Synthesis of High Molecular Weight Poly(Itaconic Acid Esters)

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Itaconic acid (IA) is a vinyl monomer obtained biotechnologically on an industrial scale. It is a non-toxic, renewable biomaterial. Due to structural similarity, IA and its esters can be used in polymerization processes as an alternative to petrochemical-derived monomers such as acrylic or methacrylic acid. IA contains an α,β-unsaturated double bond that allows it to polymerize via free-radical mechanism, while the two carboxyl groups can be modified before or after polymerization [1, 2]. Standard polymerization methods for itaconic esters produce low molecular weight polymers. The aim of the research is to develop a method for synthesis of high molecular weight poly(itaconic esters) and comparison of their properties with the polymers of typical molecular weights. In the presented alternative approach, the first step is to obtain a high molecular weight poli(itaconic acid) (PIA), followed by esterification of the carboxyl groups.

IA can be esterified directly in the presence of alcohols, e.g. using lipase enzymes such as CALB or without a catalyst by opening the ring of IA anhydride [3]. Copolymerization of IA mono- and diesters in different molar ratios in bulk was carried out in the presence of AIBN as an initiator. As a result of the reaction, polymers with molecular weights in the range of 40 000–200 000 g/mol were obtained, with the content of carboxyl groups being close to the values resulting from the type and molar ratio of monomers.

Here, we proposed a new approach to the synthesis and modification of poly(itaconic acid) esters. In this method, IA polymerization was carried out in an equimolar DMSO/H_2O solution with an azo initiator (VA-044). The molecular weight of PIA can be adjusted in the range of 30 000–700 000 g/mol by changing the initial concentration of IA in the reaction mixture [2]. PIA samples of various molecular weights were esterified using 1,1,3,3-Tetramethylguanidine (TMG) and halogenated compounds, such as methyl iodide, in DMSO solution [4]. Different temperatures and reaction times were tested (up to 50°C and 72 h). Esterification reactions were carried out on purified PIA and directly on the reaction mixture after PIA synthesis, without prior isolation and purification of the polymer.

Polymers from both synthesis paths were subjected to NMR and GPC analysis to confirm the structure and determine the degree of esterification of COOH groups. TGA and DSC analyses were also performed to compare the thermal properties of the polymers. As a result of the esterification reaction of PIA in the presence of TMG, it is possible to obtain polymers with a much higher molecular weight than in the case of polymerization of IA esters and still achieve a significant degree of esterification of COOH groups (up to 90%).

Keywords: itaconic acid, poly(itaconic acid), radical polymerization, esterification, renewable monomers

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