

Synthesis of High Solid Content Waterborne Polyurethanes with Controllable Bimodal Particle Size Distribution

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ABSTRACT: A series of waterborne polyurethane dispersions were synthesized by one-pot reaction and step-wise reaction, respectively. The effects of synthetic methods and DMPA content on the particle size distribution (PSD), solid contents and viscosity were studied by laser particle size analyzer, Brookfield viscometer and TEM analysis. High solid content and low viscosity waterborne polyurethanes (WPU) with controllable bimodal PSD were prepared by one-pot reaction using 2,2-dimethylol propionic acid (DMPA) as the only self-emulsifier. Meanwhile, 40% solid content WPU with unimodal PSD were obtained by step-wise reaction at the same formula. With the increment of DMPA content, the ratio of large particles to small particles decreased and two peaks of the particle size finally became one peak by one-pot reaction while the PSD remained unimodal by step-wise reaction. The reason leading to the difference of PSD between one-pot reaction and step-wise reaction was analyzed and the relationships among PSD, viscosity and solid content were discussed. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40420.

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INTRODUCTION

Owing to the strong call for low releasing of volatile organic compounds (VOCs) to the atmosphere, organic solvent-based polyurethanes (PUs) are increasingly being restricted.^{1–4} Waterborne polyurethanes (WPU) are the rapidly developing segment of the polyurethane industry due to environmental legislations such as the clean air act and technological advances that have made it an effective substitute for the solvent-based analogs.^{5,6} With excellent mechanical and chemical properties, WPU have gained numbers applications as coatings and adhesives for wood and automobiles as well as for numerous flexible substrates, such as textiles, leather, paper, and rubber.^{7–10}

Despite the advantages mentioned above, the drying rate of WPU is much slower compared with the solvent-based polyurethanes at the same solid content because of the high latent heat of evaporation of water.¹¹ Therefore, the drying time and energy consumption of WPU increased, which was difficult to

meet the requirement of time efficiency and economic benefit. To solve this problem, the research is mainly focused on the preparation of high solid content WPU now.

High solid content waterborne polyurethane is of growing interest owing to the following advantages: high specific productivity, short film-forming time, and low storing and transporting cost.¹² However, in most of the previous researches, the solid content of waterborne polyurethane only ranges from 20 to 40%.^{13–17} There are only several articles on WPU with solid content higher than 50% in the open literature since it is hard to synthesize WPU with a solid content above 50% as the viscosity is highly sensitive to solid content.^{11,18–20} In these articles, the preparation of WPU with high solid content was mainly by mixing sulfonate-type and carboxyl-type self-emulsifiers together or by mixing macro glycol with sulfonic group and polyester diol as soft segments, which may lead to a broad or multimodal particle size distribution. And the articles on WPU

with high solid content by using DMPA as the only self-emulsifier are difficult to find, which is hard to meet the industrial needs since only using DMPA as the self-emulsifier is low-cost and convenient for the WPU industry.

Particle size distribution is declared to be the most important parameter in determining the relationship between solid content and viscosity in an emulsion.^{21,22} Generally, the viscosity of emulsion will slowly increase as a function of the solid content until it approaches some limiting value.²³ As it gets close to this upper limit of the volume fraction of solids, viscosity begins to increase very rapidly, with a small increase in solid content leading to a huge increase in viscosity.²⁴ Emulsions with multimodal PSD usually have a lower viscosity compared to those with unimodal particle size distribution since small particles are able to fit into the interstices between large particles with multimodal PSD.²⁵ Therefore, increasing the solid content of the emulsions entails the strict control of a complex PSD which must be either broad or multimodal to obtain solid content above 50%.²⁶

In the preparation of WPUs, diisocyanates, macro glycols, self-emulsifiers and chain extenders are usually used to build up the backbone of polyurethane. According to the reaction sequence, there are two methods to prepare WPU, namely one-pot reaction and step-wise reaction. In one-pot reaction, four raw materials mentioned above are charged into the reactor by one step and reactions among four materials happen at the same time. As for step-wise reaction, diisocyanates and macro glycols are charged into the reactor to react for a period of time first, followed by the addition of self-emulsifiers and chain extenders. One-pot reaction is more eco-friendly and energy-efficient compared with step-wise reaction.^{27,28} However, few articles focused on the impact of two different methods on the particle size distribution and the solid content of WPUs.

In this study, high solid content (around 50%) waterborne polyurethanes with bimodal particle size distribution were prepared by one-pot reaction. With the increment of DMPA content, the ratio of large particles to small particles decreased gradually and the bimodal peaks finally became one peak. Meanwhile, waterborne polyurethanes with unimodal particle size distribution were prepared by step-wise reaction and the solid content was limited to 40%. The reason leading to the difference of PSD between one-pot reaction and step-wise reaction was analyzed. We hope that this work will provide a promising method to prepare high solid content WPUs by flexibly controlling the particle size distribution using DMPA as the only self-emulsifier.

EXPERIMENTAL

Material

Isophorone diisocyanate (IPDI, Analytical grade), 2,2-dimethylol propionic acid (DMPA, 98% purity) and di-*n*-butylamine (DNBA) were purchased from Aladdin reagent. Poly propylene glycol (PPG, $M_w = 1000$), 1,4-butanediol (BDO), ethanol and triethylamine (TEA) were supplied by Shanghai Chemical Reagent Corporation (Shanghai, China). Acetone, *N*-methyl pyrrolidone (NMP), and dibutyltin dilaurate (DBTDL) were purchased from J&K China Chemical. PPG and DMPA were dried in vac-

uum at 100°C for 8h before use. The solvents and chemicals were used as received unless stated.

Preparation of WPU Dispersions

WPU Dispersions by One-Pot Reaction. The synthesis of the prepolymer based on PPG, DMPA, BDO, and IPDI, catalyzed by DBTDL was carried out in the presence of N₂ atmosphere. The mixture was reacted at 80°C until the theoretical NCO content of the prepolymer was reached, as determined by the di-*n*-butylamine titration method. Then, di-butylamine was added to react for 30mins to make sure that there was no residual NCO group. The mixture was cooled to 50°C and TEA was added. Acetone was added at the same time to reduce the viscosity. The neutralization reaction proceeded at the same temperature for 30 min. Then, distilled water was added to the mixture with vigorous stirring (based on 50% solid content, except for PU-5). Finally, WPUs with high solid content was obtained after the removing of acetone. The compositions of the prepolymer were listed in Table I, and the reaction process as shown in Scheme 1.

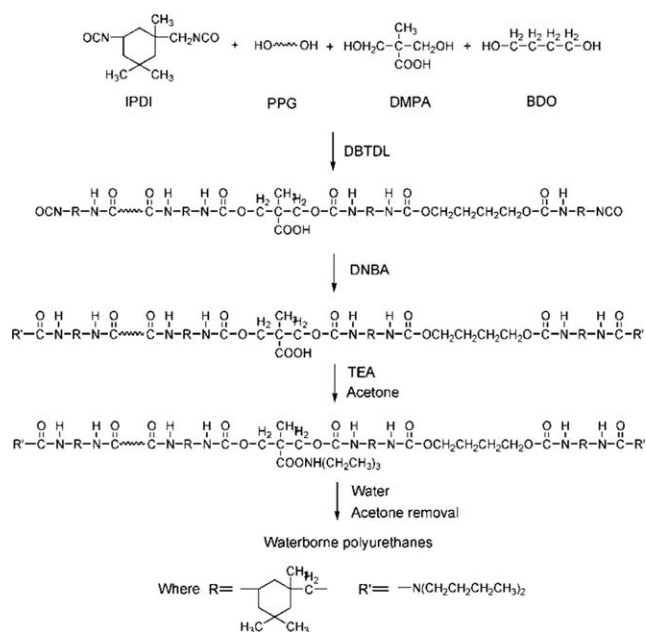
WPU Dispersions by Step-Wise Reaction. IPDI and PPG were first charged in the reactor, catalyzed by DBTDL in the presence of N₂ atmosphere. The reaction was reacted at 80°C until the theoretical NCO content of the prepolymer was reached, as determined by the di-*n*-butylamine titration method. Then, DMPA was added to react for 2 h to bring the backbone hydrophilicity. After that, BDO was added to react for 2 h. Then, di-butylamine was added to react for 30 min to make sure that there was no residual NCO group. The mixture was cooled to 50°C and TEA was added. Acetone was added at the same time to reduce the viscosity. The neutralization reaction proceeded at the same temperature for 30 min. Then, distilled water was added to the mixture with vigorous stirring (based on 40% solid content). Finally, WPUs were obtained after the removing of acetone. The compositions of the prepolymer were listed in Table I, and the reaction process as shown in Scheme 2.

CHARACTERIZATION

The FTIR spectra of the dispersions were recorded with a Thermo Fisher Nicolet 6700 type FTIR spectrophotometer. Each sample was scanned 64 times at a resolution of 4cm. All of the spectra were scanned within the range 400–4000 cm⁻¹. To ensure the reproducibility of the results, each sample was scanned at three different locations.

Table I. Synthetic Constitutions of WPUs Prepolymers

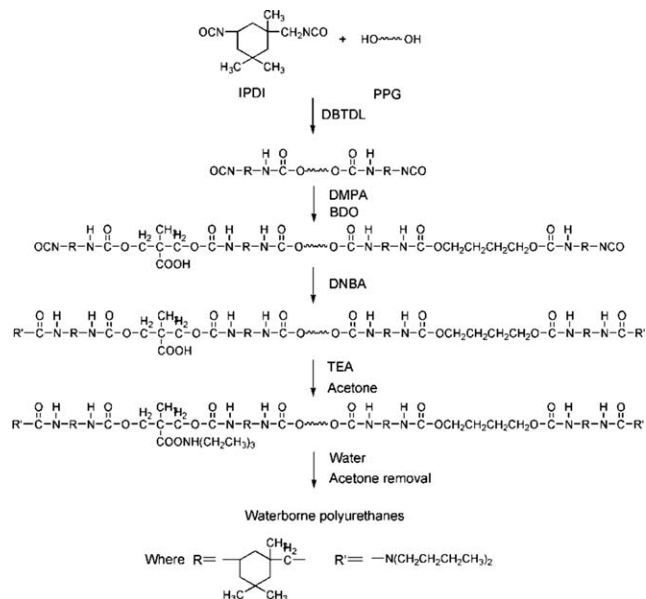
| Samples | IPDI (g) | PPG (g) | BDO (g) | DMPA (g) | DNBA (g) | DMPA content (mmol g ⁻¹) |
|---------|----------|---------|---------|----------|----------|--------------------------------------|
| PU-1 | 8.892 | 26.0 | 0.450 | 0.670 | 1.1 | 0.139 |
| PU-2 | 8.892 | 26.0 | 0.405 | 0.738 | 1.1 | 0.153 |
| PU-3 | 8.892 | 26.0 | 0.360 | 0.804 | 1.1 | 0.167 |
| PU-4 | 8.892 | 26.0 | 0.315 | 0.872 | 1.1 | 0.181 |
| PU-5 | 8.892 | 26.0 | 0.270 | 0.938 | 1.1 | 0.196 |



Scheme 1. Preparation process of waterborne polyurethanes by one-pot reaction.

The viscosity of the WPU dispersions was measured in a Brookfield digital viscometer (Modal DV-III). Measurement was carried out at 25°C, by using the spindle NO.18 at 10 rpm.

The particle size and its distribution of the dispersions were analyzed by dynamic light scattering (Malvern Zetasizer Nano-ZS), using a monochromatic coherent He-Ne laser (633 nm) as the light source and a detector that detected the scattered light at an angle of 90. The sample was first diluted in deionized water to a concentration of 0.1 wt %, followed by ultrasonic wave treatment to homogenize the dispersion.



Scheme 2. Preparation process of waterborne polyurethanes by step-wise reaction.

Transmission electron microscopy (TEM) images were obtained from a HITACHI-H7650 Microscope with an accelerating voltage of 80 kV and the samples were stained by 0.2 wt % phosphotungstic acid hydrate before observation.

The solid content of the dispersion was detected by drying it at 80°C for 3 days and calculating the weight ratio of residue to the dispersion.

RESULTS AND DISCUSSION

As seen in Figure 1, the disappearance of peaks at 2270 cm^{-1} and the appearance of peaks at 3313 cm^{-1} indicated that all the $-\text{NCO}$ groups might have sufficiently reacted with the hydroxyl groups and amino groups. The peaks at 1734 cm^{-1} were very sharp, mainly owing to the presence of $\text{C}=\text{O}$ in the urethane and urea segments. The peaks at 1108 cm^{-1} were ascribed to the stretching vibration of the $\text{C}-\text{O}-\text{C}$ of ether in the soft segment of WPUs.^{29,30} As shown in the FTIR spectroscopy, the difference between one-pot reaction and step-wise reaction was not obvious, which was ascribed to the same formula used by two methods.

Particle Size Distribution of WPU by One-Pot Reaction and Step-Wise Reaction

Varying the DMPA content, a series of WPU dispersions were prepared by one-pot reaction and step-wise reaction respectively (Table I). It was interesting to find that all samples except for PU-5 exhibited bimodal particle size distribution by one-pot reaction while all samples had unimodal particle size distribution by step-wise reaction, as shown in Figures 2 and 3.

The difference of particle size distribution between one-pot reaction and step-wise reaction at the same formula was first reported by our group. As a matter of fact, some researchers just have found that WPU may exhibit broad or bimodal particle size distribution at some specific conditions by one-pot reaction.^{19,31} However, the authors didn't make a further research on the phenomena and give a detailed explanation about the reason that caused bimodal particle size distribution by one-pot reaction.

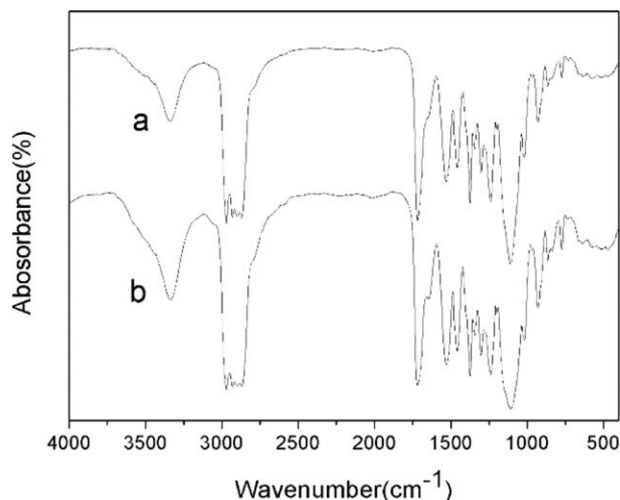


Figure 1. FTIR spectroscopy of the WPUs, (a) by one-pot reaction and (b) by step-wise reaction.

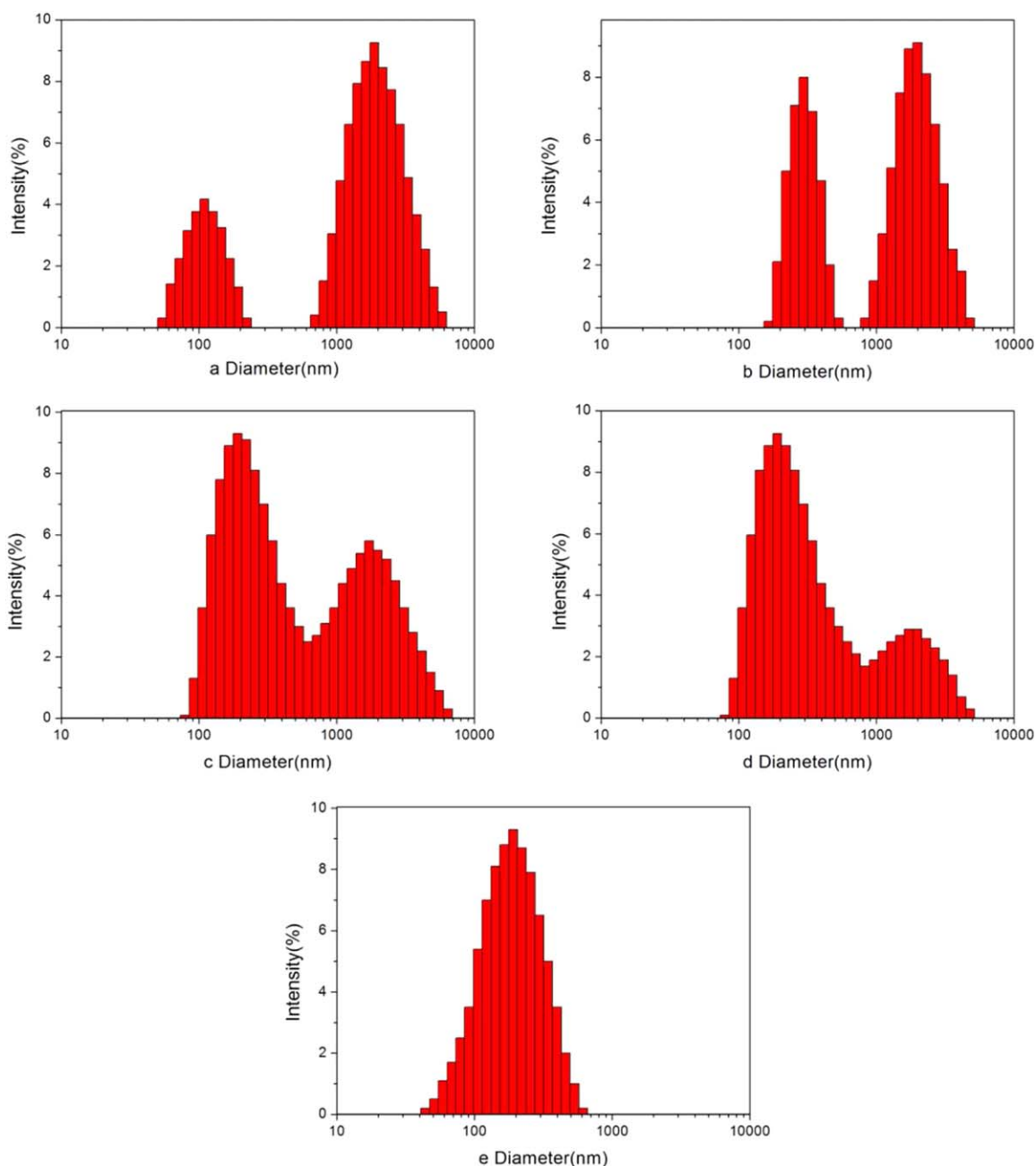


Figure 2. Particle size distribution of WPUs with different DMPA content by one-pot reaction, (a) PU-1; (b) PU-2; (c) PU-3; (d) PU-4; (e) PU-5(40% solid content). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Here, we presumed that the reason causing bimodal particle size distribution of WPU by one-pot reaction was attributed to the inhomogeneous distribution of carboxyl groups among polyurethane backbones. In one-pot reaction, four raw materials were charged into the reactor at the same time and diisocyanate (IPDI) began to react with macro glycol (PPG), self-emulsifier (DMPA) and chain extender (BDO). With secondary hydroxyl groups and a higher molecular weight, PPG has a lower reactivity with IPDI than DMPA and BDO. As a result, at the beginning of the reaction more DMPA and BDO tended to react with IPDI, leading to polyurethane backbones with high carboxyl group content. With the reaction going on, DMPA con-

tent in the mixture decreased gradually and more PPG tended to react with IPDI, leading to polyurethane backbones with low carboxyl group content correspondingly. After end-capped by di-butylamine and neutralized by triethylamine, polyurethanes with high carboxyl group content tended to generate small particles while polyurethanes with low carboxyl group content tended to generate large particles. As for step-wise reaction, PPG reacted with IPDI first, followed by the chain extending by DMPA and BDO. In this way, carboxyl groups were homogeneously distributed among polyurethane backbones, leading to unimodal particle size distribution of WPU by step-wise reaction.

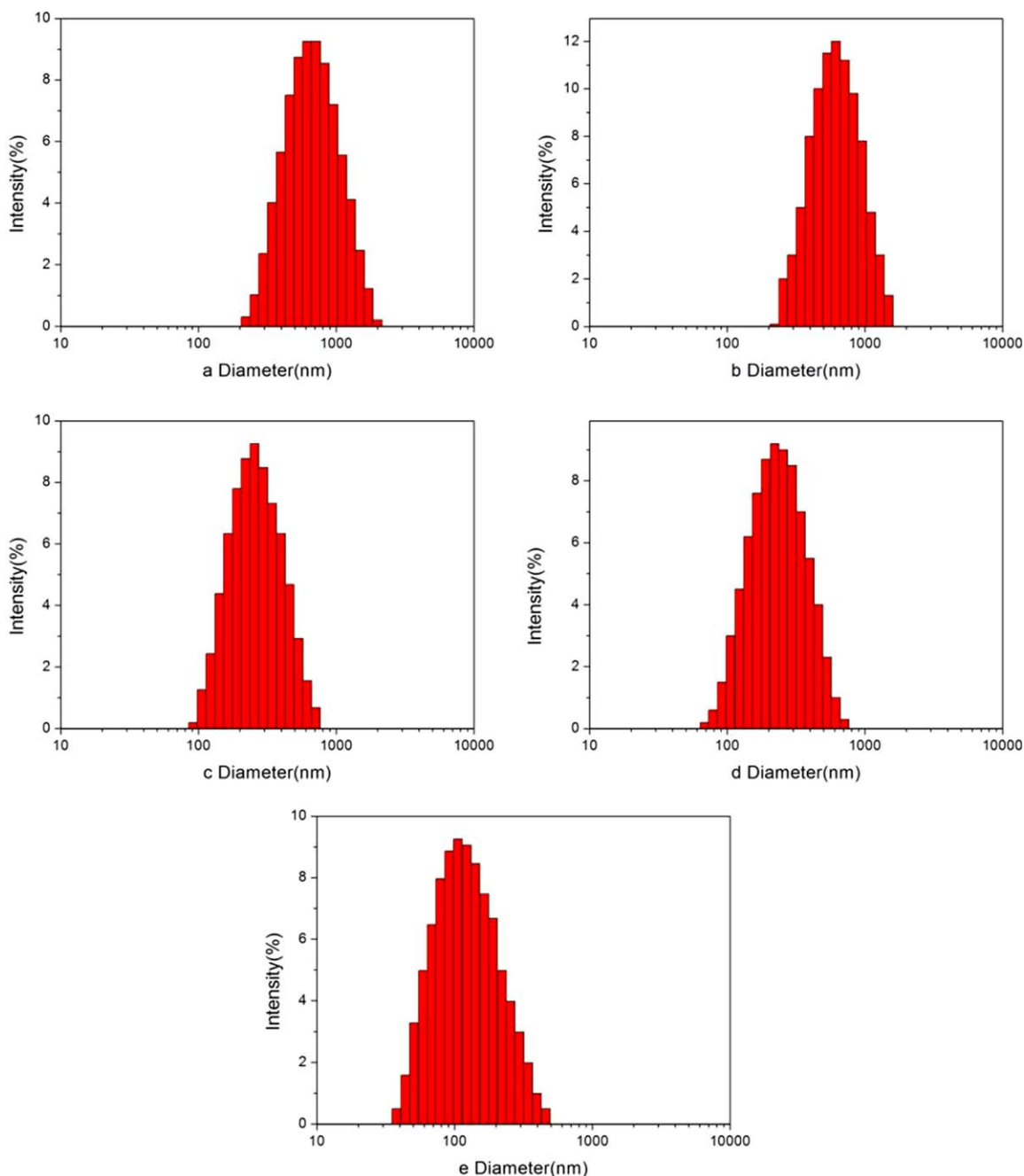


Figure 3. Particle size distribution of WPU with different DMPA content by step-wise reaction, (a) PU-1; (b) PU-2; (c) PU-3; (d) PU-4; (e) PU-5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To prove the above assumption, we set two parallel experiments of PU-2, defined as PU-6 and PU-7 to exclude the possible impact of solvent and end-capped reagent on the bimodal PSD of WPU. In the first experiment, *N*-methyl pyrrolidone (NMP) was used to dissolve the DMPA. Generally speaking, DMPA has a poor solubility in macro glycol and NMP is ordinarily used to dissolve the DMPA in industry. As a kind of solvent with high boiling point, NMP is difficult to remove from WPU, leading to a negative influence on environment and human health. As a result, NMP was not used in the former experiment in one-pot reaction, which may cause inhomogeneous distribution of car-

boxyl group on polyurethane backbone. From Figure 4(a) it was found that PU-6 still remained bimodal particle size distribution after DMPA was fully dissolved in NMP. The particle size of PU-6 (681.3 nm) was slightly bigger than PU-2 (637.7 nm), which may be caused by a decrease in surface activity of the surface of PU particles induced by NMP.³²

As a substitute for di-butylamine, ethanol was used to be the end-capped reagent in the second experiment which was defined as PU-7. From Figure 4(b), it was found that PU-7 had a bimodal particle size distribution similar to PU-2. The average

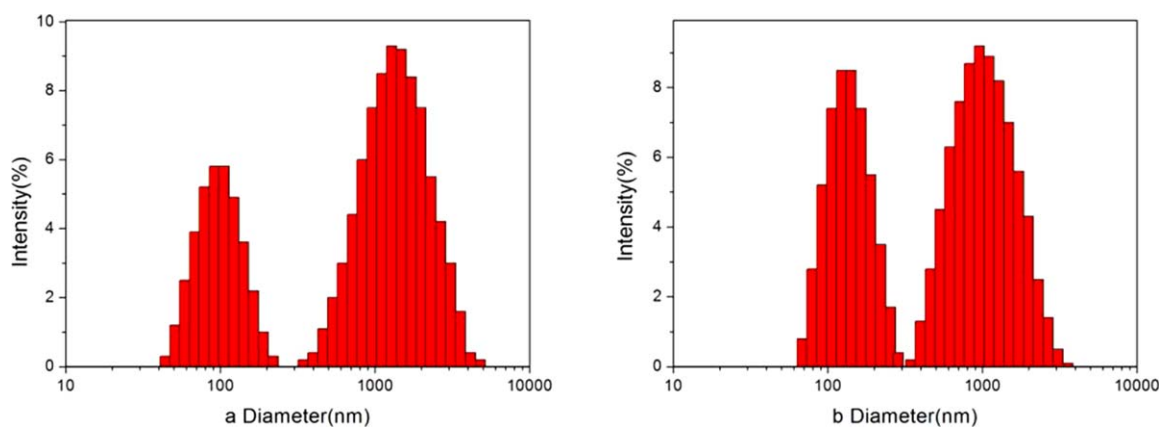


Figure 4. Particle size distribution of WPU by one-pot reaction, (a) PU-6; (b) PU-7. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

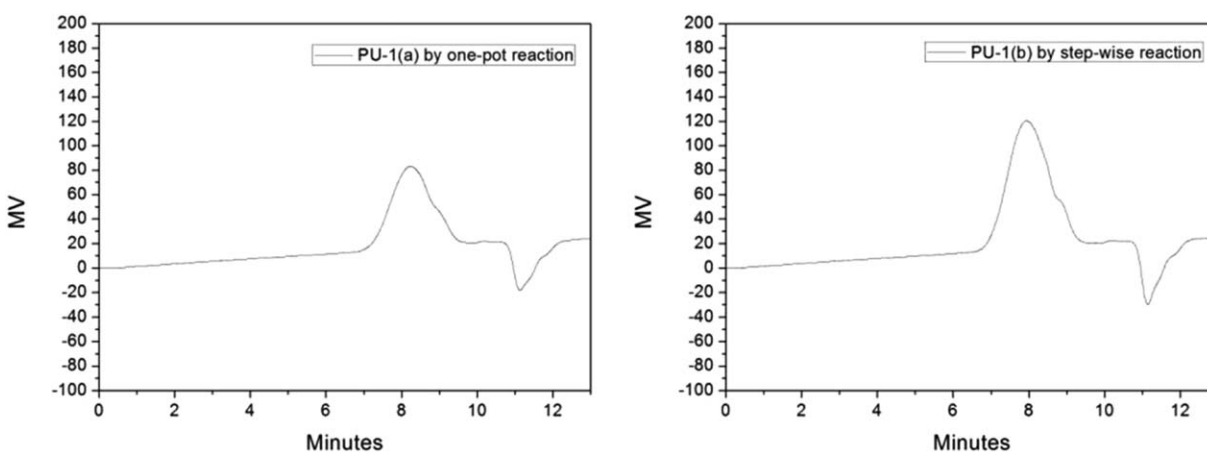


Figure 5. GPC chromatogram of PU-1 by one-pot reaction and step-wise reaction.

particle size of PU-7 was 524.6 nm, smaller than the particle size of PU-2, which was possibly induced by the different hydrophilicity of urethane linkage and urea linkage.^{33,34} Di-butylamine was used as the end-capped reagent in PU-2, generating the urea linkage at the end of the PU-2 backbone while urethane linkage was generated in PU-7 because the use of ethanol. Urethane linkage had a better hydrophilicity compared with urea linkage, resulting in a smaller particle size of PU-7.

To further confirm the assumption, the molecular weight and distribution of PU-1 prepared by one-pot reaction and step-wise reaction were tested by GPC respectively. From Figure 5, it was shown that the molecular weight of PU-1(b) ($M_w = 10,020$) by step-wise reaction was similar to PU-1(a) ($M_w = 9800$) by one-pot reaction and the molecular weight polydispersity of PU-1(a) (PDI = 1.85) and PU-1(b) (PDI = 1.83) was close. GPC data proved that molecular weight and distribution are not the reason leading to the different particle size distribution of WPU by two methods.

From Figure 2, it was interesting to see that the intensity of large particles decreased gradually and the intensity of small particles increased correspondingly with the increment of

DMPA content. Moreover, the intensity peaks of WPU were getting closer till to one peak (PU-5). Figure 6 showed that the PDI decreased gradually by increasing the DMPA content by one-pot reaction, which was in accordance with what

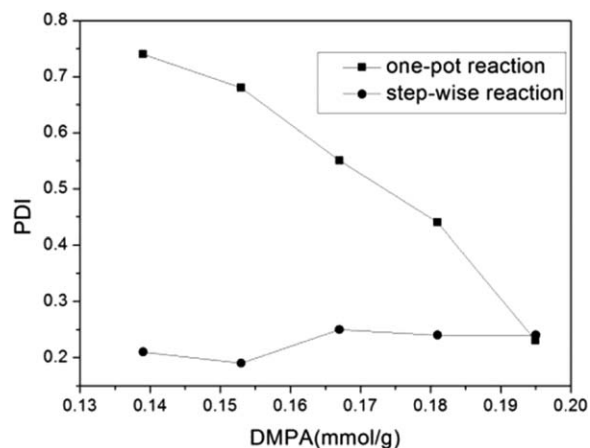


Figure 6. Particle polydispersity index (PDI) of the WPU with different DMPA content by one-pot reaction and step-wise reaction.

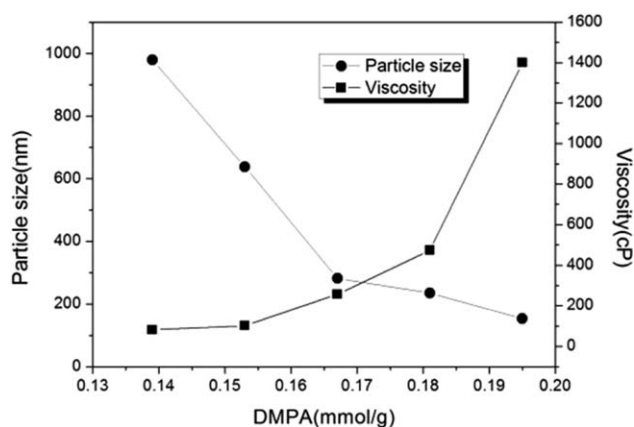


Figure 7. Particle size and viscosity of the WPU with different DMPA content by one-pot reaction.

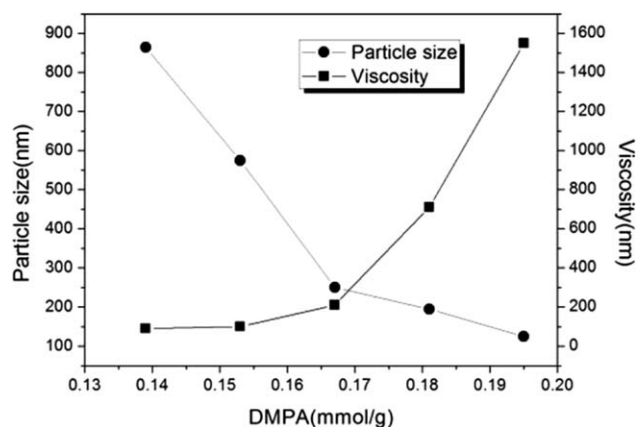


Figure 8. Particle size and viscosity of the WPU with different DMPA content by step-wise reaction.

Figure 2 showed. As stated above, the inhomogeneous distribution of carboxyl group caused the bimodal particle size distribution of WPU and DMPA content had an important impact on the inhomogeneity. By increasing the DMPA content, the inhomogeneity of carboxyl group diminished gradu-

ally, causing the changes from bimodal peaks to a unimodal peak. As for step-wise reaction, the PDI remained nearly constant around 0.2 due to two step charging sequence of PPG and DMPA.

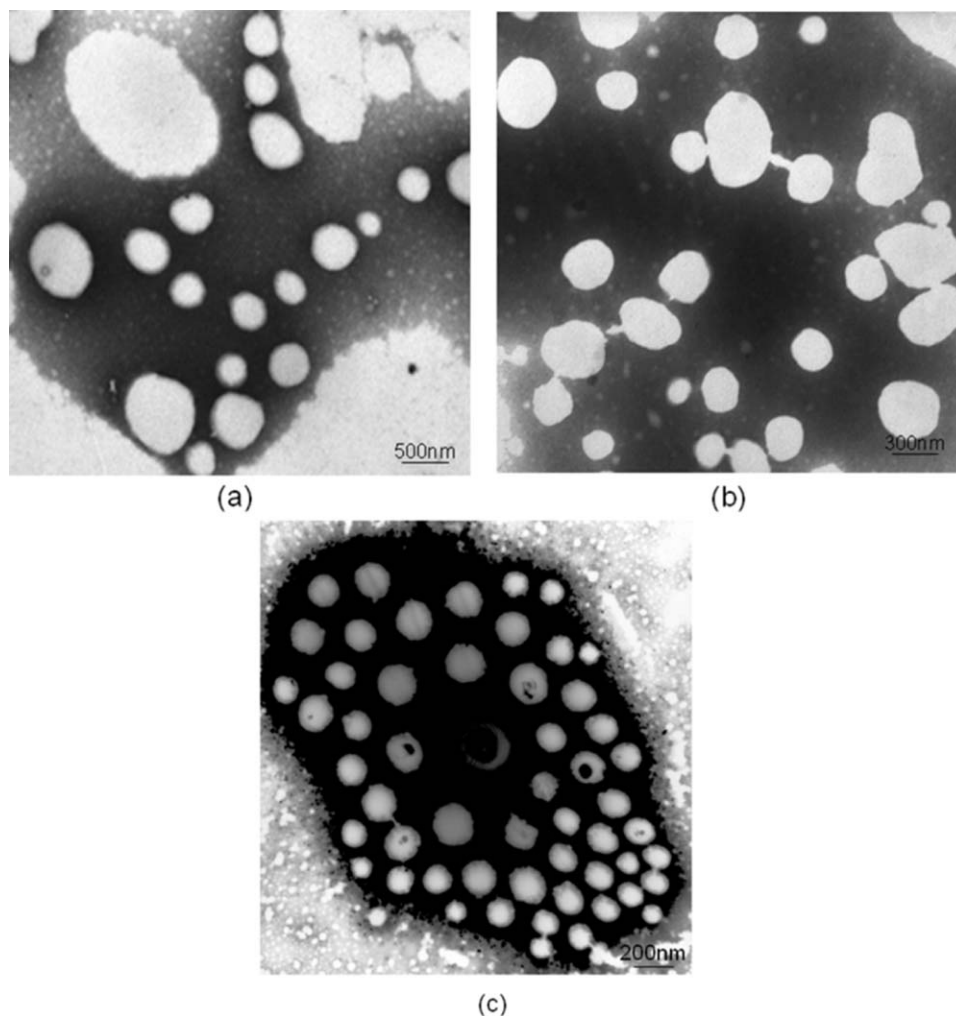


Figure 9. TEM photograph of WPU dispersions by one-pot reaction; (a) PU-1, (b) PU-3, (c) PU-5.

Particle Size, Viscosity, and Solid Content of WPU by One-Pot Reaction and Step-Wise Reaction

As mentioned above, PSD plays an important role in preparing WPU with high solid content, and broad or bimodal PSD is advantageous to keep low viscosity since small particles are able to fit into the interstices between large particles. It was found that with the increment of the hydrophilicity (DMPA content), the particle size tended to be smaller and the viscosity increased correspondingly by one-pot reaction, as shown in Figure 7. PU-1 to PU-4 kept a relative low viscosity (under 500 cP) with 50% solid content, however, the viscosity of PU-5 was high (above 1000 cP) with 40% solid content. It was worth noting that PU-5 dispersion was viscous and difficult to flow when its solid content reached 50%, which was contributed to the unimodal PSD and small particle size of PU-5. As is known, particle diameter, PSD and particle shape are three important factors to get emulsions with high solid content. Small particle diameter often leads to high viscosity, especially for waterborne polyurethanes with water swelling layer and electronic double layer.¹⁷

As for WPUs prepared by step-wise reaction, the particle size tended to be smaller and the viscosity was getting higher with the increment of DMPA content, similar to the trend of WPUs made by one-pot reaction, as shown in Figure 8. It was worth mentioning that the WPUs prepared by step-wise reaction had smaller particle size than those made by one-pot reaction. It can be explained by different position of ionic groups made by two methods. In step-wise reaction, DMPA reacted with IPDI at the second stage and carboxyl groups tended to disperse at the chain ends of polyurethanes. In this way, carboxyl groups were preferentially migrated toward to the particle-water interfaces, due to low free energy of chain ends and hydrophilic nature of carboxyl groups.³⁵ As a result, more carboxyl groups at the particle-water interfaces reduced the particle size due to the increased hydrophilicity of surface. On the contrary, DMPA tended to react with IPDI first in one-pot reaction followed by the chain extending by PPG, leading to the carboxyl groups dispersed on the middle of polyurethane backbones. Therefore, some carboxyl groups were difficult to migrate toward the particle-water interfaces, resulting in bigger particle sizes.

Particle Morphology of the Dispersions

Figure 9 is the TEM photographs of WPU dispersions with different DMPA content. From the paragraphs (a) and (b), it was obviously shown that the particles exhibited bimodal particle size distribution, which was in accordance with the previous conclusions well. With the increment of DMPA content, it was easy to find that particle sizes tend to be smaller and the difference between big particles and small particles diminished gradually. From paragraph (c) it was found that particles showed a unimodal particle size distribution and the particle size was in the range of 100–300 nm which agreed with the previous data well.

CONCLUSIONS

A series of waterborne polyurethane dispersions were prepared by one-pot reaction and step-wise reaction respectively at the same formula. It was found that WPUs prepared by one-pot

reaction exhibited bimodal particle size distribution and high solid contents (50%) at low DMPA content. With the increment of DMPA content, the intensity peaks of WPU were getting closer and finally became one peak and the solid content was limited to 40% at the same time. The reason leading to bimodal particle size distribution was attributed to the inhomogeneous distribution of carboxyl groups among polyurethane backbones which was caused by the different reaction activity of DMPA and PPG with IPDI. Meanwhile, WPUs prepared by step-wise reaction exhibited unimodal particle size distribution and the solid contents were all limited to 40%, which was ascribed to the homogeneous distribution of carboxyl groups. Therefore, compared with step-wise reaction, one-pot reaction was proved to be a promising method to prepare high solid content waterborne polyurethane by flexibly controlling the particle size distribution of WPUs using DMPA as the only self-emulsifier.

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