of the polymerization time (t) during the miniemulsion

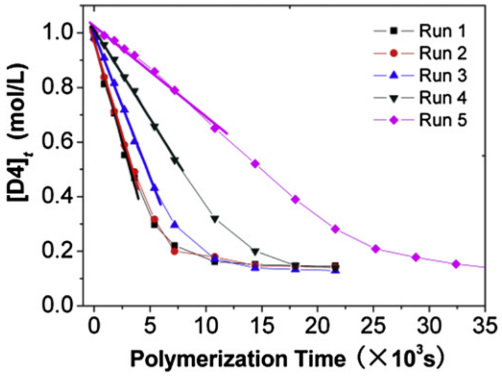


Fig. 1. Evolution of the monomer concentration as a function of the polymerization time. ($[D4]_0$ is 1.01 mol/L, [DBSA] is 0.0184 mol/L and the polymerization temperature is 60 °C. *Z*-average diameters (d) of monomer miniemulsions, Run 1: 290 nm; Run 2:234 nm; Run 3: 220 nm; Run 4: 201 nm; Run 5: 197 nm).

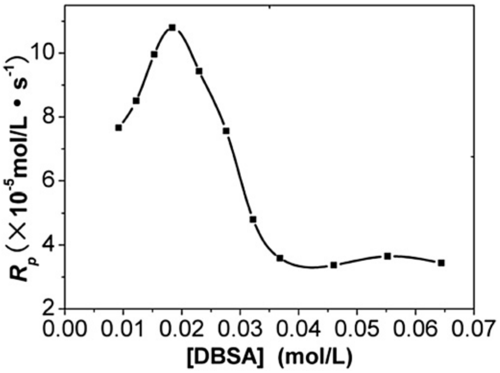


Fig. 3. Relationship between [DBSA] and R_p in cationic polymerization of $D4$ in miniemulsion (The *Z*-average droplet sizes (d) are all of 220 nm and the polymerization temperature is 60 °C).

polymerization. In each curve, an approximate linear variation of $[D4]_t \sim t$ can be obtained before the conversion reached 70%. The linearity indicates a constant polymerization rate during this process [6,23]. The average polymerization rate (R_p) during this linear period in each reaction was calculated by linear fitting on the plots before 50% conversion.

The relationship between R_p and d in the miniemulsion polymerization is shown in Fig. 2. The polymerization rates were varied in a large-scale with the variation of d. This result confirms that the ROP of $D4$ takes place at the oil/water interface: indeed, for constant concentrations of monomer and DBSA, the miniemulsions with smaller droplets size provide larger oil/water interface. As a result, the content of $D4$ molecules at the interface increases, which causes an increase of the polymerization rate with the decreasing droplet size.

3.2. *DBSA concentration and average polymerization rate*

The concentration of DBSA was changed by adding different extra content of DBSA into the monomer miniemulsions after they had been homogenized under same conditions. The monomer miniemulsions kept stable without noticeable changes on droplet sizes (Table 1, Run 6–16). Doing so, the study of the influence of the concentration of DBSA ([DBSA]) on R_p is permitted without the disturbance caused by the droplet sizes.

The evolution of R_p is shown in Fig. 3 as a function of [DBSA]. While increasing [DBSA], R_p increased to a maximum occurring at the point when $[DBSA] = 1.84 \times 10^{-2}$ mol/L. After that point, R_p decreased until [DBSA] reaches 3.68×10^{-2} mol/L, concentration at which R_p keeps constant with only slight changes upon increasing [DBSA].

The increasing part of $R_p \sim$ [DBSA] curve in Fig. 3 can be explained by an increasing concentration of active centers with the increase of initiator concentration since DBSA serves as initiator and surfactant. When [DBSA] reached 3.68×10^{-2} mol/L, the constant polymerization rates should be attributed to the saturation adsorption of DBSA at the oil/water interface [12]. The redundant DBSA molecules dissolved in water phase have negligible influence on the ROP of $D4$. However, the decreasing part in [DBSA] ranging from 1.84×10^{-2} mol/L to 3.68×10^{-2} mol/L is possibly caused both by a volume and a hindering effect of DBSA molecules at the oil/water interface [7,12], which is discussed below in more details.

DBSA is a typical amphiphilic molecule, which naturally absorbs at the oil/water interface, with the hydrophilic head-groups protruding towards in the aqueous phase whereas the hydrophobic tail-groups remain in the oil phase. Considering that the interface is of limited volume, the increase of surfactant concentration would lead to a decreasing monomer content at the interface, which would lead to the decrease of the polymerization rate: we refer this result as the volume effect of DBSA.

Further experimental results confirmed the hindering effect of DBSA molecules adsorbed at the oil/water interface. The linear relationship of $\ln R_p \sim 1/T$ (Arrhenius plots) is shown in Fig. 4. The apparent activation energy of the polymerization can be calculated

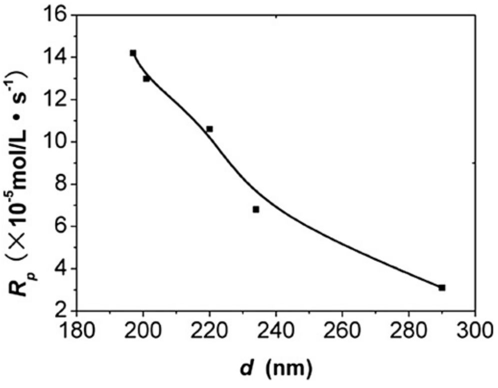


Fig. 2. Relationship between R_p and d ($[D4]_0$ is 1.01 mol/L, [DBSA] is 0.0184 mol/L and the polymerization temperature is 60 °C).

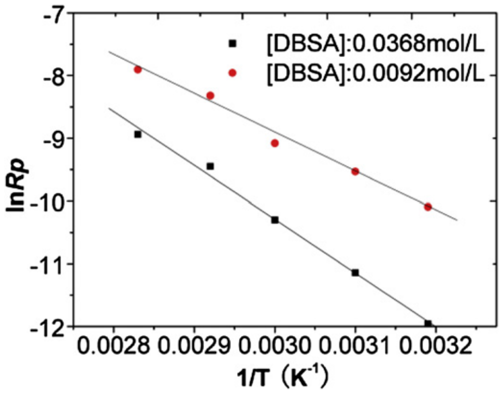
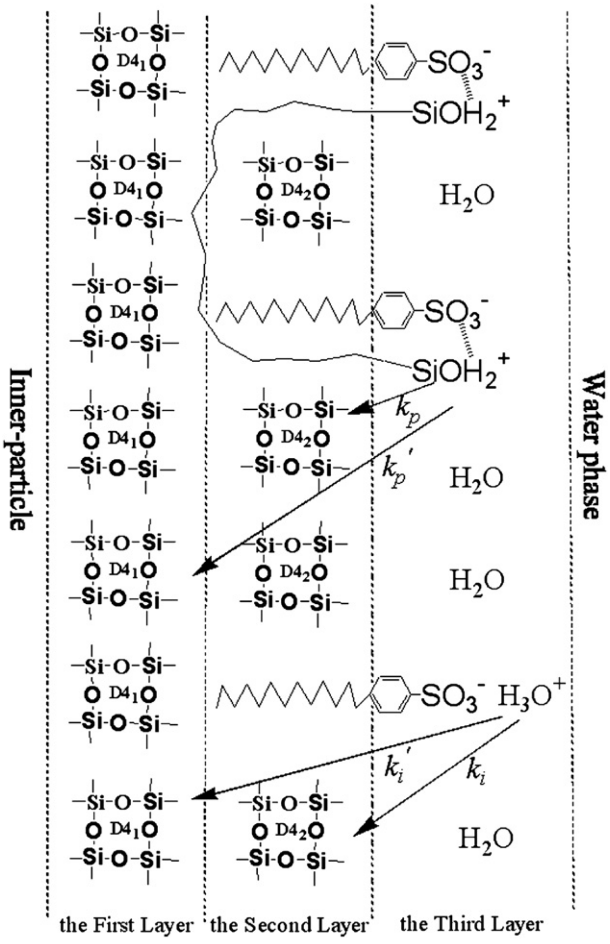


Fig. 4. Arrhenius plots for different DBSA concentrations ($[D4]_0$ is 1.01 mol/L and the *Z*-average droplet sizes (d) are all of 220 nm).

from the slope of the ln $R_p \sim 1/T$ linear fit. For monomer miniemulsions containing 9.2×10^{-3} mol/L and 3.68×10^{-2} mol/L DBSA, the apparent activation energies are 51 kJ/mol and 71 kJ/mol, respectively. The difference on the apparent activation energies means that the reaction capacity of the monomer is affected by surfactant molecules. The effective initiator, H^+ and the correspondingly active centers in an ion-pair form would prefer to stay in the aqueous phase close to the monomer droplet surface. It is reasonable to suppose that at the interface, the monomers were initiated and propagated at different rates. Those just adjacent to the aqueous phase should have a higher reactivity than those discarded from the interface by the hydrophobic tails of surfactant molecules. While increasing [DBSA], the rising coverage of surfactants on the droplet surface makes less monomer molecules reaching the surface, which leads to an overall decreasing reactivity. Correspondingly, the apparent activation energy of polymerization reaction increased.

3.3. The oil/water interface model

According to the above experimental results and analysis, a three-layer oil/water interface model was established to illustrate the volume and the hindering effects of DBSA at the oil/water interface. As shown in Scheme 1, the oil/water interface can be arbitrarily divided into three layers. From the inside to the outside of the droplet, the first layer is occupied by monomer molecules ($D4_1$); the second layer is occupied by monomer molecules ($D4_2$) and tail-groups (hydrophobic) of DBSA molecules; the third layer is aqueous layer, where H_3O^+, the head-groups (hydrophilic) of DBSA and activity centers in ion-pair form prefer to stay. Since DBSA molecules preferably adsorb in the second layer, the volume effect of DBSA is computed by the decrease of $D4_2$ concentration with increasing [DBSA] at the interface. $D4_2$ monomers have a higher reactivity due to their location close to the initiators and active centers, while $D4_1$ monomers have lower reactivity because these molecules are expelled from the aqueous phase by the molecules on the second layer. The initiation and propagation constants of $D4_1$ are defined as k_i and k_p; the initiation and propagation constants of $D4_2$ are defined as $k_i^{'}$ and $k_p^{'}$, respectively. Here, $k_i^{'} > k_i$ and $k_p^{'} > k_p$. With increasing [DBSA] and decreasing [$D4_2$], the monomer molecules with high activity, means that the polymerization reaction would proceed less readily: this is the hindering effect of DBSA.



Scheme 1. Three-layer oil/water interface model.

3.3.1. Determining the concentration of $D4_1$ and $D4_2$

Applying the three-layer oil/water interface model, the concentration of $D4_1$ and $D4_2$ were deduced. The oil/water interface can be treated as a standard spherical surface with each molecule layer perfectly occupied. The content of the polymer chains in the first and second layers are negligible, because most of the long PDMS chains entered the bulk phase at the inner-droplets. Assuming that the contribution of DBSA on the volume of monomer droplets is negligible, the density of oil phase is supposed to be constant during the polymerization. Then the total surface area (A) of monomer droplets in the miniemulsion can be expressed as:

$$A \approx \frac{3[D4]_0 \times V_e \times M_{D4}}{\pi r \times \rho} \tag{3}$$

where $[D4]_0$ is the initial concentration of $D4$ in monomer miniemulsion, V_e is the volume of monomer miniemulsion, M_{D4} is the molar mass of $D4$, r is the radius of monomer droplets and ρ is the density of oil phase.

The average coverage area of one $D4$ molecular on the spherical surface is defined as A_{D4}, and the average coverage area of one DBSA molecule is defined as A_{DBSA}. Then

$$\begin{aligned} A &= [D4_1] \times V_e \times N_A \times A_{D4} \\ &= [D4_2] \times V_e \times N_A \times A_{D4} + [\mathrm{DBSA}_2] \times V_e \times N_A \times A_{\mathrm{DBSA}} \end{aligned} \tag{4}$$

where [$D4_1$] and [$D4_2$] are the concentrations of $D4_1$ and $D4_2$, respectively, [DBSA_2] is the concentration of DBSA molecules in the second layer, and N_A is the Avogadro's number.

The coverage of DBSA on the second layer is defined as x, namely

$$x = \frac{[\mathrm{DBSA}_2] \times V_e \times N_A \times A_{\mathrm{DBSA}}}{A} (0 < x \leq 1) \tag{5}$$

According to equations (3) and (4), [DBSA_2], [$D4_1$] and [$D4_2$] can be deduced using the following relationship:

$$[\mathrm{DBSA}_2] = \frac{xA}{A_{\mathrm{DBSA}} \times N_A \times V_e} = K_{\mathrm{DBSA}} \times \frac{x[D4]_0}{r} \tag{6}$$

$$[D4_1] = \frac{A}{A_{D4} \times N_A \times V_e} = K_{D4} \times \frac{[D4]_0}{r} \tag{7}$$

$$[D4_2] = \frac{(1-x)A}{A_{D4} \times N_A \times V_e} = K_{D4} \times \frac{(1-x)[D4]_0}{r} \tag{8}$$

where

$$K_{D4} = \frac{3M_{D4}}{\pi\rho \times A_{D4} \times N_A} \tag{9}$$

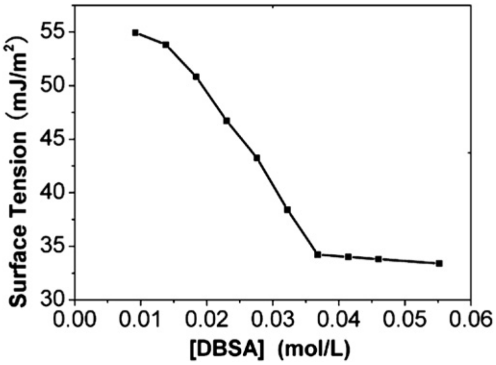


Fig. 5. Surface tension titration of monomer miniemulsion using 5% DBSA aqueous solution (the *Z*-average droplet sizes (*d*) are all of 220 nm).

$$K_{\mathrm{DBSA}} = \frac{3M_{D4}}{\pi\rho \times A_{\mathrm{DBSA}} \times N_A} \tag{10}$$

3.3.2. *On the coverage of DBSA on the second layer (x)*

In order to calculate the coverage of DBSA on the second layer (x), the value of K_{DBSA} was determined by surface tension titration method [24]. The monomer miniemulsion was prepared according to Run 6 in Table 1. The surface tension of monomer miniemulsion was titrated using 5% DBSA aqueous solution. The surface tension as a function of [DBSA] is shown in Fig. 5. With increasing [DBSA], the surface tension of monomer miniemulsion decreased until a turning point appeared when [DBSA] reached 3.68×10^{-2} mol/L. At this point, DBSA molecules absorbed on the second layer until saturation, namely $x = 1$. At the same time, DBSA dissolved in water phase reached its critical micelle concentration (CMC, 1.28×10^{-3} mol/L). Then

$$[\mathrm{DBSA}_2] = [\mathrm{DBSA}] - \mathrm{CMC}_{\mathrm{DBSA}} \tag{11}$$

By equation (6), the value of K_{DBSA} is calculated as:

$$K_{\mathrm{DBSA}} = 3.87 \times 10^{-9}\ \mathrm{m} \tag{12}$$

Before DBSA molecules in the second layer is saturated ($0 < x \le 1$), the amount of DBSA in water phase is expected to be very small. The value of x can be calculated by equation (13):

$$x = \frac{r[\mathrm{DBSA}_2]}{K_{DBSA}[D4]_0} \approx 2.584 \times 10^8 \times \frac{r[\mathrm{DBSA}]}{[D4]_0}(0 < x \le 1) \tag{13}$$

3.4. *Kinetic analysis*

3.4.1. *Reaction scheme*

Based on the three-layer interface model, the ROP scheme of *D*4 in miniemulsion with DBSA used as an inisurf is shown in Scheme 2. In this scheme, only the monomer molecules at the oil/water interface take part in the ROP of *D*4, assuming that the reaction constants of monomer molecules are different according to their location.

3.4.2. *Calculating the concentration of active centers*

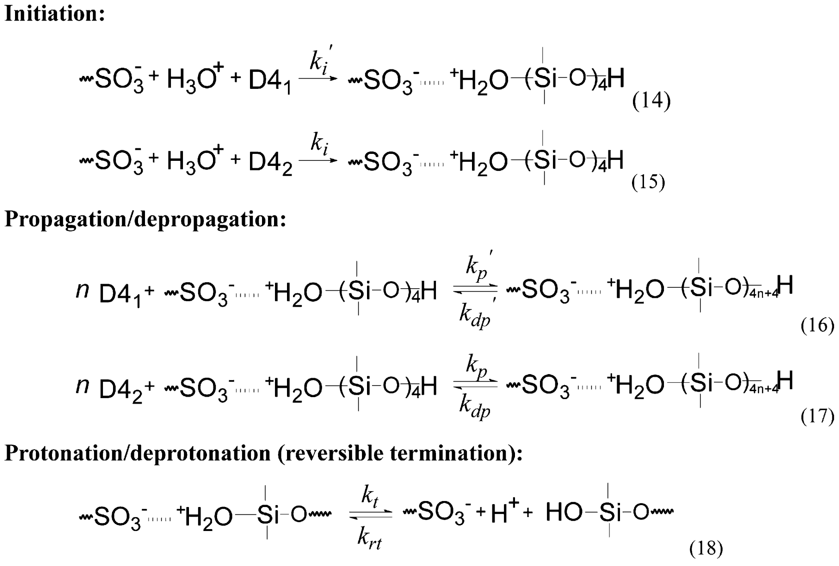
The protonation/deprotonation reaction (18) was described as a reversible termination in previous literature reports [6,15]. However considering the pK_a values in equation (19) [25], the protonation/deprotonation at the interface would sharply shift to the left under an acid condition [6]. In this way, the protonation/deprotonation reaction at the interface cannot effectively terminate the active centers but transfer the silanol end-groups to other active centers, i.e., every oligomer chain initiated at the interface would have two active centers ends, as shown in Scheme 1.

$$\begin{aligned} &\mathrm{H_2O/H_3O^+} : pK_a = 15.6 \\ &\mathrm{SiOH/SiOH_2^+} : pK_a = 11 \end{aligned} \tag{19}$$

In our point of view, the propagation is terminated only when the polymerization degree of PDMS oligomers reached 30D, a size at which the polymer chain is pulled out from the interface to the bulk phase according to their surface tension [9]. In this case, the concentration of ion-pair active centers does not be determined by the reaction (18), but the initiation rate and the average lifetime Δt of active centers. Thus, the concentration of active centers ($[\mathrm{SiOH_2^+}]$) can be expressed as equation (20):

$$\left[\mathrm{SiOH_2^+}\right] = 2\left(\frac{\mathrm{d[PDMS]_{ini}}}{\mathrm{d}t}\right) \times \Delta t \tag{20}$$

where $[\mathrm{PDMS}]_{\mathrm{ini}}$ is the concentration of the oligomer chain initiated at the interface, Δt is the average lifetime of active center.



Scheme 2. Cationic ROP of *D*4 in miniemulsion [6,15,21].

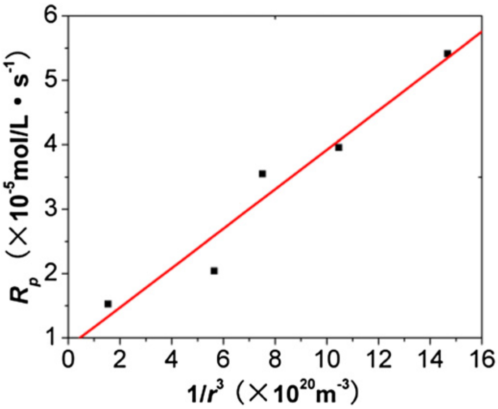


Fig. 6. Relationship between R_p and $1/r^3$ ($[D4]_0$ is 1.01 mol/L, $x = 1$ and the polymerization temperature is 60 °C).

According to the initiation equations (14) and (15), the initiation rate of oligomer chain at the interface is given by the following relationship:

$$\frac{d[\mathrm{PDMS}]_{\mathrm{ini}}}{dt} = k_i[D4_2][\mathrm{DBSA}_2] + k_i^{'}[D4_1][\mathrm{DBSA}_2] \tag{21}$$

For the ion-pair active centers would be broken up once they leave the interface, the average lifetime of active centers (Δt) is directly related to the existing time of initiated oligomer chain at the interface, which relies on the diffuse rate of the PDMS chain from interface into bulk. To simplify the calculation, we make the assumption that Δt is a constant in the beginning period. With $[D4_1]$, $[D4_2]$ and $[\mathrm{DBSA}_2]$ given by equations (6)–(8), equation (20) can be simplified to:

$$\left[\mathrm{SiOH}_2^+\right] = \frac{[D4]_0^2}{r^2} \times K_1' \left[x(1-x) + K_2' x\right] \tag{22}$$

where

$$K_1' = 2k_i K_{D4} K_{\mathrm{DBSA}} \Delta t \tag{23}$$

$$K_2' = 2k_i' K_{D4} K_{\mathrm{DBSA}} \Delta t \tag{24}$$

3.4.3. Polymerization rate

The propagation reaction is thought to be a very fast reaction which takes place at the oil/water interface [9,21]. The monomers at the interface would react quickly and the void from consumed monomer molecules would be compensated by $D4$ molecules diffusing from the bulk. The higher the diffusion rate, the more $D4$ molecules should be added on the polymer chain in the average lifetime of an active center. Thus the consumption rate of monomers would depend on the concentration of active centers and the diffuse rate of the monomer molecules from the bulk phase to interface. A constant diffuse rate of $D4$ (expressed as v_{D4}) is supposed along the radial direction of droplets. Then the polymerization rate can be expressed as:

$$R_p = K[\mathrm{SiOH}_2] \times v_{D4} \tag{25}$$

Table 2
Main parameter values (K_1 and K_2).

The results of linear fitting	$K_2 = 3.0 \times 10^{-26}$	$R^2 = 0.95$
The results of parabola fitting	$K_1 = 4.57 \times 10^{-25}$	$R^2 = 0.95$
The polymerization rate equation	$R_p = [D4]_0^2/r^3 \times 10^{-25} \times [4.57x(1-x) + 0.30x]$ (31)	

where K is a constant. The migration of $D4$ is assumed to be driven by the oil/water interfacial tension [26,27], and not affected by the local viscosity when the conversion is not much too high. In this case, v_{D4} is directly proportional to the interfacial tension of oil/water and to the radius of droplets/particles as showed in equation (26):

$$v_{D4} = K_m \times \frac{2\sigma}{r} \tag{26}$$

where K_m is a constant, $2\sigma/r$ is the ratio of oil/water interfacial tension over the droplet radius r.

With $[\mathrm{SiOH}_2^+]$ and v_{D4} given by equations (22) and (26), R_p can be reduced as:

$$R_p = \frac{[D4]_0^2}{r^3} \times [K_1 x(1-x) + K_2 x] \tag{27}$$

where

$$K_1 = 2K \times K_1^{'} \times K_m \times \sigma \tag{28}$$

$$K_2 = 2K \times K_2^{'} \times K_m \times \sigma \tag{29}$$

If droplet size variations are omitted in the miniemulsion polymerization, the coverage of DBSA on the second layer x would keep constant in a given miniemulsion polymerization process. According to equation (27), a constant monomer consumption rate would be obtained until the diffusion of monomers is affected by viscosity at high conversion range. The constant monomer consumption rate is in agreement with experimental results.

3.4.4. Determination of K_1 and K_2

For constant $[D4]_0$ and assuming that the surface of the droplets is totally occupied by DBSA, namely, $x = 1$, the equation (27) can be simplifies as:

$$R_p = K_2[D4]_0^2 \times \frac{1}{r^3} \tag{30}$$

The equation (30) shows that there should be a linear relationship between R_p and $1/r^3$. In this special case, the evolution of R_p as a function of $1/r^3$ is clearly confirmed in Fig. 6 (plotted from Table 1, Runs 14, 17–20). The value of K_2 was determined by linear fitting and the results are shown in Table 2. The coefficient of the linear regression R^2 is 0.95, which shows a good correspondence between R_p and $1/r^3$.

Keeping constant the monomer concentration and the monomer droplet size, equation (27) shows that there should be

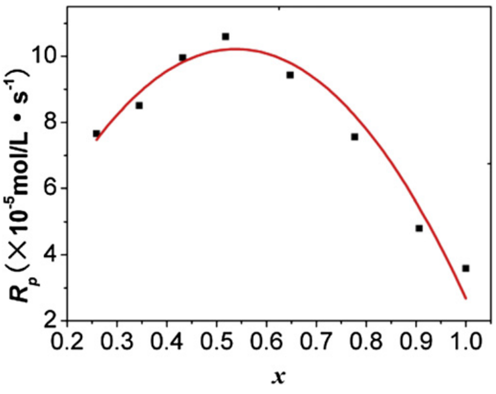


Fig. 7. Relationship between R_p and x ($0 < x \le 1$) ($[D4]_0$ is 1.01 mol/L, the Z-average droplet sizes (d) are all of 220 nm and the polymerization temperature is 60 °C).

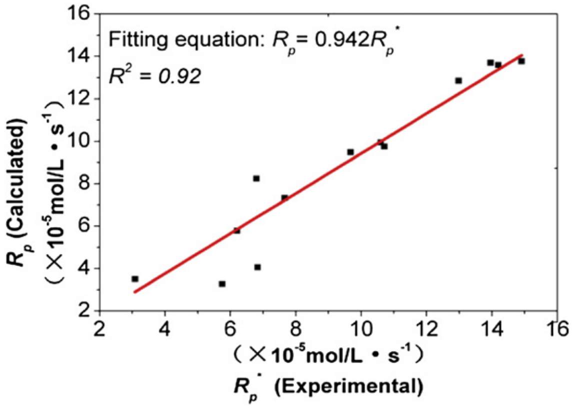


Fig. 8. Kinetic equation (31) validation by plotted the predicted values versus the experimental values.

a parabola relationship between R_p and x. The relationship between R_p and x ($0 < x \leq 1$) is shown in Fig. 7 based on the data from Fig. 3. Since the value of K_2 is known, the value of K_1 was determined by fitting the plots with a parabola equation and the result is given in Table 2. The corresponding coefficient for parabola regression R^2 is 0.95, which proves a credible curve fitting. The value of K_1 is about 15 times that of K_2, which is in agreement with the results for apparent activation energies.

3.5. Validation of the kinetic equation

Monomer miniemulsions prepared with different $[D4]_0$ and [DBSA] under different homogenization pressures, were tested: the Z-average diameter (d) of monomer droplets in miniemulsions can be determined by DLS, while the values of x can be calculated by equation (13). Then R_p in each reaction (Table 1, Run 1–6 and Run 21–27) can be predicted from equation (31) and in comparison with the measured polymerization rates (R_p^*) obtained from the monomer consumption data. The fair linearity between the calculated polymerization rates (R_p) and the experimental results (R_p^*) is shown in Fig. 8 with a corresponding regression coefficient R^2 of 0.92. The ratio of R_p to R_p^* is 0.942 which means a good agreement, the kinetic equation is verified.

4. Conclusions

The effect of droplet sizes on the polymerization rates confirmed that the cationic ROP of D4 in miniemulsion should takes place at the oil/water interface. The effect of [DBSA] on the polymerization rates and apparent energies of polymerization were discussed and attributed to the volume and the hindering effects of the inisurf molecules at the oil/water interface. A three-layer interface model was then established, where DBSA molecules were thought to locate in the middle layer at the interface with the volume of DBSA having a negative effect on the monomer concentration in the same layer (the volume effect). The monomer molecules on the first layer ($D4_1$) have a lower reactivity than the monomer molecules in the second layer ($D4_2$) since $D4_1$ were hindered by the tail-groups (hydrophobic) of DBSA from active centers (the hindering effect).

The ROP scheme of D4 in miniemulsion was reacquainted. In this scheme, only the monomer molecules at the interface can take part in the initiation and propagation of D4, and the reaction capacities of monomers were different according to their locations. The concentration of active centers and the polymerization rate equation were deduced from this model. The polymerization rate (R_p) is of zero order according to the monomer concentration ($[D4]$), but depends on the initial monomer concentration ($[D4]_0$), the droplet radius (r) and the coverage of DBSA on monomer droplets (x). The parameters in the equation were determined by carrying out various experiments. The equation was verified by the well consistency of the R_p data predicted by the kinetic equation with the experimental results under different polymerization conditions.

Besides, the values of K_1 and K_2 in the kinetic equation were determined based on DBSA used as inisurf and a polymerization temperature of 60 °C. Changing the polymerization temperature and/or initiator or surfactants types, would require recalculating the value of K_1 and K_2.

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Nomenclature

$C(t)$	conversion of monomer at polymerization time t
$[D4]_t$	concentration of D4 at polymerization time t
$[D4]_0$	initial concentration of D4 in monomer miniemulsion
[DBSA]	concentration of DBSA in the miniemulsion
R_p	polymerization rate
$[D4_1]$	concentration of D4 in the first layer
$[D4_2]$	concentration of D4 in the second layer
$[DBSA_2]$	concentration of DBSA in the second layer
k_i	initiation rate constant of D4 in the first layer
k_p	propagation rate constant of D4 in the first layer
k_{dp}	depropagation rate constant of D4 in the first layer
k_i'	initiation rate constant of D4 in the second layer
k_p'	propagation rate constant of D4 in the second layer
k_{dp}'	depropagation rate constant of D4 in the second layer
A	total surface area of monomer droplets in the miniemulsion
N_A	Avogadro's number
V_e	volume of emulsion
M_{D4}	molar mass of D4
r	radius of droplet size in miniemulsion
ρ	density of oil phase
A_{D4}	occupation area of one D4 molecule on the surface of droplets
A_{DBSA}	occupation area of one DBSA molecule on the surface of droplets
x	coverage of DBSA molecules on the second layer
CMC_{DBSA}	critical micelle concentration of DBSA
$[SiOH_2^+]$	concentration of active centers
$[PDMS]_{ini}$	concentration of the oligomer chain initiated at the interface
Δt	average lifetime of active centers
v_{D4}	diffuse rate of D4 along the radical direction of droplets
σ	oil/water interface tension when the interface is ideal flat

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