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催化、动力学与反应器

$B(C_6F_5)_3$催化Si—H/Si—OR缩聚反应机理及产物结构

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摘要

根据DFT理论，用量子化学的方法对$B(C_6F_5)_3$催化Si—H/Si—OR缩聚反应的机理进行了研究，用^{29}Si NMR对1,4-双（二甲基硅基）苯（BDSB）与二甲基二甲氧基硅烷、甲基乙烯基二甲氧基硅烷、二苯基二甲氧基硅烷缩聚产物的微观结构进行了表征，结合反应机理，对单体的结构与缩聚产物的微观结构的关系进行了讨论。$B(C_6F_5)_3$先与Si—H形成弱加合物，然后Si—OR进攻Si—H/$B(C_6F_5)_3$加合物使Si—H断裂，形成氧鎓 翁离子中间体，最后H⁻向正电中心迁移形成产物。H⁻迁移方向的不同将导致3种反应：缩合、交换、逆反应。烷氧基硅烷中的乙烯基、苯基可以增加烷氧基C的正电性，并使C—O键伸长，减少Si—H/Si—OR交换反应的发生，使得缩聚产物具有更为交替的结构。

关键词

三（五氟苯基）硼 反应机理 密度泛函理论 缩聚 聚亚苯基硅氧烷

分类号

Mechanism and polymer structure of $B(C_6F_5)_3$ catalyzed polycondensation of Si—H/Si—OR

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Abstract

The mechanism of $B(C_6F_5)_3$ catalyzed Si—H/Si—OR polycondensation reaction was studied through the quantum chemistry methods.Poly(silphenylene-siloxane)s were prepared by polycondensation of 1,4-bis(dimethylsilyl)benzene (BDSB) and dimethyldimethoxylsilane, vinylmethyldimethoxylsilane and diphenyldimethoxylsilane respectively.The microstructure of the polymer was characterized by ^{29}Si NMR and the influence of vinyl and phenyl groups of alkoxylsilane on the microstructure of the polymer was also discussed.$B(C_6F_5)_3$ first activated Si—H to form weak adduct, then Si—OR attacked Si—H/$B(C_6F_5)_3$ adduct to break Si—H and form oxonium ion complex.The decomposition of the complex occurred by the H- transfer to one of the three electrophilic centers, which explained the competition between condensation and Si—H/Si—OR exchange.Vinyl or phenyl group of alkoxysilane decreased the positive charge of Si atom and increased the positive charge of C which bonded to O, and it also reduced the strength of C—O, resulting in more alternated polymers.

Key words

tri(pentafluorophenyl)borane mechanism density functional theory polycondensation poly (silphenylene-siloxane)

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