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ARTICLE TYPE

# A Novel Alkali and Cosolvent Thickening Mechanism for Latex

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The work presented here reports the synthesis of recently developed rheology-controlled acrylic latex used in waterborne metallic coatings, which was synthesized with methacrylic acid (MAA), methyl methacrylate (MMA), butyl acrylate (BA), hydroxypropyl methacrylate (HPMA) and divinyl-benzene (DVB) via core/shell seed emulsion polymerization. Once the latex was neutralized with dimethylethanolamine (DMEA) it could be further thickened with additional solvent ethylene glycol butyl ether (EGBE), in which process the dispersion viscosity raised dramatically and the resin exhibited strong thixotropy. In order to clarify the thickening mechanism, the swelling behaviours and interfacial properties of the latex with DMEA and EGBE were investigated intensively. Dynamic Light Scattering (DLS) results revealed that DMEA swelled latex particles to some extent while EGBE could not change particle diameter but precipitate particles. Surface tension experiment demonstrated that EGBE decreased latex surface tension, and we concluded amphiphilic EGBE flocculates particles in latex system. Scanning Electron Microscopy (SEM) results showed that particles in DMEA and EGBE thickened sample retained their spherical structure and arrayed regularly. The combination of alkali swellable ability and EGBE flocculation effect were the main factors responsible for the thickening of latex.

## 1. Introduction

With environmental regulations tightened worldwide, waterborne coatings<sup>1-3</sup> have been a hot topic and widely used in the fields of building, machine, wood, food, textile, ink, adhesives, functional materials and so on.<sup>3-10</sup> The viscosity of waterborne coatings are usually low, thus thickeners have to be utilized in formulas to provide thixotropy<sup>11,12</sup>. Generally, there are mainly four kinds of thickeners<sup>12-14</sup> used in coating system: inorganic thickeners, cellulose thickeners, alkali-swellable thickeners (ASE) and hydrophobically modified ethoxylated polyurethane thickeners (HEUR). The thickening mechanism for organic thickeners<sup>15-17</sup> is mainly hydration effect. As to cellulose thickeners<sup>12, 18</sup>, the thickening mechanism is the synergy function of hydration effect and molecule chain entanglement. The thickening capacity of ASE thickeners<sup>12, 19</sup> stem from electrostatic repulsion which stretches the polymeric chains after the carboxyl groups of the polymers are neutralized. However, HEUR thickeners<sup>12, 20</sup> are quite different from the above since there are hydrophilic and hydrophobic segments in the polymer structure, and their molecules can form micelles in aqueous solution which interact with other components in the coating system, establish a kind of network and exhibit thickening capacity therefore. Besides making use of thickeners directly in coating formulas, people may also introduce acid monomers such as MAA and acrylic acid (AA) in emulsion polymerization techniques to produce alkali-swellable polymers, which could be further thickened by alkali with the same thickening mechanism as ASE thickeners<sup>19</sup>.

In recent years the research about latex thickening has been mainly focused on the interactions among thickeners, surfactants,

electrolytes and latex<sup>11, 21-25</sup> as well as their solution properties<sup>26, 27</sup>. Beshah<sup>22</sup> et al. used pulsed field gradient (PFG) NMR spectroscopy as diffusion-weighted filter to remove the signals of low molecular weight species to detect hydrophobic end groups and urethane linkers, and found that there were no HEUR transient network structures present in HEUR-latex composites with less than about 2% HEUR and 30% latex relevant for coatings applications. Crosslinked and hydrophobically modified poly(acrylic acid) was investigated by Alves<sup>26</sup> et al. with the swelling behaviour as triggered by ionization and surfactant binding. They found that viscosity, elasticity as well as transmittance of the solutions were dramatically affected when the pH exceeded 6.5, and additional anionic surfactant promoted the swelling of the polymer at low pH. Moreover, it was found that an increase in the surfactant chain length can strengthen the surfactant binding to the polymer. Wang<sup>28</sup> et al. examined the rheological characteristics of poly(acrylic acid) polymers in aqueous solutions at 20 °C, and proposed a model to simulate the rheological behaviour of the polymer solution in terms of a combination of processes involving of reptation, relaxation of the chains and normal Rouse dynamics.

However, thickeners not only increase the costs of coatings but also decrease their stability. For example, ASE thickeners are usually sensitive to electrolytes<sup>26</sup>. Cellulose thickeners and their derivatives are susceptible to enzymatic degradation<sup>29</sup> due to microbial contamination. HEUR thickeners may lead to undesired phase separation by strong bridging between particles<sup>30</sup>. In our recent work, a kind of core/shell acrylic latex with methacrylic acid-rich surface used for waterborne metallic coatings<sup>31, 32</sup> was prepared via core/shell seed emulsion polymerization according to the literature<sup>19</sup>, and the resultant latex could be directly thickened by DMEA. Later we added crosslinking agent DVB in

the shell portion of the above polymerization process and obtained crosslinked latex which was not sensitive to DMEA. However, the viscosity of the crosslinked latex increased markedly and exhibited strong thixotropy once it was treated with DMEA and EGBE together. The polymer structure of the crosslinked latex was characterized by Transmission Electron Microscope (TEM) and Fourier Transform Infrared Spectroscopy (FT-IR), and its swelling behaviours, interfacial properties as well as rheological properties with DMEA and EGBE were studied with DLS, tensiometer and rheometer respectively. The microstructure of particles in thickened dispersion was observed by SEM as well, and a novel latex thickening mechanism different from traditional thickeners is proposed.

## 2. Experimental

### 2.1 Materials

Methyl methacrylate (MMA,  $\geq 98\%$ ), butyl acrylate (BA,  $\geq 98\%$ ) and 2-hydroxypropyl methacrylate (HPMA,  $\geq 97\%$ ), methacrylic acid (MAA,  $\geq 98\%$ ), N,N-dimethylethanolamine (DMEA), ethylene glycol butyl ether (EGBE; A.P. grades, Sinopharm Chemical Reagent Co., Ltd, Shanghai), divinylbenzene (DVB,  $\geq 80\%$ , Tianjin Damao Chemical Reagent Factory), Anionic emulsifier of sodium lauryl sulfate (SLS) and reactive surfactant of sodium allyloxy hydroxypropyl sulfonate (AHPS; A.P. grade, Foshan Kodi Gas Chemical Industry Co., Ltd, Guangdong, China) were used as received. Ammonium persulfate (APS; A.P. grade, Sinopharm Chemical Reagent Co., Ltd, Shanghai) was the initiator. Deionized water was used throughout the work.

### 2.2 Synthesis of the latex

The core-shell acrylic latex was synthesized via seed emulsion polymerization, which was carried out under nitrogen atmosphere, using a 1-L four-neck flask equipped with a condenser, a mechanical stirrer and a digital thermometer. 0.54 g APS was dissolved in 24 g deionized water to prepare the initiator solution (2.20 wt%).

The polymerization process was divided into three parts. Firstly, 215 g deionized water and all emulsifiers including SLS and AHPS were charged into the flask and the reactants were heated to 76 °C under stirring, then 10 wt% mixture of the core portion consisting of MMA and BA based on Table 1 and 6 g initiator solution were fed into the flask and were stirred for 0.5 h. The resultant dispersion was used as seed latex. Secondly, the residual monomer mixture of the core portion and 10 g initiator solution were added dropwise to the same flask with two constant pressure dropping funnels respectively. The dropping process lasted for 1.5 h. Then the temperature of the system was maintained at 76 °C for another 1.5 h.

Thirdly, 160 g deionized water was charged into the same flask directly, then 8 g initiator solution and a monomer mixture of the shell portion based on Table 1 were added dropwise to the flask at a constant rate over a period of 1.5 h. Later the reactants in the flask were stirred at 80 °C for another 2 h to ensure complete monomer conversion. Later the reaction temperature was set to 40 °C and the latex was filtered with 400 mesh filter cloth. Samples with different DVB contents in the shell portion shown in Table 1 were prepared by the same method.

**Table 1** Recipes and basic properties of the core-shell acrylic latexes

Recipes	A1	A2	A3
Core portion /g			
MMA	52.0	52.0	52.0
BA	26.0	26.0	26.0
Shell portion /g			
MMA	15.0	15.0	15.0
BA	20.0	20.0	20.0
HPMA	6.0	6.0	6.0
MAA	7.0	7.0	0
DVB	6.0	0	6.0
Solid content (%)	24.8	24.8	24.8
Conversion (%)	98.5	98.9	98.5
$M_w$	$2.35 \times 10^5$	$2.16 \times 10^5$	$2.30 \times 10^5$
$M_w/M_n$	1.14	1.26	1.30

### 2.3 Characterization techniques

About 1g latex sample was added to a clean watch glass and was heated in an oven at 110 °C for 2 h, the residue was weighed. The solid content was calculated by the following formula:

$$\text{Solid content (wt\%)} = (W_2 - W_0) / (W_1 - W_0) \times 100\%$$

Where  $W_0$  is the weight of the watch glass, and  $W_1$  and  $W_2$  are the weights of sample before and after drying, respectively.

The monomer conversion was calculated by the following formula:

$$\text{Conversion (wt\%)} = [\text{Solid content (wt\%)} \times W_5 - W_4] / W_3 \times 100\%$$

Where  $W_3$  is the total weight of monomers,  $W_4$  is the weight of nonvolatile components during polymerization, and  $W_5$  is the total weight of latex.

The morphology of latex particles was observed by TEM (JEM-2100, Gatan, Acceleration voltage: 200 kV). The latex was diluted with water to about 1%, and 2% ammonium phosphotungstate was used as the staining reagent. The polymer structure was characterized by FTIR spectroscopy (Vertex 70, Bruker) with a scanning coverage from 4000 to 400  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$ . Number average mass weights ( $M_n$ ) and polydispersity index ( $M_w/M_n$ ) of polymers were determined by Size Exclusion Chromatography (SEC) calibrated with polystyrene standards with THF as eluent (1.0 ml/min) at 40 °C of columns and 50 °C of detector, and equipped with a Waters 717 plus auto sampler, a Waters 1515 isocratic HPLC pump and a Waters 2414 refractive index detector.

### 2.4 Thickening Process.

The thickening process of the core-shell acrylic latex with DMEA and EGBE was recorded with a digital camera. The latex treated with DMEA or 9 wt% (compared to the weight of the latex) EGBE was fully mixed at 25 °C and then was transferred to a clean glass bottle. All glass bottles were finally inverted to observe the flow properties of latexes.

### 2.5 Swelling Behaviour with DMEA or EGBE.

The effect of DMEA on the swelling behaviour of acrylic latex particles in water phase was investigated using DLS. In a typical sample preparation, 0.15 g DMEA was added to 10 g water to

prepare a solution of DMEA (1.48 wt%), and latex was diluted to 0.1 wt% with water, then DMEA solution was added to the diluted latex. The particle size and its distribution of the final dispersion were determined by Nano ZS Particle Sizer (Malvern, UK). The content of DMEA was expressed in terms of neutralization degree of MAA based on the neutralization reaction between DMEA and MAA.

The swelling behaviour of the latex with EGBE was also estimated using DLS: latex was diluted to 0.1 wt% with water and then absolute EGBE was added to the dispersion. The content of EGBE was expressed in terms of mass fraction compared to the solution. All DLS experiments were carried out at 25 °C.

## 2.6 Surface Tension Measurements.

The influence of EGBE on surface tension of latex was investigated using a Krüss Tensiometer K100 (Germany) at 25 °C. Latex was diluted to 0.1 wt% with deionized water, then absolute EGBE was added to the diluted latex and the changes in surface tension were measured. The content of EGBE was expressed in terms of mass fraction compared to the solution.

## 2.7 Microstructure Study and Thickening Mechanism.

The microstructure of particles in thickened dispersion was observed by SEM (Sigma, Zeiss, Germany). Samples were applied to small pieces of cover glass and dried at room temperature to form polymer film before test.

## 2.8 Rheological Behaviours.

The rheological properties of latex were investigated with a Haake RS600 rheometer (Germany). Two measurement geometries were used according to the sample viscosity: double gap cylinder system named DG41 for low viscosity sample, the radius is 17.75 mm and the length is 55 mm; plate-plate system named PP35 with 17.5 mm radius and 1° cone angle for high viscosity sample.

The shear rate in steady shear tests ranged from 0.1 to 1000 s<sup>-1</sup> in 120 s. In shear reversibility test the shear rate was firstly increased from 0.01 to 1000 s<sup>-1</sup> in 120 s, and then the shear rate was kept at 1000 s<sup>-1</sup> for another 30 s, finally the shear rate was decreased from 1000 to 0.01 s<sup>-1</sup> in 120 s, and shear viscosity vs time is shown in the picture.

The frequency sweep was carried out under constant shear stress predetermined to induce a 10% deformation at 1 Hz, which was within the linear viscoelastic regime.

For high viscosity sample centrifugation at 10<sup>4</sup> r/min was needed to eliminate bubbles before test. For each measurement, a fresh, degassed sample was prepared and kept at measurement temperature without pre-shearing or oscillating. All experiments were taken at 25 °C.

For simplicity, we take X, Y, Z as the amounts of latex, DMEA and EGBE used in each system respectively, the unit is gram. For example, X<sub>20.0</sub>Y<sub>0.27</sub>Z<sub>1.80</sub> means the amounts of latex, DMEA and EGBE in the system are 20.0 g, 0.27 g and 1.80 g respectively.

## 3. Results and discussion

### 3.1 Structure Characterization.

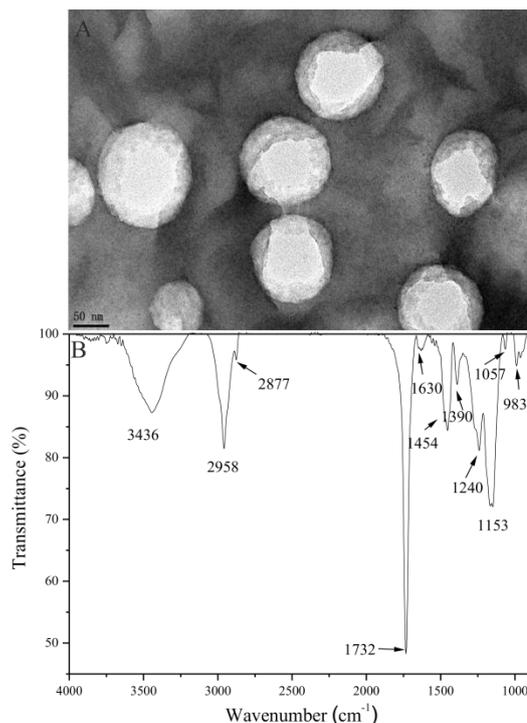


Fig. 1 (A) TEM image and (B) FT-IR spectra of A1.

The polymer structure of sample A1, which has some crosslinking monomer DVB in its shell part, was characterized by TEM and FT-IR spectra respectively. Fig. 1 (A) displays the TEM image of A1. It is clear that the latex particles were uniform spherical structures with bright core and relatively darker shell according to TEM observation. The number-average diameter of the particles was about 125 nm. As MAA and HPMA were hydrophilic and were added in the process of shell polymerization, it can be assured MAA and HPMA are concentrated in the shell region, resulting in the relatively darker image of shell part in the TEM picture.

The FT-IR spectra of A1 are shown in Fig. 1 (B). The wide band at 3436 cm<sup>-1</sup> belonged to stretching vibration of —COOH and —OH. The peaks at 2958, 2877 cm<sup>-1</sup> were attributed to stretching vibration of saturated C—H. The strong vibration absorption peak at 1732 cm<sup>-1</sup> for carbonyl, as well as the band at 1240, 1153 cm<sup>-1</sup> demonstrated there was ester group in the polymer structure. The wide band at 1630, 1530 cm<sup>-1</sup> was assigned to the stretching vibration of C=C from phenyl group, and the peaks at 1454, 1390 cm<sup>-1</sup> belonged to —CH<sub>3</sub>.

### 3.2 Thickening Process

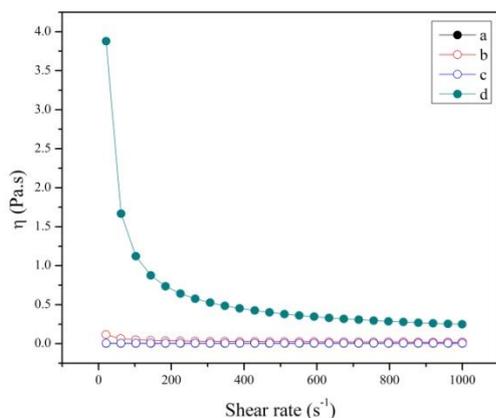
The thickening process of A1 with DMEA and EGBE was recorded with a digital camera and is shown in Fig. 2. When DMEA or EGBE was added to A1, as shown in Fig. 2 (b) and (c), the dispersion flowed down immediately when the bottle was inverted, showing DMEA or EGBE could not thicken the latex separately. In Fig. 2 (c) there was much precipitation stuck on the bottle, which is further shown in Fig. 2 (B). However, when DMEA and EGBE were both introduced in the system, the viscosity of A1 increased evidently, which flowed down the bottle quite slowly. A video of the thickening process of A1 with

DMEA and EGBE was also listed in Supporting Information for better observation of this procedure.

Rheological investigation, as a supplementary specification of the thickening process, was performed with a rotational rheometer, and the results are shown in Fig. 3. When A1 was treated with DMEA or EGBE, it exhibited capacity of low viscosity. Besides, the viscosity changed little with shear rate and



**Fig. 2** (A) Thickening process of A1, (a) A1,  $X_{20.0}Y_0Z_0$  (b) A1 added with DMEA (100% neutralization degree),  $X_{20.0}Y_{0.27}Z_0$ , (c) A1 added with 9 wt% EGBE,  $X_{20.0}Y_0Z_{1.80}$ , (d) A1 added with both DMEA (100% neutralization degree) and 9 wt% EGBE,  $X_{20.0}Y_{0.27}Z_{1.80}$ , (B) the white precipitation in the dispersion of A1 added with 9 wt% EGBE,  $X_{20.0}Y_0Z_{1.80}$ .



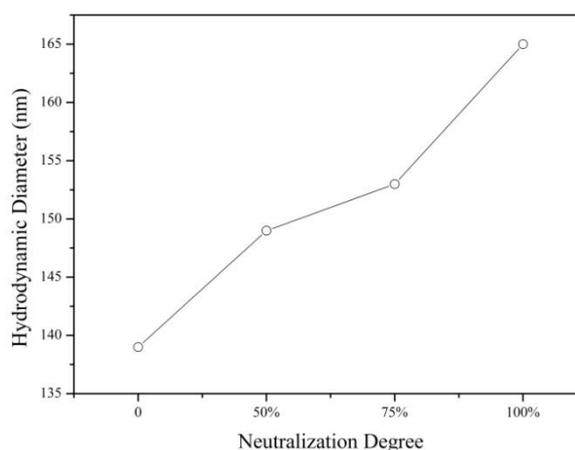
**Fig. 3** (A) Shear viscosity ( $\eta$ ) of A1 treated with different reagents, (a) A1,  $X_{20.0}Y_0Z_0$ , (b) A1 added with DMEA (100% neutralization degree),  $X_{20.0}Y_{0.27}Z_0$ , (c) A1 added with 9 wt% EGBE,  $X_{20.0}Y_0Z_{1.80}$ , (d) A1 added with DMEA (100% neutralization degree) and 9 wt% EGBE,  $X_{20.0}Y_{0.27}Z_{1.80}$ .

the latex behaved as Newtonian fluid, which suggests there is no strong interaction between the latex particles in the dispersion. However, once DMEA and EGBE were both added, viscosity of A1 elevated remarkably compared to samples in Fig. 3 (b) and Fig. 3 (c), showing a collective effect of EGBE and DMEA in latex thickening. The dispersion viscosity at moderate shear rate ( $10^3 \text{ s}^{-1}$ ) reached 0.249 Pa.s, which was much higher than that of the fully neutralized A1 sample (0.021 Pa.s) or EGBE added sample (0.004 Pa.s). Take the viscosity of all samples at  $1000 \text{ s}^{-1}$  for comparison, A1 latex viscosity is 0.003 Pa.s, only EGBE almost made no contribution to latex viscosity, while DMEA (100% neutralized) increased the latex viscosity about 7 times. However, when DMEA was added, EGBE increased latex viscosity about 80 times.

### 3.3 Swelling Behaviour

To reveal the thickening mechanism of A1, we investigated the swelling behaviours of latex particles when DMEA or EGBE was introduced in the dispersion. Variations of hydrodynamic diameter of sample A1 at different neutralization degree are showed in Fig. 4. As DMEA was added, the hydrodynamic diameters of the latex particles gradually increased from 139 to 165 nm because of carboxyl group ionization and polymer chain stretching<sup>33</sup>, which has been extensively reported in alkali-swelling thickeners<sup>26, 28, 33</sup>.

However, when EGBE was introduced in the dispersion, the swelling behaviour of the latex was quite different as shown in Table 2 and Table 3. Whatever the neutralization degree was, the average particle size of the latex was almost the same when the EGBE content increased. This indicated that EGBE can't swell the latex particles additionally. As EGBE content increased to 0.5 wt% the latex began to be unstable and there were some precipitate appeared in the dispersion. It seems that EGBE could not change particle size but destroy the stability of latex, and finally result in its precipitation (flocculation).



**Fig. 4** Hydrodynamic diameter data of the A1 sample at different neutralization degree.

**Table 2** Variations of hydrodynamic diameter with EGBE for A1 at 0% neutralization degree.

EGBE %	Diameter (nm)	PDI
0	139	0.017
0.01	135	0.026
0.06	138	0.066
0.16	136	0.022
0.25	136	0.028
0.50	aggregation	

**Table 3** Variations of hydrodynamic diameter with EGBE for A1 at 100% neutralization degree.

EGBE %	Diameter (nm)	PDI
0	165	0.026
0.02	163	0.046
0.05	165	0.003
0.16	162	0.021
0.25	158	0.018
0.50	aggregation	

### 3.4 Surface Tension Measurements

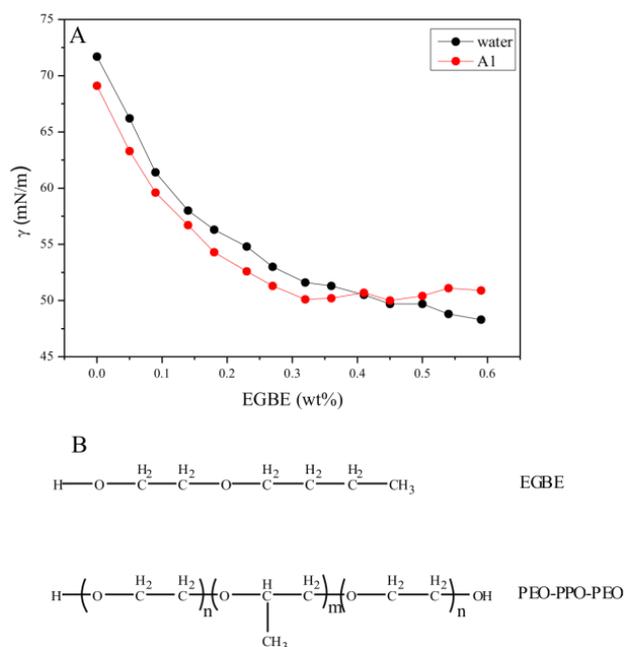
To investigate the reason for flocculation caused by introducing EGBE in the dispersion, we measured the surface tension ( $\gamma$ ) of the sample A1 and the results are shown in Fig. 5.

The initial  $\gamma$  of A1 was  $69.1 \text{ mN}\cdot\text{m}^{-1}$ , which was a little below the value of pure water ( $72 \text{ mN}\cdot\text{m}^{-1}$ ), implying that the latex stabilized by surfactants could decrease surface tension of water to some extent. Surface tension of the blank sample (pure water) continuously decreased from  $72 \text{ mN}\cdot\text{m}^{-1}$  to  $48 \text{ mN}\cdot\text{m}^{-1}$  with additional EGBE. However, for A1 sample the surface tension decreased firstly and then reached a plateau when the EGBE concentration was 0.4%. Further adding EGBE would result in evident flocculation on the surface of latex and the experiment could not continue. The experiment demonstrates that EGBE could decrease the surface tension of latex.

As we know, actually EGBE is a kind of coalescent agent<sup>34, 35</sup> widely used in coating industry. It has short hydrophobic terminal chain and hydrophilic head group —OH, which is a typical amphiphilic molecule structure (Fig. 5 (B)). Thus, the EGBE molecule can enter the interface phase to change the liquid/polymer interfacial properties. Meanwhile its short hydrophobic terminal chain is oleophilic which may interact with polymer or surfactants in the latex system. Moreover, the EGBE concentration (0.76 mol/L) was much higher than the total emulsifier (about 0.02 mol/L) in the dispersion, the flocculation phenomenon may be related to the amphiphilicity of EGBE, which makes it act as demulsifying agents<sup>36-38</sup>, impacting or competing with the emulsifiers at the liquid/latex particle interface, decreasing latex stability and inducing precipitation.

### 3.5 Microstructure Characterization

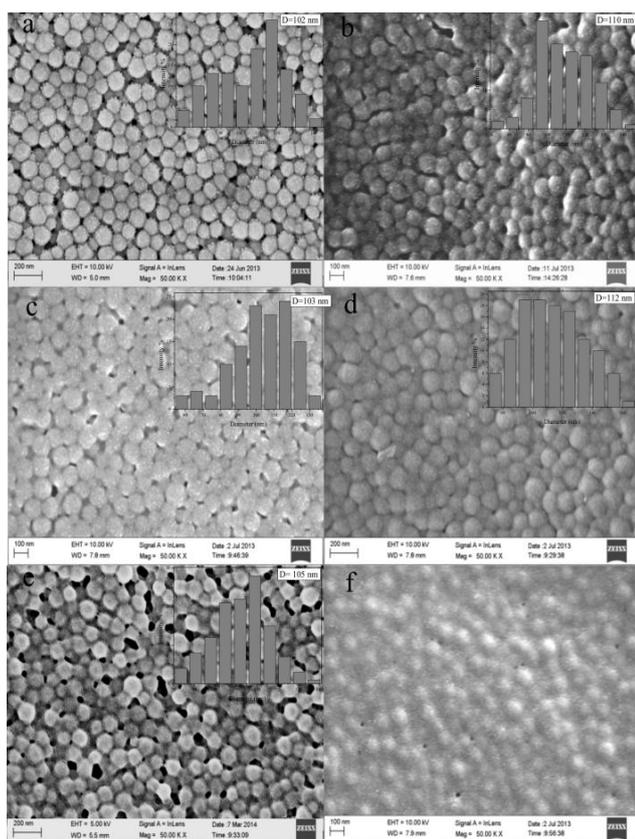
To further investigate the influence of DMEA and EGBE on the latex particles, SEM was utilized to study the microscopic morphology of sample A1 when DMEA or EGBE was added in the dispersion and the results are shown in Fig. 6.



**Fig. 5** (A) Surface tension ( $\gamma$ ), as a function of EGBE concentration for diluted A1 latex, (B) Structural formula of EGBE and PEO-PPO-PEO (a kind of demulsifier in oil extraction).

Fig. 6 (a) is the SEM image of sample A1, which shows that the latex particles were all spherical and nearly monodisperse with an average particle size of 102 nm. When A1 was neutralized with DMEA, the average diameter of the latex particles increased to 110 nm because of swelling (Fig. 6 (b)). These swollen particles retained their original spherical structures but linked together at this time. There was almost no gap between the swollen latex particles, indicating that a relatively stronger interaction between them. However, when sample A1 was mixed with EGBE without neutralizing, there was no marked change in particles size (103 nm) or morphology (Fig. 6 (c)), and the clear gap between the particles demonstrates that there is no strong interactions between them. Additionally, latex particles in the dispersion were linked to each other and their boundaries became a little vague, this should be due to the residual EGBE in aqueous phase because EGBE always contributes to polymer interdiffusion and forming film<sup>39, 40</sup> as a common cosolvent in coating industry. When A1 was added with both DMEA and EGBE, regularly packed spherical particles existed in this strongly-thickened sample (Fig. 6d), and the average diameter of the latex particles was about 112 nm. The space between particles was smaller in contrast to the ones in Fig. 6 (b) and (c), showing a relatively stronger interaction between latex particles under the combined action of DMEA and EGBE.

In order to distinguish the difference between traditional alkali thickening latex and the alkali-co-EGBE thickening sample in this work, latex A2 with better alkali-swellable ability was synthesized, whose recipe is shown in Table 1. Since there was no crosslinking agent DVB in the shell portion to limit the swelling of particles<sup>41, 42</sup>, A2 could be directly thickened by DMEA. The actual surface carboxyl groups concentration of A1 and A2 were also calculated by titration test, in which 50 mL 1.0%



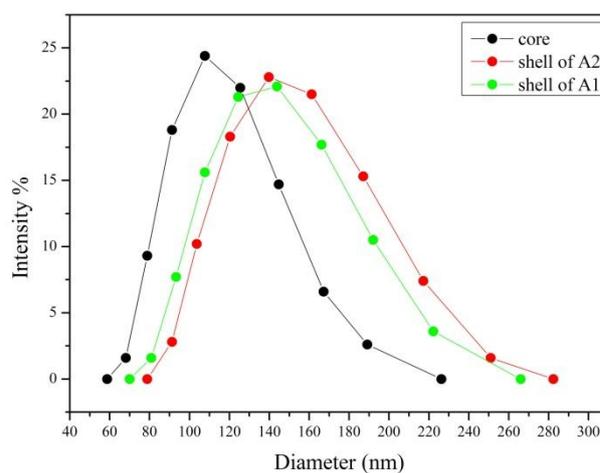
**Fig. 6** SEM images of A1 treated with different reagents, (a) A1,  $X_{20.0}Y_0Z_0$ , (b) A1 treated with DMEA (100% neutralization degree),  $X_{20.0}Y_{0.27}Z_0$ , (c) A1 treated with 9 wt% EGBE,  $X_{20.0}Y_0Z_{1.80}$ , (d) A1 treated with both of DMEA (100% neutralization degree) and EGBE (9 wt%),  $X_{20.0}Y_{0.27}Z_{1.80}$ , (e) A2,  $X_{20.0}Y_0Z_0$ , (f) A2 treated with DMEA (100% neutralization degree)  $X_{20.0}Y_{0.29}Z_0$ .

dilute solution of A1 or A2 was titrated with 0.01 mol/L NaOH standard solution, and phenolphthalein solution was the indicator. The volume consumption of NaOH solution and carboxyl groups concentration in dilute latex are shown in Table S1 (Supporting Information). The results demonstrate that A2 had higher surface carboxyl groups concentration than A1. The rheological behaviour and swelling behaviour of A2 are given in Fig. S1 and Fig. S2 (Supporting Information) as well.

The microstructure of A2 was studied by SEM further and the results are shown in Fig. 6 (e) and (f), which are A2 and A2 neutralized by DMEA respectively. It is observed that the average particle size of A2 sample was about 105 nm, which is a little bigger than A1. When DMEA was added to A2, the sample was thickened directly and all the latex particles in SEM observation (Fig. 6 (f)) were deformed because of strong swelling induced by DMEA neutralization. Compared to the A1 thickened sample (Fig. 6 (d)), particles in A2 thickened sample (Fig. 6 (f)) swelled much more and arrayed more compact than ever, the boundaries

of which almost disappeared therefore, indicating that the hydrophilic polymer chains in the shell part of the A2 latex particles can extend further and extrude with each other after being neutralized with DMEA<sup>19</sup>.

Moreover, as it is shown in Fig. 7, both the core and shell diameter distribution of A1 and A2 were quite narrow. The PDI (Polydispersity Index) for the core portion, the shell of A1 and the shell of A2 were 0.008, 0.018, 0.020 respectively, thus the above SEM results can get rid of the interference of a second population and the occurrence of water-soluble MAA oligomers.



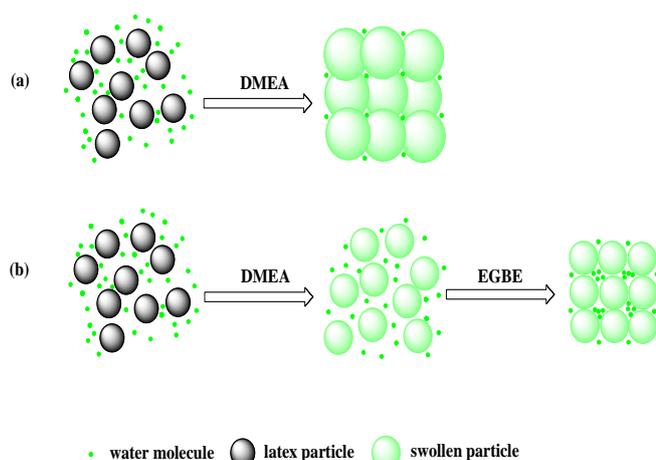
**Fig. 7** Core/shell diameter distribution for A1 and A2.

### 3.6 Thickening Mechanism.

Taking the above results into consideration, it is not difficult to find that alkali-swelling ability and EGBE flocculation effect are critical to latex thickening. When there was no acid monomer in the polymerization process of A1, the resultant latex (named A3) could not be thickened no matter what you use (Supporting Information Fig. S3). Besides, apart from DMEA, there are other alkalis such as triethylamine (TEA) and NaOH which could be used to neutralize and thicken the latex (Supporting Information Fig. S4), so we infer that there are no direct interactions between DMEA and EGBE,<sup>43, 44</sup> and alkali-swelling ability and EGBE flocculation effect are the main factors responsible for the thickening of A1. Scheme 1 was illustrated to get a better understanding of this double thickening mechanism.

Scheme 1 (a) depicts the alkali thickening process of the common alkali-swelling latex. When DMEA is added to the dispersion, the latex particles (black ball) swell with a large part of dissociative water (green dot). The electrostatic repulsion between carboxyl groups increases, resulting in polymer chain stretching and bigger hydrodynamic volumes of latex particles. Swollen latex particles (green ball) extrude with each other and the residual water molecules are restricted in the gaps of the close-arrayed swollen particles, thus a network is established in the dispersion<sup>19</sup>.

Scheme 1 (b) describes the alkali and EGBE double thickening process of A1 sample. Latex particles are dispersed in water at first, then DMEA is added and the latex particles swell a little because of the limitation of DVB in the shell part. In this process

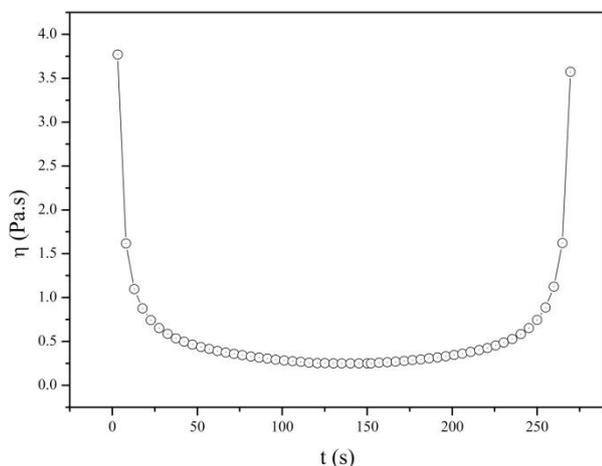


**Scheme 1** Thickening mechanism of the acrylic latex with DMEA and EGBE

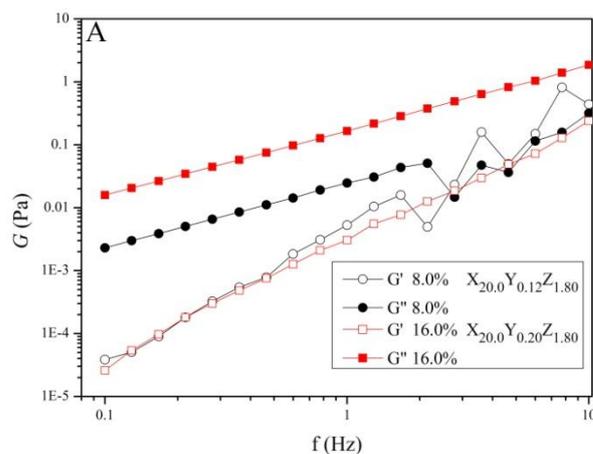
dissociative water molecules are consumed partially. Later EGBE is added and the partially swollen latex particles are inclined to precipitate because of the demulsifying effect of EGBE. The residual dissociative water molecules are restricted in the gaps of the swollen particles and a network is built up.

### 3.7 Rheological Behaviours

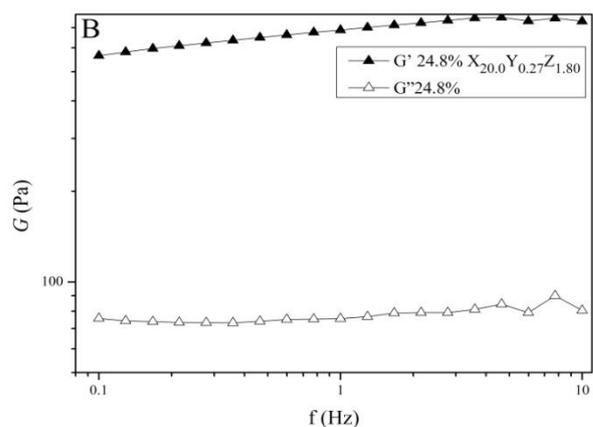
Finally we investigated the rheological behaviours of A1 thickened dispersion, whose shear reversibility is shown in Fig. 8 (the alkali used in the below rheological tests is DMEA). As we can see, in the first 120 s when the shear rate was increased from 0.01 to 1000  $\text{s}^{-1}$ , the dispersion viscosity decreased from 3.770 Pa.s to 0.252 Pa.s. The middle 30 s was the period of constant shear rate (1000  $\text{s}^{-1}$ ), and in the final 120 s when the shear rate was decreased from 1000 to 0.01  $\text{s}^{-1}$ , the dispersion viscosity increased from 0.250 Pa.s to 3.573 Pa.s, showing that the dispersion is shear reversibility with thixotropic properties.



**Fig. 8** Shear reversibility of A1 thickened dispersion,  $X_{20.0}Y_{0.27}Z_{1.80}$



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**Fig. 9** Dependence of elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) on frequency ( $f$ ) for the thickened dispersion of A1 with different volume fractions.

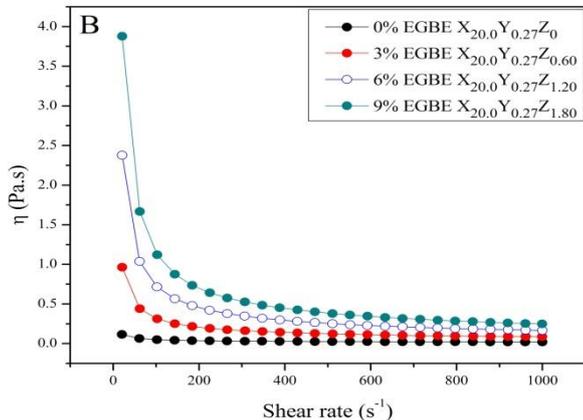
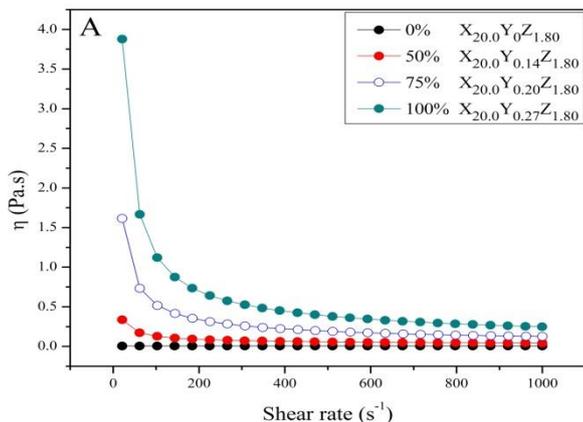
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Fig. 9 shows the dependence of elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) on frequency ( $f$ ) for the thickened dispersion of A1 with different volume fractions. When the solid content was 8.0%, the whole moduli were quite small and the latex was not thickened, at low frequency the viscous modulus  $G''$  was higher than elastic modulus  $G'$ , showing that the dispersion behaves as liquid<sup>45</sup>. When the frequency was higher than 2 Hz,  $G''$  was close to  $G'$ . When the solid content was 16.0%, the whole moduli were quite small as well and the latex was not thickened too,  $G''$  was always higher than  $G'$  in the whole scan region, showing that the viscous properties dominates in the dispersion. The whole moduli of latex with 16% solid content are a little higher than that of the latex with 8% solid content since the polymer concentration was elevated, and in both dispersions the moduli strongly depended

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on frequency. When the solid content was 24.8%, the latex was markedly thickened. Its moduli increased dramatically and  $G'$  increased to about 600 Pa.  $G'$  was always higher than  $G''$  in the whole scan region and the moduli were almost independent of frequency, showing that the dispersion behaves as solid<sup>45</sup>. The above results show that the viscoelasticity of the thickened dispersion of A1 is strongly dependent on latex concentration.

The viscosity dependence of thickened A1 dispersion on neutralization degree and EGBE content are shown in Fig. 10. Samples in Fig. 10 (A) were A1 added with 9 wt% EGBE and different contents of DMEA. When the neutralization degree of



**Fig. 10** (A) The dependence of A1 thickened dispersion viscosity ( $\eta$ ) on neutralization degree (samples in the test were added with 9 wt% EGBE and different contents of DMEA), (B) The dependence of A1 thickened dispersion viscosity ( $\eta$ ) on EGBE contents (samples in the test were 100% neutralized and added with different contents of EGBE).

the samples increased from 0% to 100%, the dispersion viscosity (at  $1000 \text{ s}^{-1}$ ) increased from 0.004 Pa.s to 0.249 Pa.s because of better swelling. However, if A1 was fully neutralized, its viscosity (at  $1000 \text{ s}^{-1}$ ) increased from 0.021 Pa.s to 0.249 Pa.s with EGBE content increasing from 0 wt% to 9 wt%, as shown in Fig. 10 (B). Further adding EGBE to the neutralized A1 dispersion would be difficult to flow owing to high viscosity (Supporting Information Fig. S5). The result shows that the A1 viscosity could be controlled by neutralization degree and EGBE content, and the latex viscosity could be easily adapted for different actual applications. Besides, the thickened dispersion of A1 is quite stable, and there was no phase separation or evident viscosity change when the sample was stored in a sealed glass bottle at room temperature for 6 months (Fig. S6, Supporting Information).

In our latest work, this co-thickening model was demonstrated effective even in traditional emulsion polymerization system without core/shell structure. The copolymer of MAA, MMA and BA, which was named B1, was prepared by traditional emulsion polymerization method using the same emulsifiers in A1. Its structure characterization and basic properties are shown in Fig. S7 and Table S2 (Supporting Information). B1 were spherical particles (diameter about 50 nm) with similar FTIR spectra with A1, and it was not sensitive to DMEA at first since its carboxyl groups were embedded inside the copolymer. When we treated B1 with DMEA and EGBE together it was thickened, whose thickening process and particles accumulation form in SEM were almost the same with A1 (Supporting Information Fig. S8 and Fig. S9). It seems that the alkali and cosolvent co-thickening mechanism is also applicable in common emulsion polymerization system. Furthermore we replaced MMA with styrene (St) in the recipe of B1 and found the resultant latex could be thickened by DMEA and EGBE as well. As a result, we infer that this co-thickening mechanism is very likely to be a universal principle.

#### 4. CONCLUSIONS

A kind of core-shell acrylic latex was synthesized through core/shell seed emulsion polymerization, when the latex was neutralized with dimethylethanolamine (DMEA), it could be thickened with additional ethylene glycol butyl ether (EGBE). Dynamic Light Scattering results revealed that DMEA swelled the particles while EGBE could not change particles diameter. Surface tension test demonstrated that EGBE could decrease the interfacial tension of latex, and we attribute the flocculation effect of EGBE to its amphiphilic properties. Scanning Electron Microscope results showed that the particles in DMEA and EGBE thickened dispersion retained their spherical structure and regularly arrayed, while particles in the dispersion which was directly thickened by DMEA were deformed and more closely packed, and their spherical boundary disappeared out of marked swelling. Alkali-swelling ability and EGBE flocculation effect are the main factors responsible for the thickening of latex.

The alkali and cosolvent co-thickened latex is shear reversibility, whose viscoelasticity is strongly dependent on latex concentration (solid content). The rheological properties of the thickened latex could be controlled by neutralization as well as cosolvent content, thus the appearance of the latex could be transformed from fluid to nearly-solid like paste. Besides, this co-thickening method was found to be effective even in traditional emulsion polymerization system. The newly thickening mechanism utilizes latex itself to thicken, which is quite different from traditional thickening mechanisms; it strengthens the alkali thickening effect by co-solvent flocculation effect, avoids the incompatibility and shortcomings of thickeners with the latex (in most case the structure of thickeners and polymer in the latex are not similar), and offers a new approach for us to thicken the latex. In addition, the method makes it possible to combine resin, thickener and coalescent in a simple and stable formula, which is hoped to bring in technological innovations in waterborne coatings field.

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## Notes and references

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*Graphical abstract*

In this work, alkali-swellable acrylic latex (resin) and coalescent ethylene glycol butyl ether were combined to thicken the coating without thickeners.

