

Waterborne Polyurethane Dispersions Obtained by the Acetone Process: A Study of Colloidal Features

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ABSTRACT: Waterborne polyurethane (PU) dispersions were prepared from isophorone diisocyanate (IPDI), 2-bis(hydroxymethyl) propionic acid (DMPA), 1,4-butane diol (BD), poly(propylene glycol) (PPG), and triethylamine (TEA) by means of phase inversion through the acetone process. Changes in DMPA content, initial PU content in acetone, phase-inversion temperature, evaporation conditions, and solvent nature were found to have a great impact on dispersion properties. Using a DMPA concentration of 0.30 mmol/g_{pol}, stable PU dispersions could only be obtained when the initial PU content in acetone was at least

60 wt %, and phase-inversion temperature was lower than 30°C. However, when increasing the PU content to 75 wt %, stable dispersions were obtained using DMPA concentrations three times lower. Finally, viscosity curves during the water addition step as well as a phase diagram were determined to understand the particle formation mechanism. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2054–2062, 2011

Key words: waterborne polyurethanes; acetone process; emulsification; particle size distribution; phase diagrams

INTRODUCTION

Owing to the strong calls for low-pollution chemical industry, organic solvent-based polyurethanes (PUs) are increasingly being restricted.^{1–4} The consciousness toward environmental care and the efforts of governmental organizations are limiting the amount of volatile organic compounds (VOCs) released in the atmosphere, forcing the development of new environmentally friendly water-based products.¹ Waterborne PUs (WPUs) are versatile environmentally friendly materials that are increasingly being used in coatings and adhesives for wood and automobiles as well as for numerous flexible substrates, such as textiles, leather, paper, and rubber.⁵

WPUs cannot be obtained by conventional synthesis methods, such as emulsion and suspension polymerizations, due to the high reactivity of isocyanate groups toward water.⁶ Therefore, several processes have been developed for achieving aqueous PU dispersions.^{6–16} Among those synthetic methods, one

of the most popular strategies is the acetone process,^{1,4,17–21} which consists of a two-step procedure. In the first step, during the PU synthesis in acetone, hydrophilic and potentially charged groups are incorporated into the polymer backbone. In a second step, water is added to the PU/acetone mixture. Thanks to the hydrophilic groups previously incorporated during the polymerization process, PU precipitation gives rise to stable dispersions. Finally, the low-boiling point of acetone allows its easy removal, yielding a product containing either a very low content of VOCs or free of VOCs. By properly fixing the conditions of the acetone process, stable dispersions can be obtained by low-energy emulsification methods.^{22–25}

The most commonly used strategy to obtain hydrophilic PU by the acetone process is the addition of an internal emulsifier containing an acidic group [2-bis(hydroxymethyl) propionic acid (DMPA)]. It is widely accepted that a minimum amount of ionic group content is required for the formation of stable PU dispersions, but this value depends on many variables such as the polymer nature and the neutralization degree.^{2,20,21} The DMPA content affects the dispersion particle size and stability, but other parameters such as the PU content in acetone, the phase-inversion temperature and the affinity toward water of the solvent used for PU synthesis also have a significant effect on the final PU dispersions. There are many reports in literature

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concerning the relationship between the nature of the dispersion and the reaction parameters.^{2,17,20,21} However, detailed studies are seldom reported.

This paper describes the preparation of WPU dispersions by the acetone process. The effects of different variables such as ionic group concentration, PU content, phase-inversion temperature, solvent evaporation conditions and solvent affinity toward water on the final particle size and stability are studied. In addition, viscosity curves during the water addition step as well as a ternary diagram have been determined to understand the particle formation mechanism.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI), 2-bis(hydroxymethyl) propionic acid (DMPA), 1,4-butane diol (BD), poly(propylene glycol) (PPG) end-capped diol ($M_n \sim 1000 \text{ g mol}^{-1}$), triethylamine (TEA), dibutyltin diacetate (DBTDA), acetone, chloroform, and tetrahydrofuran (THF) were purchased from Aldrich Chemical Corp. All materials were used as received.

Preparation of WPU dispersions

Waterborne PU (WPU) dispersions were prepared in two main steps. In the first step, the polymer was synthesized, and, in the second one, the dispersion process was carried out.

Synthesis of PU

A series of polyurethane (PU) was synthesized in a 250-mL jacket glass reactor equipped with a mechanical stirrer, a nitrogen inlet, and a condenser. In most of the cases, acetone was used as solvent to carry out the synthesis. However, chloroform and THF were also used to study the effect of solvent affinity toward water on the final dispersion characteristics. A water bath was used to control the reaction temperature.

Polyol (PPG, 45 g, 45 mmol), internal emulsifier (DMPA), and the required amount of TEA to completely neutralize DMPA acidic groups were fed into the reactor together with 700 ppm of DBTDA and solvents. Once the reaction temperature reached 60°C, IPDI (25 g, 112 mmol) was added dropwise at 1 mL min⁻¹. The reaction was carried out for 5 h under nitrogen atmosphere and mechanical stirring (250 rpm), and finally the required amount of chain extender (BD) was introduced to react with residual NCO groups. The reagent amounts are summarized in Table I. The reaction was periodically monitored by Fourier transform infrared spectroscopy (FTIR), and it was considered completed when the infrared

TABLE I
Summary of Reagent Amounts of All the PU Dispersions Prepared in this Study

DMPA (mmol/g _{poi})	PPG (g)	IPDI (g)	DMPA (g)	TEA (g)	DBTDA (mg)	BD (g)
0.58	45	25	7.0	7.0	70	3.2
0.35	45	25	3.5	3.5	70	4.6
0.30	45	25	3.0	3.0	70	4.8
0.26	45	25	2.5	2.5	70	5.0
0.21	45	25	2.0	2.0	70	5.2
0.16	45	25	1.5	1.5	70	5.4
0.10	45	25	1.0	1.0	70	5.6

absorbance of the NCO groups (around 2260 cm⁻¹) was negligible.⁶

Dispersion process

The dispersion process was carried out using several different experimental conditions. Thus, the concentration of the PU solution was adjusted to the desired value, and an aliquot of this solution was fed into the reactor. After setting the temperature and stirring rate (400 rpm), water was added at 1 mL min⁻¹. Once the dispersion was achieved, the solvent was removed by means of a rotary evaporator at different temperatures to test the effect of this parameter on the final dispersion stability. The synthesis procedure is shown in Scheme 1.

Measurements and apparatus

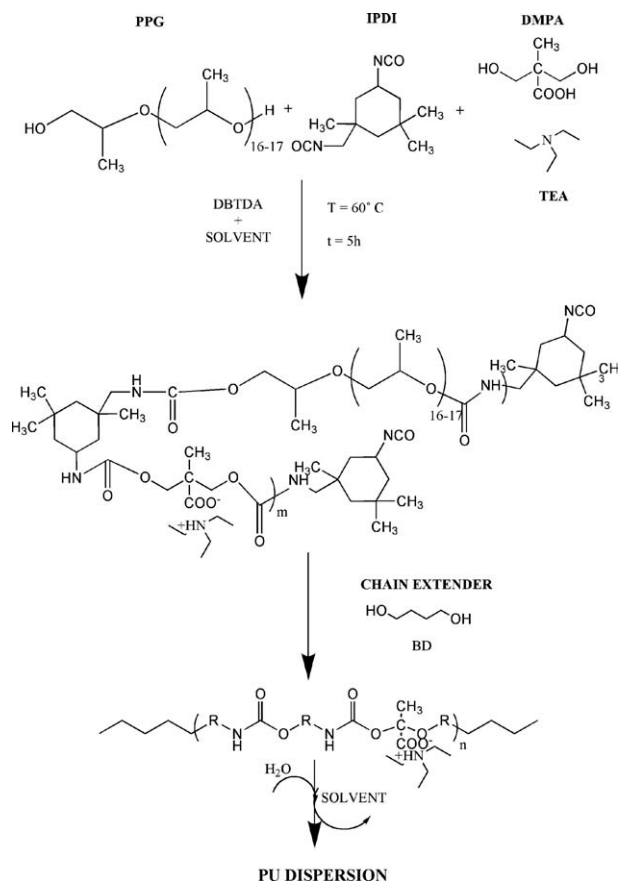
FTIR was used to study the polymerization process of WPU. FTIR spectra were recorded at different polymerization times at room temperature using a Nicolet Magna 560 spectrometer at a resolution of 2 cm⁻¹, and a total of 64 interferograms were signal averaged. FTIR spectra of the reaction mixture were obtained at different reaction times from solution casting onto KBr pellets.

Carbon nuclear magnetic resonance (¹³C NMR) spectra of the final products solved in deuterated acetone were carried out in a Fourier transform Bruker 300 MHz spectrometer (model Advance 300 DPX). TMS was used as internal reference.

The rheological behavior during the phase-inversion process was monitored using oscillatory flow measurements in cone-plate mode in a stress-controlled Thermo Haake Rheostress. Experiments were performed at sufficiently low amplitudes to reach the linear viscoelastic regime using a cone-plate geometry ($d = 35 \text{ mm}$, $\alpha = 2^\circ$).

The turbidity points were determined visually and considered as phase-separation points during the water addition process.

The particle size (D_p) and particle size distribution (Polydispersity) of the PU dispersions were



Scheme 1 Process for obtaining waterborne polyurethane dispersions.

measured by dynamic light scattering (DLS), using a Zetasizer (HS1000 from Malvern Instruments), and the data were collected using the fully automatic mode of the Zetasizer system. The samples were diluted with deionized water before the measurements to avoid multiple light scattering. The final value was an average of three measurements.

The stability of the dispersions was determined with a Turbiscan Lab^{expert} apparatus. In this equipment, the sample contained in a glass cylindrical cell was vertically scanned with a laser light and the backscattered light, which is sensitive to the particle size and dispersed phase concentration, was recorded.

RESULTS AND DISCUSSION

Chemical characterization

The characterization of the different systems was carried out by FTIR and ¹³C NMR. Figure 1 shows the infrared spectra corresponding to different reaction times of the system containing 0.3 mmol DMPA/g_{pol}.

As can be seen, the band centered at 2235 cm⁻¹, attributed to NCO stretching vibrations, decreases as

the reaction time increases and disappears once the reaction is completed. At the same time, the bands due to urethane groups increase in intensity as a function of the reaction time (NH stretching band at 3400 cm⁻¹, amide I at 1720 cm⁻¹, and amide II at 1550 cm⁻¹). However, no bands attributable to the carboxylate groups can be observed in the FTIR spectra due to their low concentration.

Figure 2 shows the ¹³C NMR spectra of two of the synthesized systems containing 0.16 and 0.58 DMPA mmol/g_{pol}, respectively, where all the signals have been assigned to their corresponding carbon atoms. Specifically, the signals of carbons 19, 20, 21, and 24 of the spectrum of the system with the higher DMPA content are directly related to the insertion of DMPA into the polymer backbone. These results evidence the polymerization reaction and the insertion of DMPA.

Effect of various parameters on the characteristics of the PU dispersions

Different experiments were carried out to better understand the phase-inversion process. These experiments are described in the following sections.

The average particle size of WPU dispersions is an important parameter that can be mainly controlled by varying the total amount of internal ionic surfactant: DMPA. However, it is also governed to some extent by emulsification conditions such as solvent affinity toward water, polyurethane (PU) content, and temperature.

To investigate the effect of the DMPA concentration, seven dispersions were prepared varying the initial amount of DMPA, while maintaining constant the concentration of the other reagents and the emulsification conditions. All the acidic groups were

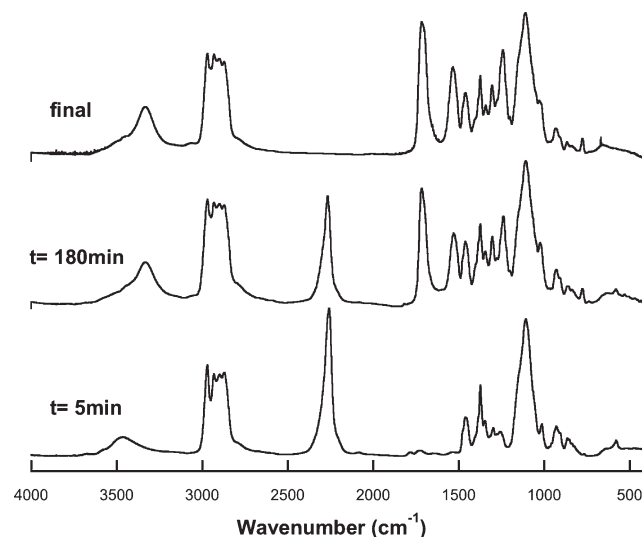


Figure 1 FTIR spectra of WPU containing 0.30 mmol DMPA/g_{pol} at different reaction times.

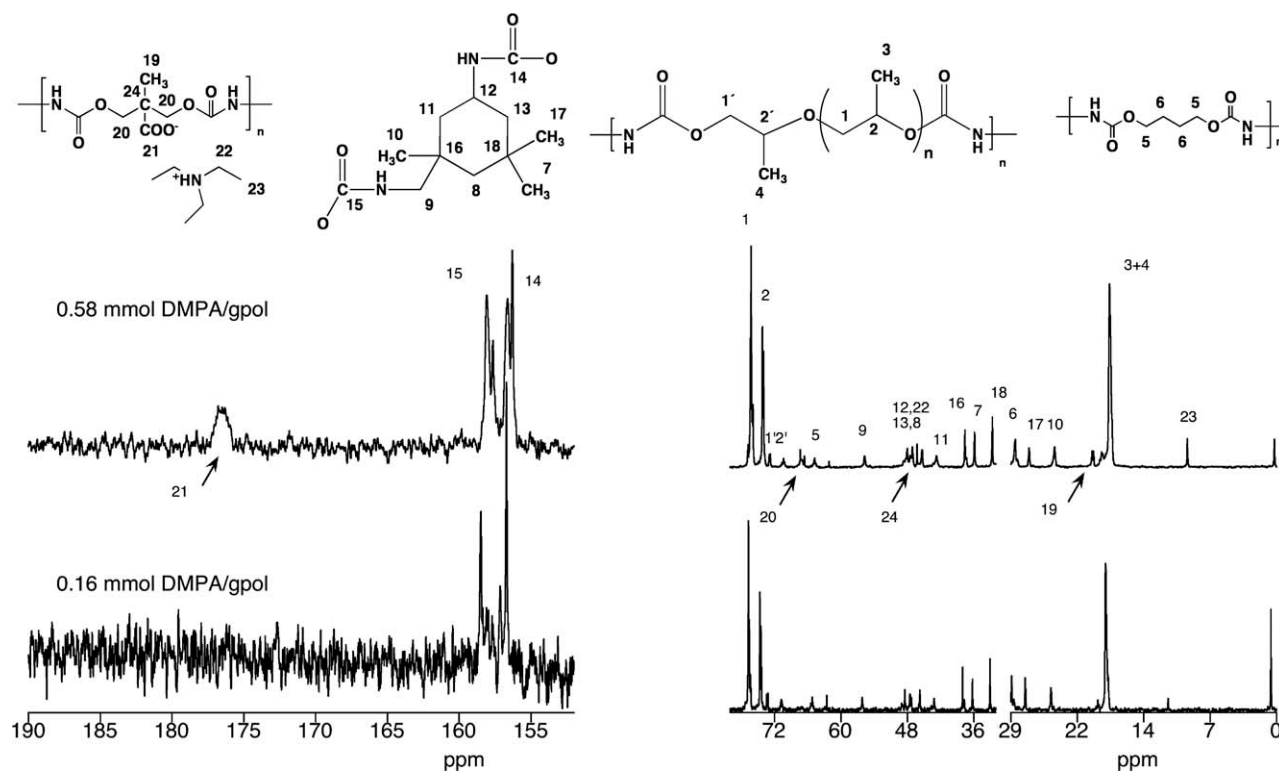


Figure 2 ^{13}C NMR spectra of WPU containing 0.16 and 0.58 mmol DMPA/ g_{pol} .

neutralized with TEA. The phase inversion was performed at 400 rpm and 25°C by adding 45 g of water at 1 mL min^{-1} to 35 g of a PU solution in acetone (60 wt %). Table I summarizes the reagents used in these reactions.

In all the reactions, the particle size was measured by DLS during the water addition process. The stability of the final product was measured using a Turbiscan. Dispersions were considered stable when no variation in the backscattering was observed for 48 h.

Figure 3 shows the evolution of the particle size during the water addition process for samples containing different DMPA concentrations as a function of f (where f is defined as the ratio of the mass of added water to the total mass of solvents). The last points of the graph ($f = 1$) were obtained after acetone removal at 25°C under vacuum using a rotary evaporator.

As shown in Figure 3, the system containing the lowest surfactant concentration (0.10 mmol/ g_{pol}) experiments a sharp increase in particle size during the phase-inversion process. On the contrary for higher DMPA amounts, particle size keeps almost constant during the whole process. In addition, it is seen that particle size decreases as the DMPA concentration increases. However, for acid concentrations higher than 0.30 mmol/ g_{pol} , no additional reduction of particle size is observed. Similar results have already been reported in the literature² and

were attributed to the greater ability of the system to stabilize larger areas, when acid concentration is increased, eventually leading to smaller particle sizes. Nevertheless, it should be pointed out that the fact of obtaining systems with a low-average particle size does not necessarily mean that the dispersion is a stable colloid. Thus, in our case for DMPA concentrations lower than 0.26 mmol/ g_{pol} , the resultant

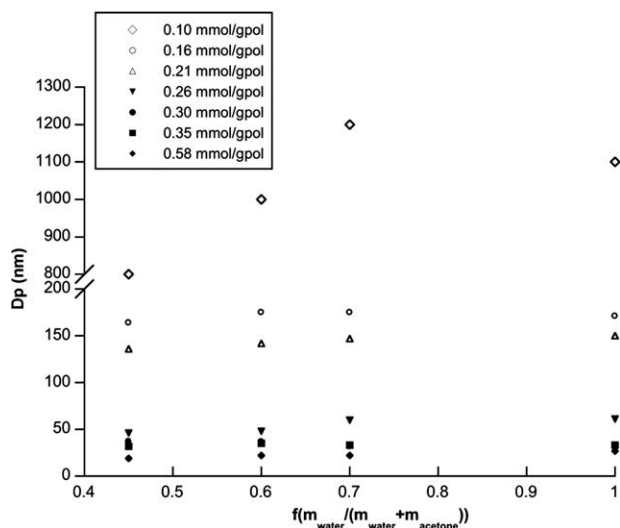


Figure 3 Particle size evolution during the phase-inversion process for different DMPA concentrations and 60 wt % PU content in acetone. The stable dispersions are represented with filled symbols.

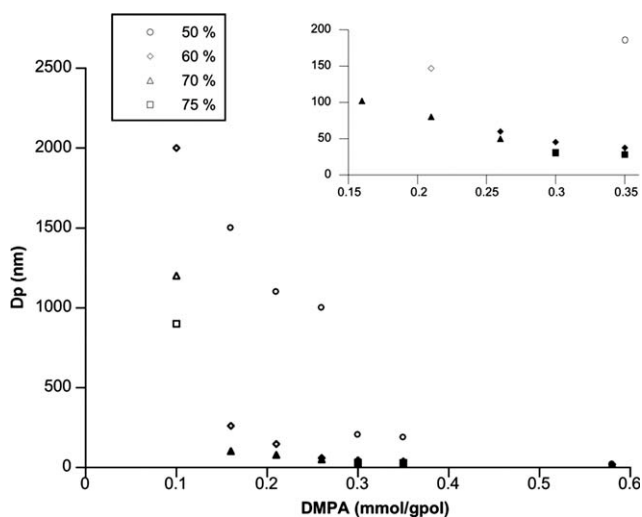


Figure 4 Final ($f = 1$) particle size versus DMPA concentration, for different initial PU contents. The stable dispersions are represented with filled symbols.

systems are highly unstable as they settle within a couple of hours.^{20,21}

Another parameter having a great effect on the phase-inversion process is the initial PU content.¹⁷ To study this parameter, the same types of experiments were carried out at different initial PU contents. As can be seen from Figure 4, for a given PU content, particle size decreases as DMPA concentration increases. Moreover, the initial PU content has a great influence on both the particle size and the stability of the final dispersion. At low-DMPA concentrations, the particle size decreases by increasing the concentration of the starting solutions. At higher DMPA concentrations the effect of the PU content is not so pronounced.

However, a small particle size does not mean that the obtained dispersion is stable. Thus, starting at 75 wt % PU, stable dispersions with mean particle sizes around 800 nm can be obtained using a low DMPA concentration. In contrast, when working at 50 wt %,

the mean particle size is around 200 nm, but it is not possible to obtain stable dispersions even with three-fold DMPA concentrations. In fact, the polydispersity index is very high and the dispersions contain aggregates ($>1 \mu\text{m}$) that precipitate rapidly. Nevertheless, as a consequence of the presence of a large amount of small particles, the mean particle size is low.

Figure 5 shows photographs of stable and unstable dispersions of different PU and DMPA contents. In all cases the adequate amount of water was added to obtain final dispersions with a 30 wt % of solids. The photographs were taken just after stirring for a few minutes (5A-left) and after leaving the samples 48 h without stirring (5B-right). Figure 5(A) shows that, regardless of the initial PU content, either soluble or two-phase systems are obtained, and this is dependent on DMPA concentration. In addition, dispersions containing the same DMPA concentration but with two different initial PU contents (vials A2 and A3) present different particle sizes. Moreover, after leaving the vials 48 h without stirring [Fig. 5(B)] the dispersion with 0.30 mmol DMPA/ g_{pol} and 50 wt % PU precipitates, probably due to the presence of large aggregates (see A3/B3). Nevertheless, when the PU content is increased (70 wt %), a stable dispersion is obtained with a lower DMPA concentration (0.16 mmol/ g_{pol} , vials A4/B4) although it has a similar mean particle size.

Figure 6 shows the minimum amount of DMPA required for obtaining a stable dispersion as a function of the PU content. As can be observed, this amount decreases as the PU content increases. This result agrees with data reported in literature^{17,20} where it is concluded that a minimum number of ionic groups is needed to obtain a stable dispersion. However, this study demonstrates that the minimum depends on the polymer/acetone ratio. Therefore, to obtain stable dispersions, both parameters (DMPA concentration and polymer acetone/ratio) must be selected altogether and not separately, as reported in

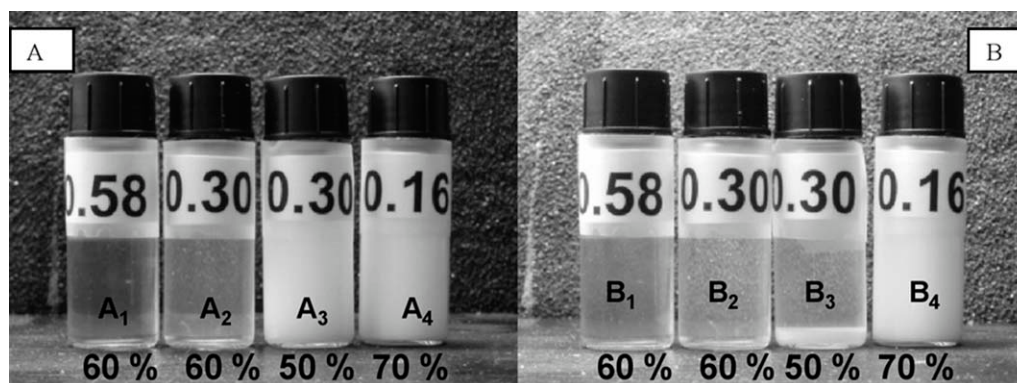


Figure 5 Photographs of samples with different DMPA concentrations and PU contents. Starting point (A-left) and after 48 h without stirring (B-right).

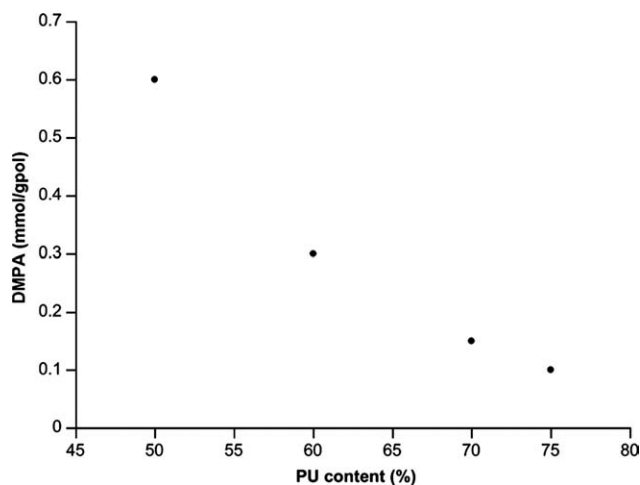


Figure 6 Minimum amount of DMPA for obtaining stable dispersions as a function of the initial PU content.

literature.^{17,20} In addition to the DMPA and acetone concentrations, the effect of the precipitation temperature was also studied. The effect of this variable both on particle size and dispersion stability has not clearly been stated in literature, so far. To study this effect, the DMPA concentration and the starting PU content were maintained constant at 0.30 mmol DMPA/g_{pol} and 60 wt %, respectively.

Figure 7 shows the evolution of the particle size during the water addition process at different temperatures. As can be seen, the temperature has an important effect on the phase-inversion process. At low temperatures (25–30°C), the particle size remains stable close to 40 nm. However, when the phase-inversion temperature is set up at 35°C or higher, there is a significant increase in the particle size, and the dispersion becomes unstable. Even

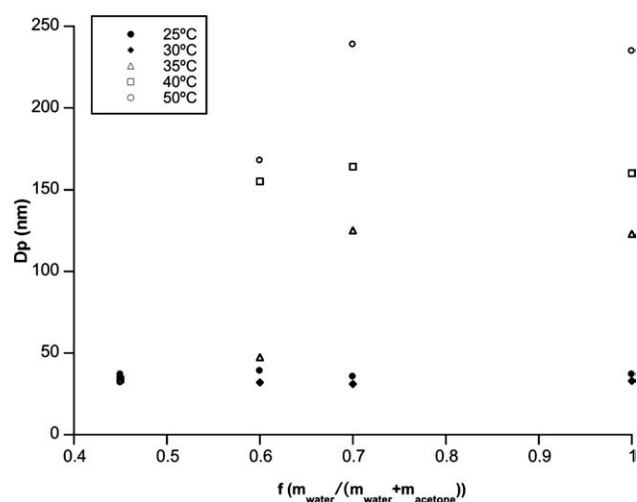


Figure 7 Particle size obtained during the phase-inversion process carried out at different temperatures, DMPA concentration 0.30 mmol/g_{pol} and PU content (60 wt %). The stable dispersions are represented by filled symbols.

though the mean particle size is not very large, the polydispersity index is high due to the presence of aggregates larger than typically 1 μm, and therefore the dispersions obtained at higher temperatures precipitate in a short period of time.

According to our results, it is clear that not only does the DMPA content control the dispersion characteristics, but the initial content of PU and the phase-inversion temperature also play an important role in the formation of stable PU dispersions.

All the results shown so far were obtained removing the acetone at room temperature. Although a higher removal temperature permits faster solvent evaporation, it can substantially affect particle size and dispersion stability because of the formation of aggregates. To prove this point, the acetone was evaporated at different temperatures for the system obtained using 0.30 mmol DMPA/g_{pol} and a starting PU content of 60 wt %. The results are shown in Table II. As can be seen, higher temperature of evaporation results in higher particle size and polydispersity index, indicating the presence of large aggregates. According to these results, low temperatures have to be used to remove the acetone from the system.

Finally, a series of experiments was carried out to study the influence of the water miscibility of the solvent used on the nanoprecipitation process. Two different organic solvents were tested in addition to acetone (totally miscible with water), that is, chloroform (water solubility: 1 g/100 mL at 15°C) and THF (miscible). The DMPA concentration and the initial PU content were maintained constant at 0.30 mmol/g_{pol} and 60 wt %, respectively.

Figure 8 shows the evolution of the particle size during the water addition process for the three different solvents at 25°C. The particle size variation during the phase-inversion process is different depending on the solvent. When using a totally miscible solvent (acetone), the particle size remains constant during the whole process (around 30 nm). In our opinion, this behavior can be explained considering that most of the acetone is in the water phase and therefore cannot swell the formed particles. When using chloroform, the particle size fluctuates

TABLE II
Particle Size and Polydispersity Index for the System Obtained Using 0.30 mmol DMPA/g_{pol} and a Starting PU Content of 60 wt %, Removing the Acetone at Different Temperatures

Sample name	Particle size (nm)	Polydispersity index
PU in acetone/water	31 ± 2	0.15 ± 0.02
PU acetone removal at T = 25°C	29 ± 1	0.14 ± 0.02
PU acetone removal at T = 35°C	38 ± 2	0.18 ± 0.03
PU acetone removal at T = 45°C	43 ± 3	0.37 ± 0.05

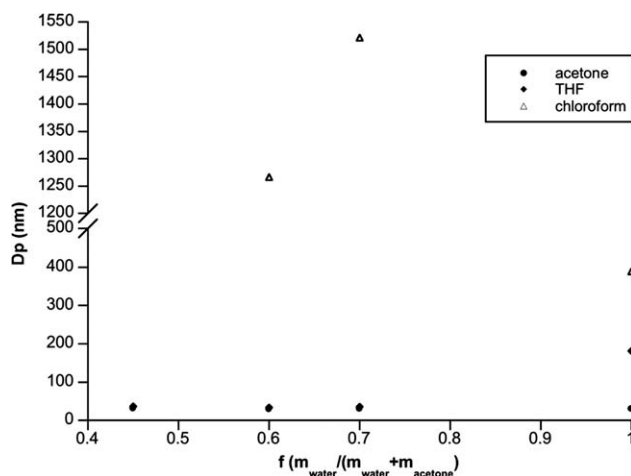


Figure 8 Particle size variation during the phase-inversion process using different solvents. The stable dispersions are represented by filled symbols.

along the process. At the beginning, large particles are obtained, but after solvent evaporation ($f = 1$), the particle size decreases substantially. We suggest that this phenomenon occurs, because the PU particles are swollen due to the presence of chloroform, and therefore, after its evaporation, the particle size is reduced. When THF is used, the particle size does not change during the water addition, but, when THF is evaporated, the particle size considerably increases (from 34 to 180 nm).

Rheological behavior of the PU during the phase-inversion process

According to literature,^{20,21} the phase-inversion process during the production of aqueous PU dispersions follows three consecutive steps. In the initial one, the first water drops are soluble in the PU/acetone solution and therefore the viscosity is slightly reduced. However, in the second one, the generation of PU particles makes the viscosity rise sharply. After reaching a maximum, the viscosity finally drops again, because the effect of adding more water is just to dilute the dispersion and not to generate new particles.

Effect of PU content

The phase-inversion point was detected by measuring the viscosity during the water-addition process.

Figure 9 shows the viscosity evolution versus f at 25°C for a system containing 0.30 mmol DMPA/ g_{pol} for three different initial PU contents. As can be seen, the three stages mentioned earlier are clearly observed only for the case of the system containing initially 70 wt % of PU. However, the three systems present an increase of the viscosity, which is more

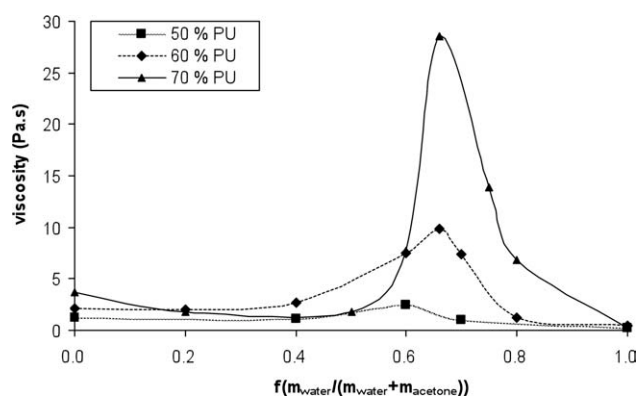


Figure 9 Viscosity evolution as a function of f for different initial PU contents and a fixed DMPA content of 0.30 mmol/ g_{pol} at 25°C.

pronounced as the initial PU content increases. Although the effect of the initial PU content on the maximum viscosity has also been discussed in the literature,¹⁷ there is no clear explanation to describe this phenomenon. From our point of view, two possible facts can be responsible for this result. First of all, as already mentioned, the higher particle size (200 nm) of the system with the lowest PU content (50 wt %) reduces the possibility of particle interaction, leading to a lower increase of the viscosity at the inversion point. However, the viscosity value corresponding to the phase-inversion point is very different for the systems containing 60 and 70 wt % of PU although their particle sizes are almost identical (30 nm). Taking into account that the polymer concentration at the inversion points varies from about 35 to 43 wt % of PU in these systems, respectively, we believe that this factor can be responsible for the viscosity difference observed at the phase-inversion points.

Effect of the phase-inversion temperature

The effect of the phase-inversion temperature was also studied. Figure 10 shows the viscosity evolution for three different phase-inversion temperatures at

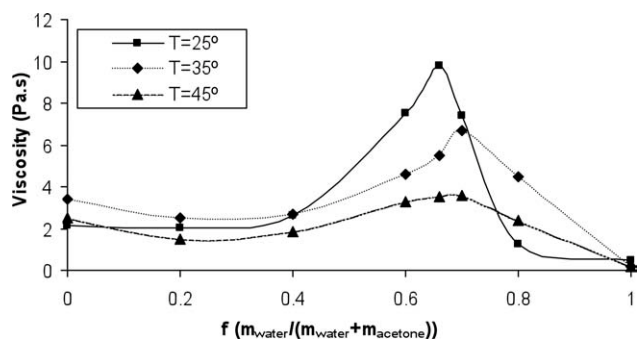


Figure 10 Evolution of the viscosity as a function of f for three different temperatures of phase inversion (60 wt % of initial PU; 0.30 mmol DMPA/ g_{pol}).

60 wt % of initial PU content for a system containing 0.30 mmol DMPA/g_{pol}. As water content increases, the viscosity reaches a maximum whose value decreases with temperature. Furthermore, this maximum remains almost constant for 35 and 45°C and shifts toward lower *f* values at 25°C. This result can be explained considering that PU solubility in the acetone/water mixture increases with temperature.

Effect of solvent affinity toward water

As mentioned earlier in the text, in addition to acetone, two other solvents (chloroform and THF) were tested to study the effect of the miscibility of the organic solvent with water. The phase-inversion process was studied at 25°C using 60 wt % and a DMPA concentration of 0.30 mmol/g_{pol}.

Figure 11 shows the viscosity curves during the phase-inversion process with the three different organic solvents. When using chloroform as solvent, the viscosity curve shifts toward lower *f* values. This result can be explained by taking into account the lower solubility of water toward chloroform. In this case, less water can be absorbed by the chloroform/PU system than in the other two cases, and therefore the particle formation occurs faster. For THF and acetone, the viscosity curves are similar, and no significant differences are observed between these two solvents. In our opinion, the solubility of THF with water is sufficient to absorb almost the same amount of water as in the case of acetone, leading to a similar phase-inversion mechanism.

Ternary diagram for the acetone process

The phase-inversion process can be represented using a ternary diagram (Fig. 12). The turbidity points were determined visually, and the maximum viscosity points by rheological studies. The connection of turbid points allows us to divide the diagram

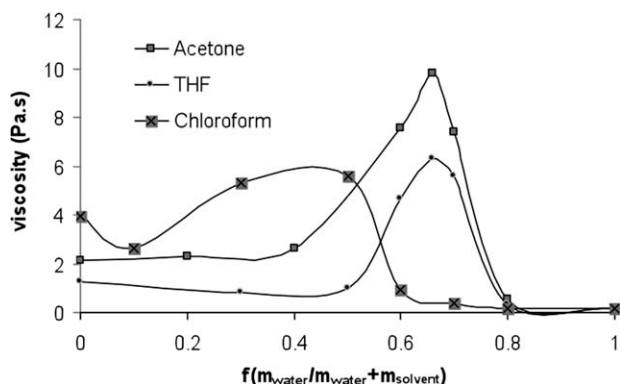


Figure 11 Evolution of the viscosity as a function of *f* for three different organic solvents at 25°C (60 wt % of PU; 0.30 mmol DMPA/g_{pol}).

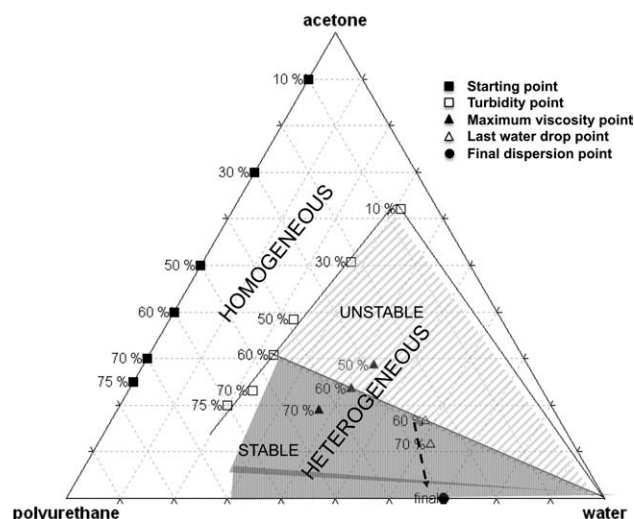


Figure 12 Schematic ternary diagram for the system containing 0.30 mmol DMPA/g_{pol} at 25°C.

into homogeneous and heterogeneous regions. The heterogeneous region can be further divided into stable (from 75 down to 60 wt % of PU) and unstable regions (from 60 down to 10 wt % of PU). Furthermore, maximum viscosity points are those at which no more PU particles are formed. The last water drop points are those where the last water drop is added to the PU/acetone mixture. The final dispersion point is taken when acetone is removed using a rotary evaporator.

According to the results summarized in Figure 12, 60 wt % of PU is needed to obtain stable water dispersions using 0.30 mmol DMPA/g_{pol} and working at 25°C. However, if DMPA concentration is varied, the diagram changes, because both PU affinity toward water and the ionic strength increase with DMPA content. In addition, when the temperature is increased, PU solubility in both solvents changes and consequently the diagram is also different.

From our point of view, the acetone concentration promotes two different particle formation mechanisms in accordance with literature results for other similar systems.^{22–25} When the acetone concentration exceeds a critical value (in our case, 40 wt %), we presume that the emulsification takes place by spinodal decomposition, which produces coarse emulsions that, therefore, separate rapidly. On the other hand, when the acetone concentration is lower than a limit value, the particle stabilization occurs by means of spontaneous emulsification (Ouzo effect), generating small stable particles.

CONCLUSIONS

This work details the preparation of waterborne PU dispersions using the acetone process. The influence of various parameters such as the concentration of

an acid functionalized diol (i.e., DMPA), the initial PU content, the phase-inversion temperature, the evaporation temperature or the solvent affinity toward water on the final particle size, and dispersion stability was studied.

It was shown that a minimum amount of DMPA is required to obtain stable PU dispersions. However, this minimum concentration depends on many other variables such as the initial PU content, the phase-inversion temperature, and the solvent affinity toward water. Moreover, it is important to take into account that the evaporation conditions, once the phase inversion is carried out, can create instability in the PU dispersions, and therefore mild temperatures (25–30°C) have to be used to avoid the generation of large aggregates.

The viscosity behavior during the phase-inversion process gives interesting information about the steps leading to particle formation, although there are still some open questions about the particle formation mechanism.

The ternary diagram enables us to fix the optimum conditions to obtain stable polymer dispersions. However, different diagrams can be obtained varying the concentration of the internal emulsifier, temperature, and solvent nature.

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