

Synthesis and stability research of reproducible aqueous polyurethane micelles with low de-blocking temperature

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ABSTRACT: Aqueous polyurethane micelles from 2,4,6-trichlorophenol blocking terminal-isocyanate pre-polymer were prepared which could be de-blocked at low temperature. The prepared aqueous blocked polyurethane micelles (BPUMs) were uniform and spherical micro-particles. The particle size was decreased with increase of the DMPA content, while it was enlarged at first and then gradually decreased by increasing *R*-value. The stability of the micelles was affected by the *R* value, blocked efficiency and DMPA content. HDI-BPUMs were more stable than HDI-BPUMs at the same condition. The stability was further researched by the zeta potential combining with technique and viscosity tracking method, and the initial zeta potential be used as the stability criterion. In addition, a stabilization mechanism of the micelles was proposed. TCP-blocked TDI-BPUMs could be initially de-blocked at about 75°C and TCP-blocked HDI-BPUMs was de-blocked at about 80°C. The de-blocking temperature could be further reduced in the presence of catalyst, but it was scarcely affected by the change of *R*-value and DMPA content. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41908

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INTRODUCTION

Waterborne polyurethanes (WPU) are versatile environmentally friendly materials that are increasingly being used in coatings and adhesives for automobiles and wood products, as well as for numerous flexible substrates, such as textiles, leather, paper, and rubber.^{1–4} Generally, WPUs exhibited inferior drying rates and their dried films were often vulnerable to water swelling and showed poor water resistance⁵ mechanical strength (tensile strength), and thermal stability⁶ for an amount of hydrophilic groups are introduced in the structures of polyurethanes. Such problems related to their properties could be largely resolved by proper molecular designs, and an effective way to contain reproducible isocyanate groups in the WPUs by selecting favorable blocking agent to block terminal isocyanate-containing polyurethanes.

Blocked-isocyanate is an adduct containing a comparatively weak bond formed by the reaction between an isocyanate and a compound containing an active hydrogen atom. At elevated temperatures, the reaction tends to proceed in such a way as to regenerate the isocyanate and blocking agent.⁷ The regenerated isocyanate could re-react with a substrate containing the hydroxyl functional group to form thermally more stable bonds. There has been some reviews^{8,9} reported in some areas of blocked isocyanates and water-dispersible blocked polyisocyanates, which was referred a large number of patents describing the applications of blocked isocyanates. Many patents and reports have revealed that phenols,¹⁰ alcohols,¹¹ amine,¹² oximes,¹³ amides,¹⁴ sodium bisulfate,¹⁵ *N*-hydroxyphthalimide,¹⁶ *N,N*-dimethylacrylamide,¹⁷ imidazole,¹⁸ and diethylene glycol monobutyl ether¹⁹ could be used as blocking agents for isocyanates. These blocked isocyanate products often need relatively high de-blocking temperature which could be advantageous in some certain applications. For example, pyrrolidone-blocked TMI is desirable as a monomer in making blocked isocyanate-functional synthetic rubber since it does not de-block at temperatures below about 160°C. Thus, the rubber is less likely to scorch during processing before vulcanization due to cross-linking.^{20,21} However, sometimes the high de-blocking temperature limited application areas of the blocked-isocyanate products for which it was necessary to use a blocking agent that should be cleaved off at lower temperatures. In order to extend the applications for blocked isocyanate, especially for the application of aqueous polyurethane, much attention should be paid to further reduce its de-blocking temperature.¹⁵ Such as solid rocket propellant which contains explosive material¹⁸; wood processing, coating processing, blocked isocyanates as stable one-component systems for poly(urea urethane)s.²² Up to now, it

has been reported that blocked isocyanate with relatively lower de-blocking temperature was the oxime blocked monomer, which could not be dispersed in aqueous solution, with de-blocking temperature of more than 110°C or so.²³

It has been reported that the de-blocking temperature of the blocked polyurethanes depends on the structures of the blocking agents and structures of the isocyanates.²⁴ At present, phenols were the most studied blocking agents because of the possibilities of introducing number of substituents on the benzene ring. The substituent had a strong influence on the de-blocking temperature of blocked isocyanates. Substituents present in the phenolic aromatic ring with electron-withdrawing tendency could decrease the de-blocking temperature while electron releasing groups increased the de-blocking temperature.^{10,25–27} In order to further reduce the de-blocking temperature of blocked aqueous polyurethane to extend the its applications in low temperature, in this study, the 2,4,6-trichlorophenol (TCP) was selected as blocking agent to synthesize functional blocked aqueous polyurethane because three electron-withdrawing groups, chlorine atom, presented in the ortho- and para- to the phenolic hydroxyl. The presence of strong electron-withdrawing substituents could make TCP more activated and had the possibility of lower de-blocking temperature. Moreover, the effect of catalyst on the de-blocking reaction was also explored. Thus terminal isocyanate-containing polyurethanes was firstly synthesized by introducing hydrophilic groups in the pre-polymer molecular structure through precise molecular design, and then the BPUMs was synthesized by using TCP as blocking agent for diisocyanate groups in the emulsification which could decompose in low temperature and stabilize more than six months. Finally, the morphology and particle size of the BPUMs was detected by SEM, Zeta/PALS and de-blocking reaction was characterized by FTIR, DSC, and simultaneously the stability and their stable mechanism in aqueous solution were researched systematically.

EXPERIMENTAL

Raw Materials

Commercial 2,4-toluene diisocyanate (TDI, supplied by shanghai Aladdin reagent co., LTD) and 2,6-hexamethylene diisocya-

nate (HDI, supplied by shanghai Aladdin reagent co., LTD) were used as hard segments. Polyethylene glycols-210(PEG-210, Mw = 1000, Fn = 2, supplied by shanghai Aladdin reagent co., LTD) was vacuum-dried at 120°C for 2 h, and used as soft segments. 2,2-Bis-(hydroxyl-methyl) propionic acid (DMPA, supplied by shanghai Aladdin reagent co., LTD) was used as the chain extender and anionic center. 2,4,6-trichlorophenol (TCP, supplied by shanghai Aladdin reagent co., LTD.) was used as blocked agent. Di-n-butylamine(supplied by Shanghai pure reagent co., LTD) were used to measure the content of free isocyanate. Triethylaniline (TEA, supplied by Tianjing BASF Chemical Co., LTD.), acetone, butanone were used as the neutralizing reagent and solvent respectively. Dibutyltin dilaurate (DBTDL, supplied by shanghai Aladdin reagent co., LTD) was used for catalytic agent.

Synthesis of Aqueous Blocked Polyurethane Micelles

The formulation was shown in Table I and II, respectively. Firstly, an appropriate amount of polyethylene glycol vacuum-dried at 120°C with a small amount of acetone and butanone was added to the dried 500-mL round-bottomed flask equipped with mechanical stirrer, thermometer and condenser with drying tube and a pipette outlet used as the reactor. The reaction was carried out in a setting-temperature oil bath. While stirring, the mixture was maintained under a nitrogen atmosphere at 60°C for about 10 min. Then the diisocyanate was dropped into the homogenized mixture. When the mixture was maintained at 80°C for about 1 h, DMPA solvent that dissolved in acetone (6 wt % based on the total weight) was charged into the flask. The mixture was continuously maintained at 80°C for 2–3 h to obtain NCO-terminated pre-polymers. The change of the NCO value during the reaction was determined using a standard dibutylamine back-titration method.²⁸ When the free NCO content was achieved to the theoretical value that was calculated from the R value ($n_{\text{-NCO}}$ of diisocyanate/ $n_{\text{-OH}}$ in polyethylene glycol) of feed, TCP and DBTDL with required quantity were added to the reaction mixture and the reaction was further carried out until the residual NCO content was nearly to be constant. Then the mixture was cooled to 45–50°C. The blocked polyisocyanate adducts with pendant COOH groups were completely

Table I. Formulation and Properties of Synthesized Aqueous Blocked Polyurethane Micelles Based on 2,4-Toluene Diisocyanate (TDI-BPUMs)

Sample no.	Formulation			Blocking rate (%)	Particle size (nm)	Viscosity (mPa·s)	Storage stability at room temperature
	R	DMPA (%)	Catalyst (%)				
TR1	1.8	6	0.3	83.1	241.9	958	Above 6 months
TR2	2.0	6	0.3	78.3	389.0	937	Above 6 months
TR3	2.2	6	0.3	64.5	404.4	963	3 months
TR4	2.5	6	0.3	59.3	393.5	987	Gelling after 7 days
TR5	3.0	6	0.3	53.5	297.8	993	Gelling after 1 day
TD1	2.2	4	0.3	62.3	619.3	558	Above 50 days
TD2	2.2	9	0.3	70.5	404.5	1107	Above 6 months
TD3	2.2	12	0.3	75.1	380.6	1144	Above 8 months
TD4	2.2	6	0.6	73.8	—	—	Above 6 months
TD5	2.2	6	0.9	77.3	—	—	Above 8 months

Table II. Formulation and Properties of Synthesized Aqueous Blocked Polyurethane Micelles Based on 2,6-Hexamethylene Diisocyanate (HDI-BPUMs)

Sample no.	Formulation			Blocking rate (%)	Particle size (nm)	Viscosity (mPa·s)	Storage stability at room temperature
	R	DMPA (%)	Catalyst (%)				
HR1	1.8	6	0.3	76.7	175.5	799	Above 9 months
HR2	2.0	6	0.3	74.2	372.3	786	Above 9 months
HR3	2.5	6	0.3	76.2	467.5	834	Above 6 months
HR4	3.0	6	0.3	67.8	390.8	825	Above 2 months
HR5	3.5	6	0.3	55.3	308.0	831	Gelling after 2 days
HD1	2.5	4	0.3	76.6	530.7	540	Above 4 months
HD2	2.5	9	0.3	73.9	394.8	989	Above 7 months
HD3	2.5	12	0.3	72.8	361.2	1103	Above 9 months
HD4	3.0	6	0.6	78.4	-	-	Above 6 months
HD5	3.0	6	0.9	78.3	-	-	Above 6 months

Note: TR1~TD5 is BPUMs based on 2,4-toluene diisocyanate and HR1~TD5 is BPUMs based on 2,6-hexamethylene diisocyanate under the different formulation.

neutralized with triethylanine TEA (equal to the total moles of DMPA *i.e.* neutralization degree = 100%). After 30 min, distilled water was added to the above adducts with vigorous stirring about 1500 rpm to form aqueous micelles. Finally, BPUMs fixed at 40 wt % solid content were obtained after acetone and butanone vacuum filtrated. The preparation procedure was shown in Figure 1.

Characterizations

Blocking rate is obtained by determining $-NCO$ value with a standard dibutylamine back-titration method. It was calculated as follows:

$$\eta = \frac{W_{-NCO,0} - W_{-NCO,t}}{W_{-NCO,0}}$$

where $W_{-NCO,0}$ is $-NCO$ value for before blocking reaction; $W_{-NCO,t}$ is $-NCO$ value for blocking reaction proceeded at t time.

The viscosity of the prepared samples is measured with NDJ-4 rotary viscometer. The sample dispersion is carefully poured into the test vessel, and then the rotor is used to insert into liquid until it is sank to the scale line. It is leveled before starting the motor and the numbers were recorded immediately until the pointer stable.

pH values of the BPUMs are measured at 20°C in a pH-meter using a silver reference electrode model HI 8418 (Hanna Instruments).

Particle Size analysis of the BPUMs samples is carried out by using a Zeta/PALS type laser particle size analyzer (BROOKHAVEN Instrument Company, USA). Adequate amounts of aqueous BPUMs samples are treated in an ultrasonic bath for 15 min before using the laser particle size analyzer to measure the particle size and polydispersity. The sample was scanned three times and the average is taken. With the same sample preparation methods, the Zeta potential analyses of BPUMs are detected before PH value of the liquids adjusted at 7.5.

The morphology and size of the BPUMs is examined by a scanning electron microscopy (SEM, FEI Quanta 200) operating at

12.5 kV. Samples for SEM were prepared by spreading a drop of dilute dispersion containing the products on aluminum foil, then sputter-coating with gold powder.

The thermal behavior of the BPUMs is analyzed by means of a differential scanning calorimeter Mettler DSC 30, equipped with a control programming unit Mettler TC10A. BPUMs sample about 3~5 mg was placed in an aluminum pan and the experiments are carried out under nitrogen atmosphere with a heating rate of 5°C/min and an nitrogen flow of 25 mL/min.

The chemical structure of the BPUMs is analyzed in a NICOLET 510 infrared spectrophotometer, provided with fourier transform analysis (FTIR). Measurements are carried out by the attenuated total reflectance technique by means of the Golden Gate Single Reflection Diamond ATR. An incidence angle of the IR radiation of 45° was used, and 64 scans are averaged.

RESULTS AND DISCUSSION

Synthesis of Blocked Isocyanate Prepolymer

A series of isocyanate pre-polymer based on aromatic diisocyanates (TDI) and aliphatic diisocyanates (HDI) were prepared. The obtained isocyanate pre-polymers were blocked by TCP in the presence of DBTDL as catalyst. Figure 2(a) shows the variations of the NCO content at different blocking reaction times. It can be seen that the NCO content drastically decreases with increasing blocking time at the beginning stage. With increasing blocking time, the reduction of the NCO content was slow down. With further proceeding blocking reaction, the free NCO content rarely remained constant over 20 min for TDI-BPUMs (sample TR3) and that of over 30 min for HDI-BPUMs (sample HD2), respectively. Thus, the optimized blocking reaction time could be determined as 30–40 min. In addition, it could be further indicated that the aromatic isocyanate pre-polymer was more reactive with phenolic hydroxyl of TCP compared to aliphatic isocyanate pre-polymer. In fact, isocyanate structures can also severely influence the blocking reaction. In the case of aromatic isocyanates, carbonyl carbon of $-NCO$ group was more electro positive because the aromatic ring drained the electron

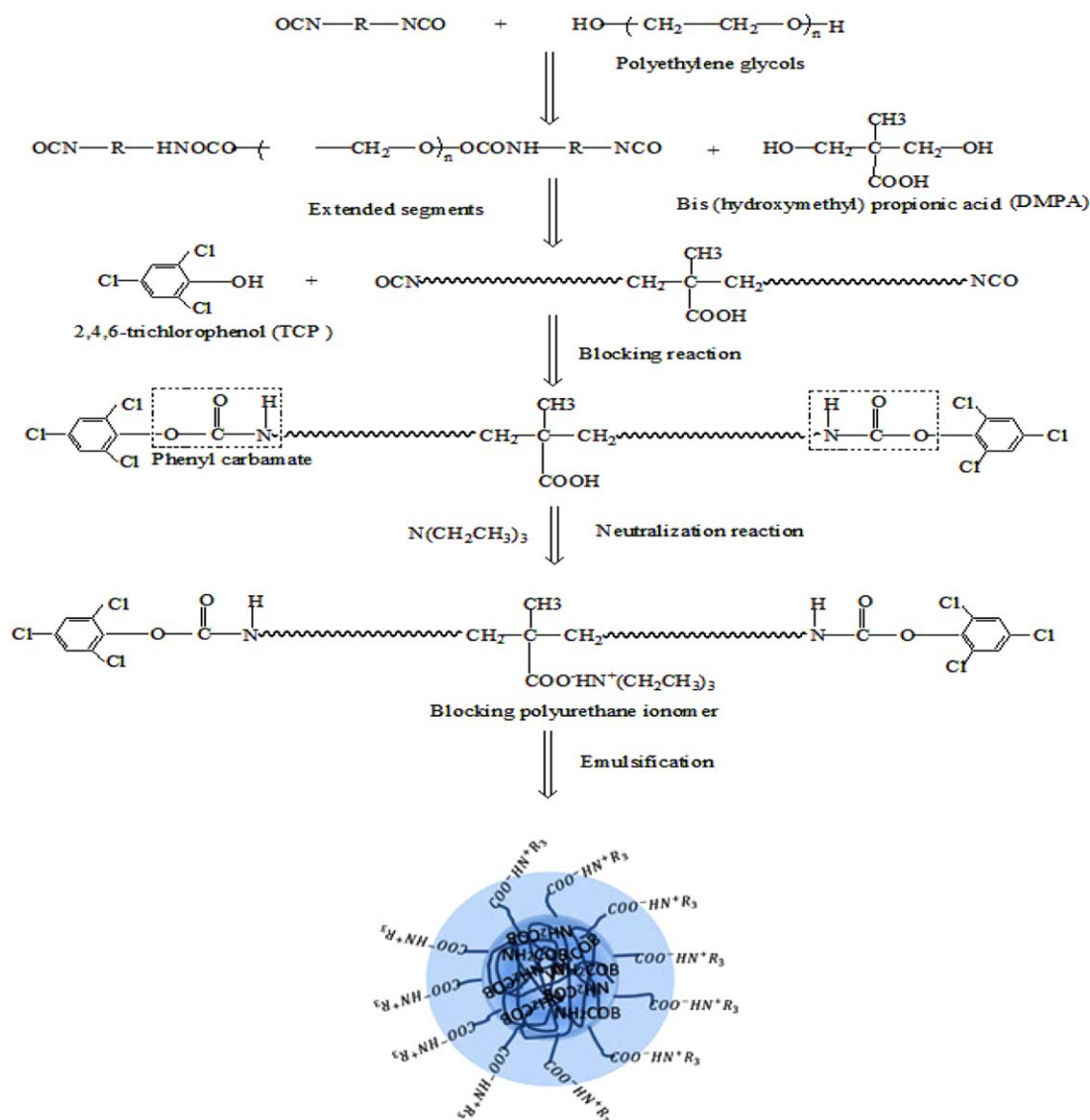


Figure 1. Preparation procedure of aqueous blocked polyurethane micelles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

density of the nitrogen atom and it facilitated the blocking reaction.²⁴

Figure 2(b) shows the FTIR spectra of the prepared blocked isocyanate pre-polymer under different blocking times. It was found that the characteristic absorption peak at the 2267 cm^{-1} could be ascribed to the antisymmetric stretching for NCO group of pre-polymer. The alkane $-\text{CH}_2$ stretching vibration at around 2871 cm^{-1} was taken as a reference for making a comparison of the content of terminal-NCO groups at different stages, because $-\text{CH}_2$ groups remain unchanged during the blocking reaction. It can be seen that the vibration absorption peak of $-\text{NCO}$ at 2267 cm^{-1} gradually becomes weak with increasing blocking reaction time, in accordance with the previous chemical-titration results, thoroughly demonstrating free isocyanate groups reacted with hydroxyl group of TCP. Furthermore, the absorption peaks at 1718 cm^{-1} ($\text{C}=\text{O}$ stretching of urethane and carboxylic groups), 2872 cm^{-1} ($-\text{CH}_2$ stretch-

ing vibration of PEG and HDI), 1145 cm^{-1} ($\text{C}-\text{O}-\text{C}$ stretching vibration of PEG), $3250\text{--}3300\text{ cm}^{-1}$ ($\text{N}-\text{H}$ stretching) and $1530\text{--}1560\text{ cm}^{-1}$ ($\text{N}-\text{H}$ bending)²⁹ confirmed the formation of blocked isocyanate pre-polymer. In addition, the result suggests that terminal-NCO group of the pre-polymer was not also completely blocked by TCP due to phenolic hydroxyl group of TCP with weak nucleophilic. Figure 3 shows FTIR spectra of blocked pre-polymer and its aqueous micelles after emulsification, respectively. The absence of characteristic NCO absorption of aqueous blocked polyurethane micelle(b) around 2267 cm^{-1} indicates the complete disappearance of free NCO groups in aqueous blocked polyurethane dispersion. Moreover there was a strong absorption peak of $\text{C}=\text{O}$ stretching at the 1637 cm^{-1} moving to right, the increase in $\text{N}-\text{H}$ stretching at the $3250\text{--}3300\text{ cm}^{-1}$ and $\text{C}-\text{N}$ stretching at the 1440 cm^{-1} compared to that of blocked pre-polymer (a), demonstrating the formation of substituted urea by the remaining isocyanate

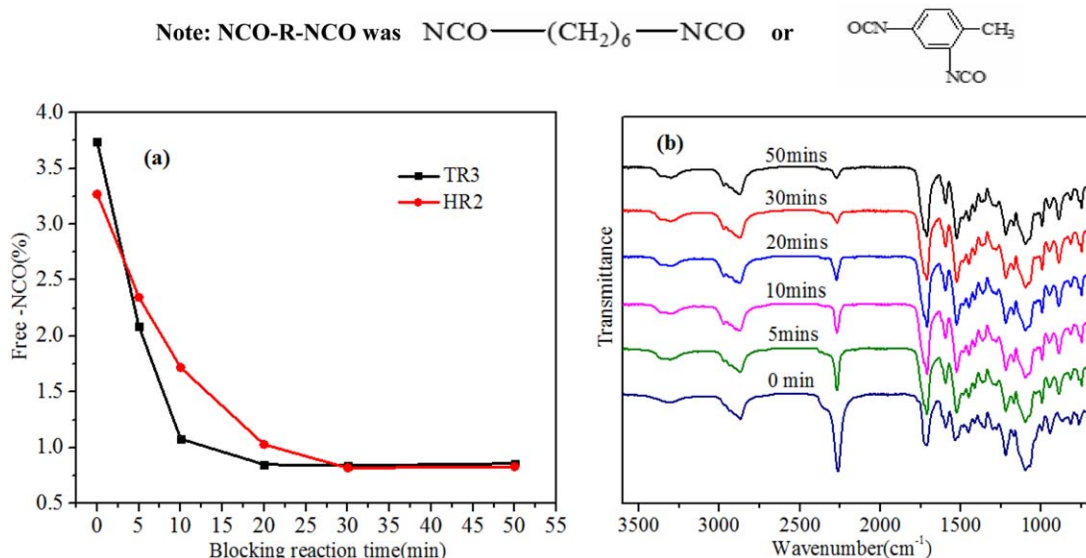


Figure 2. The variations of free NCO content of isocyanate pre-polymer with blocking reaction time (a), the FTIR spectra of isocyanate pre-polymer at the different blocking reaction time (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

group reacting with hydroxyl groups of the water molecules. Therefore, it is a necessary factor for the disappearance of remaining isocyanate groups to ensure aqueous BPUMs stable in aqueous solution.

Morphology and Size

The representative SEM micrograph and particle size of the BPUMs was shown in Figure 4. From the Figure 4(a), it can be seen that the obtained blocked polyurethane micelle is spherical micro-particles without aggregation and the observed size is about 350 nm. Furthermore, The BPUMs is a lightly yellow translucent liquid and could be stably dispersed in water maintaining up to 6 months [inset of Figure 4(a)]. The dispersion of BPUMs were probably due to that the hydrophobic segments (urethane or polyurea) in polyurethane molecular

chains were curled inside of the particles, and simultaneously, hydrophilic segments (ionic groups, hydroxy groups, ether bond) were coated on the outside of them by amphiphilic segment polyurethane in the emulsification. The particle size and particle size distribution of the BPUMs was further detected with Zeta/PALS type laser particle size analyzer, and the results were shown in Figure 4(b). It can be seen that the average particle size was 308 nm with a relatively narrow size distribution, which was consistent with that of observed from SEM micrograph.

Effect of R-Value and DMPA Content on Particle Size and Viscosity

Particle size and viscosity are important parameters for the practical application of the aqueous BPUMs. In this section, the influence of R-value and DMPA content (*i.e.* anionic group content) on the particle size and viscosity of the BPUMs fixed at 40 wt % solid content was explored. Figure 5 shows the variations of the particle size and viscosity of the TDI-BPUMs and HDI-BPUMs with R-value, respectively. It can be seen that the particle size of the BPUMs was enlarged with increase of R-value when the NCO/OH molar ratio was low. As the R-value was increased up to about 2.5, the particle size was gradually decreased. And the particle change with R-value for both TDI and HDI-BPUMs was similar. The variation of BPUMs particle size with R-value could be ascribed to polyurethane chain rigidity and polymerization degree. When the R-value was low, the hard segments in polyurethane chain were increased with increasing R-value, leading to difficult deformation of the chain in a shear field. Thus during phase inversion, the dispersed phase could difficultly be broken into small particles.³⁰ Further increasing R-value, the particle size was gradually decreased, which could be controlled by the number average degree of polymerization for the linear polyurethane chain when its terminal isocyanate blocked by TCP. It was calculated according to the following formula:³¹

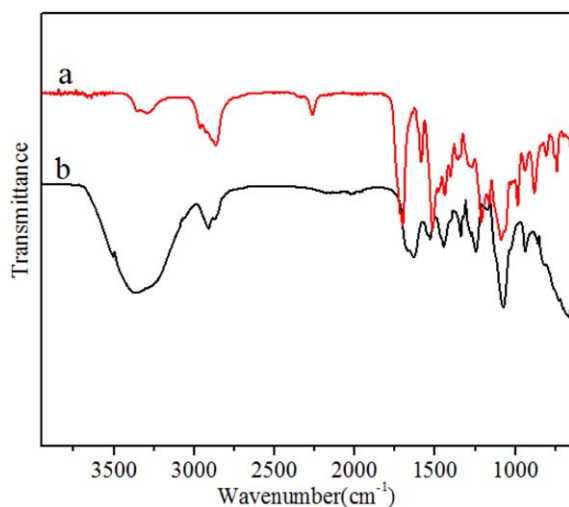


Figure 3. The FTIR spectra of blocked isocyanate pre-polymer(a) and aqueous blocked polyurethane micelle(b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

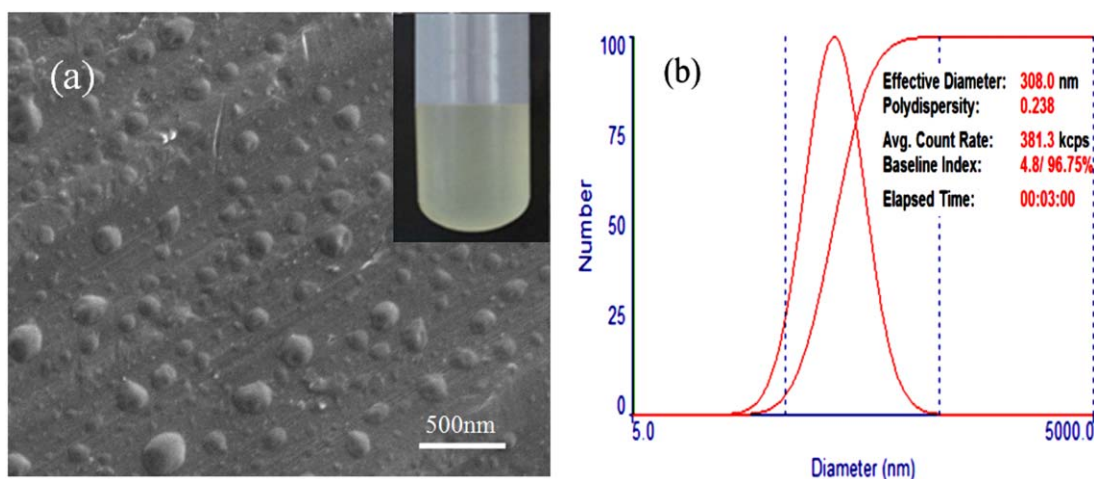


Figure 4. SEM micrograph of BPUMS (Inset: photograph of the aqueous BPUMS) (a), and Particle size distribution of BPUMS (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$DP = \frac{1 + r_a}{1 - r_a}, \quad (1)$$

$$r_a = \frac{1}{R}; \quad (2)$$

where DP is the degree of polymerization, and $r_a = [\text{OH}]/[\text{NCO}]$. So it could be obtained the following formula eq. (3) by the combination of eq. (1) and eq. (2).

$$DP = \frac{2}{R - 1} + 1; \quad (3)$$

It can be seen that DP drastically decreased with the increasing R -value. Namely, when R -value was larger, the particle sizes controlled predominantly by the number average the degree of polymerization. In addition, it can be found that the viscosity of both TDI and HDI-BPUMs was lightly increased with increase of R -value, which might be due to the increase of the effective volume of particles. But the viscosity of the TDI-BPUMs was higher than that of the HDI-BPUMs under the same R -value due to TDI-BPUMs with higher reactive to react with compound containing an active hydrogen atom compared that of HDI-BPUMs.

The effect of DMPA content on the particle size and viscosity of the BPUMs was further explored and the results had been shown in Figure 6. From Figure 6, it can be observed that the particle size of both TDI and HDI-BPUMs was decreased with increase of DMPA content, but the degree of decrease gradually became small with the continuous increase of DMPA content, in accordance with other literature results.²⁹ Actually, the particle size reduced with increasing amount of DMPA, on the one hand, due to enhance hydrophilic nature of polyurethane molecular chain when increased DMPA content. However, on the other hand, the particle size increased with increase of DMPA content is due to the increase of total ion concentration and total double layer thickness of the BPUMs. Furthermore, there is another reason that particle size increased by water-swelling of particles. Notably, it is a predominant reason for the reduction of the particle size to enhance hydrophilic nature of polyurethane molecular chain when DMPA content was lower. With continuous increase of DMPA content, the electric double layer thickness and water-swelling of particles increased which partly weak the effect of hydrophilic nature. In addition, the viscosity of the BPUMs was gradually increased with increasing

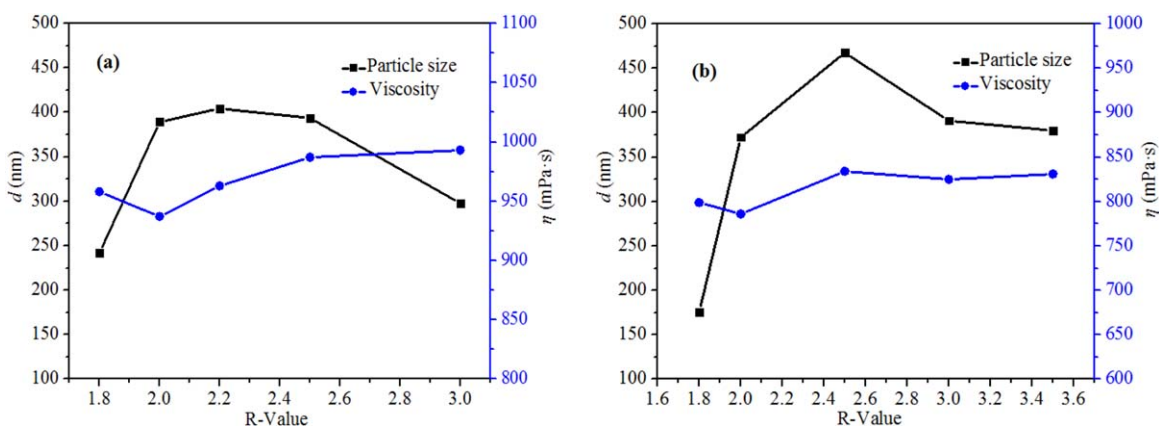


Figure 5. The particle size and viscosity of TDI-BPUDs (a), and HDI-BPUDs with R -value (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

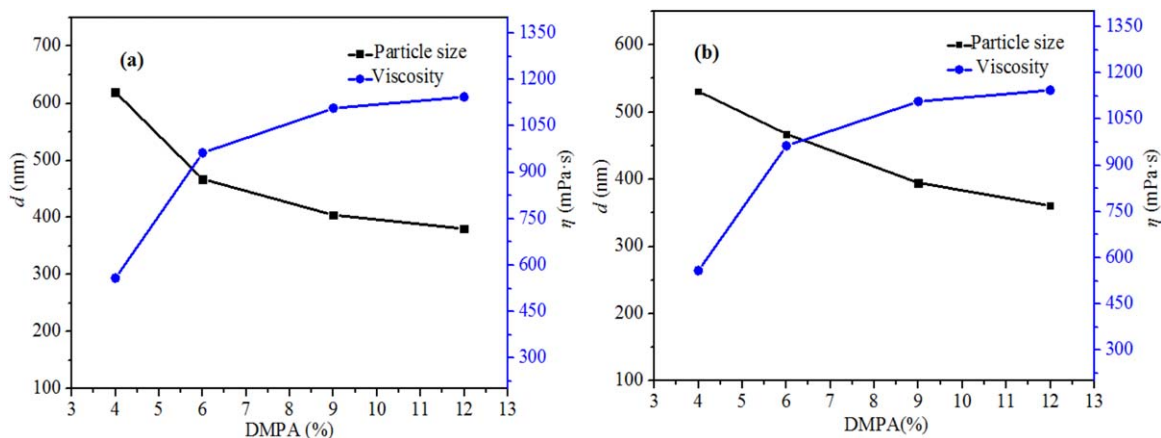


Figure 6. The particle size and viscosity of TDI-BPUDs(a), and HDI-BPUDs (b) with DMPA content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amount of DMPA, and hence, the viscosity increases due to the fact that with a reduction in the particle size, the number of electric double layers and the effective volume of the dispersed particle increased, and this lead to an increase in the viscosity. Furthermore, with the increase of ionic groups, the repulsions between the micelle could be increase which might lead to the increase of viscosity.

Storage Stability

The storage stability of aqueous BPUMs was also important for its practical application. In the experiment, it was focused on the effects of R -value, catalyst and DMPA content on the stability of the BPUMs. The variations on the storage stability of BPUMs with R -value at the fixed total ionic groups (6% DMPA content) were tabulated in Tables I and II. It can be found that the storage stability was reduced with increase of R -value. The HDI-BPUMs could be stably dispersed in aqueous solution more than six months with the increasing R -value up to 2.5, whereas the TDI-BPUMs merely could be dispersed for four months when the R -value was increased up to 2.2. It may probably indicate that the low remaining $-NCO$ groups content, which was caused by the low blocking efficiency of TCP, was depleted by water or active hydrogen-containing substance to generate polyurea or polyurethane in the emulsification, as our FTIR results indicate. So the BPUMs can be stably dispersed in an aqueous solution. The HDI-BPUMs obtained at higher NCO content ($R=2.5$) could be stable for more than 6 months. Accordingly, due to aromatic isocyanate is more reactive than aliphatic isocyanate, the TDI-BPUMs with lower NCO content ($R=2.2$) could be stabilized for only 3 months. Whereas, when remaining $-NCO$ groups content was relatively higher (*i.e.* R value is more than 2.5 for HDI-BPUMs, 2.2 for TDI-BPUMs), it had significant effect of R -value on the stability, and the BPUMs were unstable or even gel with continuous increase of R -value due to the fact that abundant remaining $-NCO$ groups react with water or active hydrogen-containing substance, leading to gel formation. In order to improve the stability of BPUMs in aqueous solution, it could be an effective way for increasing the blocking efficiency by the addition of DBTDL as catalyst. Thus, the

effect of DBTDL on the stability of the BPUMs was studied and the results were tabulated in Tables I and II. It was observed that the storage time of both TDI and HDI- BPUMs was prolonged by increasing amount of DBTDL. This was because the remaining-NCO content was decreased with improvement of the blocking efficiency, leading to the reduction of gelation. In addition, DMPA content was also an important factor for the stability of BPUMs. The variation on storage stability of the TDI-BPUMs and HDI-BPUMs with DMPA content was shown in Table I and II, respectively. The storage time increased with the increase of DMPA content. With the amount of ionic groups increasing, the repulsions among the particles were enhanced, leading to better stability. Simultaneously, the enhancement of hydrophilic nature of polyurethane molecular chains could increase hydration between the micelles and water molecules, further resulting in the improvement of stability.

The Zeta Potential

The stability of the ionomer dispersion in an electric field could be characterized by zeta potentials, which could provide the information about the electrical interaction force between dispersed particles and the stability of a particle.^{5,32} In order to systematically study the relationship between the zeta potential and stability, the viscosity and zeta potential of the BPUMs were detected and their variations with storage time were shown in Figure 7. It can be seen that the initial zeta potential of TDI-BPUMs for sample TR2 and sample TD1 presented at -20.04 mv and -16.78 mv, as shown in Figure7(a), respectively. As prolonged storage time, the zeta potential of sample TR2 became more negative, and then it reached at a plateau of about -23.65 mv. However, the zeta potential of sample TD1 became rapidly more negative with prolonging storage time up to 10 days, and then it was less negative until reached at another plateau of about -24.25 mv. Accordingly, from the inset of Figure 7(a), it can be observed that the viscosity of sample TR2 was increased and then reached at a plateau, but for sample TD1, the viscosity was rapidly increased up to form gel as prolonged storage time, implying that sample TR2 can be stably dispersed in aqueous solution but for sample TD1 with poor stability.

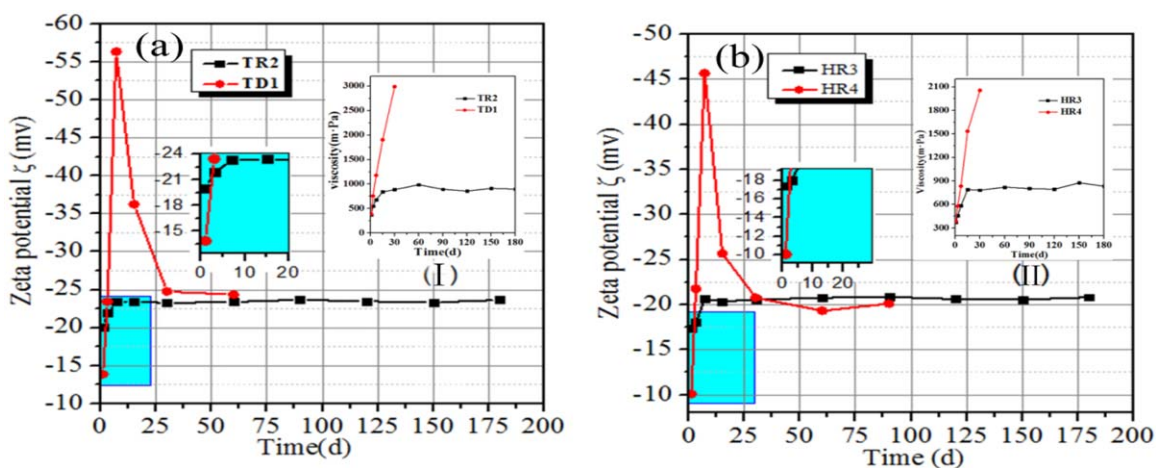


Figure 7. The variations in zeta potential and viscosity of TDI-BPUMs (a) and HDI-BPUMs (b) with storage time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

This was further improved by previous experimental result as shown in Table I. Similarly, the variation of zeta potential and viscosity of HDI-BPUMs for sample HR3 and HR4 were agreed with that of TDI-BPUMs as shown in Figure 7(b). However, it was found that initial zeta potential was more obvious change for the blocked micelles with stable or not than final zeta potential. Therefore, it could be reasonably concluded that the stability of the BPUMs could be determined by the initial zeta potential.

The effect of R -value on the initial zeta potential of the BPUMs at the fixed total hydrophilic ionic groups (DMPA content as 6%) was studied and the results were shown in Figure 8(a). When the R -value was less than or equal to 2.2, the initial zeta potentials of the TDI-BPUMs had little change, approximately maintaining at below -19.18 mV. At this condition, the TDI-BPUMs could be stably dispersed in aqueous solution as shown in Table I. With continuous increase of R -value (above 2.2), the initial zeta potential became less negative rapidly, and then it reached -13.9 mV when R -value increased up to 2.5. Simultaneously,

the TDI-BPUMs could be unstable in aqueous solution. The electric double layer structure to keep micelles stable was destroyed by the formation of substituted urea when R -value increased up to 2.5. Accordingly, the variation of initial zeta potential with increase of R -value for HDI-BPUMs was similar to that of TDI-BPUMs, but they were unstable when the initial zeta potential was less negative than -17.38 mV. Furthermore, the influence of DMPA content on the initial zeta potential was researched and the results were represented in Figure 8(b). The initial zeta potential of both TDI-BPUMs and HDI-BPUMs became more negative with increasing amount of DMPA content. Especially, the initial zeta potential became rapidly more negative as the DMPA content was lower than 6%. However, with continuous increase of DMPA content, the degree of initial zeta potential became negative was slow down. As corresponds, the storage stability was improved with increasing amount of DMPA and this was also demonstrated in Tables I and II. Summarily, it could be concluded that when the initial zeta potential became more negative than -19.18 mV for TDI-BPUMs and

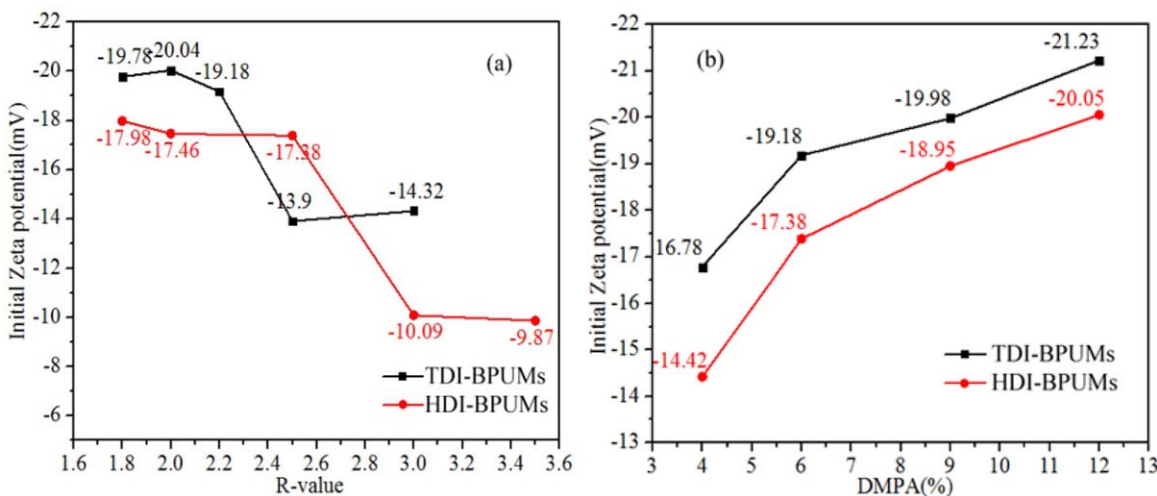


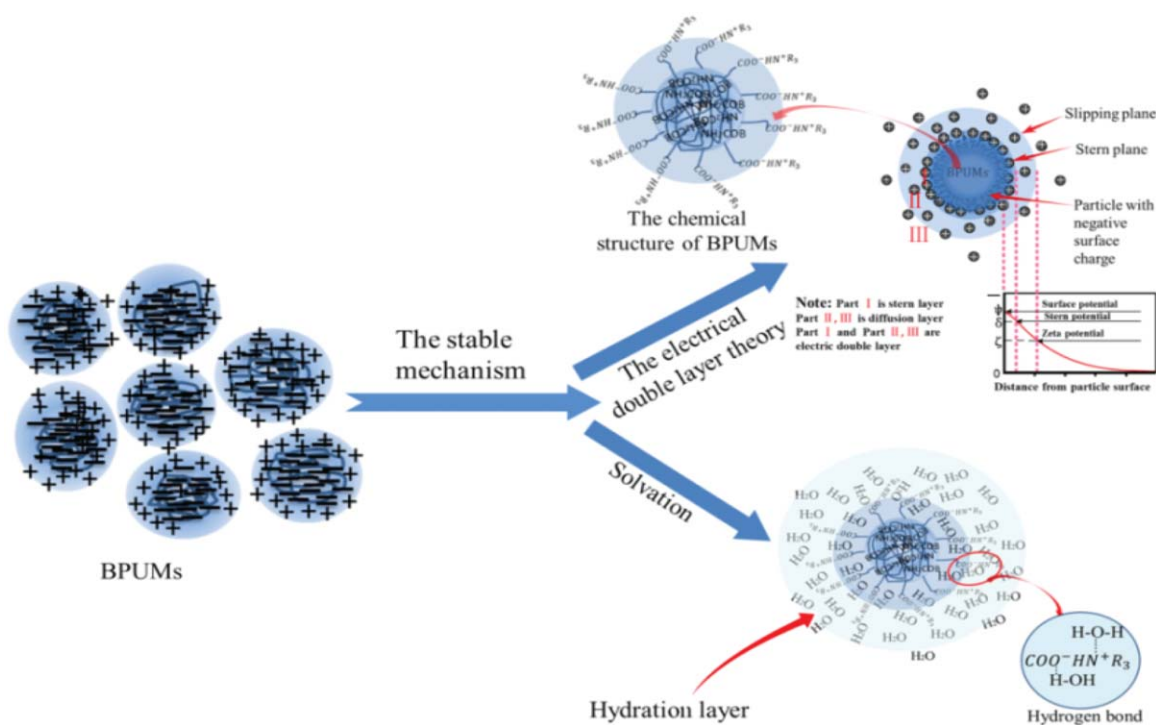
Figure 8. Initial Zeta potential of BPUMs with R -value (a), and DMPA content (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

−17.38 mV for HDI-BPUMs, they could be dispersed stably in aqueous solution for above 6 months, respectively.

Stabilization Mechanism

The BPUMs could be stably dispersed in aqueous solution due to that hydrophilic ionic groups ($-\text{COO}^-$) were incorporated into polyurethane chains through molecular design during chain extension process. Therefore, it could be considered that the micelles were stabilized by the formation of electrical double layers between the ionic constituents which were chemically bounded to the polyurethane chains, and their counterions which were migrated into the water phase around the micelles.³³ The interference of the electrical double layers of different micelles resulted in particle repulsion, leading to the stabilization mechanism of micelles. In addition, the micelles could also keep stable in aqueous solution due to the formation of loose hydration layer around them to provide steric hindrance by the solvation which generated via hydrogen bonds and electrostatic attraction between the hydrophilic groups and water molecules.³⁴ The stability mechanism for the micelles in aqueous solution was schematically proposed as shown in Scheme 1. According to Gouy-Chapman-Stern model,³⁵ which was used to describe the structure of electric double layer at the junction of charged particles with aqueous solution, it could be conceived the layer was composed of two elements, in addition to the sheet of anionic groups in micellar surface. The inner element, known as the “compact layer” or “stern layer”, was formed by absorb counterions ($\text{N}^+\text{HCH}_2\text{CH}_3$) solidly via the electrostatic interaction and Van der Waals’ force, which was distributed between micellar surface and the stern plane and this region was shown as the

part I. The potential was approximately linearly dissipated in this region according to the Langmuir adsorption theory, and the potential of the micellar surface was denoted as ψ . The outer element, the “diffuse layer” or “Gouy-Chapman layer” was semiinfinite in extent, and contained anions ($-\text{COO}^-$, OH^-) and counter-cations ($\text{N}^+\text{HCH}_2\text{CH}_3$, H_3O^+) which was distributed unequally in obedience to the laws of Poisson and Boltzmann and this region was shown as part II and III in structure of electric double layer model. The boundary of part II and III was denoted as the slip plane where hydrodynamic motion became possible and the potential of this plane was zeta potential (ζ potential) or electrokinetic potential. Therefore, the zeta potential was related to the quantity of electricity of particle, and the magnitude of the zeta potential could provide information about the potential stability of the micelles. All the charged particles with negative or positive zeta potential would repel each other to disperse stably due to the formation of a relatively thick electrical double layers around the micelles. It was a main reason to improve stability of the BPUMs by enhancement of the zeta potential, as demonstrated by the previous results. In addition, there is another factor that made the BPUMs stable by the formation of loose hydration layer through hydrogen bonds between abundant hydrophilic groups on the micellar surface and aqueous molecular. The formation of the hydration layer could resist the micelles aggregation because of steric hindrance among micelles. Therefore, the hydration enhanced with increasing amount of the hydrophilic segment and ionic groups, and simultaneously the interfacial tension between micelles and aqueous phase reduced, which could contribute to the stability of micelles.



Scheme 1. Schematic diagram of stable mechanism for BPUMs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

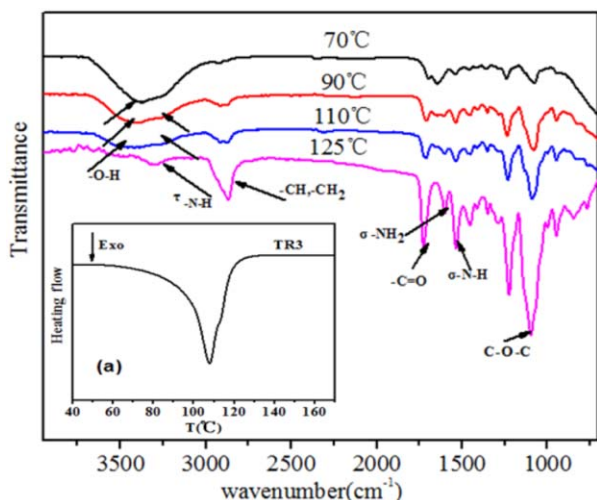


Figure 9. FTIR spectra of de-blocking of BPUMs at different temperature and DSC curve of de-blocking (inset). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The De-Blocking Reaction

The thermal regeneration of the BPUMs was analyzed by a hot-stage FTIR spectroscopy, and simultaneously its thermal dissociation was studied by the differential scanning calorimetry (DSC). Figure 9 showed the FTIR spectra of de-blocking of the BPUMs at 70°C, 90°C, 110°C, 125°C, respectively, and DSC curve of thermal decomposition process of the BPUMs (inset in Figure 9). It can be found that there was no indication of stretching vibration of the —NCO (2273 cm^{-1}) in the de-blocking product under different temperatures. The stretching vibration peak of —C=O at 1720 cm^{-1} , $3250\text{--}3323\text{ cm}^{-1}$ ($\tau\text{-N-H}$ stretching vibration), 1540 cm^{-1} ($\sigma\text{-N-H}$ deformation vibration) and 1605 cm^{-1} ($\sigma\text{-NH}_2$ deformation vibration) was increased and the stretching vibration peak of O—H at $3375\text{--}3503\text{ cm}^{-1}$ was decreased with elevated temperature. Meanwhile, from the DSC, it can be seen that there is a significant exothermic peak in the thermal decomposition process at the range of about 70–125°C. Therefore, the results proved that the de-blocking reaction did occur with rising temperature, but free isocyanate groups from the de-blocking reaction immediately reacted with active hydrogen-containing or water to form carbamate or substituted urea, which made the isocyanate groups directly not detected by Infrared spectroscopy.

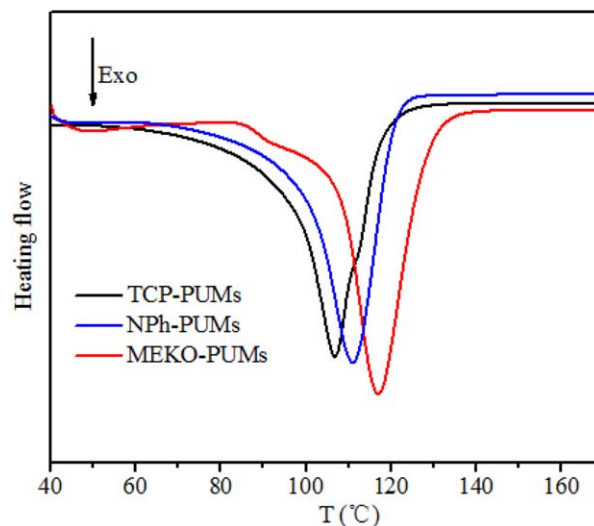


Figure 10. The FTIR spectra of the BPUMs with the different blocking agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Furthermore, the de-blocking temperatures of the BPUMs were shown in Table III. When the fracture of chemical bond happened, the temperature could be represented as the initial de-blocking temperature.³⁶ TCP-blocked TDI-BPUMs were initially de-blocked at about 75°C, and the range of de-blocking temperature was about 70–120°C, and HDI-BPUMs could be initially de-blocked at about 80°C and the de-blocking temperature range was about 80–125°C, which were lower than those of other blocking agents of blocked diisocyanate adducts (110–145°C).^{8,37} Moreover, it was found that the low initial de-blocking temperatures of the blocked isocyanate series TR1, TR3, TR4, TD1 and TD3 were due to the presence of aromatic ring in the structures and the high initial de-blocking temperature of the blocked isocyanate series HR1, HR3, HR5, HD1 and HD3 were due to the use of aliphatic isocyanates. Among the isocyanate used, TDI based blocked isocyanate undergo de-blocking at lowest temperature and are due to the methyl group present in the isocyanate moiety, which accelerates the de-blocking reaction, through steric factor.²⁴ In addition, there were basically no variation on de-blocking temperature of the BPUMs with the different *R*-value and DMPA content. So it can be concluded that the ratio of hard and soft segments and ionic

Table III. The De-Blocking Temperatures of the BPUMs

Sample no.	De-blocking temperature (°C)			Sample no.	De-blocking temperature (°C)		
	T_i	T_p	T_f		T_i	T_p	T_f
TR1	70.9	109.8	121.5	HR1	75.8	103.6	126.8
TR3	70.6	107.7	126.5	HR3	76.2	107.1	124.7
TR4	68.5	105.6	119.3	HR5	80.3	101.9	118.1
TD1	65.4	102.0	124.5	HD1	78.2	102.2	119.3
TD3	62.3	106.1	123.7	HD3	80.8	104.5	119.7
TD4	76.4	101.7	117.1	HD4	76.4	99.6	109.8
TD5	69.7	97.1	117.2	HD5	65.3	93.6	109.3

groups content in the chain of polyurethane molecular has no effect on de-blocking reaction. In addition, from Tables I, II, and III, it was found that the de-blocking temperatures of TDI-BPUMs series TR3, TD4, TD5 and HDI-BPUMs series HR3, HD4, HD5 were reduced with increasing amount of catalyst. It could be ascribed the de-blocking reaction was accelerated in the presence of DBTDL.

Finally, we further study the effects of the blocking agent on the de-blocking reaction of the BPUMs. The results are shown in Figure 10. The peak de-blocking temperature of the blocked diisocyanates determined by DSC was in the following order:



TCP blocked PUMs could be de-blocked at lower temperature than nitro phenol resulting from the greater electron-withdrawing potential of three chlorine substituent presented in the phenolic aromatic ring compared to a nitro substituent. However, MEKO blocked PUMs de-blocked at higher temperature than the former because of the formation of relatively stable bond carbamic acid phenyl ester which was caused by relatively strong nucleophilic O atom in hydroxyl of the MEKO as blocking agent compared to TCP and NPh. Therefore, the de-blocking temperature related with the type of blocking agent.

CONCLUSIONS

Aqueous polyurethane micelles from TCP blocking terminal —NCO pre-polymer based on aromatic isocyanate (TDI) and aliphatic isocyanate (HDI) are prepared and characterized. The optimized blocking time of TCP blocking isocyanate is determined as 30–40 min and the TDI-BPUMs is more reactive with phenolic hydroxyl of TCP compared to that of the HDI-BPUMs. The particles are uniform and spherical microparticles. Both of particle sizes for TDI and HDI-BPUMs increase to its maximum and then gradually decrease with the increasing *R*-value, and the viscosities gradually increase with increase of *R*-value and DMPA content. The storage stability gradually reduces with increasing amount of *R*-value. Specifically, the HDI-BPUMs can disperse stably more than six months with the increasing *R*-value up to 2.5, but the TDI-BPUMs merely disperse stably for four months when *R*-value increase up to 2.2. In addition, initial zeta potential also provided particular information about stability of the BPUMs. The blocked micelles can stable when the initial Zeta potential become more negative than −19.18 mv for TDI-BPUMs and −17.38 mv for HDI-BPUMs, The blocked TDI and HDI-BPUMs initially de-blocked at about 75°C and 80°C, respectively. The de-blocking temperatures is about 70–125°C, which are lower than those of other blocking agents of blocked diisocyanate adducts. The de-blocking temperatures are reduced with increasing amount of DBTDL as catalyst, however their de-blocking temperature are scarcely affected by the change of *R*-value and DMPA content.

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