

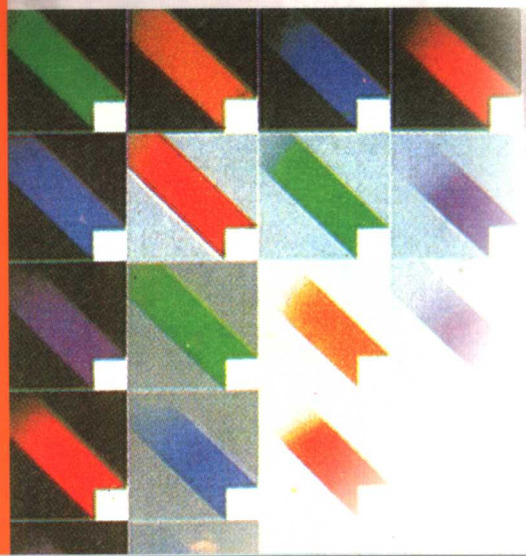
斛兵博士文丛

HUBING BOSHI WENCONG

# 有机聚合物 / $\text{SiO}_2$ 有机无机杂化材料的研究

著 王华林 ● 导师 史铁钧

合肥工业大学出版社



合肥工业大学研究生科技创新基金资助出版

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**图书在版编目(CIP)数据**

有机聚合物/SiO<sub>2</sub>有机无机杂化材料的研究/王华林著. —合肥:合肥工业大学出版社, 2007. 10

(斛兵博士文丛)

ISBN 978-7-81093-683-5

I. 有… II. 王… III. ①有机硅化合物:高聚物②有机材料—杂化研究③无机材料—杂化—研究 IV. 0627.41063 TB32

中国版本图书馆 CIP 数据核字(2007)第 161881 号

**有机聚合物/SiO<sub>2</sub>有机无机杂化材料的研究**

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出 版	合肥工业大学出版社	版 次	2007 年 10 月第 1 版
地 址	合肥市屯溪路 193 号	印 次	2007 年 10 月第 1 次印刷
邮 编	230009	开 本	710×1000 1/16
电 话	总编室:0551-2903038	印 张	9.5
	发行部:0551-2903198	字 数	145 千字
网 址	www.hfutpress.com.cn	印 刷	安徽江淮印务有限责任公司
E-mail	press@hfutpress.com.cn	发 行	全国新华书店

ISBN 978-7-81093-683-5

定价: 25.00 元

如果有影响阅读的印装质量问题,请与出版社发行部联系调换。

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《斛兵博士文丛》的出版,得到了相关兄弟院校和有关专家的大力支持,也得到了研究生导师和研究生的热情支持,我们谨此表示感谢,希望今后能继续得到他们的支持与帮助。

我们力求把这项工作做好,但由于我们经验不足和学识水平有限,书中难免存在不足之处,敬请读者给予批评指正。

合肥工业大学研究生学位论文出版编辑委员会

2007 年 11 月

# 总 序

当今世界科学技术突飞猛进,知识经济飞速发展,以经济和科技为基础的综合国力的竞争日趋激烈。而科技的竞争、经济的竞争乃至综合国力的竞争,归根结底是人才的竞争。面对新的形势、新的要求,党中央先后作出了实施“科教兴国”、“人才强国”战略和走自主创新道路,建设创新型国家的重大决策。胡锦涛同志在党的十七大报告中又提出,建设人力资源强国和创新型国家是我国全面夺取建设小康社会新胜利的两大新目标。高等学校是国家创新体系的重要组成部分,肩负着培养自主创新型人才的历史使命。研究生教育处于高等教育的最高层次,是国家培养高层次创新型人才的主要渠道。研究生,特别是博士研究生的科研工作,一般处于本学科的前沿,具有一定的创造性。为鼓励广大研究生,特别是博士研究生选择具有重大意义的科技前沿课题进行研究,进一步提高研究生的创新意识、创新精神、创新能力,激励、调动我校博士研究生及其指导教师进一步重视提高博士学位论文质量和争创优秀博士学位论文的主动性和积极性,展示我校博士研究生的学术水平,为他们的尽快成才搭建平台,学校经过精心策划,编辑出版了《斛兵博士文丛》。

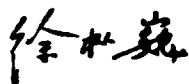
此次入选《斛兵博士文丛》的论著,均为2006年毕业并获得博士学位的博士研究生学位论文,是在广泛动员、严格把关的基础上,根据质量第一、公平公开、规范评审的原则认真遴选出来的。同时这些论著注重坚持基础研究与应用研究并举,是兼顾理论价

值与实践意义的最新研究成果。可以说,这套《斛兵博士文丛》(第一卷)虽然也可能有这样或那样的不足,但基本反映了我校博士研究生所具有的坚实的理论基础、系统的专门知识,以及较高的学术造诣和分析能力;体现了他们崇尚学术、追求真理、勇于创新的科学精神,实事求是、严谨认真的治学态度,不断进取、追求卓越的学术品格;展现了我校“勤奋、严谨、求实、创新”的校风学风。

建校 62 年来,学校充分发挥人才培养、科学研究和服务社会的功能,为国家和社会培养了一大批杰出人才,一代又一代的莘莘学子在这里勤奋耕耘、茁壮成长。出版《斛兵博士文丛》也是我校实施研究生教育创新工程、培养研究生创新精神、提高研究生创新能力的一个重要举措。合肥工业大学经过 62 年的建设和发展,逐步形成自身的办学特色,也取得许多令人瞩目的成就。我们正在不断改善办学条件,逐步完善相关政策,营造有利于高层次创新型人才尽快成长的良好环境,确保学校多出人才、快出人才、出好人才。

我衷心希望广大研究生特别是博士研究生,发扬我校优良的传统、校风、学风,在合肥工业大学自由宽松、开放和谐、充满生机和活力的学术环境中奋发努力、锐意进取、勇于创新,通过自己的辛勤劳动和刻苦钻研写出更好的论文,为进一步提高我校的学术水平、科研创新能力和综合实力作出更大的贡献,努力把学校建设成为国内先进、国际知名的创新型高水平大学。

合肥工业大学校长  
教授、博士生导师



二〇〇七年十一月

## 致 谢

我的博士学位论文的研究工作是在导师史铁钧教授的悉心指导和热情关怀下完成的,尤其在论文的成文阶段,导师对论文进行了逐字修改,倾注了大量的心血。导师严谨求实的治学态度、一丝不苟的敬业精神和丰富的经验、渊博的知识、无私的品格、高尚的修养,豁达开朗的大家风范,使我受益匪浅,并将影响到我以后的学习和工作。多年来,本人在学习、生活、工作等方面都得到了导师无微不至的关怀和帮助,让我能得以在繁忙工作的同时,挤出时间学习和研究,撰写完成论文,感激之情难于言表,在此,谨致以最诚挚的敬意和谢意。

感谢中国科技大学结构中心、安徽大学结构中心、合肥工业大学理化测试中心在测试方面给予的帮助。

感谢杨善中、马海红、于少明、翟林峰、汪瑾、曹金燕、宋秋生、谢红璐师弟、师妹们的支持与帮助。

感谢王继植老师在实验方面给予的帮助。

感谢我的家人,感谢他们长期以来对我的理解、支持和对家庭的无私奉献,使我得以顺利完成本论文。

感谢所有曾经帮助过我的朋友和同事们,并致以诚挚的谢意和祝福。

王华林

2006 年 9 月



# 摘要

有机无机杂化材料是一种分散均匀的多相材料,兼备有机聚合物或无机聚合物的性能优势。它可以是无机改性有机聚合物,也可以是有机改性无机玻璃。可以通过调节有机相与无机相的组分及比例,实现对材料功能的“剪裁”和“组装”。论文以正硅酸乙酯(TEOS)为硅源,制备出系列有机聚合物/SiO<sub>2</sub>有机无机杂化材料,并研究其制备原理、杂化与聚合机理、结构与性能。

1. 基于溶胶凝胶法,以 TEOS 为硅源,利用甲基丙烯酸- $\beta$ -羟丙酯(HPMA)与 TEOS 直接杂化,再引发 HPMA 聚合,制备出以共价键结合的块状聚甲基丙烯酸- $\beta$ -羟丙酯(PHPMA)/SiO<sub>2</sub>均质有机无机杂化材料。这种方法是制备以共价键结合的有机无机杂化材料的一种最简洁的方法,对制备类似的有机无机杂化材料,具有重要参考价值。

HPMA 分子中的—OH 可以与 TEOS 分子中的—OCH<sub>2</sub>CH<sub>3</sub>发生缩合反应,且 HPMA 与 TEOS 的缩合反应是分步进行的。PHPMA/SiO<sub>2</sub>杂化材料中有机组分与无机组分间形成以 Si—O—C 链结合的杂化网络,热稳定性能优良,耐热性能达到 350℃左右,具有广阔的应用前景。

2. 基于两步法,以 TEOS 为硅源,制备硅溶胶,然后与 HPMA 及 MMA 进行杂化反应,制备出活性 PHPMA—MMA/SiO<sub>2</sub>杂化溶胶,再将 PHPMA—MMA/SiO<sub>2</sub>杂化溶胶与尼龙 6(PA6)混合、加工,制备出 PA6/SiO<sub>2</sub>有机无机杂化材料。这种两步法制备 PA6/SiO<sub>2</sub>有机无机杂化材料工艺,未见其他相关报道。研究结果将会为有机无机杂化材料的制备提供一种崭新的方法,为聚合物增强增韧开辟一条新途径。

用于改性 PA6 的是含有 PMMA 的 PHPMA—MMA/SiO<sub>2</sub>杂化溶胶,并不是传统意义上的无机纳米粒子。在杂化溶胶内部,PMMA 是通过共价键

与无机组分 SiO<sub>2</sub> 发生作用,形成有机无机杂化网络。PMMA 与无机组分 SiO<sub>2</sub> 间的共价键作用将 SiO<sub>2</sub> 纳米粒子固定在杂化网络中,限制了 SiO<sub>2</sub> 纳米粒子的团聚,使其在与 PA6 基体复合时保持粒子尺寸稳定;在 PA6/SiO<sub>2</sub> 有机无机杂化材料内部,PA6 与无机 SiO<sub>2</sub> 组分以氢键或间接通过共价键结合。

发现 PHPMA - MMA/SiO<sub>2</sub> 有机无机杂化材料能诱导 PA6 由  $\alpha$  晶型转化为  $\gamma$  晶型,当 SiO<sub>2</sub> 含量达到或超过 3wt% 时,PA6 基本上转化为  $\gamma$  晶型 PA6,这对研究 PA6 的晶型转化具有重要价值。当相对结晶度  $X(t)$  接近或超过 60% 左右时,Jeziorny 法不能有效地描述 PA6 和 PA6/SiO<sub>2</sub> 有机无机杂化材料的非等温结晶过程,但在  $X(t)$  小于 60% 左右时,仍然有效,而 Liu 法却能成功地描述 PA6 和 PA6/SiO<sub>2</sub> 有机无机杂化材料的非等温结晶全过程。

PHPMA - MMA/SiO<sub>2</sub> 有机无机杂化材料对 PA6 具有增强增韧效果, SiO<sub>2</sub> 的含量为 1wt% 时,PA6/SiO<sub>2</sub> 有机无机杂化材料的拉伸强度较 PA6 提高 12.6%,冲击强度较 PA6 提高 2.9 倍,断裂伸长率较 PA6 降低 13.9%。

PHPMA - MMA/SiO<sub>2</sub> 杂化材料与 PA66 基体具有很好的相容性,在 PA66/SiO<sub>2</sub> 有机无机杂化材料内部,PA66 与无机 SiO<sub>2</sub> 组分以氢键或间接通过共价键结合。

Jeziorny 法能有效地描述 PA66 非等温结晶过程,不能有效地描述 PA66/SiO<sub>2</sub> 有机无机杂化材料非等温结晶过程,但  $X(t) < 1 - 1/e$  时仍然有效。Ozawa 法能够成功地描述 PA66 的非等温结晶过程,对 PA66/SiO<sub>2</sub> 有机无机杂化材料无效。Liu 法却能成功地描述 PA66 和 PA66/SiO<sub>2</sub> 有机无机杂化材料的非等温结晶全过程。PHPMA - MMA/SiO<sub>2</sub> 有机无机杂化材料对 PA66 具有异相成核作用,使 PA66 结晶能力增强,加速 PA66 的结晶过程。

PHPMA - MMA/SiO<sub>2</sub> 有机无机杂化材料对 PA66 也具有一定增强增韧效果, SiO<sub>2</sub> 的含量为 1wt% 时,PA66/SiO<sub>2</sub> 有机无机杂化材料的拉伸强度较 PA66 提高 15.6%,冲击强度较 PA66 提高 2.5 倍,断裂伸长率变化相对较小。

3. 以 TEOS 为硅源,乙烯基三乙氧基硅烷(VTEOS)为偶联剂,乙醇和乙酸乙酯为分散介质,采用分散聚合,制备核壳型聚丙烯酸(PAA)/聚苯乙烯(PS)/SiO<sub>2</sub> 有机无机杂化微球。核壳型 PAA/PS/SiO<sub>2</sub> 有机无机杂化微球

以  $\text{SiO}_2$  粒子为核,壳层分别由 PAA 和 PS 组成。在对极性聚合物共混改性时,外壳层极性 PAA 对聚合物基体具有良好的相容性,保证了  $\text{SiO}_2$  纳米粒子在聚合物基体中分散的均匀性。PS 具有优良的加工流变性能,在  $\text{SiO}_2$  核与外壳层 PAA 间起润滑作用,从而使 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球在改性聚合物时具有良好的加工性能。这种多层核壳型 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球的制备,未见其他相关报道,研究结果将为多层核壳型有机无机杂化微球的制备,提供理论依据。

当分散介质  $v(\text{乙酸乙酯})/v(\text{乙醇})=1:1$ ,搅拌速率为 300rpm,大多数 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球的  $\text{SiO}_2$  核的直径为 15nm,PS 层厚 7.5nm, PAA 层厚 5nm,且  $\text{SiO}_2$  核与 PS、PS 和 PAA 间均以共价键键合。这种核壳型 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球耐热性能优良,当温度超过  $420^\circ\text{C}$  时,才发生热氧化分解。

核壳型 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球的制备分为 core stage、shell stage I、shell stage II 三个阶段,相应形成表面带有的乙烯基活性  $\text{SiO}_2$  粒子、带有活性自由基的核壳型 PS/ $\text{SiO}_2$  有机无机杂化微球和核壳型 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球。当 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球增大到一定的程度,从乙醇和乙酸乙酯中析出,发生相分离。在散聚合过程中,由于均聚 PAA 对 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球具有稳定作用,不需要另外再加分散剂。这种无分散剂的分散聚合是对传统分散聚合方法的一种有益的补充,为制备类似的有机无机杂化微球提供一种新方法。

搅拌速率和分散介质的组成对核壳型 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球粒径具有一定的影响,搅拌速率过低,会致使微球粒径偏大,搅拌速率过高时,会导致  $\text{SiO}_2$  粒子偏离 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球的中心。随着  $v(\text{乙酸乙酯})/v(\text{乙醇})$  比值的增大,PAA/PS/ $\text{SiO}_2$  有机无机杂化微球的粒径有减小的趋势,且  $v(\text{乙酸乙酯})/v(\text{乙醇})$  比值介于 1~1.5 时,可以得到单分散的核壳型 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球。

**关键词:**溶胶凝胶技术 PHPMA/ $\text{SiO}_2$  有机无机杂化材料 两步法 PA6/ $\text{SiO}_2$  有机无机杂化材料 PA66/ $\text{SiO}_2$  有机无机杂化材料 分散聚合 核壳型 PAA/PS/ $\text{SiO}_2$  有机无机杂化微球

## ABSTRACT

Organic-inorganic hybrid material is an even multiphase material with the advantageous properties over organic and inorganic polymers. This hybrid material can be ranged from organic polymer modified by inorganic substance to inorganic glass modified by organic substance, and the properties of material are able to be tailored and constructed by adjusting the component and ratio of organic and inorganic phase. In this book, a series of organic polymer/SiO<sub>2</sub> organic-inorganic hybrid materials were prepared with tetraethoxysilane (TEOS) as silica source, moreover, the preparation principle, hybrid and polymerization mechanisms, structures and properties of the organic polymer/ SiO<sub>2</sub> organic-inorganic hybrid materials were investigated.

1. Based on sol-gel method, using TEOS as silica source to hybridize with poly (2-hydroxy propylmethacrylate) (HPMA) before the polymerization of HPMA, the bulk poly (2-hydroxy propylmethacrylate) (PHPMA)/SiO<sub>2</sub> organic-inorganic hybrid material bonded by covalents was prepared in fully transparent homogeneous form. This method is the simplest method to prepare organic-inorganic hybrid material bonded by covalents and will have important references on the preparation of the similar organic-inorganic hybrid materials.

HPMA and TEOS could be hybridized and reacted completely by step polycondensation between the hydroxyl group of HPMA and ethoxyl group of TEOS. The organic-inorganic network in the hybrid material was formed by Si—O—C chains. This PHPMA/SiO<sub>2</sub> organic-inorganic hybrid material

possesses advantage thermal properties and can be used even at about 350°C, implying good application future.

2. Based on two-step method and using TEOS as silica source, the poly 2-hydroxy propylmethacrylate-methyl methacrylate (PHPMA-MMA)/SiO<sub>2</sub> hybrid sol was prepared by the hybrid reaction among the silica sol, HPMA and MMA at first, then the hybrid sol was used to synthesize polyamide 6(PA6)/SiO<sub>2</sub> organic-inorganic hybrid materials via blending method. No other reports were found about this two-step method to prepare PA6/SiO<sub>2</sub> organic-inorganic hybrid material. This research result will provide a new method for preparing organic-inorganic hybrid material and a new way for reinforcing and toughening polymer.

The material used to modify PA6 is PHPMA - MMA/SiO<sub>2</sub> hybrid sol and not traditional nano-inorganic particles. The stable organic-inorganic hybrid network dispersed by nano-SiO<sub>2</sub> particles have been formed in the hybrid sol, and the SiO<sub>2</sub> inorganic dispersion phase and the organic component were bonded by covalents. The covalents among PMMA and SiO<sub>2</sub> inorganic dispersion phase fix the nano-SiO<sub>2</sub> particles in the organic-inorganic hybrid network, so the assembling phenomena of nano-SiO<sub>2</sub> particles can be avoided and this characteristic structure can limit the nano-SiO<sub>2</sub> particle size when blended with PA6 matrix. Moreover, nano-SiO<sub>2</sub> particles and PA6 matrix are bonded by hydrogen bonds directly or covalents indirectly in PA6/SiO<sub>2</sub> organic-inorganic hybrid material.

It was found that PHPMA-MMA/SiO<sub>2</sub> organic-inorganic hybrid material could induce PA6 to transit from  $\alpha$  to  $\gamma$  crystal form, and when the content of SiO<sub>2</sub> was approximately 3 wt% or more, PA6 was changed into  $\gamma$  crystal form almost completely. This finding will be very important in studying the crystal transition of PA6. Based on our experimental data, if the relative degree of crystallinity was approximately 60% or more, the Jeziorny method was not valid to describe the nonisothermal crystallization process, while Liu's method was successful to describe the whole noniso-

thermal crystallization process.

PHPMA - MMA/SiO<sub>2</sub> organic-inorganic hybrid material has both reinforcing and toughening effects on PA6. Compared with PA6, when the content of SiO<sub>2</sub> is 1wt%, the tensile strength and impact strength of PA6/SiO<sub>2</sub> organic-inorganic hybrid material are improved by 12.6% and 290% respectively, while the tensile elongation PA6/SiO<sub>2</sub> organic-inorganic hybrid material is decreased by 13.9%.

3. Based on two-step method and using TEOS as silica source, the PHPMA - MMA/SiO<sub>2</sub> hybrid sol was prepared by the hybrid reaction among the silica sol, HPMA and MMA at first, then the hybrid sol was used to synthesize polyamide 66(PA66)/SiO<sub>2</sub> organic-inorganic hybrid materials via blending method. No reports were found about this two-step method to prepare PA66/SiO<sub>2</sub> organic-inorganic hybrid material also.

There exists good compatibility between PHPMA - MMA/SiO<sub>2</sub> organic-inorganic hybrid material and PA66 matrix. Moreover, nano-SiO<sub>2</sub> particles and PA66 matrix were bonded by hydrogen bonds directly or covalents indirectly in PA66/SiO<sub>2</sub> organic-inorganic hybrid material.

Jeziorny method was suitable to describe the nonisothermal crystallization process of PA66 and not suitable for PA66/SiO<sub>2</sub> organic-inorganic hybrid material, but when  $X(t)$  was less than  $1 - 1/e$ , Jeziorny method was still valid. Ozawa method was suitable to describe the nonisothermal crystallization process of PA6, and not suitable for PA66/SiO<sub>2</sub> organic-inorganic hybrid material. Liu's method was successful to describe the nonisothermal crystallization processes for both PA66 and PA66/SiO<sub>2</sub> hybrid material. It was conformed that the presence of PHPMA - MMA/SiO<sub>2</sub> composite could increase crystallization rate and had hetero phase nucleation effect on PA66 matrix.

PHPMA - MMA/SiO<sub>2</sub> organic-inorganic hybrid material has both reinforcing and toughening effects on PA66 also. Compared with PA66, when the content of SiO<sub>2</sub> is 1wt%, the tensile strength and impact strength of

PA66/SiO<sub>2</sub> organic-inorganic hybrid material are improved by 15.6% and 250% respectively, but the change of the tensile elongation is not obviously.

4. Using TEOS as silica source and vinyltriethoxysilane (VTEOS) as silane agent, core-shell poly (acrylic acid)/polystyrene/SiO<sub>2</sub> (PAA/PS/SiO<sub>2</sub>) organic-inorganic hybrid microspheres were prepared by dispersion polymerization in ethanol and ethyl acetate mixture medium. In the core-shell PAA/PS/SiO<sub>2</sub> hybrid microsphere, the core is silica particles and the shell is composed of PAA and PS. When polarity polymer is modified by these hybrid microspheres, there exists good compatibility between the polarity PAA outermost shell and polymer matrix, which makes it possible for silica particles to disperse evenly in polymer matrix. Moreover, PS layer may work as lubricant owing to its superior processing rheological property between silica core and PAA outermost shell and contributes superior processability in polymer modifying.

These core-shell PAA/PS/SiO<sub>2</sub> hybrid microspheres have potential as new materials for polar polymer modification. No other reports were found about the preparation of these multilayer core-shell PAA/PS/SiO<sub>2</sub> organic-inorganic hybrid microspheres. This research result will provide fundamental theory for preparing multilayer core-shell organic-inorganic hybrid microsphere.

When  $v(\text{ethyl acetate})/v(\text{ethanol}) = 1 : 1$  and stirring rate is 300rpm, most PAA/PS/SiO<sub>2</sub> hybrid microspheres are composed of silica cores about 15nm in diameter, a layer of PS shell about 7.5 nm thick and a layer of PAA outermost shell about 5 nm thick. Moreover, the silica core, PS shell and PAA outermost shell are bonded by covalents. This PAA/PS/SiO<sub>2</sub> hybrid microsphere possesses advantage thermal properties and it begins to decompose when the temperature exceeds 420°C.

The preparation of PAA/PS/SiO<sub>2</sub> organic-inorganic hybrid microsphere includes three stages, that is core stage, shell stage and shell stage, the

functional organic-inorganic silica particles structured vinyl groups on surfaces, PS/SiO<sub>2</sub> organic-inorganic hybrid microspheres with active free radicals and PAA/PS/SiO<sub>2</sub> organic-inorganic hybrid microsphere were formed correspondingly in these three stages. When the PAA/PS/SiO<sub>2</sub> hybrid microsphere increased at a certain size, they were separated out in ethanol and ethyl acetate mixture medium, then the phase separation phenomena was obtained. Because the homogeneous polymer PAA has stable effect on PAA/PS/SiO<sub>2</sub> organic-inorganic hybrid microsphere, no dispersion agent is needed in dispersion polymerization. This dispersion polymerization without dispersion agent is a useful supplement to traditional dispersion polymerization, which will provide a new method for preparing similar organic-inorganic hybrid microsphere.

The stirring rate and the component of dispersion medium have certain effects on the size of PAA/PS/SiO<sub>2</sub> organic-inorganic hybrid microsphere. When the stirring rate is too slow, the hybrid microsphere size is bigger, while the stirring rate is too fast, the SiO<sub>2</sub> core will shift from the centre of the hybrid microsphere. The size of PAA/PS/SiO<sub>2</sub> organic-inorganic hybrid microsphere is decreasing with the increase of volume ratio value of ethyl acetate and ethanol, and when the volume ratio of ethyl acetate and ethanol is between 1 and 1.5, monodisperse PAA/PS/SiO<sub>2</sub> organic-inorganic hybrid microsphere can be obtained.

**KEYWORDS:** Sol-gel method; PHPMA/SiO<sub>2</sub> organic-inorganic hybrid material; Two-step method; PA6/SiO<sub>2</sub> organic-inorganic hybrid material; PA66/SiO<sub>2</sub> organic-inorganic hybrid material; Dispersion polymerization; PAA/PS/SiO<sub>2</sub> organic-inorganic hybrid microsphere



## 目 录

摘 要 .....	(001)
第 1 章 绪论 .....	(001)
1.1 有机无机杂化材料分类 .....	(001)
1.2 有机无机杂化材料的制备 .....	(003)
1.2.1 溶胶-凝胶法 .....	(003)
1.2.2 插层复合法 .....	(005)
1.2.3 物理共混复合法 .....	(007)
1.3 有机无机杂化材料的性能 .....	(009)
1.3.1 力学性能 .....	(009)
1.3.2 热学性能 .....	(010)
1.3.3 光学性能 .....	(010)
1.3.4 电学性能 .....	(011)
1.3.5 阻隔性能 .....	(011)
1.3.6 成膜性能 .....	(012)
1.3.7 成纤性能 .....	(013)
1.3.8 生物性能 .....	(013)
1.4 论文课题来源 .....	(014)
1.5 论文主要内容、方法和意义 .....	(014)
1.5.1 主要内容与方法 .....	(014)
1.5.2 主要意义 .....	(016)
参考文献 .....	(017)