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基于 POSS 嵌段共聚物的溶液自组装及
环氧树脂改性研究

Study on Self-Assembly Behavior of POSS-Based Block
Copolymer in Solutions and Modification of Epoxy Resin by
POSS-Based Block Copolymer

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摘要

有机/无机纳米杂化材料因其综合了有机聚合物轻质、良好加工性、柔韧性和无机成分的良好热稳定性、抗氧化性等优点而受到愈来愈多的重视，这一领域的研究已成为当今高分子研究领域的热点，继续深入探究有机/无机纳米杂化材料的制备和应用是一项富有意义的工作。本文的工作围绕着 POSS 基嵌段共聚物展开，目的在于采用 RAFT 聚合制备具有 P4VP 嵌段的 POSS 基嵌段共聚物，并探究所得的 POSS 基两亲嵌段共聚物的溶液自组装，同时，研究具有 PMMA 嵌段的 POSS 基嵌段共聚物对 POSS 与环氧树脂共混相容性的改善。本文工作具体如下：

1. PMAiBuPOSS-b-P4VP 两嵌段共聚物和 PMAiBuPOSS-b-PS-b-P4VP 三嵌段共聚物的合成与溶液自组装。采用 RAFT 聚合法探究了 PMAiBuPOSS-b-P4VP 两嵌段共聚物和 PMAiBuPOSS-b-PS-b-P4VP 三嵌段共聚物的合成，通过 NMR、GPC、TEM 和 TGA 等表征方法对聚合物的结构和热性能进行了表征，结果表明，我们成功合成了 PMAiBuPOSS-b-P4VP 和 PMAiBuPOSS-b-PS-b-P4VP，而这一聚合物的合成尚未见报道。目前，关于纯有机嵌段聚合物的溶液自组装研究较多，而关于具有有机/无机杂化特征的嵌段共聚物自组装研究依然较少。于是，我们利用两亲性 PMAiBuPOSS-b-P4VP 两嵌段共聚物和 PMAiBuPOSS-b-PS-b-P4VP 三嵌段共聚物在盐酸溶液中制备了自组装胶束，并采用荧光光谱法、DLS、TEM 等表征方法对共聚物胶束临界聚集浓度 (CAC)、pH 响应性和自组装形貌等进行了表征。结果表明，共聚物亲疏水链长均对共聚物胶束 CAC 有着直接的影响。在盐酸溶液中，随着 pH 值的增大，胶束尺寸会经历一个先减小后增大的变化过程，并认为尺寸减小是由于 pH 增大时质子化程度减弱、链间斥力减小引起的 P4VP 链收缩，尺寸再增大是由于吡啶环的疏水作用和 π - π 堆积作用增强所引起的更多数量 P4VP 链段参与疏水核形成所致。研究还发现在 pH=1 的盐酸溶液中，共聚物胶束会发生特殊相分离，我们认为这一现象是由与嵌段共聚物酯基水解后形成的 POSS 团聚微区所造成的。我们的工作进一步丰富了两亲性嵌段共聚物在溶液自组装领域的研究。

2. 基于 POSS 嵌段共聚物的环氧共混改性。采用 RAFT 聚合方法成功合成

具有 PMMA 嵌段的 POSS 基嵌段共聚物 (BCP): PMAiBuPOSS-b-PMMA。致力于克服直接共混法制备 POSS 改性环氧树脂时共混相容性差的缺点,我们创新性地采用 BCP 作为增容剂改善 POSS 与环氧树脂共混相容性。通过 SEM 观察,我们发现,随着 BCP 添加量的增加,POSS 的微米级富集区减少,纳米级富集区增多;当 BCP 为 10 phr, POSS 单体 5 phr 时,POSS 在环氧基体内的富集区全部为纳米尺寸,即 POSS 以纳米尺寸均一分散于环氧基体内。由于两亲性 PMMA 嵌段和 POSS 嵌段的存在,BCP 在 DGEBA 中,确实可对 POSS 与环氧树脂共混相容性起到一定改善作用。我们还发现,随着 BCP 含量的增多,POSS 改性环氧树脂的断裂行为逐渐由脆性断裂转变为韧性断裂,然而,玻璃化转变温度和橡胶态储能模量有所下降。

关键词: POSS; 嵌段共聚物; 溶液自组装; 环氧树脂

Abstract

Organic/inorganic hybrid material has attracted more and more attentions in recent years, because of its combination of organic components of light, good processability, flexibility, etc. and inorganic components of good thermal stability, oxidation resistance, etc.. It is no doubt that this field of research has become the hottest area in polymer science. Apparently, continuous work in the preparation and application of organic-inorganic hybrid material is very meaningful. Our work in this thesis is all about POSS-based block copolymers. We studied the synthesis of POSS-based block copolymers with P4VP block via RAFT polymerization and their self-assembly behaviors. Besides, we studied the improvement of the compatibility of epoxy/POSS blends by using POSS-based block copolymers with PMMA block as compatibilizer. The main achievements of our work are shown as below:

1. The synthesis of PMAiBuPOSS-b-P4VP diblock copolymers and PMAiBuPOSS-b-PS-b-P4VP triblock copolymers and their self-assembly behaviors. In this part, the synthesis of PMAiBuPOSS-b-P4VP diblock copolymers and PMAiBuPOSS-b-PS-b-P4VP triblock copolymers via RAFT polymerization were investigated seriously, furthermore, the structure and thermal properties of these products were characterized by NMR, GPC, TEM and TGA. Results of these characterizations showed that the PMAiBuPOSS-b-P4VP and PMAiBuPOSS-b-PS-b-P4VP have been synthesized successfully, which has not been reported by other researchers yet. As we know, studies in the self-assembly behaviors of pure organic polymers are abundant, but studies about the self-assembly behaviors of organic-inorganic hybrid block copolymer are still few. Herein, we prepared the aggregates of PMAiBuPOSS-b-P4VP and PMAiBuPOSS-b-PS-b-P4VP in aqueous solution, and carefully investigated the critical aggregate concentration (CAC), pH sensitive behaviors and self-assembly morphology by fluorescent spectrometry, DLS, TEM, etc.. It was shown that CAC was influenced by the chain length of hydrophilic and hydrophobic chains directly. With the increase of pH, the size of aggregates

would firstly decrease and further increase in aqueous solution. Size decrease was supposed to be caused by the shrink of P4VP chain at higher pH value, but the subsequent increase of aggregate size was caused by π - π stacking interaction of pyridine ring, which made much more molecules aggregate as a result. We were also surprised to find special dot-like phase separation in aggregates of block copolymers at pH=1, which was considered to be the POSS-rich area formed after the hydrolysis reaction of ester group of block copolymer. Certainly, our work enriched studies about self-assembly behaviors of block copolymer in solution.

2. The blending modification of epoxy resin based on POSS-based block copolymer. First, we successfully synthesized the POSS-based block copolymer with PMMA block: PMAiBuPOSS-b-PMMA (BCP). Aiming to overcome the shortcomings brought by bad compatibility of epoxy/POSS blends prepared by blending methods, BCP were creatively used as compatibilizer to improve the compatibility of epoxy resin and POSS. We found that the number of micro aggregation areas of POSS decreased with BCP content, whereas the number of nano aggregation areas of POSS increased. For example, all the aggregation areas of POSS were in nano size when the content of BCP was 10 phr and POSS monomer was 5 phr. It indicated that POSS were distributed in epoxy matrix in nano size uniformly. Therefore, it was confirmed that BCP could effectively improve the compatibility of epoxy resin and POSS utilizing its amphiphilicity in DGEBA, which was provided by PMMA block and PMAiBuPOSS block. It was also found that the fracture behavior transformed from brittle fracture to ductile fracture gradually with the increase of BCP content, but the T_g and E' decreased.

Keywords: POSS; block copolymer; self-assembly behavior; epoxy resin

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第一章 绪论

1.1 多面体齐聚倍半硅氧烷 (POSS) 简介

1.1.1 POSS 的结构与性能

伴随着高分子科学的日益发展,人们在享受着高分子科学带来的无数创新作品的同时,也对生产和生活提出了更高的要求。从 20 世纪 90 年代开始,纳米材料开始映入我们的眼帘。纳米材料的尺寸在 100 nm 以下,与电子的相干长度和光的波长相近,使得纳米材料会表现出特殊的纳米效应,与物质在宏观状态下表现出来的热学、力学、导电性能等都有着极大的不同^[1-6]。纳米材料的优异性能使得纳米材料的开发研究一直是全世界研究的热点。而今,有机/无机纳米杂化材料开始在纳米材料的中占据重要的地位。有机/无机纳米杂化材料因其综合了有机聚合物轻质、良好加工性、柔韧性和无机成分的良好热稳定性、抗氧化性等优点为人们所发现并重视。可控结构的无机纳米粒子团簇,尤其是多面体齐聚倍半硅氧烷 (Polyhedral oligomeric silsesquioxanes, 简称 POSS) 的出现为有机/无机纳米杂化材料应用和发展提供了一种新的途径。

倍半硅氧烷(silsesquioxane)是一类具有经典结构式为 $(\text{RSiO}_{1.5})_n$ 的化合物,其中 $n=6, 8, 10, 12$, R 可以是 H 或者烷基、烯基、芳基、芳烯基以及它们的有机衍生物^[7]。其结构主要包括无定形结构、梯形结构、半笼结构、笼状结构,如图 1.1 所示。

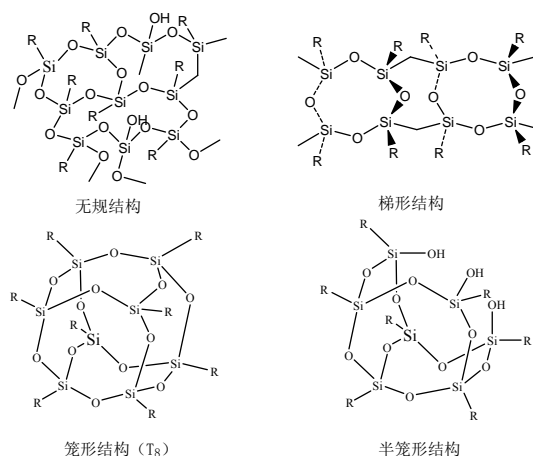


图 1.1 倍半硅氧烷的结构

Figure 1.1 The structures of silsesquioxane

POSS 是倍半硅氧烷的一种，主要指具有笼形结构和半笼形结构的倍半硅氧烷。它包括无机和有机两个部分，硅和氧构成无机结构中心，此结构中心被有机取代基所覆盖；在笼型骨架中，Si-O-Si 键和 O-Si-O 键的键角分别约为 114° 和 111° ，POSS 分子的直径从 1 nm 到 3 nm，分子量可高达 1 000，每个 POSS 分子外围所含有的有机基团^[7,8]，可以使 POSS 纳米结构与聚合物、生物系统或者表面有很好的相容性。

一般根据角基团的不同将 POSS 分为不同的种类。用 X 代表角基团，n 代表 POSS 笼型主体结构的 Si 原子数，则当 X 全部为氢原子 (H) 时，POSS 表示为 T_n^H (图 1.2(a))；当 X 全部为一种有机官能团时，POSS 表示为 T_n (图 1.2(b))；当 X 为 2 种或 2 种以上的有机官能团，如果其中一个官能团与其他 7 个相同的官能团不同时，POSS 表示为 Q_n (图 1.2(c))。 T_8 ，是笼形倍半硅氧烷中的六面体倍半硅氧烷 (如图 1.2(b))，结构对称性非常强，六面体的每个面都由硅氧八元环组成，与二氧化硅类中的沸石或分子筛的结构最为相近，是目前研究最多的一类笼形倍半硅氧烷。

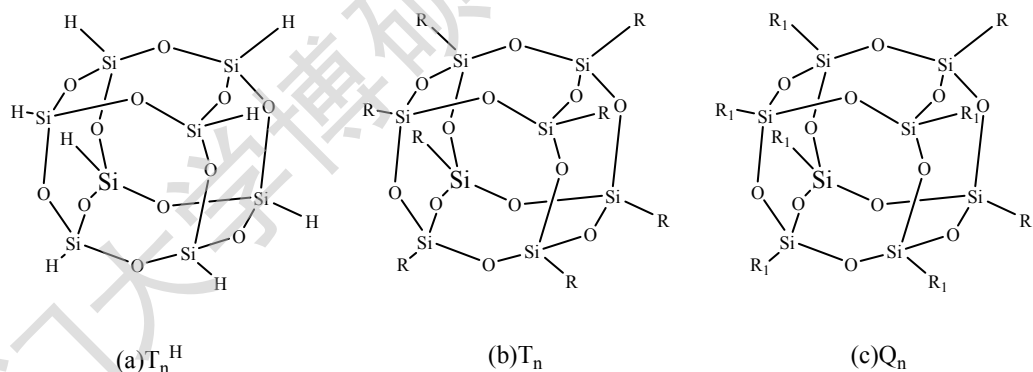


图 1.2 带不同角基团的 POSS

Figure 1.2 POSS with different groups

POSS 的特殊结构给其带来了特殊的性能，下面结合 POSS 的结构来阐述其优异的性能。

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