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硕 士 学 位 论 文

基于双茂金属联合催化剂的长支链聚丙烯大分子过  
程模型

Process Model of Long Chain Branched Polypropylene  
Macromolecule Based on Combined Metallocene Catalysts

李华荣

指导教师姓名: 罗正鸿 副教授

专 业 名 称: 工业催化

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李华荣

指导教师: 罗正鸿 (副教授)

厦门大学

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## 摘 要

Ziegler-Natta 催化制备线性等规聚丙烯 (IPP) 的模拟及实验工作已经开展多时, 并取得了许多研究成果。然而, IPP 的使用范围存在一定的局限性。目前可以通过长支链化来拓宽 IPP 的使用范围。公开报道主要是采用线性催化剂和长支链催化剂 (限制几何构型催化剂 CGC-Ti) 联合催化制备长支链聚丙烯 (LCBPP)。以往在 LCBPP 制备方面的报道主要集中在国外, 采用的技术手段是实验研究, 相关制备过程的模拟工作非常匮乏。

对于所研究的 LCBPP 聚合体系而言, 催化剂的配比及其物理变化、反应所对应的一整套参数, 以及反应过程中质量和热量传递阻力等都足够对聚合过程和聚合产物特性产生重要影响。本论文基于微观尺度对丙烯原位制备 LCBPP 过程进行工程模拟, 主要研究内容包括三部分:

第一部分, 建立单颗粒模型: 基于以往的PP单颗粒模型, 结合茂金属联合催化剂特点, 建立改进的多粒模型。利用改进的多粒模型分别对CSTR反应器内的PP颗粒和LCBPP颗粒内部的传质、传热进行模型化研究。此外, 本文模型结果还与公开报告结果进行了对比, 验证了该模型对LCBPP体系的适用性。模拟结果体现了模型的优势, 其更详细的描述LCBPP聚合体系的变化, 如催化剂颗粒的破碎、存在一个不能忽略的引发阶段、聚合过程是一个反应-扩散-反应控制过程、聚合过程中催化剂活性中心浓度变化很小以及验证传热阻力小等。

第二部分, 基于摩尔衡算方程的生成函数法建模 (简称粒群衡算模型): 首先提出聚合反应机理, 得到体系中各种物质的摩尔衡算方程, 结合生成函数法建立粒群衡算模型。采用该模型分别考察了 LCBPP 聚合体系产物的稳态和动态变化。结果表明, 稳态下粒群衡算模型就足以描述产物特性, 动态情况下, 该模型的结果没有说服力, 因而, 有必要考虑颗粒内部的阻力和催化剂的物理变化等因素的影响, 即需要结合单颗粒模型。

第三部分, 单颗粒与粒群衡算耦合模型: 对前述建立的两类模型进行耦合建立单颗粒与粒群衡算耦合模型, 使得模型能考虑单颗粒内部的扩散效应同时又能反映本征反应, 利用该模型对体系进行了稳态和动态模拟。结果证明了稳态条件下, 粒群衡算模型具有优越性。动态条件下, 该模型得到了较好的结果:

所得到的各个结果曲线图体现了扩散作用的影响、体现了催化剂大颗粒的破碎对反应产物特性的影响；对于确定体系达到稳态的时间具有很好的指导意义；能够跟踪大颗粒内部我们所划分的每一层上每一时刻的反应情况。

此外，单颗粒模型结合粒群衡算模型还可以进一步分析体系的其他特性，对生产的指导意义不可小觑。目前，该模型也并非完美无暇，计算耗时和对计算机硬件的要求都提示我们思考能不能对模型进行改进。

**关键词：**联合茂金属催化剂；LCBPP 聚合机理建模；单颗粒模型；粒群衡算模型

## Abstract

The simulation and experimental study of linear polypropylene (IPP) catalyzing by Ziegler-Natta catalyst has been developed such a long time, and has obtained many research results. However, the use of IPP has some limitations. Currently, long chain branching can greatly improve the property of IPP. Publicly reported is mainly long-chain branched polypropylene (LCBPP) prepared by combining of linear catalyst and long chain branched catalyst (CGC-Ti) catalyst. Report on the preparation of LCBPP is mainly in overseas. The technology is experimental study, and the simulation work related to preparation is extremely deficient.

For the LCBPP system we studying, except for fraction of LCB catalyst as well as physical change of catalyst particles, the corresponding entire set of parameters, the mass and heat transfer resistance during the reaction could make significant impact on the propylene polymerization and the polymer properties. Based on the microscopic modeling of in-situ preparation of LCBPP by propylene, most relevant content and results obtained in this work are summarized as follows:

In the first section, we set up a single particle model. Referring to the PP pellet model research by the predecessor and carrying on the reasonable supposition, we set up an improved multigrain model. With the improved multigrain model, the mass and heat transfer effect during the reaction in the PP pellet and the LCBPP pellet in the CSTR reactor were studied respectively. In the same simulation condition, we compared the results obtained by this model between these two polymerization systems. And on the research of the predecessor, we were sure that this improved multigrain model was suitable for the LCBPP system. The results showed that the model we set up had its superiority. Because it could describe the process of the LCBPP formation more detailed, such as the fracture of the macroparticle of catalyst, the initiation stage that could not be neglected, the controlling rule of the reaction was reaction- diffusion-reaction, the change of catalyst concentration and

the heat transfer resistance were both little.

In the second section, we set up a model by the Generating Function Method based on the mole balance calculation equations (i.e. particle population balance model). After proposing the reaction mechanism, we obtained the mole balance calculation equations of all the material in the system, and then obtained the particle population balance model. On this model the steady-state and the dynamic change of the product in LCBPP polymerization system was described. The result indicated that, only the particle population balance model can describe the product characteristic sufficiently in the situation of steady-state, however in the dynamic situation, the result was not good enough. Thus, it was necessary to consider the influence of the resistance internal the pellet and the physical change of the catalyst and so on, and to unify the single pellet model might be good choice.

In the third section, we obtained the steady-state and the dynamic solution of the product in the same system by combining the single particle model and the particle population balance model in the last two sections. With the coupled model the diffusion effect within the single particle could be considered while reflecting the intrinsic reaction. Result showed that the particle population balance model was more superior when describing the steady-state system. In the situation of dynamic, this model obtained better result: Effect of the diffusion resistance as well as the fracture of macroparticle of catalyst were both manifested by the results curves obtained. It could help us determine the time to achieve the steady-state, and track the polymerization process at any time and any layer we divided.

In addition, more properties of the polymer in this system could be further studied and analyzed by the coupled model, and it might give great help to the practical production. However, this coupled model suffers from some limitations. Such long computation time and the requirement of good computer hardware both prompted us that the model might need further effort to be improved.

**Keywords:** Combined Metallocene Catalyst; Mechanism Modeling for LCBPP Polymerization; Single Particle Model; Particle Population Balance Model.

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## 第一章 绪论

介绍课题相关的背景知识和研究现状，主要有长支链聚丙烯的制备工艺、制备催化剂、物理模型等。

### 1.1 引言

#### 1.1.1 相关背景

聚丙烯（PP）是目前世界上应用最为广泛，产量增长最快的树脂之一。与其他热塑性树脂相比，PP具有无味无臭、低密度、高熔点、来源广、价格低以及机械性能优越、化学稳定性好且较易回收等特点，已经成为包装、轻工、建筑、电子、电器和汽车等行业不可缺少的基本原料，其产量仅次于聚乙烯（PE）聚氯乙烯（PVC）<sup>[1]</sup>。

但是，由于 IPP 是一种部分结晶聚合物，软化点与熔点非常接近，超过熔点后熔体强度迅速下降，导致在加热成型时器壁厚度不均匀，挤出涂布时边缘卷曲、收缩，挤出发泡时泡孔塌陷等等问题<sup>[1]</sup>。由于这些缺陷，严重限制了聚丙烯在热成型、吹塑成型和发泡等成型加工领域的应用。

研究发现，提高 IPP 其他特性的关键技术就在于如何使线形聚丙烯产生长链支化（LCB）结构。大量资料显示，少量长支链结构的存在就能使 PP 的熔体强度大大提高，而短支链结构对分子的熔体强度影响不大。对于不同的测试方法或不同的体系，长支链的定义是不同的。目前规定当分子量在缠结分子量 2.5 倍以上时的支链称为长支链<sup>[2]</sup>。在初期的工作中，人们曾试图将有机过氧化物、交联剂与聚丙烯树脂通过挤出机混合或通过电子射线辐照加有交联剂的聚丙烯来达到产生长支链的目的，但效果并不好，聚丙烯熔体强度或者提高幅度不大，或者产生大量凝胶，导致加工困难。

到目前为止，国内外所开发出的最成功的使聚丙烯产生长支链的方法是高能射线辐照法。但采用这种方法，在最后阶段需对聚丙烯加热或加入甲硫醇等助剂，使残留的未完全反应的自由基失去活性，降低聚丙烯的降解和交联等副反应发生的几率。即使这样，需要指出的是，使用这种方法所制备的长链支化



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