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硕　士　学　位　论　文

偶氮苯基双亲共聚物的溶液自组装及其多重刺激响应研究

Study on Self-assembly Behavior and Multiple-stimuli-responsive Property of Azobenzene-based Amphiphilic Copolymers in Solution

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摘要

环境响应聚合物分子链中含有特殊的响应基团，能够对外界环境的改变做出结构和性质的调整。许多科研团队致力于设计这类聚合物，并以此来丰富其在药物传送与释放方面的应用。偶氮苯由于有独特的光响应性和还原响应性，将其嵌入到聚合物中，通过光照或加入还原性物质便可调控其自组装聚集体的结构与实现药物分子的释放等，使其成为自组装领域的研究热点。本文先合成活性的偶氮苯单体，再将其与其他响应性单体通过 RAFT 法进行共聚，制备出含偶氮苯基团的多重刺激响应双亲共聚物，研究了共聚物的自组装行为、胶束的荧光及控制释放性能。以下是本文的主要内容：

1. 借助重氮化反应与偶合反应，制得羟基偶氮苯 HOAZO。将其与酰氯反应，转变为有聚合活性的乙烯基偶氮苯单体 AZOMA。通过 NMR、FTIR 和 MS 对其结构进行表征。

2. 采用 RAFT 法，以 AZOMA、甲基丙烯酰氧丙基七异丁基笼形倍半硅氧烷 POSSMA 和甲基丙烯酸二甲基氨基乙酯 DMAEMA 为共聚单体，以二硫代苯甲酸枯基酯 CDB 为 RAFT 链转移剂，将具有光响应和还原响应的偶氮苯基团、强疏水性的 POSS 基团和 pH 响应的叔胺基团设计到同一个聚合物链中。制得一系列具有多重刺激响应性的双亲性无规共聚物 P(POSSMA-co-AZOMA-co-DMAEMA)。通过 NMR、FTIR 和 GPC 对其组成和结构进行分析。

3. 采用溶剂挥发诱导自组装法制备核壳结构的纳米胶束。通过分析胶束的紫外吸收特点，确定偶氮苯基团在胶束中形成“J 型聚集”结构。据此，分析了胶束的聚集诱导荧光发射现象，并将其用于测定胶束形成过程中的临界水含量 CWC，通过传统的浊度法对实验结果进行验证。选用尼罗红 Nile Red 作为荧光探针测定 P(POSSMA-co-AZOMA-co-DMAEMA)的临界胶束浓度 CMC。借助 DLS 和 TEM 讨论了胶束形貌和尺寸的影响因素，结果表明：初始浓度和分子量的增加均有利于形成更大粒径的胶束。

4. 借助 DLS 和 UV-Vis 光谱研究了胶束的光响应性，发现紫外光照能够诱发偶氮侧基的构型转变，导致胶束粒径减小。DLS 和 TEM 分析了胶束的 pH 响

应性，结果表明：pH 在 6.9~5.5 范围内，pH 降低，胶束的粒径呈现先增大后减小的趋势，球形核壳结构被破坏，形成不规则的聚合物团聚体；当 pH 值降至 5.5 时，胶束会发生解组装，表现出敏感的 pH 响应性。这一敏感性来源于聚合物链中有较多的叔胺基团。UV-Vis、NMR 和 FTIR 研究胶束的还原响应性，双亲共聚物经 $Na_2S_2O_4$ 还原后，偶氮侧基断裂，生成取代苯胺，增加分子链的亲水性，诱导胶束解组装过程。

5. 基于 P(POSSMA-co-AZOMA-co-DMAEMA)胶束的多重刺激响应性，选取 Nile Red 作为疏水模型分子，探索胶束包覆和释放疏水分子的性质。结果表明：弱酸性或还原性环境均能诱导胶束快速高效地释放出 Nile Red 分子。

关键词：偶氮苯；POSS；双亲共聚物；聚集诱导荧光发射；多重刺激响应

Abstract

Stimuli-responsive polymeric systems integrating with special responsive moieties can undergo alteration of their chemical structures and physical properties in response to external stimulus. A great deal of work has been done to design multi-stimuli-responsive polymeric systems to enrich applications in the fields of drug controlled release. Azobenzene, as a special light and reduction dual-stimuli-responsive moiety undergo trans–cis isomerization under UV light irradiation and cleavage in reducing environment. Owing to dual-stimuli-responses, incorporation of azobenzene into a polymer chains to generate a multi-stimuli-responsive amphiphiles have been an active research in the field of macromolecular self-assembly. Here, we synthesized an azobenzene monomer with polymerization activity and prepared a series of azobenzene-based amphiphiles via RAFT polymerization. Furthermore, we researched the self-assembly behaviors of these amphiphiles, fluorescence and release properties of self-assembly nanoaggregates. The main achievements of this work are shown as follows:

1. Hydroxyazobenzene HOAZO was synthesized by diazo reaction and coupling reaction. Azobenzene monomer AZOMA was prepared by the reaction between HOAZO and methacryloyl chloride. The structures of HOAZO and HOAZO were characterized by NMR, FTIR and MS.

2. Azobenzene-based copolymers, P(POSSMA-co-AZOMA-co-DMAEMA), were synthesized with comonomers of AZOMA, POSSMA and DMAEMA via RAFT polymerization. In this way, the light and reduction dual-responsive azo group, pH-responsive tertiary amine group and super hydrophobic POSS moiety were incorporated into the polymer chain to generate multi-stimuli-responsive amphiphiles. Furthermore, the structures of these amphiphiles were characterized by NMR, FTIR and GPC.

3. Spherical micelles with core-shell structure were prepared by self-assembly process based on P(POSSMA-co-AZOMA-co-DMAEMA). The UV absorption

property of micellar aggregates was analyzed by UV-Vis spectroscopy and the results showed that the azo groups tend to form J-Aggregation structure. This stacking interaction endows the micelles with Aggregation Induced Emission **(**AIE) property. The Critical Water Content **(**CWC) was measured according to AIE property and the result was validated by Turbidity Test. The Critical Micelle Concentration (CMC) was measured with Nile Red as a fluorescent probe. The effects of initial concentration and molecular weight on micellar morphology and size were investigated by TEM and DLS. The results indicated that the sizes of micelles tend to increase as the concentration or molecular weight increased.

4. The light-responsive property of micelles has been studied by DLS and UV-Vis spectroscopy. The azo groups can undergo fast trans–cis isomerization under UV light irradiation and the diameter of micelles decreased. The pH-responsive property of micelles was researched by DLS and TEM. We found that the diameter of micelles tend to increase as the subtly decrease of pH value in the range of 6.9 to 5.5. The spherical core-shell structure of micelles can be destroyed and formed irregular polymer aggregates. When pH value decreased to 5.5, the micelles disassemble. Owing to the large proportion of tertiary amine groups in amphiphiles, the micelles showed sensitive pH-responsive property. The structures of copolymers upon reduction of $Na_2S_2O_4$ were analyzed by UV-Vis, NMR and FTIR. The azo group cleavaged into substituted anilines, resulting the increase of overall hydrophobicity in copolymer chains, consequently induced micelles disassembly.

5. Based on the multi-stimuli-responses of micelles, we explored the release properties of self-assembly micelles. Nile Red was selected as a hydrophobic molecular model to study the properties of encapsulating and releasing hydrophobic molecules in response to the pH and reductive stimulus. As expected, acid or reducing environment can induce the rapid and efficient release of Red Nile molecules.

Keywords: azobenzene; POSS; amphiphilic copolymer; Aggregation Induced Emission; multi-stimuli-responsive

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