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Functionalization of syndiotactic polystyrene

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ABSTRACT

Syndiotactic polystyrene (sPS) is a promising material that has been commercialized and widely studied by the academic community. Several drawbacks can however restrict its practical use: its brittleness, in areas where mechanical properties are important, the lack of polar groups, for adhesion and compatibility with other polymers, and the need to process sPS at high temperatures. These drawbacks can be overcome by the introduction of relevant functional groups into sPS. We present in this review the various strategies reported for the functionalization of syndiotactic polystyrene: statistical and sequential block copolymerization, chain transfer and chain-end functionalization, polymerization of substituted styrenic monomers and chemical modification of sPS.

Contents

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1. Introduction

Syndiotactic polystyrene (sPS) is a promising semi-crystalline engineering plastic that was synthesized for the first time 20 years ago [1]. Its fast crystallization rate, around two orders of magnitude greater than isotactic polystyrene, enables its use as raw material for the plastic industry. The excellent balance between mechanical and dielectric properties, solvent and heat resistance confers high potentialities to its applications. Its relatively low cost combined to such properties has motivated the commercialization of this unique material by Dow Chemical Co. (Chestra™) and Idemistsu (Xarec™) together with a substantial interest of the scientific community [2–5]. Several drawbacks can however restrict its practical use as performance plastic. Syndiotactic polystyrene (sPS) has to be processed at high temperatures, greater than 290 °C due to its melting point of 270 °C, which approaches its degradation temperature. The brittleness of sPS can be detrimental in areas where mechanical properties are of prime importance. The lack of polar groups may also disfavor its use in applications where adhesion and compatibility with other polymers are concerned. The introduction of functional groups in sPS can enable to overcome these drawbacks.

Functionalization of syndiotactic polystyrene can be achieved by various routes that are summarized Fig. 1. Functional groups can be introduced directly in the reactive medium, as described by the *in situ* functionalization pathway. This includes statistical copolymerization with other monomers as well as catalytic chain transfer to a chain transfer agent. The former pathway implies the design of highly versatile catalytic systems, able to selectively polymerize a large variety of monomers. The latter pathway has been reviewed recently for polyolefins [6]. It presents potential disadvantages in terms of catalyst poisoning or deactivation, but leads to a higher degree of sophistication. Subsequent reactions can indeed be performed considering the chemistry of the metal/functional group bound at the polymer chain end, including polymerization. Another way consists in the derivatization of the polymer once formed. It includes sequential block copolymerization, and chemical modification of the polymer. The former implies the design of catalytic systems that enable a *living* polymerization, and remains rare keeping in mind that the first living syndiospecific polymerization of styrene was discovered only recently [7]. The latter suffers from the unreactive nature of hydrocarbon polymers, leading to difficult reactions and poor selectivities. Another pathway consists in the polymerization of a functionalized monomer, involving a first step of chemical modification of the monomer.

Although several reviews have been done on one hand on the synthesis of syndiotactic polystyrene and related catalysis [2–5], and on the other hand on different strategies used for the functionalization of polyolefins [6,8–12], the functionalization of syndiotactic polystyrene has never been reviewed so far. This article reports the state of the art in this field. The different strategies are classified in the following way: copolymerization, including statistical and sequential block copolymerizations, functionalization via chain transfer, polymerization of a functionalized monomer and post-polymerization functionalization. The different catalyst precursors used in the studies reported in this review are presented in Fig. 2.

2. Copolymerization

Statistical copolymerization presents a one-step, simple and convenient way of polyolefin functionalization. It implies the use/development of highly versatile catalytic systems able to (co)polymerize a large variety of monomers. If the functionalization of sPS with diene and ethylene has been reported using this route, the synthesis of poly(styrene-*co*-1-alkene) containing styrene–styrene syndiotactic sequences was never reported so far. The statistical copolymerization of polar monomers with olefins also remains a difficult task [8]. The copolymerization of styrene with carbon monoxide using palladium based catalysts can lead to a syndiotactic poly(styrene-*alt*-carbon monoxide) [13], in the absence of styrene–styrene syndiotactic sequences however. Apart from a patent [14] where analytic details have been omitted, attempts to copolymerize styrene with methyl methacrylate [15] and methyl acrylate [16] using titanium based syndiospecific catalytic systems lead to statistical copolymers where styrene–styrene syndiotactic sequences are absent. Sequential block copolymerization also needs highly versatile catalytic systems, and the polymerization has to be living with at least one of the monomer. A sPS-*block*-polar polymer can in principle be synthesized via this pathway, but there is to date no such example as far as we know. This is probably due to the fact that only few catalytic systems are able to polymerize styrene syndiospecifically and in a living manner.

Random as well as sequential block copolymerizations of styrene with olefins and dienes leading to materials