

Influence of chain extenders on the molecular weight distribution in polyethylene terephthalate

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SUMMARY:

An experimental study of the influence of chain extenders on the molecular weight distribution in polyethylene terephthalate is presented. Using bislactamates and bisoxazoline as chain extenders the molecular weight increases during coupling whereas the polydispersity didn't change significantly. By isolating and quantifying the low molecular fraction it could be shown that the oligomer content didn't change significantly during coupling.

KEYWORDS:

Chain extender, polyethylene terephthalate, coupling, molecular weight distributions

INTRODUCTION

Poly(ethylene terephthalate) is one of the most common polyester in use today. After the synthesis the molecular weight can be increased by a solid state polymerization process (SSP). The SSP process, however, is energy and time consuming leading to high costs in producing high molecular weight PET. An alternative to increase the molecular weight is the addition of chain extenders to the PET melt directly after the polycondensation step or afterwards during the extrusion process. A chain extender is a low molecular weight compound with highly reactive end groups connecting the end groups of the polymer chains.

Figure 1 shows an idealized coupling schema up to the second reaction stage where it is assumed that the reaction between two polymer end groups is excluded. The two terminal groups of chain extender are denoted by *B* whereas the polymer end groups are denoted by *A* with *X* and *Y* being an arbitrary number of repeating units in the polymer chain.

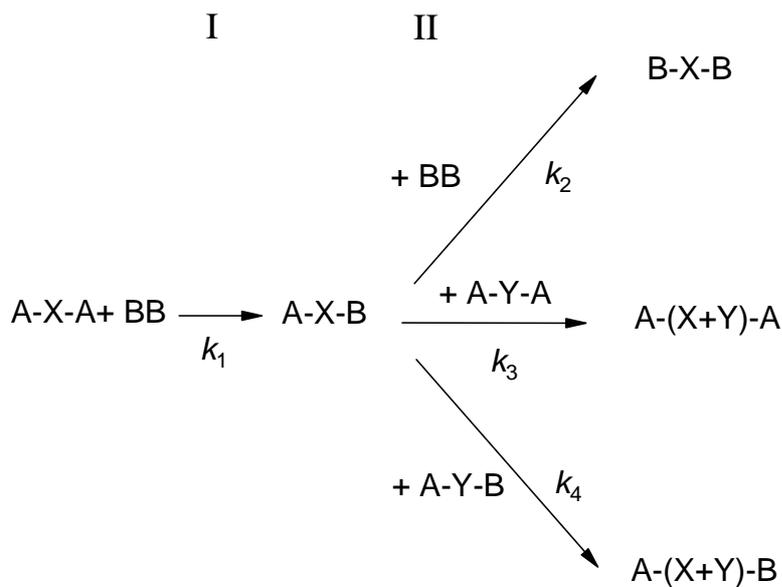


Figure 1 Reaction schema of coupling (shown up to the second reaction stage)

Along with factors such as temperature and reaction time, the magnitude of the increase of the molecular weight during coupling depends strongly on the molar ratio r of chain extender end groups to polymer end groups. If the kinetics of all reactions in Figure 1 can be described with only one kinetic constant ($k_1 = k_2 = k_3 \dots$) it can be shown theoretically that an equimolar ratio leads to the highest increase of the molecular weight in dependence of the extent of coupling.

Experimentally it is found, however, that the most efficient ratio r of chain extenders end groups to polymer end groups is approximately 1.5 : 1. This slight higher amount of chain extender end groups may be attributed to the fact that the reaction schema of coupling can not be described adequately with only one kinetic constant or may be attributed to the experimental uncertainties discussed later. Figure 2 shows the coupling and blocking reactions of the carboxyl end groups of a PET chain with 2,2'-(1,3-Phenylene) bis(2-oxazoline).

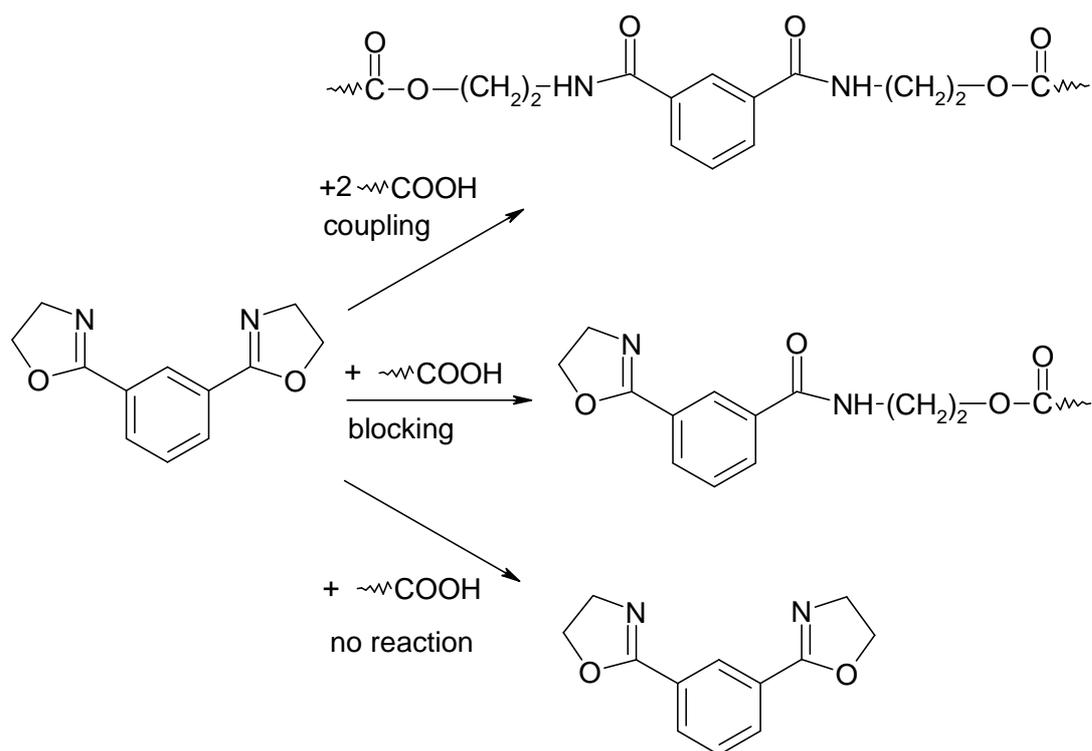


Figure 2 Coupling and blocking of the carboxyl end groups of a PET chain with 2,2'-(1,3-Phenylene) bis(2-oxazoline)

If the reaction rate of the coupling reaction is higher than the blocking reaction (see Figure 1, $k_1 < k_3$ or $k_1 < k_4$) one would expect an increase of the molecular weight despite of an excess of coupling agent. However, there are also many experimental uncertainties mentioned before which can lead to a deviation of the equimolar ratio r predicted by the theory for one kinetic constant. Such experimental uncertainties are for example (a) that a certain amount of the low molecular weight chain extender can be evaporated or decomposed during the addition to the polymer melt, (b) that there are simultaneously chain building and degradation reactions in the polymer melt changing permanently the number of polymer end groups during the coupling reaction (for example it is well known that the number of carboxyl end groups increase during an extrusion process).

For the coupling of PET many suitable chain extenders are known in literature. In this paper we focus our investigations on the most important chain extenders for PET, namely bisoxazolines and bislactamates where we apply explicitly terephthaloyl biscaprolactamate and 2,2'-(1,3-Phenylene) bis(2-oxazoline). As a consequence of their molecular structure, chain extenders such as bisoxazolines react with the end standing carboxyl groups whereas the bislactamates react preferably with the hydroxyl end groups in PET.

Nowadays, it has become clear that many properties of polymers (tensile strength, etc.) are influenced not only by the average molecular weights but also by the width and the shape of the molecular weight distribution¹⁻³. Since previous investigations on chain extenders and PET determine only an average molecular weight (mostly the viscosity average), this paper focuses on a systematic study of the influence of bisoxazolines and bislactamates on the complete molecular weight distribution during the coupling of PET, especially on the polydispersity. Furthermore, we want to clarify the important aspect if it is possible to change the oligomer content by the coupling reactions by isolating the oligomers and quantifying it by HPLC. This is also important for practical use since oligomers can lead to troubles, for examples, during spinning where the oligomers may sublime and condense at cold places in the spinning line.

RESULTS AND DISCUSSION

The coupling reactions were carried out in a double screw extruder for different retention times from 1 min up to 10 min at a defined temperature of 280°C. The molecular weight distribution before and after coupling was determined by gel permeation chromatography (GPC).

According to the GPC curves obtained for different retention times t_e in the extruder we can estimate that the quantity of the low molecular weight fraction eluted at high

retention times t_g can not be influenced by the coupling reaction under the experimental conditions and chain extenders applied. To confirm this we isolate the oligomers by two different methods and quantified the oligomer fraction by HPLC: (a) solution of the samples in HFIP and precipitation of the high molecular weight fraction with dioxane; (b) extraction of the samples with dioxane using a Soxhlet apparatus. The low molecular weight fraction obtained was separated and quantified by high pressure liquid chromatography (HPLC).

CONCLUSION

Under the experimental conditions applied and chain extenders used we could show that it is not possible to change significantly either the oligomer content nor the polydispersity by the coupling reaction.

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