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ORIGINAL RESEARCH

m-Cresol-substituted triethyl aluminum/$MoCl_5$/TBP catalytic system for coordination polymerization of butadiene

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Abstract

Coordination polymerization of butadiene was initiated by a catalyst system consisting of tributyl phosphate (TBP) as ligand, molybdenum pentachloride as primary catalyst and triethyl aluminum substituted by *m*-cresol as co-catalyst. The effects of the substitution of *m*-cresol on the activity of the catalyst system, molecular weight and molecular weight distribution, intrinsic viscosity and microstructures of the resulting polymers were investigated in details. The molecular weight and molecular weight distribution of the polymerization products were determined by GPC. The microstructure of the polymerization products was characterized by FTIR, ^{13}C NMR and DSC techniques. The experimental results indicated that the polymerization activity of the reaction system and the molecular weight of the polymerization products gradually increased with the increase of the substitution content of *m*-cresol, namely, $Al(OPhCH_3)_2Et > Al(OPhCH_3)Et_2 > Al(OPhCH_3)_{0.5}Et_{2.5} > AlEt_3$. The 1,2-structure contents of the polymerization products could be adjusted between 89 and 91% through the control of the substitution of *m*-cresol, and there was minute quantities of crystalline structures in the resulting polymers due to the increasing content of the syndiotactic 1,2-polybutadiene. In a word, the existence and increase of steric hindrance of *m*-cresol made it easier for polymerization products to form interdisciplinary 1,2-structure.

Keywords Mo-based catalyst · 1,2-Polybutadiene · *m*-Cresol · Catalytic activity · Crystalline structure

Introduction

In the case of the conjugated dienes, the stereo- and regioselective polymerization initiated by the excessive metal complexes has received considerable attention from both academic and industrial communities [1, 2]. However, a challenging issue about the relevance of such materials as plastics and synthetic rubbers has been put forward. Particularly, a large amount of importance has been attached to *cis*-1,4-butadiene polymerization due to the industrial advantages, while the 1,2 polymerization has not been extensively investigated. Moreover, it is noteworthy that the 1,2 polymerization of 1,3-butadiene can generate three stereoisomers, including syndio-, isotactic- and syndio-1,2-polybutadiene, which can better satisfy the requirements of high-performance rubber materials.

1,2-Polybutadiene (1,2-PB) with 1,2-structure content over 80% is provided with excellent wet skid resistance, low heat build-up and aging resistance attributed to fewer double bonds on its backbone and dense vinyl side groups, which can, therefore, partly replace SSBR to meet the requirements of high-performance rubber materials for its application in manufacturing high-performance high-speed tires and aircraft tires [3–5]. The catalytic systems in initiating the 1,2-polybutadiene polymerization are mostly the transition metal materials such as Co-based [6, 7], Ti-based [8, 9] and Fe-based [10–12] catalytic systems. Among them, the polybutadiene prepared by Mo-based catalytic system contains 1,2-structure more than 80% and is an amorphous polymer. However, with the Mo-based catalyst as catalytic system, the 1,2-stereoselective polymerization is still a challenging work due to some deficiencies, such as poor 1,2-regularity, strict reaction conditions and low polymerized activity, etc. Accordingly, the effective actions taken to overcome these unfavorable factors and to improve the catalytic efficiency have become the focus of this study.

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