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Molecular modelling of polyphthalamides thermal properties: Comparison between modelling and experimental results

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ABSTRACT

The aim of this study was to investigate new polyphthalamides (PPA) through the use of molecular modelling techniques and comparison with experimental data. The objectives were to provide a computer simulation method that can be used to predict the properties of polyphthalamides with a good reliability with respect to the experimentally synthesized materials. Several PPA with a variable amount of aromatic units derived from condensation with hexamethylene diamine (HMDA) and terephthalic acid (TPA) or isophthalic acid (IPA) were synthesized. These polymers were characterized using thermal analysis, size-exclusion chromatography, NMR and viscosimetry techniques. The same PPA were modelled at the atomistic level and molecular dynamics simulations were run. The glass transition temperature (T_g) of the various materials was used to make comparisons between simulations and experiments. The results were found to be in good agreement and the simulation method can be used to predict thermal properties of this class of polyamides.

1. Introduction

In the last few years, a new class of polymer has been successfully developed and commercialized. These are known as polyphthalamides (PPA), which are polyamides (PA) containing aromatic rings in their backbones, giving them high mechanical strength and thermal resistance. This leads to polymer materials that have a high commercial potential, competing with metals, especially in the automotive industry where the reduction of weight is a big issue [1,2]. Usually the process that leads to development of a new material starts with several steps of chemistry optimization, choice of the monomers, etc., followed by an extensive characterization of these polymers. This process is time-consuming and has a substantial cost. Moreover, in nowadays situation of quick development of new biobased polymers, a large screening of monomers is required. This is a common new trend of research in polymer and material science, and lot of companies and academic laboratories (including ours) are currently working on this subject.

Simulating polymer properties is considerably less time-consuming than preparing real systems and, therefore, a-priori simulations would allow the development of new materials according to the output of those simulations. In order to speed up this process, recent developments in molecular modelling and computer simulations can be a useful tool. Since macromolecules are by definition molecules composed of a large number of atoms, so the computational cost of their simulation is big (computational time-scales as a power law from 2 to 4 of the number of particles simulated), but in the last few years the exponential increase in computer power has made it possible [3].

In this study we will focus on the one hand on the synthesis and characterization of amorphous PPA and on the other hand on their molecular modelling mainly by molecular dynamics (MD).

PPA are formed by the reaction of aromatic acids with aliphatic diamines. Additional monomers can be used, but usually the term polyphthalamide is used when more than 60% mol of the carboxylic acid portion of the repeating unit in the polymer chain is composed of a combination of terephthalic (T) and isophthalic (I) acids. The resulting PPA may be either amorphous or semi-crystalline depending on the actual combination of monomers used, and several examples of each category exist commercially [4]. The semi-crystalline PPA are based on PA6T, obtained through condensation of hexamethylene diamine (HMDA) and terephthalic acid. These polyamides are generally characterized by higher melting points, higher glass transition temperatures, better chemical resistance,

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lower moisture absorption and better thermal stability compared to common aliphatic polyamides such as nylon 6 and nylon 66 [5]. When more than 55% of the acid part of the PPA is composed of isophthalic acid, the resulting copolymer is amorphous [6].

The aim of this study was to investigate PPA properties with the use of molecular modelling and computer simulation methods in comparison with experimental data. On this account, only amorphous PPA were synthesized and studied. These amorphous PPA are not really interesting for their thermal and mechanical properties, but they are important for the molecular modelling. Indeed the atomistic simulation cannot take into account the crystallization process, which occurs on a much larger space and time-scale.

The molecular modelling approach is separated into two axes: the first one through the use of the group contribution method, and the second one using molecular dynamics simulations. The group contribution method applies the theory developed by Van Krevelen and Fedors [7,8] in the 70s. A group contribution method uses the principle that some simple aspects of the structures of chemical components are always the same in many different molecules. So by following this principle, a wide variety of properties of a polymer can be predicted by knowing only its repeating unit. This method is empiric and uses data collected on several polymers that have been extensively studied. Of course this method is over simple and does not take into account polydispersity effects, etc., but its main advantage is its speed (additive method, with group interactions for evolved models). On the other hand, molecular dynamics is the most convenient method of simulation for relatively complex molecules such as polymers. These simulations are based on strong theoretical background [9]. They should use an appropriate forcefield to describe the interactions between atoms. In this study the forcefield that has been used is named COMPASS, and has been especially developed for dense organic systems, such as polymer melts. The goal of the different simulations performed is to simulate a PVT (Pressure-Volume-Temperature) diagram of PA6T and PA6I as well as their copolymers. To achieve this goal, MD simulations were performed: variations of the density as a function of temperature were calculated [10]. This leads to the calculation of the glass transition temperature of the different tested polymers through MD simulations. This method is much more accurate than the group contribution theory but it takes a much longer time to complete.

The ability of the two methods to reproduce experimental data for our "model" PPA is discussed in the results and discussion part, and thus its possible use as a prediction tool for quick evaluation of PPA properties. However, the reader should keep in mind that this method only applies to polyamides, composed of rigid diacid segments and flexible diamine (or aminoacid) segments. It is possible to change the structure of monomers studied as long as they follow these requirements.

2. Experimental methods

2.1. Synthesis

2.1.1. Materials

The different monomers used for the purpose of the synthesis of high performance polyamide materials were hexamethylene diamine (HMDA), terephthalic (TPA) and isophthalic (IPA) acids. The HMDA was purchased from Sigma–Aldrich and is a white solid at room temperature, highly soluble in water. The terephthalic and isophthalic acids were purchased from BP Chemicals. They come as white crystalline powders, insoluble in water. Trifluoroacetic anhydride was purchased also from Sigma–Aldrich. All products were used as received.

2.1.2. Protocol

The synthesis of the different polyamides was carried out in bulk in 200 mL glass tubes equipped with a mechanical stirrer, electrical heating device, a distillation device (fractionating column, condenser and a receiving flask) and under inert atmosphere (N_2). The monomers (50 g) were introduced in proportions close to the stoichiometric proportions, i.e., the diamine was put in with a slight excess of 2% to compensate its loss during the reaction process due to its volatility. HMDA was first introduced in the glass tube with approximately 20 g of deionized water. Then the acid(s) were poured into the solution. The water was used in the reaction mixture in order to help the formation of the polyamide salt and the stirring. At the beginning of this reaction, a heterogeneous biphasic medium was observed. One phase contains the aqueous solution of diamine, and at the bottom of that phase a suspension of the acid powders was present. The reaction medium was first heated to 170 °C for 30 min, in order to form the polyamide salt and the first oligomers. During this heating, the disappearance of the acid suspension was observed, which confirms the formation of the water soluble polyamide salt. The glass tube was further heated to 300 °C and the reaction was carried out during 2 h. During the reaction and the heating process, water was distilled and the fusion of the polyamide salt was observed after the removal of water. At the end, after cooling the reactor, the glass tube was broken to retrieve the polyamide. The general formula of resulting copolymers synthesized from HMDA and isophthalic and/or terephthalic acids is shown in Fig. 1.

In this study, all the copolymers synthesized had between 60 and 100% of IPA (x) and the complementary co-monomer was TPA (y).

2.2. Characterization

2.2.1. NMR

^{1}H was performed on several polymers modified by N-Trifluoroacetylation [11]. It was necessary to derivatize the polymers because polyamides are insoluble in most common solvents, due to very high hydrogen bonding and non-bonded interactions. In order to bypass this problem, reactions between the different polyamides and trifluoroacetic anhydride (TFAA) were performed in $CHCl_3$. This chemical modification consists to replace all the hydrogen atoms of amide, primary amine and carboxylic acid groups by a $COCF_3$ group as showed in Fig. 2. This modification avoids intermolecular hydrogen bounding and allows the solubilization of the modified PA.

Solutions for ^{1}H were prepared using $CDCl_3$ with excess TFAA to achieve the solubilization of the polymers by using the following procedure. The different PA were weighted (20 mg for ^{1}H) and

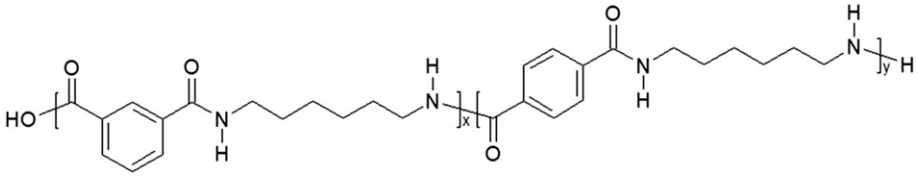

Fig. 1. Copolymers synthesized PA6I(x)/6T(y).