



Multiblock copolymers of polyamide 6 and diepoxy propylene adipate obtained by solid state polymerization



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ABSTRACT

Polyesteramide multiblock copolymers based on polyamide 6 and diepoxy propylene adipate blocks were synthesized. For this purpose a carboxyl-terminated polyamide 6 ($M_n = 2400$ g/mol, $T_m = 205.5$ °C) and diepoxy propylene adipate ($M_n = 450$ g/mol) were separately synthesized and characterized. The incorporation of the oligoester into the polyamide 6 backbone was performed by solid state polymerization (SSP) well below the melting temperature of the polyamide (80–140 °C) so that the physical and thermal properties of the original polyamide 6 block were retained. Formation of the multiblock structure was confirmed by following the increase in molecular weight by SEC, reaction of the end groups by ^1H NMR and by following the maintained melting temperature after the copolymerization. These segmented copolymers have molecular weights up to 10 kg/mol, thermal stability of 325 °C at 5% weight loss and a melting temperature of 205 °C.

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1. Introduction

Polyamide 6 (PA6) is an important engineering plastic and as such mainly used for automotive, electrical and packaging applications. However it is not susceptible to degradation like some other industrial plastics. It would be desirable for PA6 to be environmentally biodegradable, especially for the packaging applications.

The biodegradation of PA6 can be enhanced by the incorporation of hydrolyzable ester groups into the polyamide backbone [1–5]. However, if this is done via melt polymerization random copolymers are obtained which results in the deterioration of the crystallization behavior of the PA6 [6–9]. This finally negatively affects the good mechanical and physical properties of PA6 which is not desired for the applications. This behavior is well described by Flory [10] and Jo and Baik [11] theoretically. This depression might be prevented by blending two types of homopolyamides for just a sufficient time, or by sequential addition of monomers and preventing transamidation reactions, by which block-like copolymers can be obtained [12,13]. The advantage of such blocky structures is that the physical properties of both original polyamides are still present in the final material, whereas a completely random copolyamide might lose the crystallinity and favorable physical properties of both blend components. Segmented polyesteramides based on caprolactam were prepared via anionic polymerization [14] and polycondensation reactions [15,16] but yielded in copolymers with low melting temperatures.

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Incorporation of degradable ester groups into the amorphous part of a relatively low molecular weight PA6 below the melting temperature of the PA6 crystals is possible without a significant deterioration of the crystalline region of the PA6. In our previous study we have shown the incorporation polycaprolactone into the PA6 backbone by using this approach [17]. In this way, multiblock copolymers were obtained for which the high melting temperature and crystallinity of the PA6 blocks can still be maintained.

The same approach can be used by making use of epoxide-carboxyl reactions. These reactions are widely used to produce crosslinked coatings from epoxy resins [18–24]. It is also possible to synthesize linear polymers in bulk without crosslinking if moderate temperatures and proper reaction times are used [25–34]. In this study we used a similar stepwise approach as used in our previous study where the functional end groups were changed. A low molecular weight carboxyl end-capped PA6 and a degradable oligoester with epoxide end groups were synthesized separately. This oligoester (diepoxy propylene adipate) was synthesized as described before [35]. Both components were mixed in a common solvent at room temperature with the addition of a tertiary amine as a catalyst. After the complete evaporation of the solvent solid state step growth copolymerization [36–38,41] was performed well below the melting temperature of the PA6 as shown in the reaction scheme in Fig. 1. In this way, multiblock polyesteramides were prepared where the degradability of PA6 is enhanced by the incorporation of the hydrolyzable ester groups. Molecular weights of the synthesized polymers were determined by using SEC, NMR and titration methods. SEC was also used as a useful tool to monitor reactions with time. Thermal analysis was performed by using TGA and DSC.

2. Experimental

2.1. Materials

Dry ϵ -Caprolactam (CL) was kindly provided by DSM (Geleen, The Netherlands). Adipic acid (AA) was purchased from Sigma. Irganox 1330 was purchased from Ciba Speciality Chemicals. 4-dimethylaminopyridine (DMAP), triethylamine

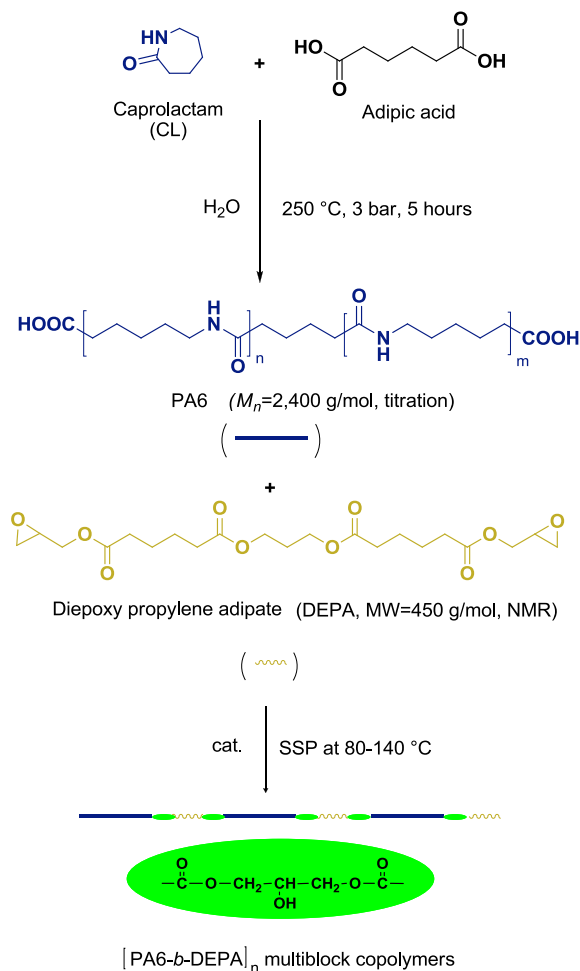


Fig. 1. Schematic overview of the stepwise synthesis of polyamide 6-diepoxy propylene adipate multiblock copolymers obtained by solution and solid state polymerization.

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