聚苯胺衍生物及无机物/聚苯胺纳米复合材料的制备及性能研究

论文标题:聚苯胺衍生物及无机物/聚苯胺纳米复合材料的制备及性能研究
Studies on Preparation and Properties of Polyaniline Derivatives and Inorganic Matters/Polyaniline Nanocmposites
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Polyaniline; N-β-cyanoethylaniline; N-phenylglycine; 2-aminobenzyl alcohol; attapulgite; nano silica; chemical oxidative polymerization; emulsion polymerization; conductivity
本文回顾了聚苯胺的发展历史，简述了聚苯胺的合成方法及聚合机理。对聚苯胺的结构及掺杂方法、掺杂机制进行了概述。讨论了反应条件对合成聚苯胺的影响。就目前聚苯胺存在的溶解难、加工难的问题简要介绍了几种常用的改性方法及制备聚苯胺／无机物复合材料的概况。从八个方面叙述了聚苯胺的应用进展状况。按照N-取代苯胺、苯环取代苯胺与苯胺进行化学氧化共聚得到聚苯胺类衍生物和制备聚苯胺与纳米无机物的复合材料两个大的方面详细讨论了本人对聚苯胺的改性研究。基于对聚苯胺的认识，就其目前存在的问题及今后的应用提出了一些看法。 本文选用N-取代苯胺、苯环取代苯胺作为反应物可简便地得到所需要的聚合产物。直接由N-取代苯胺均聚或共聚得到的N-取代聚苯胺具有更好的溶解性能，但同时电导率下降的程度也较大。在苯环上引入取代基能有效地降低聚苯胺链的刚性，减小链间作用力，从而提高其溶解性；并能有效阻止在取代位置可能发生的副反应，从而有利于整个分子大共轭体系的形成。本文还对聚苯胺复合纳米无机材料做了探索性研究。采用红外吸收、紫外吸收、X射线衍射、电子自旋振动、扫描电镜、透射电镜、热失重、差热分析手段进行了表征，并系统研究了聚苯胺类衍生物的溶解性及电导率，取得了如下研究成果： (1)首次以N-取代苯胺为单体，即N-β-氰乙基苯胺和N-苯替甘氨酸，分别与苯胺进行化学氧化聚合，得到的聚合物随引入单体的比例不同，电导率及溶解性呈现一定的规律性。其中，共聚物的溶解性比纯的聚苯胺有显著提高：光谱吸收也呈现一定的规律性。为进一步研究在氮的位置上引入吸电子基团的聚苯胺类衍生物的物理性质与化学结构之间的关系提供了依据。该法简便，可望用于导电、防腐、抗静电材料等领域之中。 (2)首次使用苯环取代的2-氨基苄醇与苯胺进行化学氧化聚合，得到聚合物的光谱吸收及电导率、溶解性能都呈规律性变化。设想引入的羟基官能团可作为制备其他聚苯胺类衍生物的活性点。 (3)首次使用凹凸棒石原土及有机改性凹凸棒石分别与苯胺进行原位复合及乳液聚合反应，得到凹凸棒石／聚苯胺纳米复合材料。该种材料随凹凸棒石的引入量不同，电导率、耐热性均呈现规律性变化。这种复合材料有望在压电陶瓷、阻燃、隔气领域中得到应用。 (4)首次使用一种新方法合成了聚苯胺包裹纳米SiO_2复合材料。SiO_2与聚苯胺之间的相互作用与传统的物理吸附作用不同之处在于，本文通过化学键合的方法制备了该种复合材料，使这种复合材料更加稳定，不易分离。并对该材料的导电性进行了测试。该种材料有望在耐热、防腐及半导体材料中得到应用。

In this paper, description relating to the history of development, synthetic methods, and mechanism of polymerization, chemical structure, doped methods and mechanisms of polyaniline were reviewed. The effect of reaction conditions on chemical structure of polyaniline were discussed in detail. One of the key problems related to the application of polyaniline is its poor processability due to the rigid-rod macromolecular chains and strong interchain interactions. Several approaches were mentioned to solve the problem and also the preparations of nanocomposites as polyaniline/inorganic materials were described. The applications of polyaniline in recent years were concluded from eight different aspects. Modification to polyaniline was achieved successfully by copolymerization of N-substituted aniline and aniline, ring-substituted aniline and aniline. As well, preparation of the nanocomposites composed of attapulgite and polyaniline, and nano silica and polyaniline were studied in detail in this paper. The research direction on polyaniline in the near future was also previewed. Homopolymerization of N-substituted anilines or their copolymerization with aniline resulted in improved solubility while decreased conductivity of the polymers obtained. Ring-substituted polyaniline had a lower rigidity compared to polyaniline and the substituents could weaken interchain interactions between polymer chains, resulting in increased solubility. And also ring-substituted aniline could hinder the side reactions happened on the ring during polymerization procedure, which was benefit for formingπ-electron conjugated system. Besides these, the nanocomposites composed of polyaniline and inorganic materials were prepared. The solubility and conductivity of the polymers and nanocomposites were studied systematically. Techniques of FT-IR, UV-Vis, XRD, ESR, TEM, SEM, TGA and DSC were applied in this paper. (1) Monomers as N-β-cyanoethylaniline and N-phenylglycine copolymerized with aniline by chemical oxidative method, respectively. With introducing different molar ratio of aniline to the comonomers, the conductivity, solubility and spectral absorptions properties of the copolymers appeared a few of regularity. The copolymers had better solubility while poorer conductivity than pure polyaniline. It can be provided with some information on studying of the relationship between physical properties and chemical structure by introduction of the electron-withdrawing groups to the nitrogen of aniline. These polymers prepared in this paper were looking forward to be used as semiconductor, anticorrosion and antistatic materials. (2) 2-Aminobenzyl alcohol and aniline as comonomers were polymerized firstly by chemical oxidative method in this paper. The copolymer showed some regularity on conductivity, solubility and spectral absorptions properties. The hydroxyl groups on the polymer chains were looking forward to be used as a new reaction site to prepare other conductive polyaniline derivatives. (3) The nanocomposites based on polyaniline and attapulgite (including organic attapulgite) were obtained by in situ and emulsion polymerization, respectively. With various weight of attapulgite or organic attapulgite added, the conductivity and heat-resistance of the composites showed special regularity. They were looking forward to be applied in the field of ceramic, fire-resistance, low gas permeability and so on. (4) Composite of polyaniline coated nano silica was firstly prepared by chemical method. There existed chemical effect between SiO_2 and polyaniline but not physical absorption, leading to the composite exist more stable in the environment. Also the conductivity of it were studied. The composite was wished to be used as heat-resistance and anticorrosion materials.

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