

Synthesis and characterization of biodegradable poly(ester-urethane)s based on poly(ϵ -caprolactone)

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Introduction

Nowadays there is a great interest in the scientific and technological world to develop biodegradable materials that can be use in the biomedical area. Polyurethanes constitutes an important family for these applications [1-2]. Polyurethanes are step polymers that can be obtained from the reaction between diols and diisocyanates. α - ω telechelic PCL diols (HOPCLOH), prepared from ϵ -caprolactone and diols can be used to prepare biodegradable polyurethanes [3]. Properties of these derivatives are similar to those observed for desirable biodegradable materials [4,5].

This work is concerning with: a) preparation of α - ω telechelic PCL diols (HOPCLOH) with molecular weights of 530, 1250 and 2000 g/mol, by ring opening polymerization of ϵ -caprolactone, using ethylene-diamine, hexamethylene-diamine and 1,10-diaminodecane as initiators, and $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$ or tin(II)-2-ethylhexanoate as catalysts, and b) preparation of polyurethanes by reaction of macrodiols with 1,6-diisocianate-hexane.

Experimental

Materials. ϵ -caprolactone (CL, Sigma-Aldrich) was dried over calcium hydride and distilled under vacuum before use. $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$ (Fluka) was grounded in a mortar and passed through a 100 mesh sieve. The catalyst was dried in an oven at 80°C overnight before use.

Ethylene-diamine, hexamethylene-diamine, 1,10-diaminodecane, Tin(II)-2-ethylhexanoate and 1,6-diisocyanate-hexane (Sigma-Aldrich) were used as received.

Synthesis.

α - ω telechelic PCL diols (HOPCLOH). All experiments were carried out in glass vials. In a typical experiment, 1 mL of CL (1.03g, 9.024mmol), ethylenediamine (29.3 μ L, 0.4328mmol for HOPCLOH of 1250 g/mol) or hexamethylene-diamine (67.5 μ L, 0.4542mmol for HOPCLOH of 1250 g/mol) or 1,10-diaminodecane (0.0849g, 0.4779mmol for HOPCLOH of 1250 g/mol) and catalyst ((NH₄)₈[Mo₁₀O₃₄] or Tin(II)-2-ethylhexanoate) were placed in glass vials. CL/catalyst molar ratios were 1250, 2500 and 5000 for Tin(II)-2-ethylhexanoate and 5000, 10000, 20000, and 40000 for (NH₄)₈[Mo₁₀O₃₄]. The vials were stoppered at room temperature and placed in thermostated baths at 120°C and 150°C, respectively. Vials were removed from the baths at different reaction times (1, 2, 4, 6, 8, 10 and 24 hours). No inert atmosphere was used. The obtained polymer (HOPCLOH) was characterized by ¹H and ¹³C NMR, and MALDI-TOF.

Synthesis of polyurethanes. Polyurethanes were obtained from 1g of HOPCLOH diol (0.7616mmol for the PCL of 1250 g/mol), 1,6-diisocyanate-hexane (129 μ L, 0.80mmol), catalyst (Tin(II)-2-ethylhexanoate) (0.0031g, 0.0076mmol), and 3mL of CH₃Cl. Reaction mixture was stirred until homogenization. The vial with this mixture was stoppered at room temperature and placed in a thermostated bath at 80° C. Vials were removed from the bath every 3 hours to test the disappearance of the signal peak for di-isocyanate in the FTIR spectrum (at 2250-2280 cm⁻¹). Polyurethane films were obtained by casting in a leveled glass within a fume cupboard. The cast solution was placed in a box to protect it from dust and allowed to stand at ambient temperature for 24 hours. The film was then released. Samples for physical characterization were cut from films unless otherwise stated. Film thickness ranged from 50 to 250 μ m.

Results and discussion

Figures 1, 2 and 3 shows the kinetics curves obtained for the 1250 g/mol PCL diols (HOPCLOH), using ethylenediamine, hexamethylenediamine and 1,10-diaminodecane as initiator respectively. In the three systems, it is observed that when catalyst concentration increases, polymerization rate increases too. The catalyst used in this experiments was $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$, and the catalyst concentration was fixed at $\text{CL}/\text{catalyst}=20000$. The formation of the polyurethanes was followed by FTIR, and diols were characterized by ^{13}C RMN.

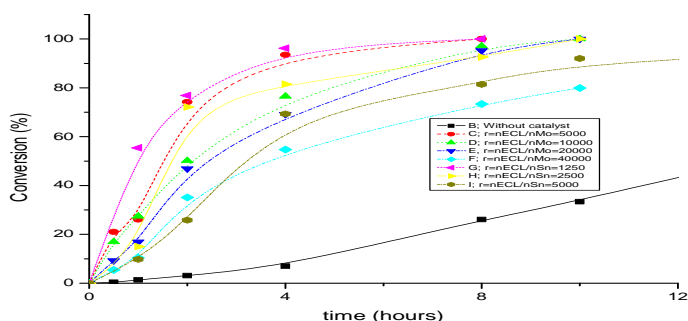


Figure 1. Kinetic plots for the synthesis of HOPCLOH (1250 g/mol) with ethylenediamine as initiator.

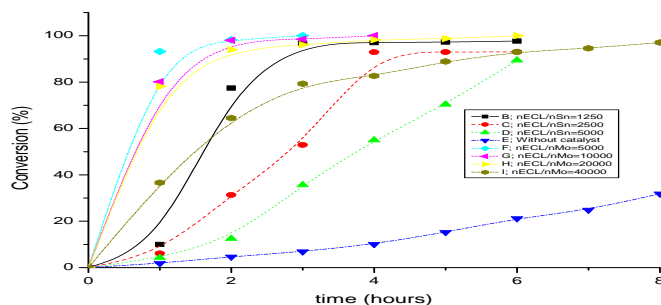


Figure 2. Kinetic plots for the synthesis of HOPCLOH (1250 g/mol) with hexamethylenediamine as initiator.

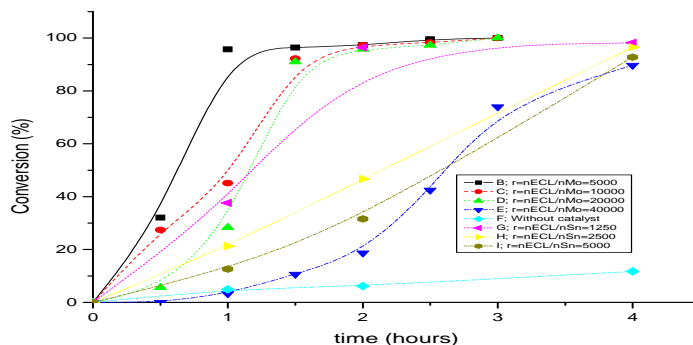


Figure 3. Kinetic plots for the synthesis of HOPCLOH (1250 g/mol) with 1,10-diaminodecane as initiator

In Figure 4, it can be seen that polymerization rates increase as a function of the increment in diamine length.

The same behavior was observed for the synthesis of HOPCLOH diols of 530, and 2000 g/mol

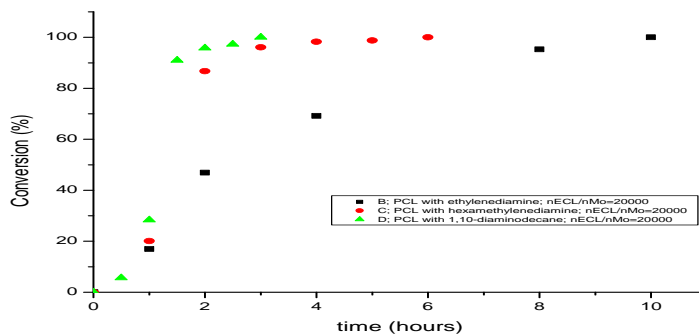


Figure 4. Comparison of polymerization rate as a function of diamine length

Conclusions

α - ω telechelic PCL diols (HOPCLOH) with molecular weights of 530, 1250 and 2000 g/mol were prepared by ring opening polymerization of CL. Ammonium decamolybdate $(\text{NH}_4)_8[\text{Mo}_{10}\text{O}_{34}]$ is better catalyst than Tin(II)-2-ethylhexanoate, as lower concentrations (molar ratio of CL/catalyst=20000) are needed to obtain high conversions in relatively short reaction

times. HOPCLOH diols were characterized by ^{13}C NMR. The different HOPCLOH diols were successfully used as macromonomer to obtain poly(ester-urethane)s films. Degree of crystallinity, mechanical properties and biodegradability behavior are under evaluation.

References

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