Prediction of the Droplet Size of Nonionic Urethane Acrylate Emulsions

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Abstract: To predict emulsion droplet size of PEG-modified urethane acrylate (PMUA) which are emulsified in the absence of surfactants, when the steric repulsive potential is dominant, simulation methods and various equations of steric hindrance of nonionic surfactants were used. Lennard-Jones potential was used to describe the interactions of hydrophilic-hydrophilic, hydrophilic-hydrophobic, and hydrophobic-hydrophobic and the movements of chains. Various equations for description of the steric hindrance of polyoxyethylene chains are also used as correction parameters of interaction between other droplets. The results of simulations were relatively similar to those of measured. Most of correction parameters were determined by experiments, and several parameters were treated as variables.

1. Introduction

Computer simulation has been widely used as a prediction method for experimental results. Especially, in the fields of polymer science, computer was available to describe the invisible movement of polymer chains. These days, many computer simulation methods are used for the interpretation of dynamics of macromolecules. Representatively, Molecular dynamics (MD) [1, 2] and Monte-carlo (MC) [3] simulation are prevailed. In MD simulations, static as well as dynamic properties of molecules can be calculated, while in MC simulations, only static properties can be determined. That is, MC simulations are widely used to calculate the thermodynamical state of systems and molecules.

Aggregation of self-associating polymers is of considerable current research interest, because of their unusual macroscopic material properties. To describe the colloidal aggregation which has ionic groups, over the past decades, diffusion-limited aggregation (DLA) [4, 5] models have been extremely used in elucidating the structures and the kinetics of aggregation for associating colloidal particles. Because ionic sites work as sticker sites, before adding water, ionic sites are aggregated each other. However, as water is added, ionic sites which is oriented toward the water phase are dissociated and work as repulsive site, internal aggregated ionic sites are maintained on the state of aggregation. In this way, emulsion is formed and stabilized by repulsive force between outer ionic sites. In the case of nonionic colloidal aggregation, because sticker sites do not exist, the formation of droplets can not be elucidated as aggregation of sticker sites. Lennard-Jones potential [6-8] which shows the interaction between hydrophilic-hydrophilic, hydrophilic-hydrophobic, and hydrophobic-hydrophobic is widely used to described the formation of droplets. Emulsion which has hydrophilic polyoxyethylene chain is stabilized by steric repulsion of hydrophilic polyoxyethylene chains. The chain length of polyoxyethylene is an important factor for droplet formation because it dominates the degree of steric hindrance.

In this study, the droplet size of emulsions of resins possessing a long, flexible, and hydrophilic polyoxyet-
hylene chain was predicted. Lennard-Jones potential and steric hindrance potential were used and several assumption were laid in order to simplify the simulation. The assumptions are as follows: 1) The angle between each segments was fixed either at 90° or 180°, 2) The movement of chains was 2-dimensional, and 3) The thermodynamic state is not considered.

2. Experimental part

2.1. Materials
Poly(tetramethylene) glycol (PTMG, Mw=1000, Hyosung BASF) was dried and degassed at 60°C under vacuum. 2,4-toluene disocyanate (TDI, Junsei) was purified by filtration. 2-hydroxyethyl methacrylate (2-HEMA, Aldrich) was used without further purification. Polyethylene glycol (PEG, Mw=600, 1000, 2000, 4000, and 6000 Junsei Chemical Co.) was used without further purification. Dibutyldilaurate also used as a catalyst.

2.2. Synthesis of PEG-modified Urethane Acrylate

PEG-modified urethane acrylates (PMUAs) were synthesized by the following three-step processes. The molar ratio of reactants was summarized in Table 1. These reactions were carried out in the 4-necked glass reactor equipped with stirrer, a reflux condenser, thermometer, and nitrogen inlet system.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TDI</th>
<th>PTMG</th>
<th>HEMA</th>
<th>PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMUA600</td>
<td>0.2</td>
<td>0.1</td>
<td>0.12</td>
<td>0.08</td>
</tr>
<tr>
<td>PMUA1000</td>
<td>0.2</td>
<td>0.1</td>
<td>0.12</td>
<td>0.08</td>
</tr>
<tr>
<td>PMUA2000</td>
<td>0.2</td>
<td>0.1</td>
<td>0.12</td>
<td>0.08</td>
</tr>
<tr>
<td>PMUA4000</td>
<td>0.2</td>
<td>0.1</td>
<td>0.12</td>
<td>0.08</td>
</tr>
<tr>
<td>PMUA6000</td>
<td>0.2</td>
<td>0.1</td>
<td>0.12</td>
<td>0.08</td>
</tr>
</tbody>
</table>
* At PMUAx, X means the molecular weight of PEG.

In the first step, TDI was poured into the 4-necked glass reactor under a N₂ atmosphere. Then, PTMG was dropped into the reactor at 35°C and the reaction temperature was raised to 45°C so that the isocyanate group of TDI reacted with the hydroxyl groups of PTMG. This temperature was maintained for 7 h to retain an acceptable rate of reaction and then the temperature was lowered slowly to reduce isocyanate levels. The change of NCO value during the reaction was determined using the dibutyamine back titration method to find out the end point of reaction.

In the second step, 2-HEMA was added slowly into the reactor to react with residual isocyanate group at 45°C for 4 hrs, which introduce reactive vinyl group into the molecular end. The temperature was raised again to 75°C in order to eliminate unreacted isocyanates.

In the third step, PEG was a slowly added into the reactor to react the hydroxy group of PEG with the residual isocyanate, which made it possible to introduce polyoxyethylene chains into the molecular end as hydrophilic groups. The reaction end point was determined by the disappearance of NCO stretching peak (2270 cm⁻¹) by IR spectroscopy. In our previous study [9-18], the molecular structure of PEG-modified urethane acrylate was analyzed, and molecular structure of PMUA was illustrated as in Fig. 1.

![Fig. 1. The structure of PEG-modified urethane acrylate (PMUA).](image)

2.3. Emulsification
All emulsions were prepared by phase inversion emulsification process[20]. Resin was placed in a 100ml beaker and stirred slowly until the resin was melted. Then distilled deionized water (DDI water) was dropped slowly while stirring at 380 rpm at room temperature. Silicon rubber plate was used for covering the beaker to protect the water evaporation. All emulsions were prepared without using any surfactant. Solid content of emulsions was fixed at 30 wt%.

2.4. Measurements
1H-NMR spectra were recorded at 500MHz on an NMR 500 (AMX 500, Bruker) instrument from CDCl₃ solution at 303K. IR spectra were recorded using a Shimadzu IR 470 FDU-3 spectrometer. The molecular...
weight distributions of PMUA were measured by Model 410 GPC equipped with Syragel. Flow rate of THF was maintained at 0.5mL/min. The average molecular weights of PMUA determined by GPC were Mw = 3751-6074 and Mn = 1855-3002. The droplet size of emulsions was measured using Brookhaven laser light scattering instrument (BI9000AT, 2MF98631 PM-tube, Ar-Ne laser).

2.5. Prediction of Droplet Size

Each molecules of polymeric surfactants are composed of hydrophobic and hydrophilic parts. PMUA are also composed of hydrophobic and hydrophilic polyoxyethylene parts. So, PMUA could be simplified as the combination of hydrophobic particles (●) and hydrophilic (○). A schematic drawing of the O/W system was presented below.

○ ● ● ● ● ○ ○ ○ ○

where ● : hydrophobic particle
○ : hydrophilic particle

Each particles are interacted by Lennard-Jones potential and this is available in the radius of cut-off (Rc)[21, 22] which means the limitation radius of interactions.

\[ \vartheta = 4 \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

where \( \sigma \), \( \varepsilon \) : constant for materials
\( r \) : radius between two particles

The cut-off radii for o-o and o-w interactions are set to 2.5 and 1.12, respectively. In the general system, the radius is set to 1. To simplify the simulation, following several assumptions were made.
1) \( \sigma \) and \( \varepsilon \) are constants which depends on materials, however, in this study, these constants are fixed to 1.
2) All simulations are executed in 2-dimensional plane.
3) Interactions of o-o are equal to those of w-w.
4) Number of hydrophobic particles are constant irrespective of molecular weight of PEG. That is to say, polydispersity of PEG is 1.

Movement of chains is followed Eden cluster formation dynamics (ED) and excluded volume theory[23].

The simulation was executed according to the above assumptions using IBM compatible personal computer equipped pentium-150 MHz processor, and Borland C compiler was used as a programming language.

3. Results and Discussion

3.1. Synthesis of PEG-modified Urethane Acrylate

PMUA is mainly comprised of two-types of macro molecules, type A and B which are represented in Fig. 2. 1H-NMR spectra and the peak assignments of PMUA are shown in Fig. 2. The assignments of the proton are based on those reported by Chokki et al.[24-26] In the case of the unmodified urethane acrylate, the chemical shift corresponding to \(-\text{CH}_2\text{CH}_2\text{O}\) is not detected. However, the signal at 3.64 ppm appears in the NMR spectra of PMUA, indicating that polyoxyethylene groups are introduced into the urethane acrylate.

3.2. Prediction of Droplet Size

Generally, there are two kinds of theories in estimating the emulsion stability; one is the energy dissipation theory based on the DLVO theory or the disjoining pressure, and the other is the hydrodynamic theory. The results of these studies have made it possible quantitatively to argue the contribution of the steric stabilization to the stability of the thin liquid film with nonionic surfactant. Friberg et al.[27] explained the stability of emulsion by the idea that the liquid crystal-like multilayers formed on the O/W interface reduce the coalescence potential based on van der waals force.

The present papers make an attempt to measure the rate of rapid coalescence of emulsions stabilized with sample nonionic surfactant, so as to elucidate the steric stabilization in the emulsions. The stability of the emulsion droplets can be expressed in terms of the energy balance between the attractive potential and the steric repulsive potential, if the electrostatic repulsive potential can be allowed to diminish.

In this study, variables are determined by simulation and the droplets size of emulsions are determined by

using the estimation of repulsive energy.

Let us now consider two oil droplets of radius \(a\), the surface of which are further covered with a hydrophilic layer of polyoxyethylene groups of thickness \(\delta\). The total energy worked on the two oil droplets, \(G_t\) \cite{28}, is generally given by:

\[
G_t = G_e + G_v + G_s
\]

where, \(G_t\) : Total energy between two droplets  
\(G_e\) : Electric double layer repulsion  
\(G_v\) : Van der waals attraction  
\(G_s\) : Steric repulsive potential

However, in our system, electric double layer repulsion and van der waals attraction are affected relatively little, so those parameter are removed and only steric repulsive potential is considered in the process of simulation.

When the droplets are in direct contact with each other, the contribution of the \(G_v\) term to the total potential must be carefully accounted for. In such a case, the interactions between the hydrophilic layers of adsorbed surfactants may be described by the \(G_s\) \cite{22} term as an additional repulsive potential.

\[
G_s = G_{VR} + G_M
\]

where \(G_{VR}\), the so-called volume restriction defined by Mackor, denoted the entropically free energy generated due to the restrictive mobility of polyoxyethylene moieties in hydrophilic layers of the surfactant adsorbed on both droplet surfaces overlapped each other by compression. Otewill et al.\cite{29} proposed the following expression for \(G_{VR}\):

\[
G_{VR} = N_o kT \theta \left(1 - \frac{H_0}{2\delta}\right) \times S_0
\]

\[
S_0 = \pi \left(\delta + \frac{H_0}{2}\right) (2\delta - H_0)
\]

where \(N_o\) : Number of adsorbed molecules per unit area at O/W interface  
\(\theta\) : The coverage of adsorbed molecules  
\(\delta = H_0 - 2\delta\)

Recently, Hesselink et al.\cite{30} have proposed a statistical treatments to estimate the \(G_M\) and \(G_{VR}\) values for the overlapping interaction between the long-chain polyoxyethylene coiling. Since the polyoxyethylene chains of adsorbed surfactants in the present study are relatively short, the overlapping layers of polyoxyethylene groups is treated as a dilute polymer solution. Therefore, the \(G_M\) \cite{28} term may be expressed by:

\[
G_M = \frac{4\pi kT}{3V_1} \phi_v^2 \left(1 - \chi\right) \left(\delta - \frac{H_0}{2}\right)^2 (3a + 2\delta + \frac{H_0}{2})
\]

where \(a\) : Radius of micelle  
\(V_1\) : Molar volume of water  
\(\chi\) : Interaction parameter of polyoxyethylene

Several variables are determined by simulation in equilibrium that is to say, Lennard-Jones potential is zero in our system. Droplet sizes of emulsions are obtained by using above equations. At \(G_{VR} + G_M = 0\), above formulations are rearranged as follow:

\[
\phi_v = \left(\delta - \frac{H_0}{2}\right) \left(\frac{3a + 2\delta + \frac{H_0}{2}}{4\pi kT V_1}\right)^{1/2}
\]

Fig. 3. The flow chart for PMUJA simulation.

Fig. 4. The graphical representation of PMUA simulation.

\[ a = \frac{\theta \cdot N_b \cdot V \cdot (1 - \frac{H_b}{2 \cdot \delta}) \cdot (\delta + \frac{H_b}{2}) \cdot (2 \cdot \delta - H_b)}{4 \cdot \phi \cdot \left( \frac{1}{2} - \delta \right) \cdot (\delta - \frac{H_b}{2})^2} \]

\[ = \frac{(2 \cdot \delta + H_b)}{3} \]

where \( \theta \), \( N_b \) are determined by simulation and \( \phi \) is proportional to cube of the length of polyoxyethylene chains. \( H_b \) is inversely proportional to the length of polyoxyethylene chains.

PMUA simulation is executed through algorithm which is illustrated in Fig. 3. The simulation results are illustrated in Fig. 4 and Fig. 5. In our simulation, value is changed between 0 and 1 because \( \delta \) is unknown. The results of simulation are similar to those of measured and as \( \delta \) value increases, the results become close to those of measured. In our study, electrical terms are ignored, so results of simulation are slightly different from those of measured.

4. Conclusions

In our study, Lennard-Jones potential are used for simulation in order to predict the droplet size of PMUA emulsion. And various steric hindrance equation of polyoxyethylene chains are used some correction parameters to calibrate the steric hindrance among neighboring droplets. Several assumptions are made to simplify the simulation.

The results of simulation are similar to those of measurement. As \( \delta \) value increased, the results get more closer to those of measured. However, when \( \delta \) is 0, the measured droplet size is most similar to that obtained by simulation. These results may be attributed to several assumptions and removal of electrical terms.
Fig. 5. Comparison of the results of PMUA simulation and those of measurement
- ▲ : = 0
- ○ : = 0.2
- ▼ : = 0.4
- ▼ : = 0.6
- ▲ : measurement

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References