

Synthesis and characterization of bisester-amide segments of uniform and random length

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Abstract

The synthesis and characterization of bisester-oligoamides segments with varying segment length that can be used in segmented block copolymers were studied. The bisester-oligoamides segments were made from diamines and terephthalate or isophthalate esters. The diamines used were *p*-xylylene diamine, *m*-xylylene diamine and hexamethylene diamine. The esters used are dimethyl terephthalate, diphenyl terephthalate, dimethyl isophthalate and diphenyl isophthalate. Uniform bisester-diamide, bisester-(tetra-amides) and bisester-(hexa-amide) segments were synthesized in steps and characterized by ¹H NMR, MALDI-TOF and DSC. The uniformity of these segments was studied by MALDI-TOF.

With the uniform amide segments and polypropylene oxide segments, block copolymers were prepared by high temperature melt polymerization. The amide segment length distribution, which is susceptible to randomization was studied. The analysis of the amide segment distribution after hydrolysis of the ester-linkage groups was by MALDI-TOF. The amide segments were found to have the same narrow distribution as the starting bisester-oligoamide, which strongly supports the fact that randomization of the amide segments during melt polymerization does not take place. The uniformity of the amide segments is, therefore, preserved during high temperature melt polymerization.

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1. Introduction

Segmented polyether(ester)s (PEE) synthesized from diesters and telechelic polyethers like Arnitel[®] and Hytel[®] are examples of commercial PEE's. These segmented blockcopolymers belong to the class of so-called thermoplastic elastomers (TPE's) [1]. Normally, commercial TPE's contain rigid crystallisable segments, which have a broad segment length distribution. The majority of these segmented blockcopolymers is synthesized from poly(tetramethylene oxide) (PTMO) or poly(ethylene oxide) (PEO) as the polyether segment and a minor part is made from poly(propylene oxide) (PPO). PPO contains secondary

hydroxyl end groups and has, therefore, a lower reactivity in the PEE syntheses as compared to PTMO and PEO. Recently, a PPO end-capped with ethylene oxide (PEO-*b*-PPO-*b*-PEO) has become commercially available which has an enhanced reactivity [2]. However, this PPO still contains a small amount of secondary hydroxyl groups [3], which hinders the formation of high molecular weight PEE block copolymers [4,5]. High molecular weight PPO-based polyether(ester) (PEE) and polyether(ester-amide) (PEEA) segmented block copolymers can be obtained if a terephthalic diester is used that contains phenolic ester end groups, like: diphenyl terephthalate [5].

The properties of segmented polyurethanes, PPE and PEEA segmented block copolymers depend strongly on the structure regularity of the crystallisable segment used. The higher the structure regularity the faster the crystallization and the higher the crystallinity in the resulting block copolymer [1]. The structural regularity of the crystallisable segments is usually higher for those containing *p*-phenylene groups as compared to *m*-phenylene groups. Another kind of structure regularity can be found in the segment length

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distribution of the crystallisable segments. The smaller the segment length distribution, the faster the crystallization and the higher the crystallinity [6–8]. A third parameter of interest is the length of the crystallisable segment used in segmented block copolymers. Block copolymers with tetra-amide segments were found to have enhanced elasticity over block copolymers with di-amide segments [9].

New and interesting types of TPE's are block copolymers, which comprise crystallisable segments with narrow segment length distribution; the so-called uniform segments [9–13]. A major problem of block copolymers with segments of uniform length is the loss of uniformity at high temperatures due to transreactions. These transreactions are fast for segmented polyurethanes, polyureas and polyesters [14]. However, with oligoamide segments melt polymerization and melt processing seems possible without losing the uniform character of these segments [9,11].

Segmented block copolymers with crystallisable amide segments of uniform length can be made by a conventional copolymerization using uniform bisester-amide segments. The synthesis of some biester-diamide and bisester-(tetra-amide) segments have been reported before [15,16]. These bisester-oligoamides segments were synthesized, starting with a diamine and a diester. The reaction of a diamine (X) with a terephthalic diester (T) may proceed by the following reaction scheme [15]:

1. $X + 2 T \rightarrow TXT$ (diamide).
2. $2 X + T \rightarrow XTX$.
3. $XTX + 2 T \rightarrow TXTXT$ (tetra-amide).
4. $2 X + TXT \rightarrow XTXTX$.
5. $XTXTX + 2 T \rightarrow TXTXTXT$ (hexa-amide).

A very large excess of diamine favors oligo-amide sequences having amine end groups and vice versa with a large excess of diester. If bisester-oligoamides of uniform length are required, the longer segments can best be prepared in steps. For instance, the tetra-amide segments ($x=2$) can be synthesized in two steps [16]. First, by reacting an excess diamine with the diester and subsequent purification (2). Secondly, the extended diamine, here XTX, was added to an excess diester (3). Even if a large excess of diamine or diester is used there may still be a distribution of segment length. One hundred percent uniform segments are, therefore, difficult to obtain and purification steps are needed to obtain a high uniformity. The uniformity of the synthesized bisester-oligoamide segments was determined by ^1H NMR and MALDI-TOF and is defined as the mol fraction of segments with the desired segment length. In a one-pot synthesis bisester-oligoamide segments with a random segment length distribution can be prepared. The extent of randomization of the amide segments during the polymerization is difficult to determine by ^1H NMR as the average length of these segments remains constant.

For the synthesis of segmented block copolymers based on the low reactive poly(propylene oxide) the use of

uniform bisester-amide segments with phenolic ester end groups is an advantage [5]. The bisester-oligoamide segments in our studies are segments with varying structural regularity and length (Fig. 1). The structure regularity of bisester-oligoamides was varied by using either isophthalic or terephthalic groups and *p*-xylylene diamine, *m*-xylylene diamine or hexamethylene diamine groups. Also the uniform length bisester-oligoamides is varied ($x=1, 2$ or 3).

In this paper, the preparation of random and uniform bisester-oligoamide segments is studied. Also studied is whether the uniformity of the segments is maintained on copolymerization at high temperature with a telechelic hydroxyl functionalized poly(propylene oxide). The uniformity of the segments is studied by ^1H NMR and MALDI-TOF. For analysis of the amide segment length distribution in the block copolymers, the polymers were first hydrolyzed before the remaining blocks were analyzed by MALDI-TOF.

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT), diphenyl isophthalate (DPI), terephthaloyl dichloride, phenol, *p*-xylylene diamine, 1,6-diamino hexane, tetra-isopropyl orthotitanate ($\text{Ti}(\text{i-OC}_3\text{H}_7)_4$), ethanol, *m*-xylene, toluene, chloroform, *N*-methyl-2-pyrrolidone (NMP) and dimethyl formamide (DMF) were purchased from Aldrich (BIOSOLVE). Irganox 1330 was obtained from CIBA. *m*-Xylylene diamine was a gift from Mitsubishi Gas Chemical Company (Japan). These materials were used as received. Poly(propylene oxide) end capped with 20 wt% ethylene oxide (EO) and a molecular weight of approximately 2300 g/mol (PPO-2300) was a gift from Bayer AG (Acclaim Polyol PPO-2220 N).

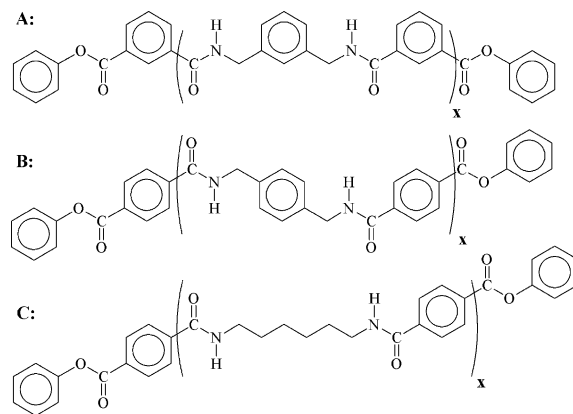


Fig. 1. Structure of the bisester-oligoamide monomers with amide segment length x and phenolic ester end groups. A, isophthalic ($\text{I}(\text{X}_m\text{D})_x$); B, terephthalic ($\text{T}(\text{X}_p\text{T})_x$); C, terephthalic/aliphatic ($\text{T}(\text{6T})_x$).

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