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超支化聚碳硅烷结构、交联方法及其应用研究进展

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摘要: 超支化聚碳硅烷(Hyperbranched Polycarbosilane, HBPCS)作为一种 SiC 陶瓷先驱体, 因其具有可自交联、低粘度、高陶瓷产率、末端基团功能化等特殊性能, 广泛用于制备 SiC 陶瓷及其复合材料。本文对 HBPCS 的结构、交联方法和应用做了系统综述, 展望了未来 HBPCS 的发展方向, 指出面向功能化需求和应用性能要求将是未来 HBPCS 合成及应用的主体方向, 其交联方法将向低温、快速、无氧、低成本等方向发展。

关键词: 超支化聚碳硅烷; 交联方法; 单体; 结构; 应用

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Research Progress on Structural, Crosslinking Methods and Applications of Hyperbranched Polycarbosilane

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Abstract: As a polymer precursor of SiC, hyperbranched polycarbosilanes (HBPCS) have been widely applied to the fabrication of SiC ceramics and SiC matrix composites, due to their excellent properties, such as self-crosslinking, low viscosity, high ceramic yields and functional terminal groups. In the present work, the structures, crosslinking methods and applications of HBPCS were reviewed systematically. The development direction of HBPCS in the near future was prospected. Functionalization requirement and application properties of the HBPCS were the main object of future synthesis and application. Crosslinking method would be developed in the direction of low temperature, fast, anaerobic and low cost.

Key words: hyperbranched polycarbosilane; crosslinking methods; monomer; structure; applications

0 引言

近年来, 高度支化的聚合物由于具有独特的性质和结构, 一直是广大学者关注的热点^[1-3]。高度支化的聚合物通常可分为树枝状聚合物(Dendrimers)和超支化聚合物(Hyperbranched Polymer, HBP)两种。其中, 树枝状聚合物具有较为完美的结构, 理论支化度(Degree of branching, DB)为 1, 合成条件苛刻, 需要进行多步反应才能获得; 与树枝状聚合物相比, HBP 通常可用“一锅法”制得^[4], DB 在 0-1 之间, 具有与树枝状聚合物许多相似的性质^[5]; 与 HBP 相比, 线性聚合物虽然具有优异的物理化学性能, 但存在黏度大、

与其它聚合物相容性差、反应活性低等缺点。HBP 分子内存在大量支化结构, 具有分子内存在空腔、分子间缠绕少、较难结晶、低粘度、高反应活性等优点, 更受研究者的青睐^[6,7]。超支化聚碳硅烷(Hyperbranched Polycarbosilane, HBPCS)作为超支化聚合物中的一种, 成为近年来的研究热点。

陶瓷材料具有高强度、高模量、耐高温、抗氧化等优越的性能, 广泛应用于航空航天、国防等高新技术领域^[8,9]。碳化硅陶瓷作为陶瓷材料中的一种, 不仅具有高强度、高模量、耐高温、抗氧化等性能, 还具有耐酸碱、电阻率可调、与陶瓷基及金属基复合材料相容性好等优越的性能, 在国防、航空航天、军事武器等高新技术领域有着广

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泛的应用^[10-12]。HBPCS 作为 SiC 陶瓷先驱体之一, 在高温惰性气氛或真空条件下转化为 SiC 陶瓷, 在氨气气氛下发生碳氮置换反应转化为 Si₃N₄ 陶瓷。为了提高 HBPCS 热解的陶瓷产率, 在热解前对 HBPCS 进行交联是一种提高陶瓷产率和减少小分子在热解过程中挥发的有效措施。对于线性聚碳硅烷的交联, 通常采用热空气氧化交联、电子束辐照交联、化学气相交联等方法。与线性聚碳硅烷不同的是, HBPCS 的交联除了可用上述交联方法来提高陶瓷产率外, 还可通过自交联、自由基引发无氧交联等交联方式提高陶瓷产率, 自交联或自由基引发无氧交联过程中没有氧的引入, 1200 °C 时不发生 Si_xO_yC_z 相的分解, 所得陶瓷的耐温性能相较于热氧化固化得到的陶瓷更好。HBPCS 通常由含多官能团的 A_mB_n 型^[13]、A_m+B_n 型^[14-16]等(m≥1, n≥2)硅烷单体聚合而成, 分子外围带有大量的末端功能基团, 可根据实际要求对末端官能团进行修饰改性进而获得具有特定功能的材料, 如催化剂载体^[17]、含硅陶瓷材料先驱体^[18]、药物载体^[19]、膜分离材料^[20,21]、激光防护涂层^[22]、吸波材料等^[23-27]。本文依据近年来 HBPCS 的发展, 对其结构、交联方法和应用做了系统综述, 并展望了 HBPCS 未来的发展方向。

1 HBPCS 结构类型

HBPCS 是由单体聚合而成, 其结构组成与所选单体密切相关, 特定的单体可以制备出含特定结构的 HBPCS, 结构的不同导致 HBPCS 性能上存在差异, 进而决定了其用途的不同。根据现有研究资料可把合成 HBPCS 的单体分为无环单体和含环单体, 通过这些单体的聚合可以合成无环或含环的 HBPCS。

1.1 无环 HBPCS

20 世纪 70 年代, Yajima 等^[28]首次以聚碳硅烷 (Polycarbosilane, PCS) 作为先驱体制备 SiC 陶瓷纤

维, 该 PCS 制备的 SiC 富 C, 影响了 SiC 在高温下的耐温性能。为了提高 SiC 的耐温性能、减少产品含 C 量, 设计合成化学计量比的先驱体应运而生。Whitmarsh 等^[29]以氯甲基三氯硅烷在乙醚溶剂中发生格氏偶合反应, 并采用 LiAlH₄ 还原, 首次制备出了氢化 HBPCS (称 HPCS)。该 HBPCS 结构中含有 SiH₃CH₂—、—SiH₂CH₂—、=SiHCH₂— 和 ≡SiCH₂— 结构单元, 实质上是一种无环的 HBPCS, 平均结构式为 [SiH_{1.85}Et_{0.15}CH₂]_n, 与原设计结构中化学计量比 SiC 有少许偏离。随后, Interrante 课题组^[30]对 HPCS 进行了衍生, 得到无环、高陶瓷产率 (陶瓷产率达 90%) 的烯丙基取代的 HBPCS (Allylhydriodopolycarbosilane, AHPCS), HPCS 和 AHPCS 的结构如图 1 所示。此外, 美国的 Starfire 公司也研发出了化学计量比的 HBPCS, 商品名为 SMP-10, 但遗憾的是其合成路线尚未公布。

自 Interrante 课题组制备出 HBPCS 以来, 格氏偶合法^[31]、硅氢加成法^[32]、开环聚合^[33]等也相继用于合成 HBPCS。在其合成策略上不只限于以 Si、C 化学计量比进行合成, HBPCS 的结构也不断发展优化。其中, 无环 HBPCS 的合成是目前研究最多的, 其合成主要以无环单体为原料进行合成, 无环单体包括烷基卤硅烷(4)、卤代烷基卤硅烷(1,2,3)、卤代烯基(炔基)卤硅烷(5,6)或烯(或炔)基硅烷(12,14)、含硅氢键的烯(或炔)基硅烷(7,8,9,10,11,13)等, 无环单体如图 2 所示。

从图 2 中可知, 以单一单体或者两种单体为反应物, 都可以制备出无环的 HBPCS, 这给其结构的可设计性带来了优势。Xiao 等^[34]采用硅氢加成法, 以单体 7 为原料, 制备了末端含有乙炔基功能团的 HBPCS, 其路线如图 3 所示, 通过热重分析得出该 HBPCS 在 1300 °C 失重仅为 13%。继无环 HBPCS 被合成出来后, 含环 HBPCS 的合成也应运而生。

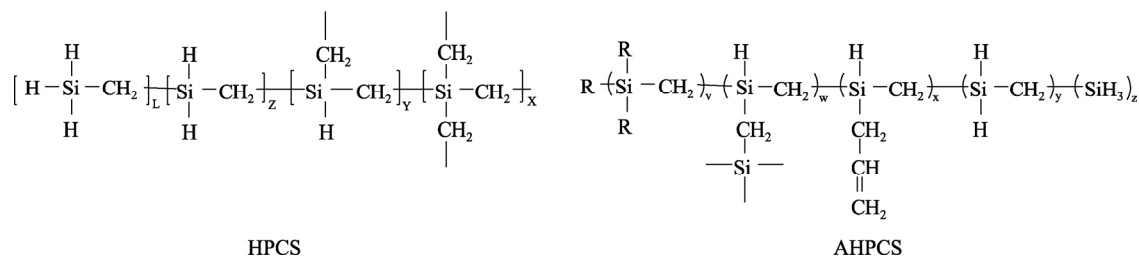


图 1 HPCS 和 AHPCS 的结构
Fig.1 Structures of HPCS and AHPCS

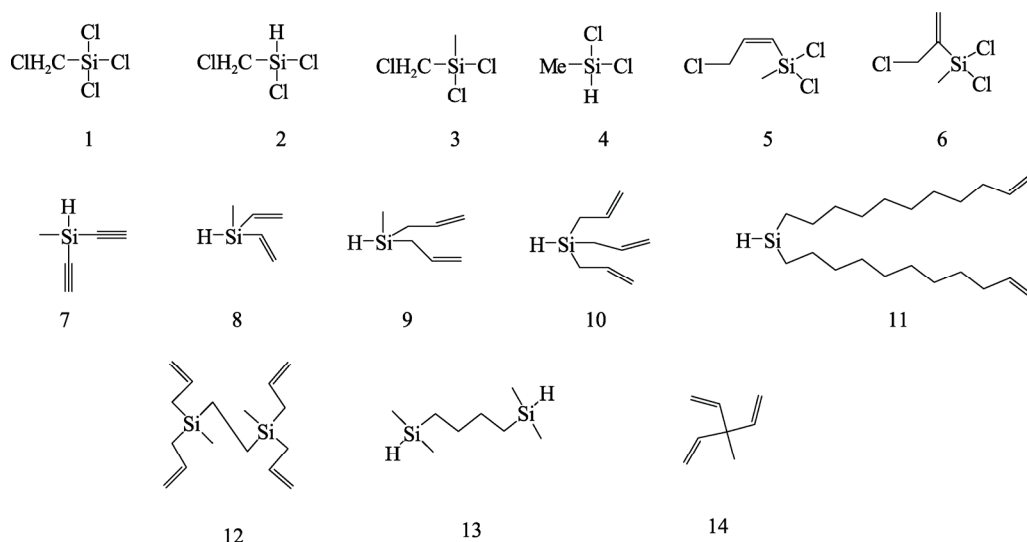


图 2 用于制备无环 HBPCS 的单体

Fig.2 Monomers for aliphatic hyperbranched polycarbosilanes

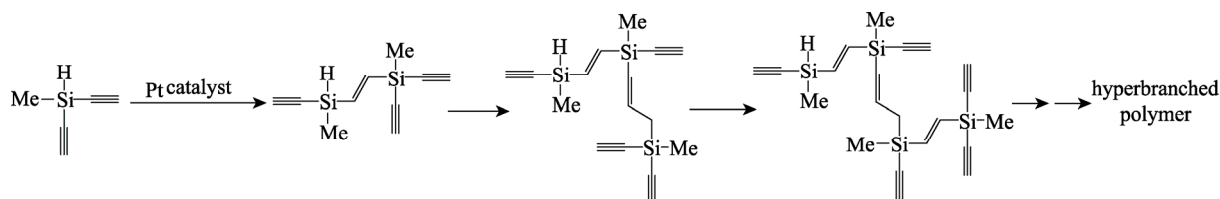


图 3 末端含乙炔基的 HBPCS

Fig.3 HBPCS with ethynyl terminal groups

1.2 含环 HBPCS

HBPCS 中环的来源主要有四种形式：在无环 HBPCS 中引入含环的核、以含环的单体为原料合成含环 HBPCS、用含环化合物对 HBPCS 末端活性基团改性以及通过无环单体间反应合成含环 HBPCS。Lach 等^[35-37]以无环单体 10 为主要反应原料，以含恶唑啉官能团的化合物为核，通过硅氢加成法制备出 DB 为 0.48 ± 0.05 的含恶唑啉的 HBPCS，添加核(如 1,3,5-苯三甲酸)可进一步提高 HBPCS 的聚合度。此外，通过硅氢加成法结合格氏偶合法还可以进一步控制 HBPCS 的 DB。Yoon 等^[38]为了研制性能优越的高温弹性体，通过使用含有芳环的多功能硅烷单体合成了主链中含有芳环的 HBPCS，其过程如图 4 所示；Lam 等^[39]制备了含噻咯环的 HBPCS，该 HBPCS 结构中含有大量的共轭结构，可在聚集诱导发光方面获得应用，其合成过程如图 5 所示；Moreno 等^[40]合成的 HBPCS 链结构中含有芳环和 O 元素，其合成过程与结构如图 6 所示。Baldwin 等^[41]以无环单体 9 合成了 HBPCS，然后，在该 HBPCS 中添加含硅氢键的无环单体与之反应后形成了分子间的环状结构，最终形成凝胶化的 HBPCS，该凝胶化的

HBPCS 可在喷墨打印方面获得应用。

2 交联

对于线性 PCS 和 HBPCS，为了提高最终烧成的陶瓷产率，交联是必不可少的环节。交联的目的在于使分子量增大，形成三维网状的不溶不熔结构，减少小分子组分的挥发，提高高温裂解产率。通常线性 PCS 的交联方法有热氧化交联^[42]、化学气相交联^[43]、电子束辐照交联^[44]、强氧化剂氧化交联^[45]等。这些方法由于在 PCS 结构中引入氧元素，最终导致烧成陶瓷的耐温性能受到影响；或者由于交联所需能量高、交联设备昂贵，限制了其规模化和商业化应用。与线性 PCS 交联不同，HBPCS 由于末端基团的存在，除了可以用上述方法进行交联外，还可以通过热交联^[46]、添加引发剂^[47]、紫外辐照^[48]等方法进行交联。

2.1 热氧化交联

热氧化交联是 HBPCS 中的 Si-H 键与氧反应形成 Si-OH, Si-OH 间进一步脱水缩合形成 Si-O-Si 结构，从而使 HBPCS 形成不溶不熔的三维网状结构。虽然热氧化交联可以达到交联的目的，但因

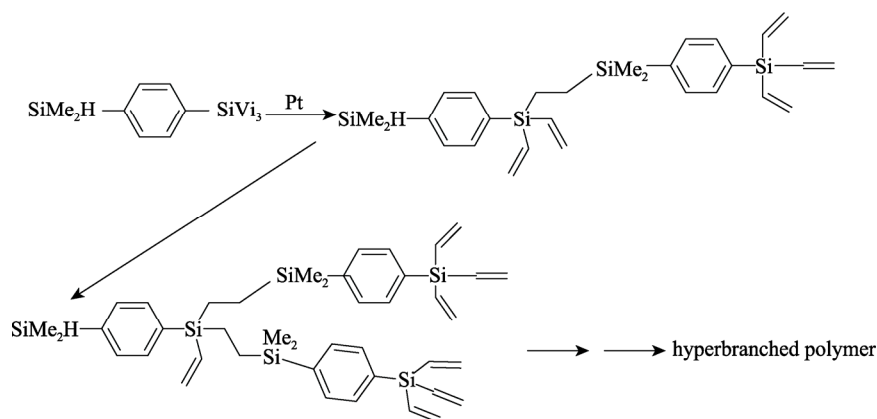


图 4 含有芳环的 HBPCS
Fig.4 Ring-containing HBPCS

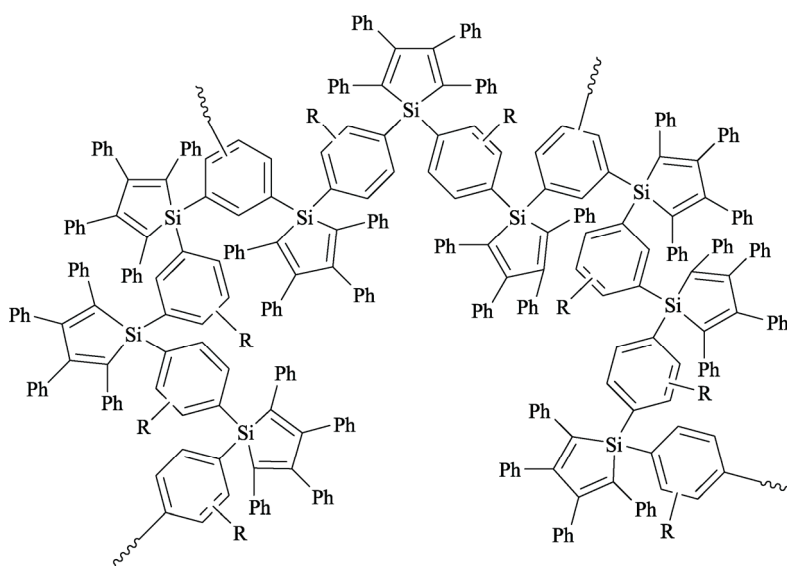


图 5 含噻咯的 HBPCS
Fig.5 Silole-containing HBPCS

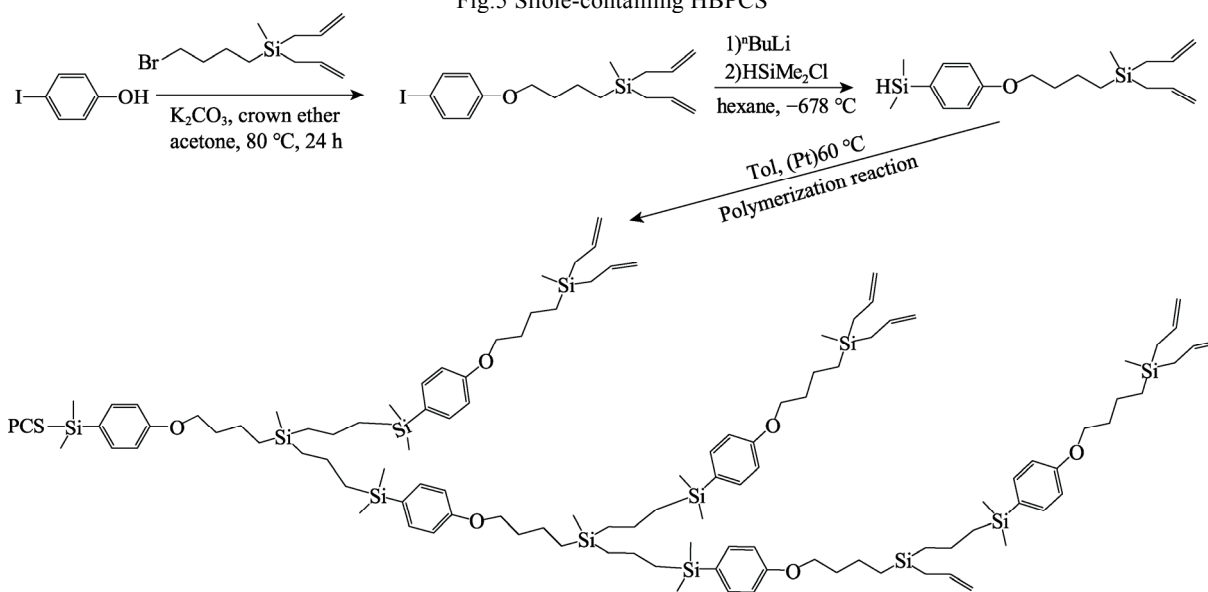


图 6 含苯环和氧元素的 HBPCS
Fig.6 HBPCS with structure containing aromatic units and oxygen element

过紫外辐照的方法进行交联，并研究了紫外交联的机理，认为 HBPCS 在紫外辐照时主要发生了脱氢耦合反应、硅氢加成反应和乙烯基的加聚反应，反应过程如图 11 所示。

对于 HBPCS 的交联而言，紫外辐照交联作为一种低温交联方法，不仅具有低成本、低能耗、高效率等优点，而且可以在 HBPCS 中添加引发剂或者含不饱和官能团的化合物，进而提高 HBPCS 的陶瓷产率。

3 应用

3.1 陶瓷先驱体

SiC 具有高强度模量、耐高温、抗氧化等优越

的性能，广泛应用于航空航天、核工业等高新技术领域^[60]。HBPCS 作为制备 SiC 的先驱体之一，具有 Si-H、C=C 等活性官能团，可在无氧环境下实现的交联，以交联后的 HBPCS 制备 SiC 陶瓷时，其热解过程的失重与 Yajima 方法制备的固态 PCS 热解时相似，即热解过程的失重为三个阶段^[55,58]，室温至 400 °C 为 HBPCS 的进一步交联；400-800 °C 为 HBPCS 从有机转化为无机的过程；800-1400 °C 为 SiC 从无定形向 β-SiC 转变，且随着温度的升高，β-SiC 晶粒逐渐生长。无氧环境下交联的 HBPCS 高温热解后无 SiC_xO_y 相存在或 SiC_xO_y 相含量很低，在 1200 °C 处理时结构几乎不受影响，因此，具有更好的耐高温性能。此外，HBPCS 还

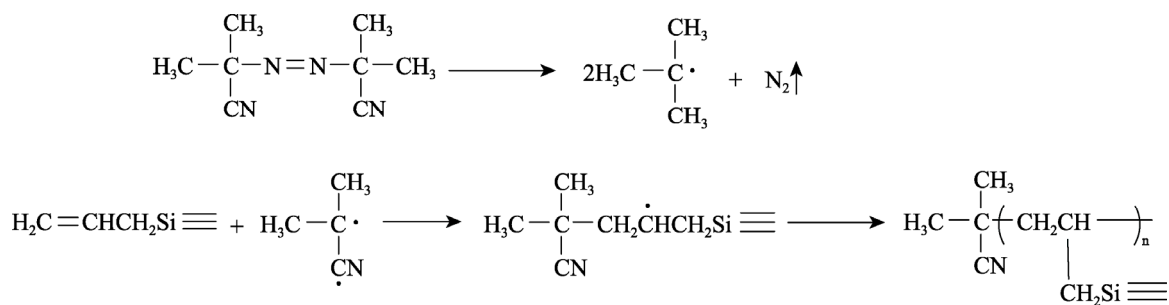


图 8 偶氮二异丁腈引发 HBPCS 交联

Fig.8 Mechanism of HBPCS crosslinked by azodiisobutyronitrile as initiator

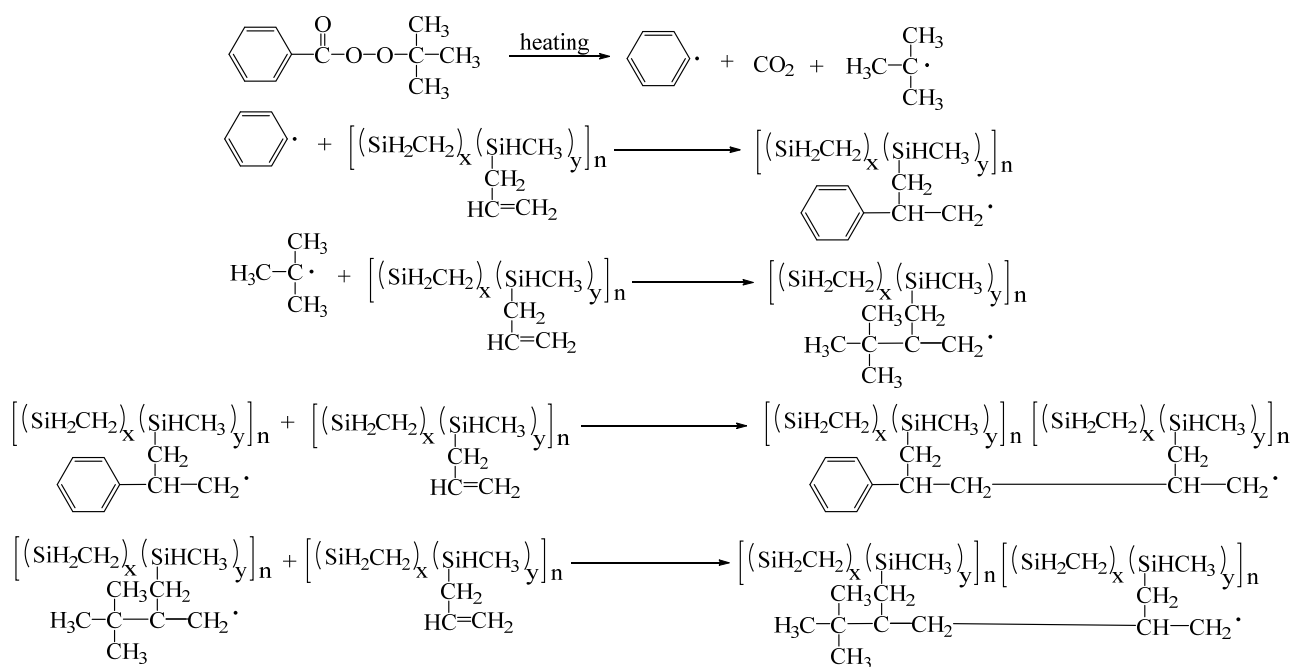


图 9 过氧苯甲酸叔丁酯引发 LHBPCS 交联

Fig.9 LHBPCS crosslinked by tert-butyl peroxybenzoate

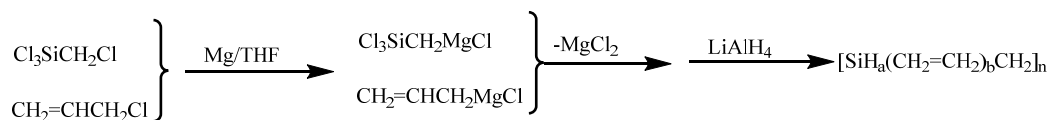


图 10 LHBPCS 的合成路线(a + b = 2)

Fig.10 Synthesis route for LHBPCS (a + b = 2)

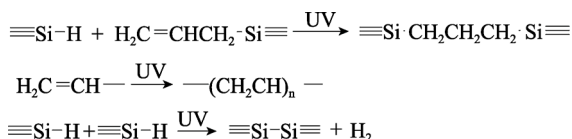


图 11 紫外辐照下 HBPCS 发生的反应

Fig.11 Main reaction of HBPCS under UV irradiation

广泛用于制备含硅陶瓷及其复合材料^[61-65]。由于 HBPCS 具有一定的流动性,其可单独热解,也可与其它先驱体共混共热解或与 SiC 颗粒混合热解等^[41,51,66]。此外,HBPCS 具有大量的活性官能团,采用含异质元素的化合物(含金属或非金属)对这些活性基团加以改性,可以制备出含异质元素的 HBPCS,将含异质元素的 HBPCS 热解可以进一步得到性能优越的 SiC(Ti)、SiBCN 等含异质元素的陶瓷^[67-69]。

Kong 等^[26]为提高陶瓷产率,利用超支化聚二茂铁基聚碳硅烷与聚硅氮烷发生交联反应热解,制备出的陶瓷含有 Fe₅Si₃、Si₃N₄、SiC 相。其中,Fe₅Si₃ 相由无定型 SiCN 相与铁原子反应生成,在 1300 °C 处理后,Fe₅Si₃ 转变为稳定的 Fe₃Si 磁性颗粒,有良好的铁磁性,具有极低的磁滞损失接近 0,在电磁系统、信息存储和磁制冷等领域具有实际应用潜力。2017 年,其课题组^[70]研制出了富碳无金属具有优越吸波性能的 SiCN 陶瓷,当样品厚度为 2.30 mm 时,在频率为 12.5 GHz 处的反射衰减为 -59.59 dB。该陶瓷在恶劣环境下的电子设备、天线外壳和雷达罩等领域有着巨大潜力。

3.2 HBPCS 的其它应用

HBPCS 具有良好的相容性、流动性,结构内存在大量空腔,可用于制备膜分离材料^[21-22]、磁流变流体^[71,72]、激光防护涂层^[22]、药物控制释放剂^[73-75]、抗菌剂^[76,77]、手性毛细管电泳柱包覆材料^[78]、催化剂^[79-81]、高分子硅烷偶联剂^[82]等。此外,因 HBPCS 主链中主要含有 -Si-C-、-Si-C-C- 等结构,原子间的电负性相差不大,多呈疏水性,可用于制备超疏水材料和高湿气体分离材料^[83]。若将亲水性的基团或者物质与 HBPCS 活性末端基团反应,可以制备出具有双亲性的材料^[84]。为了拓宽 HBPCS 的应用领域,还需要广大科技工作者

不断尝试和探索。

4 展望

HBPCS 分子内存在空腔,不仅在药物控释靶向给药等方面有着潜在的应用,而且在分离、过滤、细菌培养等方面也有一定的优势。在合成策略方面,虽然现在的合成技术已相对成熟了,合成出的 HBPCS 种类繁多,但多涉及到使用贵金属催化剂或有机金属试剂。因此,如何降低 HBPCS 的制备成本,使其能规模化、产业化、商业化是目前存在的挑战之一。此外,为了提高交联效率和减少 HBPCS 小分子在交联和热解过程中的挥发,其交联工艺将向低温、快速、无氧、低成本、高陶瓷产率等方向发展。随着研究的深入与材料应用环境的要求的提高,对现有 HBPCS 也提出了挑战。在陶瓷方面,HBPCS 具有大量的活性官能团,通过对活性官能团进行改性,不仅可以实现 HBPCS 的交联,而且能提高 SiC 陶瓷的现有性能,适用于某些极端环境,还可以拓展 SiC 陶瓷新的应用领域。HBPCS 具有许多线性 PCS 所不具备的物理化学性能,可用作 SiC 陶瓷先驱体,在制备无氧陶瓷方面具有广阔的应用前景;且其末端存在大量的活性官能团,对 HBPCS 的末端活性官能团进行改性,不仅可用于制备含硅陶瓷、含硅陶瓷复合材料,而且在药物包覆释放载体、催化剂载体、膜材料等领域也有广泛的应用。

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