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蒸气诱导相分离法制备聚合物微球
材料研究

Preparation and Characterization of Polymer Microspheres
via Vapor-Induced Phase Separation

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摘要

近年来，嵌段共聚物自组装制备各种类型的聚集体，在纳米反应器、纳米材料、药物缓释和生物组织等方面具有广泛的应用前景。在嵌段共聚物的自组装过程中，总是涉及多种类型的相分离。其中，蒸气诱导相分离(vapor-induced phase separation, VIPS)经常被用来制备多孔薄膜和其它多种聚合物材料。通常，水是作为 VIPS 过程沉淀剂的首选，然而水与许多有机溶剂都不相溶，从而限制了 VIPS 的应用。本论文改用可与有机溶剂互溶的甲醇或乙醇作为沉淀剂来研究嵌段共聚物溶液在沉淀剂蒸气诱导下的相分离行为。在溶剂挥发过程中，甲醇或乙醇气体遇冷被聚合物溶液吸收，改变了溶剂的性质，使溶液发生了相分离；同时结合 Marangoni 对流的剪切作用，初步探讨了聚合物溶液相分离的机制。并在此基础上制备了聚合物微球、二氧化钛空心微球、药物缓释微球以及超疏水薄膜。具体研究结果如下：

蒸气诱导相分离法制备嵌段共聚物微球

将苯乙烯-丁二烯四臂星形嵌段共聚物溶解在甲苯溶液中，配制成 1 wt% 溶液。将聚合物溶液在沉淀剂甲醇蒸气中挥发溶剂，待甲苯和甲醇都挥发完全后即可制备嵌段共聚物微球。采用光学、电子显微镜对微球进行观察，发现微球表面比较光滑致密，球形结构良好，直径分布在几百纳米到几微米之间。采用高温固化的办法，快速固化聚合物溶液，从而对微球的形成过程进行实时观察。实验结果表明，随溶剂的挥发，聚合物溶液表面温度降低，导致沉淀剂甲醇蒸气冷凝并进入聚合物溶液；随甲醇的不断冷凝，溶剂热力学性质变差，逐渐成为不良溶剂，从而产生相分离；在 Marangoni 效应的作用下，产生宏观相分离。随溶剂进一步挥发，相分离后的聚合物溶液粘度急速增大失去流动性，并在固化过程中为降低表面能而成为球形，这即是最终所得的微球材料。

蒸气诱导相分离法制备二氧化钛空心微球及其对甲基橙的降解性能研究

将苯乙烯-丁二烯嵌段共聚物与前驱体钛酸正丁酯共同溶解于甲苯中，并将混合溶液在甲醇蒸气中挥发溶剂。待甲苯和甲醇挥发完后转移至高温水蒸气浴中使钛酸正丁酯充分水解，得到二氧化钛/聚合物复合微球，最后煅烧除去聚合

物即制得二氧化钛空心微球。采用扫描电镜(SEM)对微球进行观察,结果显示,所得复合微球在各处理阶段的形貌发生显著改变。最终产物二氧化钛空心微球表面带有裂纹,壳层粗糙,厚度约为 80 nm,微球表面留有聚合物烧除后形成的多孔结构。采用能谱分析仪(EDS)对微球样品不同区域元素含量进行分析,结果显示,在新制备的钛酸正丁酯/嵌段共聚物复合微球表面、内部及玻璃基片上均存在钛元素,证实了钛酸正丁酯在整个溶液体系中的扩散。这部分结果表明,沉淀剂蒸气冷凝进入聚合物溶液导致体系产生相分离,从而形成了聚合物复合微球。最后,利用二氧化钛空心微球对甲基橙进行紫外光降解实验,以研究二氧化钛微球的光催化活性。结果显示,甲基橙的降解效果良好,降解动力学符合准一级反应动力学模型,表观动力学常数为 0.085 h^{-1} 。

聚(乳酸-乙醇酸)载药微球的制备及其体外释药性能研究

将聚(乳酸-乙醇酸)与布洛芬共同溶解于四氢呋喃中,通过在沉淀剂甲醇蒸气中挥发溶剂,成功制备了负载布洛芬药物的聚(乳酸-乙醇酸)微球。采用电子显微镜观察,发现微球球形结构良好、表面光滑,部分微球发生粘连。经测定,微球的载药率为 6.08%,布洛芬的包封率为 20.9%。以 0.1 mol/L 磷酸缓冲溶液作为释放介质,模拟药物在体外的释放,结果显示,布洛芬在最初 10h 内为突释阶段,累积释药约 75%,10h 后布洛芬释放减慢,3d 累积释放约 80%,使布洛芬完全释放则需更长的时间,体现了微球的良好释药作用。

蒸气诱导相分离法制备高粘性超疏水嵌段共聚物薄膜

将苯乙烯-丁二烯-苯乙烯线形三嵌段共聚物溶解在聚苯乙烯段的选择性溶剂丁酮中,使其自组装成核-壳结构的胶束,这种胶束以收缩的聚丁二烯段为核,伸展的聚苯乙烯段为壳。将胶束溶液在乙醇蒸气中挥发溶剂,制备了高粘性、超疏水聚合物薄膜。采用扫描电镜(SEM)对薄膜表面及断面进行观察,结果显示:薄膜由(亚)微米级纺锤形纤维连接形成三维网络结构,具有大量纳米/亚微米级凸起和孔洞,为聚合物基质和孔洞构成的双连续微观结构。通过接触角测试仪测定薄膜的疏水性,发现水滴的接触角超过 150° ,薄膜具有超疏水性。当薄膜倾斜甚至翻转时,水滴仍然可以牢牢沾在薄膜上,表现出了优异的粘附性。对这种高粘性、超疏水的性能,可通过 Wenzel 和 Cassie 复合模型进行解释。利用薄膜的高粘附力,以薄膜为“机械臂”,成功地从疏水荷叶上提起水滴。通过本方法还可制备大面积的聚合物薄膜。

本论文聚合物复合微球及薄膜的制备与表征研究均属于原创性探索研究。

关键词： 蒸气诱导相分离 聚合物微球 形成机理 新方法

厦门大学博硕士学位论文摘要库

Abstract

Lately, aggregates of block copolymers have attracted extensive attention based on their potential applications as nanoreactors, nanomaterials, drug delivery systems, polymeric tissue scaffolds and so on. Preparation of block copolymer aggregates always involves some types of phase separation technique during the self-assembly process. Among them, the vapor-induced phase separation (VIPS) is widely applied to manufacturing porous membrane and/or other polymer materials. Water is always a preferential nonsolvent in a VIPS process. However, water is immiscible with many organic solvents, which restricts the application of VIPS. In this work, methanol and/or ethanol were used as nonsolvents instead of water. The phase separation behaviors of block copolymer solutions induced by the nonsolvent vapor have been investigated. During this process, the solvent evaporation cooling of block copolymer solution would induce condensation of methanol or ethanol vapor, which would lead to the phase separation of the polymer solution. Simultaneously, the shearing caused by the Marangoni convection has been combined in order to understand the mechanism of phase separation of polymer solution. Then, the separated phases would be sphered due to the interfacial tension during solidification. Based on the VIPS, polymer microspheres, hollow TiO₂ microspheres, controlled-release microspheres and superhydrophobic membranes were prepared, respectively. The specific researches are as follows:

Preparation and characterization of block copolymer microspheres induced by vapor phase separation

Star-shaped poly(styrene-block-butadiene) copolymer was dissolved in toluene, with a typical concentration in solution of 1 wt%. The polymer solution was cast onto glass substrate in a static methanol vapor atmosphere. After the complete evaporation of toluene and methanol, a thin layer of polymer microspheres was obtained. The microspheres were observed by optical and scanning electron microscopes. It shows that microspheres present good spherical structure with smooth and compact surfaces, and range from several hundred nanometers to several micrometers in diameter. A real time observation of the formation of microspheres was carried out. Those results indicated that solvent evaporation cooling would lead to condensation of methanol

vapor, which would result in thermodynamically worse solvent of the polymer solution system gradually. Along with the Marangoni convection, macroscopic phase separation occurred. With the continuous evaporation of solvent and condensation of nonsolvent, the separated phases would form spherical micro-droplets due to interfacial tension, and then solidify to form the final microsphere product.

Preparation and characterization of hollow TiO₂ microspheres using novel polymer microsphere templates and their photocatalytic degradation of methyl orange

In this work, composite microspheres were prepared by casting a toluene solution of tetrabutyl titanate and poly(styrene-block-butadiene) copolymer in a static methanol vapor atmosphere. After evaporation of toluene and methanol, the obtained composite microspheres were subjected to a water vapor phase hydrothermal treatment to completely hydrolyze tetrabutyl titanate. Then, the composite TiO₂/polymer microspheres were calcined in air at 550 °C to remove the polymer; thus, hollow TiO₂ microspheres were fabricated. The SEM images of microspheres indicate that the morphology of microspheres has changed a lot after a series of experimental treatments. The final TiO₂ microspheres are mostly with cracks, and the shell is rough with a thickness of approximate 80 nm. The shell exhibits a porous texture because of the removal of the polymer. The elemental distribution in the as-prepared tetrabutyl titanate/polymer composite materials was examined with the energy dispersive spectrometer (EDS). It has been found that Ti element exists in all regions including microsphere's surface, microsphere's crack and the substrate, which confirms the diffusion of tetrabutyl titanate in the whole solution. The photocatalytic activity of the hollow TiO₂ microspheres was studied by measuring the photo-degradation of methyl orange. The degradation kinetics of the methyl orange aqueous solution exhibited pseudo-first-order behavior and the apparent degradation rate constant was determined to be 0.085h⁻¹.

Preparation and characterization of PLGA microspheres and their sustained release performance *in vitro*

Ibuprofen-loaded poly(lactide-co-glycolide) (PLGA) microspheres were prepared by casting a tetrahydrofuran solution of ibuprofen and PLGA in a methanol vapor atmosphere. The morphology of the microspheres was investigated by scanning electron microscope. The surface is smooth and some microspheres stack together. The drug loading efficiency and encapsulation efficiency were determined to be

6.08% and 20.9%, respectively. PBS buffer solution with a concentration of 0.1 mol/L was used as a releasing media *in vitro*, and UV-visible spectrophotometer was used to measure the ibuprofen during the release process. In the first 10h, an initial burst release was observed, 75% ibuprofen was released. Subsequently, drug release dramatically slowed down. The accumulative release ration was up to 80% after 3 days. The result shows that PLGA is an appropriate controlled-release material.

Preparation and characterization of a block copolymer surface with superhydrophobicity and high adhesive force via vapor-induced phase separation

Poly(styrene-*b*-butadiene-*b*-styrene) was dissolved in selective solvent methyl ethyl ketone. Micelles were formed with the inner polybutadiene blocks while the shell of polystyrene blocks. Phase separation occurred as solidifying the micellar solution in a static ethanol vapor, resulting in a polymer surface with superhydrophobicity and high adhesive force. The SEM images of the resultant membrane exhibit that small spindle-like protrusions in micron size connect together and cover the surface, and such membrane is totally built up by a bi-continuous network with polymer matrix and interlinked grooves. Water contact angle (CA) was measured by using sessile drop method with a water droplet of 5 μL . Water CA of the membrane is higher than 150° , which can be defined as superhydrophobic surface. The water drop could be pinned on the membrane when the substrate was tilted even when it was turned upside down, which showed the high adhesive force of the surface. We attributed the observation to the mixed Wenzel and Cassie model. The as-prepared membrane was used as a “mechanical hand” to carry out water transport. A $10 \times 10 \text{ cm}^2$ membrane was fabricated by the same method to expand the application of the membrane.

In this thesis, the preparation and characterization of the composite microspheres and membranes are original researches.

Keywords: vapor-induced phase separation; polymer microspheres; formation mechanism; novel preparation

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