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Modeling and simulation of activated anionic polymerization of laurylllactam in the presence of a macroactivator

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HIGHLIGHTS

- Presentation of a detailed kinetic mechanism for the PDMS-PA12 copolymerization.
- Development of a mechanistic model for the chain length and branching developments.
- Model validation in terms of experimental measurements and statistical analysis.
- The combined effect of branching side reactions and Claisen's reactions is shown.
- Conversion, functional end-group concentrations and Mn are successfully predicted.

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ABSTRACT

In the present work, a comprehensive theoretical and experimental study is carried out on the anionic polymerization of laurylllactam in the presence of a macroactivator ($\alpha,\omega-$dicarbamoyloxy caprolactam polydimethylsiloxane), which was carefully synthesized and characterized prior to its use. Following the developments of a previous study, a predictive model is developed on the basis of an analytical kinetic scheme that takes into account important branching and condensation side reactions, resulting in a number of different functional end-groups on the produced macromolecules. A series of batch polymerization experiments, carried out under different operating conditions in terms of temperature and macroactivator concentration, are used for the identification of the kinetic parameters of the model as well as for its subsequent validation. Through these experiments, it becomes apparent that the proposed model and kinetic mechanism are capable of describing the behavior of the system with accuracy.

1. Introduction

The production of different polyamides, most notably polyamide 6 (PA6) and polyamide 12 (PA12), via the ring-opening polymerization of lactams remains a subject of great interest and activity, mainly due to their vast range of applications as well as to the significant number of related production processes such as reactive extrusion (Du and Yang, 2010; Hornsby and Tung, 1995), reactive thermoplastic pultrusion (Dave et al., 1997; Luisier et al., 2003), reaction injection molding (Macosko, 1989) and reactive rotational molding (Barhoumi et al., 2013).

The chemical synthesis of PA12 and its copolymers is mainly carried out via the ring-opening polymerization (ROP) of laurylllactam (LL). In a previous publication (Rached et al., 2005), it has been shown that a number of side reactions, including Claisen's condensation reactions, need to be taken into account in order to describe the complexity of the chemical phenomena that occur during the synthesis of a PA12 matrix via this route. The present work is an extension of the previously developed mechanistic model to the activated anionic polymerization of LL using a polydimethylsiloxane (PDMS) prepolymer (or macroactivator) for the synthesis of a block copolymer of the general structure '*PA12-PDMS-PA12*'. The produced copolymer will serve as an in-situ synthesized compatibilizer in a subsequent blending process

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of the PA12 matrix with PDMS (*to be the subject of a forthcoming publication*), within the framework of an overall theoretical and experimental investigation of the synthesis of PA12/PDMS blends by anionic polymerization of LL by reactive extrusion.

A key factor for the successful outcome of the blending process is the compatibilization of the participating phases. It has been shown that the in-situ formation of block copolymers during the melt processing is a very fast, easy, and cost effective alternative to classical compatibilization methods that can lead in increased adhesion between the two phases (Du and Yang, 2010). Moreover, anionic polymerization has proven to be a valuable method for preparing block copolymers from a functional polymer containing active species at its ends (a macroactivator), which can allow the polymerization of another monomer.

Multiphase copolymers based on PDMS are receiving an increasing interest, mainly due to their unique combination of properties that is related to their chemical structure and macromolecular architecture. Several works (Kang and Park, 2010; Kajiyama et al., 1990; Mougin et al., 1993; Otsuki et al., 1991; Policastro and Hernandez, 1987; Stehlíček et al., 1990; Veith and Cohen, 1991) have already reported the synthesis of block copolymers composed of PDMS and various polyamides (PA). Veith and Cohen (1991) described the synthesis of a ω-acyllactam PDMS by anionic polymerization of hexamethylcyclotrisiloxane, which was then terminated by a chlorosilylacyllactam. A different macroactivator, of higher functionality (i.e., equal to 2) was obtained by Mougin et al. (1993) via the reaction of a α,ω-dihydro PDMS and undecylenoyl-caprolactam by hydrosilylation.

The successful synthesis of a well-defined block copolymer via anionic polymerization of lactams on the growth centers of α,ω-functionalized PDMS macroactivators requires a high chain-end reactivity and efficient polymerization of the second monomer. The prepolymer that was synthesized in terms of this study, contains isocyanate blocked caprolactam end-groups, which can act as propagating centers for the subsequent LL polymerization and the final formation of the block '*PA12-PDMS-PA12*' copolymer.

Although activated anionic polymerization (AAP) of lactams has been extensively studied, particularly for the synthesis of PA6 and only occasionally for PA12, only a few modeling approaches of this system, principally concerning the AAP of ε-caprolactam, have been presented in the literature. They mainly consist of an empirical approach, also called "macrokinetics" (Malkin et al., 1982; Puffr and Kubanek, 1991), and of a number of mechanistic-modeling approaches (Cimini and Sundberg, 1986; Greenley et al., 1969; Lin et al., 1985) in all of which the reaction mechanisms were oversimplified (i.e. the main side reactions were neglected and the polymerization was simplified by combining the addition reactions with the hydrogen transfer reaction). This study presents as attempt to completely describe the complex kinetic developments of the synthesis of PA12 via the activated anionic polymerization of lauryllactam with a macroactivator, in terms of a detailed mechanistic model.

In the sections that follow, the experimental part of the study is presented first, which includes the description of the synthesis procedure of both the catalyst and the PDMS macroactivator as well as a brief description of the polymerization process. Subsequently, in the following section, the adopted kinetic scheme is established and the model elaboration is analytically presented. Finally, the results of both experimental characterizations and theoretical simulations are presented in the results and discussion section of the publication.

2. Experimental part

2.1. Materials

The α,ω-dihydroxy PDMS was purchased from ABCR and dehydrated under vacuum at 70 °C during 6 h prior to use. Its number-average molecular weight was determined by ^{1}H NMR (M_n=3100 g mol^{-1}) while its kinematic viscosity was equal to 120 cSt.

The dibutyltin diacetate ($>$98%) was purchased from Fluka. All other chemicals were purchased from Aldrich and used as received. They consisted of:

- Lauryllactam (LL), stored under nitrogen atmosphere,
- ε-caprolactam (ε-CL),
- Sodium bis (2-methoxyethoxy) aluminium hydride ($[(OtBu)_2\text{-}AlH_2]Na$),
- 4,4′-diphenylmethane diisocyanate (MDI),
- Tetrahydrofurane (THF).

2.2. Synthesis of the catalyst

The catalyst (Cat) was prepared just before each polymerization, according to the following procedure (Mougin et al., 1992):

5×10^{-4} mol of ε-CL were dissolved in 2 ml of THF and added drop-wise, at ambient temperature, to 5×10^{-4} mol of Sodium bis (2-methoxyethoxy) aluminium hydride. The reaction was considered finished when the hydrogen release ceased.

2.3. Synthesis of α,ω_dicarbamoyloxy caprolactam PDMS (macroactivator, MA)

In a glass reactor, 1.75 g of MDI and 10 g of α,ω-dihydroxy PDMS were dissolved in 10 ml of toluene under dry nitrogen and allowed to react at 90 °C for 2 h in the presence of 0.05 g (0.5% wt) of the dibutyltin diacetate catalyst. Next, 0.83 of ε-CL were added and the reaction was carried out at 90 °C during another 5 h. At the end, the mixture was cooled at ambient temperature. The solvent was finally evaporated under reduced pressure at 60 °C. The produced α,ω-dicarbamoyloxy caprolactam PDMS (henceforth denoted as MA) was characterized by IR and ^{1}H NMR, with the aid of spectra of similar molecules (e.g. di-εCL MDI), as well as by elementary analysis.

2.4. Polymerization procedure

PA12-*b*-PDMS-*b*-PA12 triblock copolymers were synthesized by anionic polymerization of LL in the presence of the α,ω-functionalized PDMS. 10 g of lauryllactam and various percentages in weight of macroactivator were introduced in a glass reactor under nitrogen and heated by means of a high-temperature oil bath. The mixture was stirred magnetically. Then an appropriate volume of catalyst was added to the molten monomer by use of a syringe. The polymerization was quenched at appropriate time intervals by immersing the reactor into a small container of liquid nitrogen.

2.5. Analysis techniques

The infra-red spectra were recorded on a Bruker IFS 25 FTIR spectrometer. NMR experiments were performed using a Bruker Avance 300 spectrometer with TMS as internal reference. Elementary analyses were carried out by the Central Analysis Service of the National Center of Scientific Research (CNRS) at Vernaison, France.

For the measurement of the monomer conversion, the residual monomer was extracted from the polymer sample with methanol, during a period of 24 h, via a Soxhlet extractor and the resulting polymer sample was recovered and dried under vacuum at 80 °C during 24 h.