

About the mode of incorporation of silanol-terminated polysiloxanes into butylene terephthalate-*b*-dimethylsiloxane copolymers

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Abstract

The modality of the incorporation of silanol-terminated siloxanes into copolymers with butylene terephthalate were investigated and determined. Besides siloxanes, the other participants in this well-known copolymerization, called the catalyzed two-step transesterification/polycondensation reaction, are dimethyl terephthalate and 1,4-butanediol. The employed approach to this problem was to exactly examine all the possibilities of the reactions between particular pairs of reactants, as well as of single reactants. The final results were, firstly, that reactions between siloxanes and dimethyl terephthalate did not occur and, secondly, that the only possibility for silanol-terminated siloxanes to be incorporated into the copolymers was by means of their condensation with 1,4-butanediol. This means that siloxanes are incorporated into the copolymer by ether and not by ester linkages.

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1. Introduction

Poly(butylene terephthalate)-*b*-poly(dimethylsiloxane)s, PBT-*b*-PDMS, are block copolymers which consist of two chemically very different and incompatible polymer blocks. Stiff, inflexible and crystallizable polymer chains characterize the PBT block. The

PDMS block, because of its low glass transition temperature, is at room temperature amorphous and possesses a rubber-like consistency, characterized by high flexibility and mobility of the polymer chains. These two different polymer blocks are usually defined as hard and soft blocks or segments, respectively. Such type of block copolymers demonstrates some specific features, as for example, the microphase separation phenomenon, and possesses a number of interesting and useful properties, the most important of which is the so-called thermoplastic elasticity.

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The synthetic route for the preparation of PBT-*b*-PDMSs is the catalyzed two-step transesterification/polycondensation reaction, whereby dimethyl terephthalate, DMT, 1,4-butanediol, BD, and some appropriate siloxane compound are used as the reactants. In order to incorporate siloxane compounds, which are very poorly compatible with PBT, a large number of reactive, chain-end functionalized oligo- and polysiloxanes have been used. To the best of our knowledge, the use of the following siloxanes has been described in the literature: different hydroxyalkyl terminated oligo- and polysiloxanes [1,2], hydroxyl terminated poly(ether-siloxane-ether) block copolymers [3–7], alkyloxy terminated polysiloxanes [8], as well as polysiloxanes with epoxy [2], amino [2,9], hydrosilyl [10] and carboxypropyl [11–13] end-groups.

The remaining group of siloxane compounds used for the preparation of PBT-*b*-PDMS copolymers consists of silanol, Si–OH, terminated oligo and polysiloxanes, PDMS–OH [14–20]. They represent just the group of siloxane compounds which especially attracted our interest, because some of us were also engaged in the preparation of copolymers using silanol-terminated siloxanes [16,20]. However, all the time we were confronted with the problem that the results obtained by investigating the synthesized copolymers were in part somewhat curious. Specifically, the copolymers were inhomogeneous and, secondly, there was a very poor reproducibility of the obtained results. Further, it was noticed that in none of the published reports on this subject, a clear explanation of the reaction route by which silanol-terminated siloxanes are incorporated into the polymer chains, was given. It seems, based on general reaction

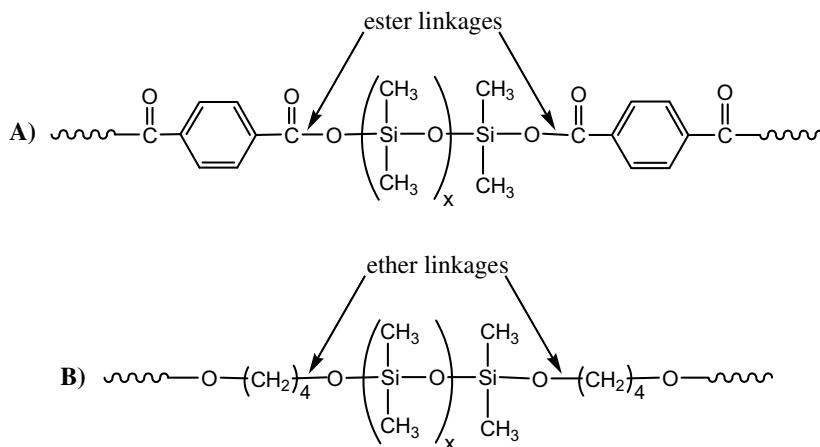
schemes shown in some of these articles [14–16,20], that the authors believed that silanol esters were formed (COOSi, A in Scheme 1), either as a product of DMT transesterification with PDMS–OH in the first reaction step, or, if PDMS–OH was added in the second reaction step, as a result of combined transesterification/polycondensation reaction with butylene terephthalate originating from the first reaction step. In the case that the first of the above-mentioned possibilities is correct, then the transesterified terephthalates with either BD or PDMS–OH should yield the desired copolymers in the second reaction step. Only Schiraldi [17,18] expressed some doubts and speculated about another reaction pathway, namely the formation of butanediol bisether of the silanol-terminated siloxanes (COSi, B in Scheme 1), which then, just in the same way as BD molecules do, acts as a diol and participates in the transesterification reaction with DMT.

Due to these conflicting opinions, it was decided to perform a more detailed experimental study in order to determine the true incorporation mode of silanol-terminated siloxanes into the PBT-*b*-PDMS copolymers. The plan was to examine all possible reactions which could occur in the usually used starting reaction mixture, while maintaining the normally employed reaction conditions, as described in the literature.

2. Experimental

2.1. Materials

α,ω -Disilanol-poly(dimethylsiloxane) (PDMS–OH), from ABCR, was dried over molecular sieves



Scheme 1. Ester linkage formation between DMT and PDMS–OH (A) and ether linkage formation between BD and PDMS–OH (B).

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