

Ultrasound assisted miniemulsion polymerization to prepare poly(urea-urethane) nanoparticles

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Abstract

Recently, the physical and chemical effects of ultrasound in polymeric materials synthesis have attracted great attention. This work presents the synthesis of novel polymeric materials by polymerization of isophorone diisocyanate with different polyols. Polymers were synthesized by step miniemulsion polymerizations, using ultrasound bath and thermostatic bath. The effects of ultrasound, temperature and polyol type were evaluated by Fourier transform infrared spectroscopy, gel permeation chromatography, dynamic light scattering and titrimetry. Polymerization under ultrasound bath showed that different reaction temperatures in the range between 50 °C and 80 °C directly influence the molecular weight of the polymers, urea/urethane formation and increase of diisocyanate consumption rate. In addition, different polyols used in polymerizations in miniemulsion had a significant effect on the characteristics of the resulting poly(urea-urethane) nanoparticles. Finally, ultrasound assisted polymerizations showed a faster diisocyanate consumption rate, but did not lead to enhanced molecular weights.

Keywords: miniemulsion polymerization, poly(urea-urethane), ultrasound.

1. Introduction

Synthesis of new polymeric materials have attracted the interest of researchers, chemical and pharmaceutical industries. Continuous improvement of polymers and polymerization methods is a still growing field of interest. Production of materials with different characteristics, as surface characteristics, molecular weight, crosslinking degree and inorganic materials addition is a very active research field^[1-7].

Miniemulsion is a polymerization technique that has been gaining much attention due to some advantages when compared to conventional emulsion polymerization^[8,9]. Miniemulsions are described as aqueous dispersions of relatively stable oil droplets within a size range (from 50 to 500 nm), prepared in a system containing a dispersed phase (organic), continuous phase (aqueous), an emulsifier and a co-stabilizer^[10,11]. To obtain this dispersion, a mechanism of high shear stress is required to break the monomer droplets into submicron droplets, reaching a steady state obtained by balancing the rates of coalescence and breakage of droplets that are kinetically, but not thermodynamically stable. In this way, since these droplets are protected against molecular diffusion (Ostwald Ripening) and coalescence, the size of polymeric particles formed after reaction is expected to remain practically the same as that of the droplets formed during miniemulsification^[12,13]. In addition, the latex formed by miniemulsion polymerization may also exhibit viscosity and colloidal stability different from those of conventional emulsion polymerizations, resulting in more stable latexes with same surfactant concentration, possibility of obtaining latexes with a high solids content and hybrid organic/inorganic and organic/organic materials^[13,14].

The development of poly(urea-urethane) (PUU) has been extensively studied in the last decades due to their excellent physical properties^[2,15-17] ranging from very soft elastomers to very rigid plastics^[4,16,18]. Poly(urea-urethane) nanoparticles obtained by miniemulsion polymerization are being used in different areas such as pharmaceutical, medical and cosmetic, especially as a means of drug delivery because of their excellent physical and biocompatibility properties^[2,4,19-21].

In PUU synthesis, the main reaction involves the formation of urethane segments in the reaction between isocyanates (NCO) and OH groups from a polyol, Figure 1. Urea groups may be formed in a secondary reaction with water and with the release of CO₂, as shown in Figure 2, wherein water reacts with a diisocyanate to form an amine and CO₂. The formed amine can rapidly react with an isocyanate group to generate a compound with a urea bond, modifying the final properties of PUU^[22].

The use of ultrasound bath in organic synthesis has been broadly expanded in recent years since it may enhance the reaction rate and selectivity of the product rather significantly^[23-25]. Many studies have been carried out and advantages of ultrasound procedures as good yields, short reaction times and mild conditions have been reported^[24,26]. In this way, the use of ultrasound in organic synthesis is now recognized as a viable environmentally benign alternative^[27]. When ultrasound propagates in sound-bearing media, it can cause some effects on this media including mechanical, thermal and cavitation effect^[23,26,28,29]. Few works report the use of ultrasound with the aim to affect the course of

580 g mol⁻¹ and 3,800,000 g mol⁻¹ were used to calculate average molecular weights.

Average diameters (intensity averages – Dpz) of PUU nanoparticles were measured at 25 °C using dynamic light scattering equipment (DLS, Zetasizer Nano S, from Malvern). Analyses were carried out in duplicate. Fourier transform infrared spectroscopy (FTIR, IR Prestige-21, Shimadzu), using the resolution of 4.0 cm⁻¹, was used to identify features of IPDI, the absorption band with peak location at 2270 cm⁻¹, related to N=C=O stretching vibration of isocyanate groups was used. At the end of the reaction, the band located between 1680-1650 cm⁻¹ relative to N-H group of urea and the absorption band between 1740-1700 cm⁻¹ due to stretching vibration of C=O group of urethane, were used to identify peaks of poly(urea-urethane)^[4].

3. Results and Discussions

3.1 Influence of polyol type in the PUU synthesis using ultrasound and thermostatic bath

For the study of the polyol type influence on the synthesis of PUU nanoparticles, reactions were carried out in ultrasound bath and thermostatic bath, using as monomers castor oil/PEG 400, castor oil/PEG 1000, 1,6-hexanediol, and glycerol, besides IPDI. Reactions were conducted at 70 °C for both reaction systems and when in ultrasound bath, power was kept constant at 132 W. When thermostatic bath was used, reactions were kept under magnetic stirring. FTIR (Figure 3 and Figure 4) was used to confirm urethane and urea formation during these miniemulsion polymerizations.

The characteristic carbonyl stretching was observed at 1740-1700 cm⁻¹, indicating the presence of urethane linkage. The absorption band of urea groups (-NH) was observed between 1680-1650 cm⁻¹. When reactions were conducted under ultrasound bath, absence of absorbance at 2270 cm⁻¹ (N-C-O stretching vibration) indicates that all isocyanate groups were consumed during the reaction. In the reactions conducted in the thermostatic bath, the absorption band located at 2270 cm⁻¹ was still found and that could be explained by the fact that these reactions were slower when compared with the same reactions in as ultrasound bath, thereby the isocyanate groups were not completely consumed at the end of reaction time.

Figure 5 shows urethane/urea area ratios calculated from FTIR spectra of PUU synthesized by step miniemulsion polymerization using ultrasound bath at 132 W or thermostatic bath, both at 70°C. To obtain such ratios, the areas of the respective peaks (1740-1700 cm⁻¹ for urethane bonds and 1680-1650 cm⁻¹ for urea groups) were integrated and then compared. When the water soluble polyols, 1,6-hexanediol and glycerol were used, it was not possible to separate the peaks related to urethane linkages in the FTIR spectra. Therefore, the ratio between urethane/urea peaks was calculated only for reactions using castor oil/PEG 400 and castor oil/PEG 1000 as polyols. It can be observed that reactions conducted under ultrasound bath resulted in a slightly lower ratio between the urethane/urea peaks. This indicates that the use of ultrasound bath led to a small increase in the reaction between isocyanate groups and OH from water, generating higher amount of polyurea.

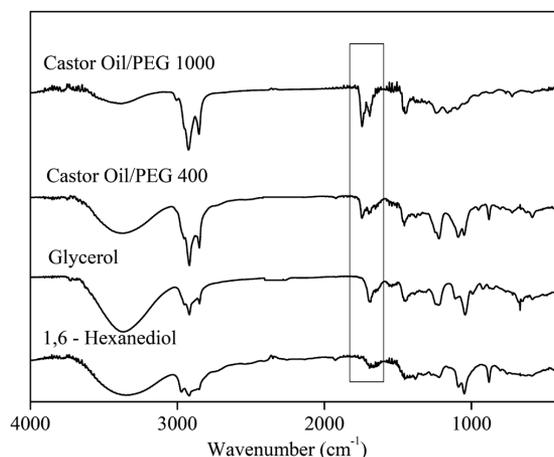


Figure 3. FTIR spectra of PUU synthesized by step miniemulsion polymerization using ultrasound bath at 132 W at 70 °C with different polyols type.

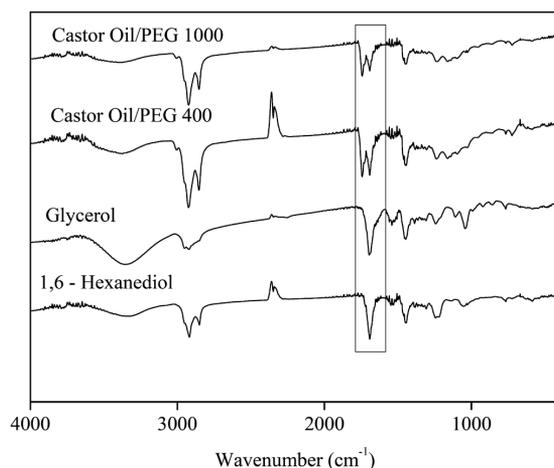


Figure 4. FTIR spectra of PUU synthesized by step miniemulsion polymerization using thermostatic bath at 70 °C with different polyols type.

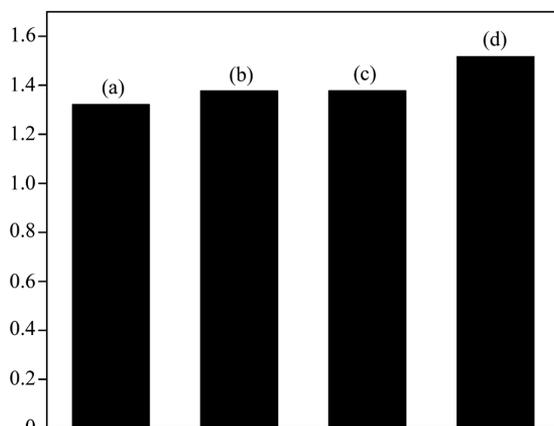


Figure 5. Urethane/urea ratio calculated from FTIR areas of PUU produced using (a) castor oil/PEG 400 (ultrasound bath), (b) castor oil/PEG 400 (thermostatic bath), (c) castor oil/PEG 1000 (ultrasound bath) and (d) castor oil/PEG 1000 (thermostatic bath).

As can be observed in Table 1, when replacing 1,6-hexanediol (molecular weight 118 g mol^{-1}) by the mixture of castor oil/PEG 400 and castor oil/PEG 1000 as monomers (molecular weight 928/400 and 928/1000 g mol^{-1} , respectively) PUU molecular weight was increased. Moreover, reactions conducted in US bath resulted in lower molecular weight values when using 1,6-hexanediol and castor oil/PEG 1000 as monomers, probably due to the increase of the reaction forming urea bonds, as observed in the FTIR results. This reaction uses two NCO groups for each OH group from water, thus reducing the molecular weight. Due to the fact that these reactions were conducted in miniemulsion (using water as continuous phase) these results are different from those of Price et al.^[31] who polymerized different isocyanates with different diols in bulk using an ultrasound and observed that the rate of reaction could be accelerated and molecular weights were increased in comparison with reactions without the use of ultrasound.

3.2 Effect of temperature in the PUU synthesis using ultrasound and thermostatic bath

Initially, the influence of temperature in a range from 50°C up to 80°C was studied and the results using ultrasound bath were compared with conventional reaction at 70°C . The use of thermostatic bath at 70°C was based on previous studies that related 70°C as optimum for PUU synthesis^[4]. The polyol used to study the influence of temperature was castor oil/PEG 400 in a molar ratio of 9:1. Results in terms of NCO consumption are shown in Figure 6.

As shown in Figure 6, lower reaction rates were obtained at 50°C , what can be explained by the fact that this temperature will not result in an efficient mobility of monomer molecules hindering the reaction between functional groups (NCO-OH), as reported in the literature^[19]. Results obtained for reactions at 70°C using ultrasound bath showed higher NCO consumption rate when compared with the same reactions using thermostatic bath. The increase in NCO consumption rate can be explained by the ultrasound effect, since it causes an increase in molecules mobility, and at 70°C the effect of cavitation and bubble collapse are higher, enhancing the reaction of NCO groups with OH groups of the polyol and with water to form, respectively, urethane and urea linkages. Another explanation for the higher NCO consumption under ultrasound bath would be the heating caused by sonication: the collapse of micro bubbles formed by cavitation results in an elevation of local temperature and, thus, local reaction rate, but does not affect the system temperature as a whole. Increasing reaction temperature further to 80°C did not lead to a further

increase of the NCO consumption rate, as already observed for reactions under conventional heating^[4]. This behavior is attributed to the higher water solubility at 80°C increasing the contribution of side reactions generating urea bonds.

The ratio between the diameter of PUU nanoparticles and the initial diameter of the monomer droplets at different reaction temperatures is shown in Figure 7, it is possible to see that PUU nanoparticles size remained constant during the reaction indicating that droplets/particles remained stable

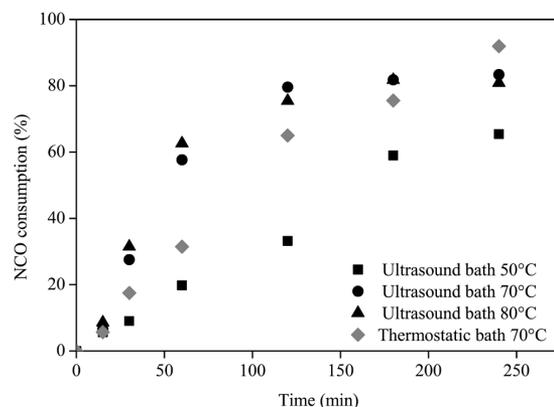


Figure 6. NCO consumption for poly(urea-urethane) reactions obtained by miniemulsion using thermostatic bath at 70°C and ultrasound bath at 132 W at different temperatures.

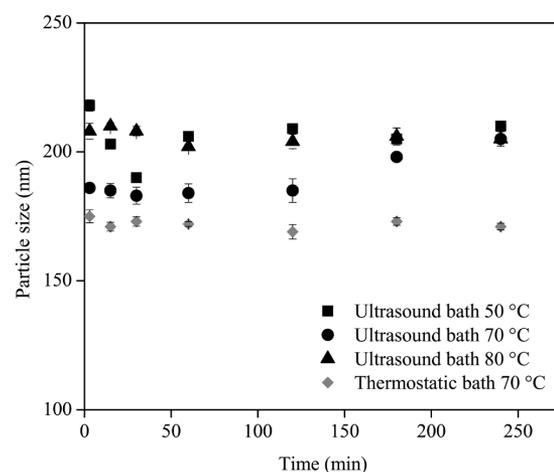


Figure 7. Diameter evolution of PUU nanoparticles during step miniemulsion polymerizations with thermostatic bath at 70°C and ultrasound bath at 132 W at 50, 70 and 80°C .

Table 1. Weight average (Mw) and number average (Mn) molecular weights and dispersities (Đ) of PUU nanoparticles obtained in ultrasound bath at 70°C , using different polyols as monomers.

Polyol	US 132 W			Thermostatic bath		
	Mw (g mol^{-1})	Mn (g mol^{-1})	Đ	Mw (g mol^{-1})	Mn (g mol^{-1})	Đ
1,6-hexanediol	6200	3500	1.7	12600	5500	2.3
Glycerol	*	*	*	9100	4500	2.0
Castor oil/PEG 400	19100	9450	2.0	20400	9600	2.1
Castor oil/PEG 1000	20650	9400	2.2	29700	10700	2.8

*not soluble in THF.

Table 2. Weight average (Mw) and number average (Mn) molecular weights and dispersities (Đ) of PUU nanoparticles obtained by step miniemulsion polymerizations using ultrasound bath at different temperatures using isophorone diisocyanate and castor oil/PEG 400 as monomers.

Temperature (°C)	Mw (g/mol)	Mn (g/mol)	Đ
50	10800	6900	1.56
70	19100	9450	2.02
80	9690	6550	1.48

during polymerization and that the ultrasound bath did not affect their size (around 200 nm).

Table 2 shows the molecular weights of PUU nanoparticles obtained using ultrasound bath at 132 W and at different temperatures. When the temperature was increased from 50 °C to 70 °C, one can observe an increase in molecular weight from 10800 to 19100 g mol⁻¹. On the other hand, a further increase in temperature led to a decrease of molecular weight to around 9690 g mol⁻¹. This decrease can be attributed to side reactions of isocyanate group with water to form urea linkages with the release of carbon dioxide, resulting in lower molecular weights, since two isocyanate groups are consumed in the formation of each urea group. This occurs because the concentration of water in the organic phase increases with temperature^[4].

4. Conclusions

In this work, the effect of ultrasound bath in step miniemulsion polymerization of IPDI with different polyols was evaluated. Results show that molecular weights of poly(urea-urethane) was strongly influenced by the polyol type. Higher molecular weights were obtained using the mixture of castor oil/PEG 400 and castor oil/PEG 1000 as polyols. In addition, the reaction temperature also affected the molecular weight and reaction rates of materials produced. Results obtained for reactions at 70°C using ultrasound bath showed higher reaction rates when compared with the same reactions using thermostatic bath.

Finally, the samples produced using ultrasound bath showed lower values of molecular weight when compared with those produced when thermostatic bath was used, because ultrasound waves facilitate the hydrolysis of isocyanate, thus forming urea. Ultrasound bath, besides of accelerating the reaction, led to formation of larger fractions of urea and this can be a useful tool for producing polymers with different urea/urethane ratios, creating materials with distinctive characteristics.

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