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Polloni, André Eliezer; Valério, Alexsandra; Oliveira, Débora de; Araújo, Pedro Henrique Hermes de; Sayer, Claudia

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

André Eliezer Polloni¹

Universidade Federal de Santa Catarina , Brazil

Alexsandra Valério¹

Universidade Federal de Santa Catarina , Brazil

Débora de Oliveira¹

Universidade Federal de Santa Catarina , Brazil

Pedro Henrique Hermes de Araújo¹

Universidade Federal de Santa Catarina , Brazil

Claudia Sayer^{1*} claudia.sayer@ufsc.br

Universidade Federal de Santa Catarina , Brazil

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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 Rippening) 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].

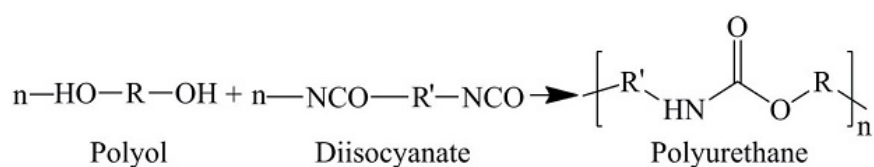
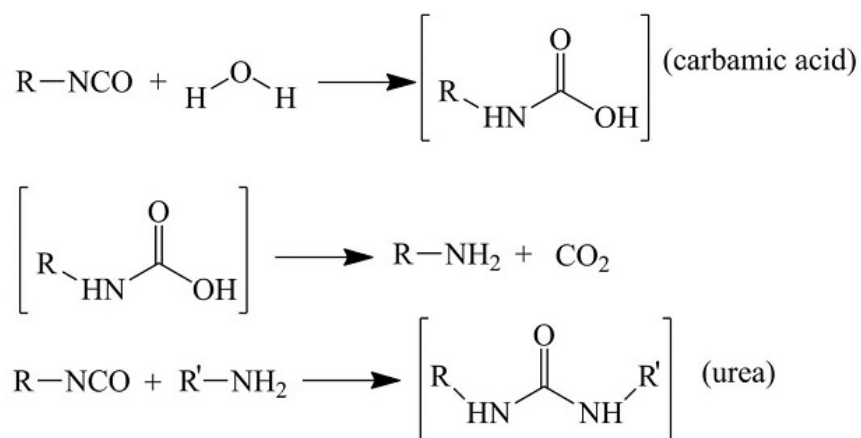


Figure 1.

Polyurethane formation by the reaction between a polyol and a diisocyanate.

**Figure 2.**

Urea formation by reaction between a isocyanate group and water.

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 polymerization reactions^[23,24,30,31]. Price et al.^[31] present an investigation of the effect of ultrasound on the synthesis of polyurethane in bulk polymerization using a diisocyanate:diol molar ratio of 1:1. The ultrasound system used was a sonic horn system operating at 23 kHz. Polymerization times and molecular weights have been improved by the use of high intensity ultrasound, and increasing the ultrasound intensity lowered the reaction times but had no significant effect of the molecular weight of the polymers formed. The authors attributed this effect of ultrasound heating to local heating around collapsing cavitation bubbles together with the enhanced mass transfer caused by the fluid motion.

In this work the influence of ultrasound bath, temperature and different polyols on NCO consumption rate and on final characteristics (urea/urethane ratio, molecular weight and particle diameter) of poly(urea-urethane) nanoparticles produced by step miniemulsion polymerization were evaluated. Among the polyols used some were oil soluble and others water soluble leading to interfacial polymerization.

2. Materials and Methods

2.1 Materials

For the synthesis of poly(urea-urethane) nanoparticles the following reactants were used: castor oil (100%, Mw 928 g mol⁻¹) from Linfar, isophorone diisocyanate (IPDI, 98%, Mw 222 g mol⁻¹), poly(ethylene glycol) diol with nominal molecular weights of 400 Da (PEG400) and 1000 Da (PEG1000), 1,6-hexanediol (99%), glycerol (99%), and surfactant sodium dodecyl sulfate (SDS, from Sigma–Aldrich). N-Dibutylamine (Vetec, 99%), toluene (Vetec, 99.5%), propanol (Synth, 99.5%), chloridric acid 1N (HCl, Cronoline, PA), and bromophenol blue 0.1% (Lafan) were used for free NCO quantification. All reagents were used as received.

2.2 Methods

2.1.1 Synthesis of PUU nanoparticles by miniemulsion polymerization

PUU nanoparticles were prepared by miniemulsion step polymerization according to a procedure based on a previous work^[4]. Aqueous phase (90 wt % relative to the total formulation) was prepared with 10 wt % of surfactant (SDS) relative to the organic phase. The organic phase was prepared with IPDI and polyol, keeping the molar ratio NCO:OH constant for all reactions at 1.5:1. When castor oil/PEG 400 and castor oil/PEG 1000 were used as polyols, they were dissolved in organic phase along with IPDI and remained inside the monomer droplets; thereby the polymerization was inside monomer droplets. When 1,6-hexanediol and glycerol were used as polyols, they were dissolved in the aqueous phase while the IPDI was dispersed in the organic phase and polymerization occurred in the organic/aqueous phase interface.

At first, the aqueous phase was added slowly to the organic phase under magnetic stirring and kept for 5 min at room temperature to form a coarse emulsion. In sequence, the miniemulsion was prepared by sonication of the previous emulsion for 120 seconds at 70% of amplitude (Ultrasonic Dismembrator model 500, Fisher Scientific – 400 W). This miniemulsification step was conducted using an ice bath to prevent polymerization. After that, the miniemulsion was placed in two different reactors: a jacketed reactor with constant magnetic stirring at 70 °C unless mentioned, for 3 h at low pressure (1 atm) or in glass vials inserted in an ultrasound bath (without agitation) (USC-1880A, 37 kHz, 132 watts, 3.8 liters, UNIQUE) at 70 °C unless mentioned, for 3 h at low pressure (1 atm). Special care was taken with samples inserted in ultrasound bath, i.e.; samples were always placed in the same position inside the ultrasound bath and the amount of distilled water inside the bath was always the same, avoiding differences in cavitation formation during the reactions.

A schematic representation of miniemulsification and polymerization processes is presented in Scheme 1.

Scheme 1.

Schematic representation of PUU nanoparticles synthesis via miniemulsion polymerization.

2.1.2 Characterization

Free NCO concentration was quantified based on the NCO standard dibutylamine back-titration method^[32], titrations were conducted in duplicate. The molecular weight was evaluated by gel permeation chromatography (GPC in a High Performance Liquid Chromatograph (HPLC, model LC-20A, Shimadzu, equipped with a RID-10A detector in tetrahydrofuran (THF) at 35 °C). GPC analyses were carried out by injecting 20 μL of a 0.5 wt% polymer solution (solvent THF, Merck), previously filtered through a Teflon-filter with a mesh size of 450 nm. A column set was employed consisting of three 300 x 8 mm columns in series (GPC-801, GPC-804 and GPC-807). Polystyrene standards between 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 $\text{N}=\text{C}=\text{O}$ 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 $\text{C}=\text{O}$ 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.

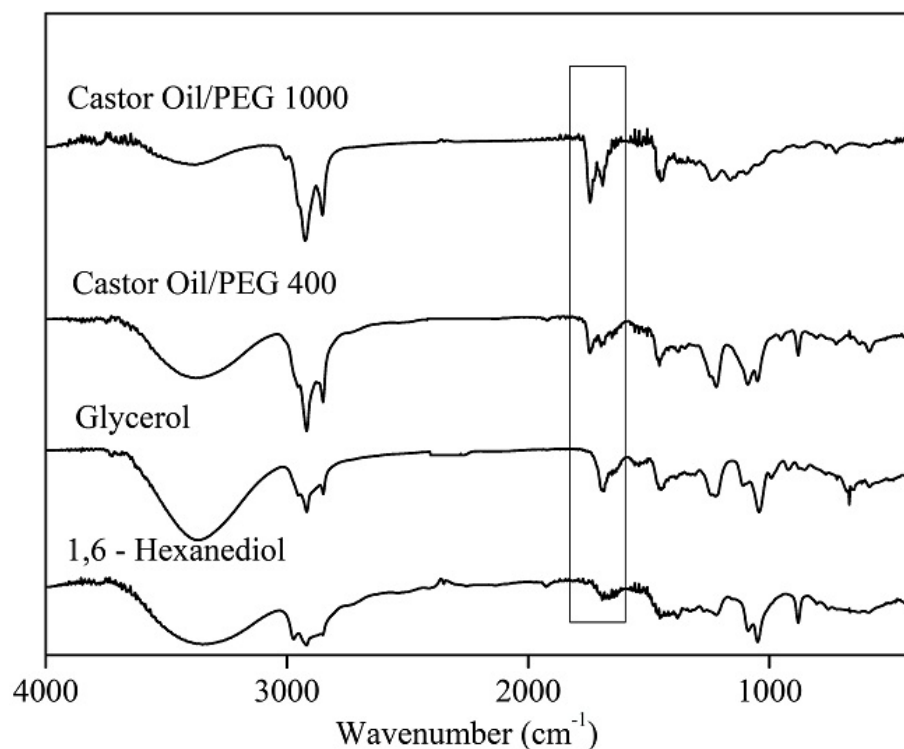


Figure 3.
FTIR spectra of PUU synthesized by step miniemulsion polymerization using ultrasound bath at 132 W at 70 °C with different polyols type.

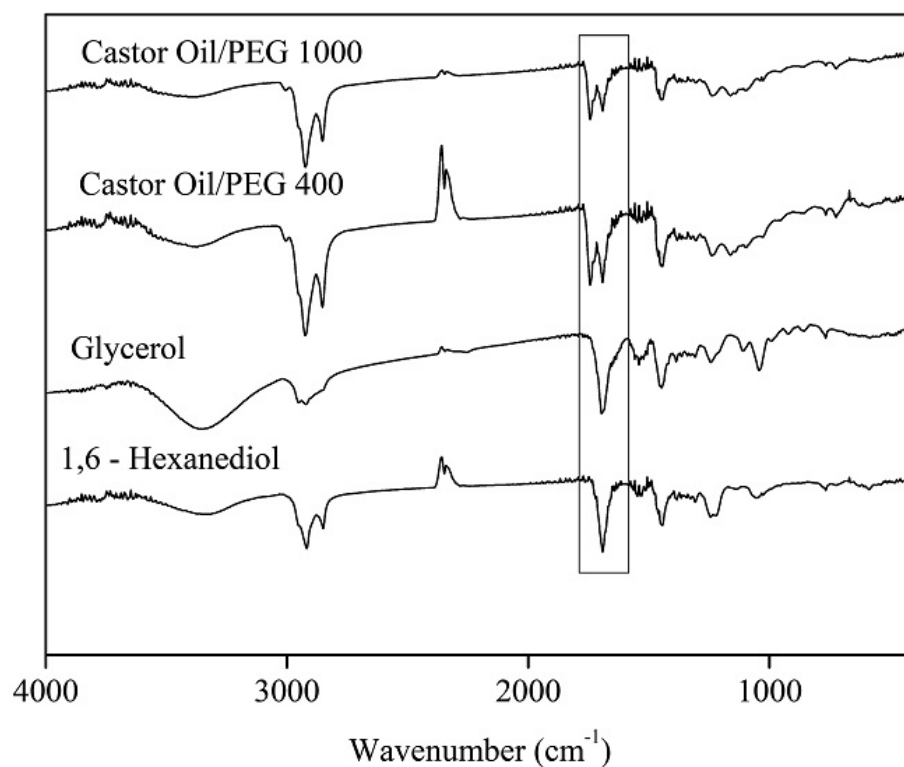


Figure 4.
FTIR spectra of PUU synthesized by step miniemulsion polymerization using thermostatic bath at 70 °C with different polyols type.

The characteristic carbonyl stretching was observed at 1740-1700 cm^{-1} , indicating the presence of urethane linkage. The absorption band of urea groups ($-\text{NH}$) was observed between 1680-1650 cm^{-1} . When reactions were conducted under ultrasound bath, absence of absorbance at 2270 cm^{-1} ($\text{N}-\text{C}-\text{O}$ 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.

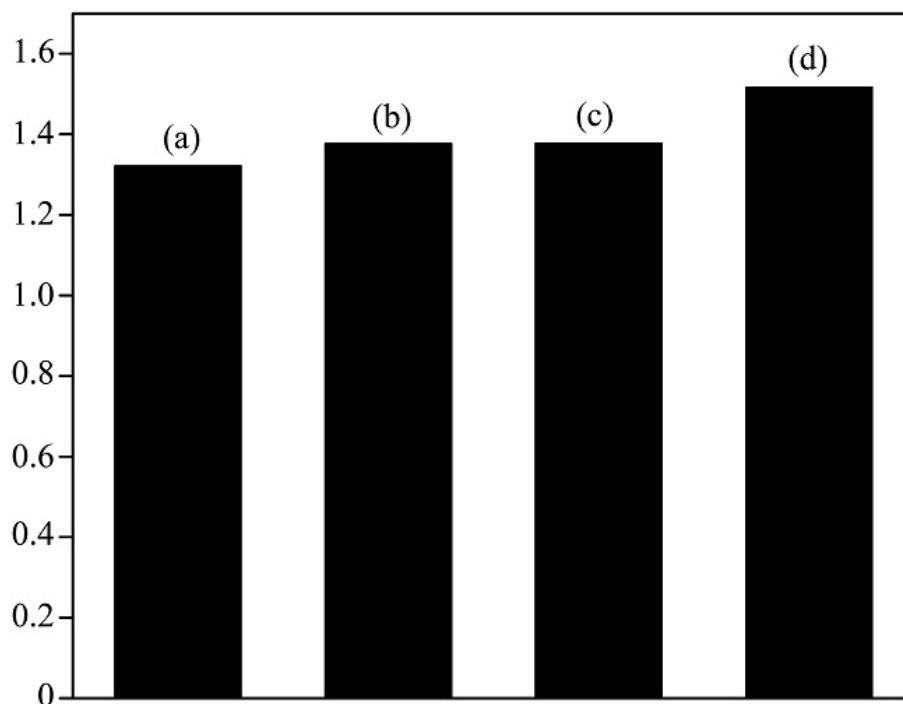


Figure 5.

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.

Table 1.

Weight average (Mw) and number average (Mn) molecular weights and dispersities (\bar{D}) 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)	\bar{D}	Mw (g mol ⁻¹)	Mn (g mol ⁻¹)	\bar{D}
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

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.

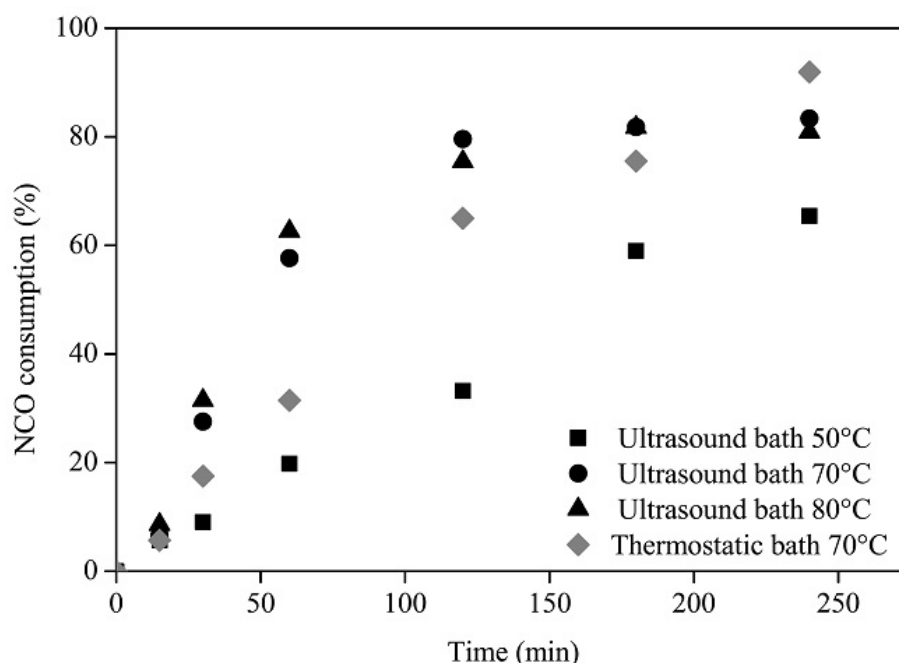


Figure 6.

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.

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

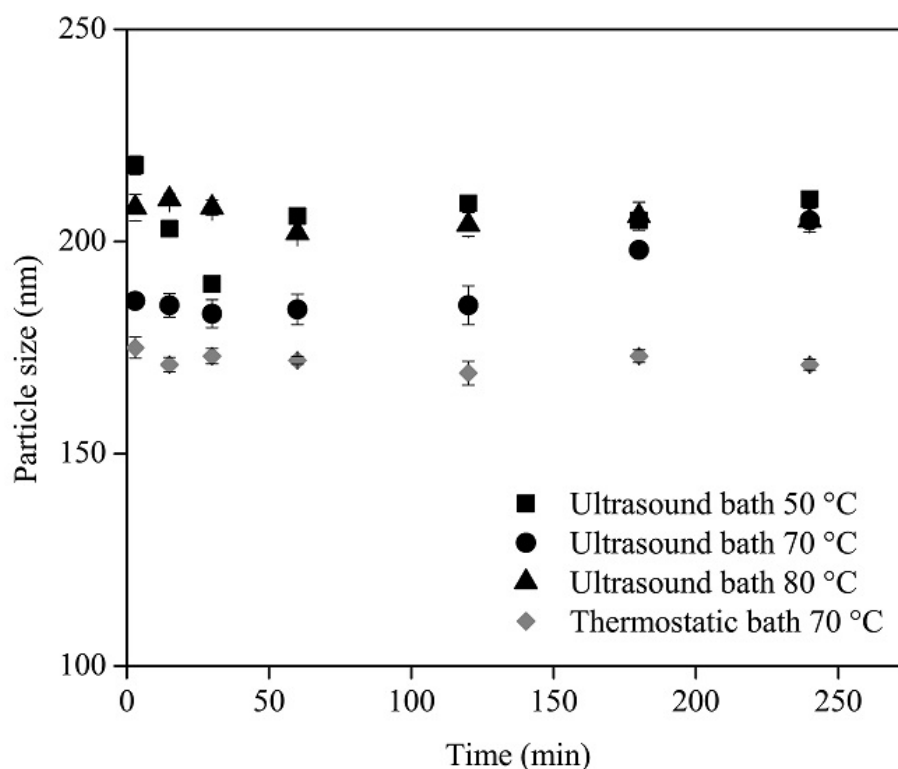


Figure 7.

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 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].

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

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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6. References

- 1 Gaudin, F., & Sintez-Zydowicz, N. (2008). Poly(urethane-urea) nanocapsules prepared by interfacial step polymerization in miniemulsion. The droplet size: a key-factor for the molecular and thermal characteristics of the polymeric membrane of the nanocapsules?. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 384(1-3), 698-712. <https://doi.org/10.1016/j.colsurfa.2011.05.050>.
- 2 Ding, M., He, X., Wang, Z., Li, J., Tan, H., Deng, H., Fu, Q., & Gu, Q. (2011). Cellular uptake of polyurethane nanocarriers mediated by gemini quaternary ammonium. *Biomaterials*, 32(35), 9515-9524. PMID:21907404. <http://dx.doi.org/10.1016/j.biomaterials.2011.08.074>.
- 3 Souto, E. B., Severino, P., & Santana, M. H. (2012). Preparação de nanopartículas poliméricas a partir da polimerização de monômeros: parte I. *Polímeros: Ciência e Tecnologia*, 22(1), 96-100. <http://dx.doi.org/10.1590/S0104-14282012005000006>.
- 4 Valério, A., Araújo, P. H. H., & Sayer, C. (2013). Preparation of poly(urethane-urea) nanoparticles containing açaí oil by miniemulsion polymerization. *Polímeros: Ciência e Tecnologia*, 23(4), 451-455. <http://dx.doi.org/10.4322/polimeros.2013.088>.
- 5 Mishra, A., Singh, S. H., Dash, D., Aswal, V., Maiti, B., Misra, M., & Maiti, P. (2014). Self-assembled aliphatic chain extended polyurethane nanobiohybrids: Emerging hemocompatible biomaterials for sustained drug delivery. *Acta Biomaterialia*, 10(5), 2133-2146. PMID:24374322. <http://dx.doi.org/10.1016/j.actbio.2013.12.035>.
- 6 Kucinska-Lipka, J., Gubanska, I., Janik, H., & Sienkiewicz, M. (2015). Fabrication of polyurethane and polyurethane based composite fibres by the electrospinning technique for soft tissue engineering of cardiovascular system. *Materials Science and Engineering C*, 46(1), 166-176. PMID:25491973. <http://dx.doi.org/10.1016/j.msec.2014.10.027>.
- 7 Trinca, R. B., & Felisberti, M. I. (2015). Segmented polyurethanes based on poly(L-lactide), poly(ethylene glycol) and poly(trimethylene carbonate): physico-chemical properties and morphology. *European Polymer Journal*, 62, 77-86. <http://dx.doi.org/10.1016/j.eurpolymj.2014.11.008>.
- 8 Hecht, L. L., Winkelmann, M., Wagner, C., Landfester, K., Gerlinger, W., Sachweh, B., & Schuchmann, H. P. (2012). Miniemulsions for the production of nanostructured particles. *Chemical Engineering & Technology*, 35(9), 1670-1676. <http://dx.doi.org/10.1002/ceat.201200196>.
- 9 Steinmacher, F. R., Bernardy, N., Moretto, J. B., Barcelos, E. I., Araújo, P. H. H., & Sayer, C. (2010). Kinetics of MMA and VAc Miniemulsion Polymerizations Using Miglyol and Castor Oil as Hydrophobe and Liquid Core. *Chemical Engineering & Technology*, 33(11), 1877-1887. <http://dx.doi.org/10.1002/ceat.201000256>.
- 10 Landfester, K., Bechthold, N., Tiarks, F., & Antonietti, M. (1999). Formulation and Stability Mechanisms of Polymerizable Miniemulsions. *Macromolecules*, 32(16), 5222-5228. <http://dx.doi.org/10.1021/ma990299+>.

- 11 Asua, J. M. (2002). Miniemulsion polymerization. *Progress in Polymer Science*, 27(7), 1283-1346. [http://dx.doi.org/10.1016/S0079-6700\(02\)00010-2](http://dx.doi.org/10.1016/S0079-6700(02)00010-2).
- 12 Suter, U. W. (2001). *Advances in polymer science: new polymerization techniques and synthetic methodologies*. New York: Springer-Verlag Berlin Heidelberg.
- 13 Schork, F. J., Luo, Y., Smulders, W., Russum, J. P., Butté, A., & Fontenot, K. (2005). *Advances in polymer science: miniemulsion polymerization*. New York: Springer-Verlag Berlin Heidelberg.
- 14 Ouzineb, K., Lord, C., Lesauze, N., Graillat, C., Tanguy, P. A., & McKenna, T. (2006). Homogenisation devices for the production of miniemulsions. *Chemical Engineering Science*, 61(9), 2994-3000. <http://dx.doi.org/10.1016/j.ces.2005.10.065>.
- 15 Xu, D., Wu, K., Zhang, Q., Hu, H., Xi, K., Chen, Q., Yu, X., Chen, J., & Jia, X. (2010). Synthesis and biocompatibility of anionic polyurethane nanoparticles coated with adsorbed chitosan. *Polymer*, 51(9), 1926-1933. <http://dx.doi.org/10.1016/j.polymer.2010.03.008>.
- 16 Zhou, L., Yu, L., Ding, M., Li, J., Tan, H., Wang, Z., & Fu, Q. (2011). Synthesis and characterization of pH-sensitive biodegradable polyurethane for potential drug delivery applications. *Macromolecules*, 44(4), 857-864. <http://dx.doi.org/10.1021/ma102346a>.
- 17 Miao, S., Wang, P., Su, Z., Liu, Y., & Zhang, S. (2012). Soybean oil-based shape-memory polyurethanes: Synthesis and characterization. *European Journal of Lipid Science and Technology*, 114(12), 1345-1351. <http://dx.doi.org/10.1002/ejlt.201200219>.
- 18 Wang, Z., Yu, L., Ding, M., Tan, H., Li, J., & Fu, Q. (2010). Preparation and rapid degradation of nontoxic biodegradable polyurethanes based on poly(lactic acid)-poly(ethylene glycol)-poly(lactic acid) and L-lysine diisocyanate. *Polymer Chemistry*, 2(3), 601-607. <http://dx.doi.org/10.1039/C0PY00235F>.
- 19 Valério, A., da Rocha, S. R. P., Araújo, P. H. H., & Sayer, C. (2013). Degradable polyurethane nanoparticles containing vegetable oils. *European Journal of Lipid Science and Technology*, 116(1), 24-30. <http://dx.doi.org/10.1002/ejlt.201300214>.
- 20 Zanetti-Ramos, B. G., Lemos-Senna, E., Cramail, H., Cloutet, E., Borsali, R., & Soldi, V. (2008). The role of surfactant in the miniemulsion polymerization of biodegradable polyurethane nanoparticles. *Materials Science and Engineering C*, 28(4), 526-531. <http://dx.doi.org/10.1016/j.msec.2007.04.041>.
- 21 Gaudin, F., & Sintès-Zydowicz, N. (2011). Poly(urethane-urea) nanocapsules prepared by interfacial step polymerization in miniemulsion: the droplet size: a key-factor for the molecular and thermal characteristics of the polymeric membrane of the nanocapsules? *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 384, 698-712. <http://dx.doi.org/10.1016/j.colsurfa.2011.05.050>.
- 22 Barrère, M., & Landfester, K. (2003). High Molecular Weight Polyurethane and Polymer Hybrid Particles in Aqueous Miniemulsion. *Macromolecules*, 36(14), 5119-5125. <http://dx.doi.org/10.1021/ma025981+>.

- 23 Price, G. J. (1996). Ultrasonically enhanced polymer synthesis. *Ultrasonics Sonochemistry* , 3(3), 229-238. [http://dx.doi.org/10.1016/S1350-4177\(96\)00031-4](http://dx.doi.org/10.1016/S1350-4177(96)00031-4).
- 24 Price, G. J., Lenz, E. J., & Ansell, C. W. G. (2002). The effect of high-intensity ultrasound on the ring-opening polymerisation of cyclic lactones. *European Polymer Journal* , 38(9), 1753-1760. [http://dx.doi.org/10.1016/S0014-3057\(02\)00056-3](http://dx.doi.org/10.1016/S0014-3057(02)00056-3).
- 25 Barkade, S. S., Naik, J. B., & Sonawane, S. H. (2011). Ultrasound assisted miniemulsion synthesis of polyaniline/Ag nanocomposite and its application for ethanol vapor sensing. *Colloids and Surfaces. A, Physicochemical and Engineering Aspects*, 378(1-3), 94-98. <http://dx.doi.org/10.1016/j.colsurfa.2011.02.002>.
- 26 Bhanvase, B. A., & Sonawane, S. H. (2014). Ultrasound assisted in situ emulsion polymerization for polymer nanocomposite: A review. *Chemical Engineering and Processing: Process Intensification*, 85, 86-107. <http://dx.doi.org/10.1016/j.ccep.2014.08.007>.
- 27 Luzzio, F. A., & Moore, W. J. (1993). Ultrasound in oxochromium(VI)-mediated transformations. 2. Ultrasound-mediated preparation and applications of chromyl chloride. *The Journal of Organic Chemistry*, 58(2), 512-515. <http://dx.doi.org/10.1021/jo00054a043>.
- 28 Price, G. J. (2003). Recent developments in sonochemical polymerisation. *Ultrasonics Sonochemistry*, 10(4-5), 277-283. PMID:12818394. [http://dx.doi.org/10.1016/S1350-4177\(02\)00156-6](http://dx.doi.org/10.1016/S1350-4177(02)00156-6).
- 29 Loganathan, S., & Rajendran, V. (2013). Ultrasound assisted polymerization of N-vinyl imidazole under phase-transfer catalysis condition - A kinetic study. *Ultrasonics Sonochemistry*, 20(1), 308-313. PMID:22922071. <http://dx.doi.org/10.1016/j.ultsonch.2012.07.004>.
- 30 Lerin, L. A., Loss, R. A., Remonatto, D., Zenevich, M. C., Balen, M., Oenning, V., No., Ninow, J. L., Trentin, C. M., Oliveira, J. V., & Oliveira, D. (2014). A review on lipase-catalyzed reactions in ultrasound-assisted systems. *Bioprocess and Biosystems Engineering* , 37(12), 2381-2394. PMID:24906428. <http://dx.doi.org/10.1007/s00449-014-1222-5>.
- 31 Price, G. J., Lenz, E. J., & Ansell, C. W. G. (2002). The effect of high intensity ultrasound on the synthesis of some polyurethanes. *European Polymer Journal*, 38(8), 1531-1536. [http://dx.doi.org/10.1016/S0014-3057\(02\)00039-3](http://dx.doi.org/10.1016/S0014-3057(02)00039-3).
- 32 American Society for Testing and Materials – ASTM. (2003). *ASTM D-2572: Standard Test Method for isocyanate Groups in Urethane Materials or Prepolymers* . West Conshohocken: ASTM.

Author notes

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claudia.sayer@ufsc.br