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乙二醇纯化用自具微孔高分子渗透汽化膜的
制备及性能研究

Preparation and Pervaporation Performance of the PIMs
Membranes for Purification of Ethylene Glycol

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摘 要

乙二醇是一种重要的化工原料,被广泛作为一种难挥发型防冻剂和冷却介质使用,也常用于多聚物的合成过程,在许多领域扮演重要的角色且需求量也在逐年增大。目前,乙二醇的工业生产方式主要有两种:一是乙烯直接氧化为环氧乙烷,然后环氧乙烷水解得到乙二醇;二是通过合成气直接制备乙二醇。这两种方法会分别产生副产物水和甲醇。因此,从乙二醇溶液中分离水或者甲醇得到以获得高纯度乙二醇产品就变得十分必要。渗透汽化膜过程作为一种低能耗、分离效率高、过程简单的新型膜分离技术,为乙二醇纯化提供了新的方法。渗透汽化膜过程中最关键的是高性能膜材料。

本文致力于开发高效乙二醇纯化的膜材料,合成了自具微孔高分子(PIM-1),并用于渗透汽化脱除乙二醇中的水和甲醇。利用核磁共振(HNMR)、X-射线衍射(XRD)、红外光谱(FT-IR)、扫描电镜(SEM)、热重分析(TGA)、水接触角仪等仪器对膜的物化性质和微观结构进行了表征,分析了上述表征结果与分离性能之间的内在关系。其主要研究内容和实验结果如下:

1) 根据双亲核取代反应合成了自具微孔高分子 PIM-1 并对其结构进行了表征,使用相转化法制备了 PIM-1 致密膜并探究了对分离甲醇/乙二醇和水/乙二醇的渗透汽化性能。实验结果表明:合成的 PIM-1 纯度较高,平均分子质量和分散度分别是 64.7 kDa 和 1.87;所制备膜机械性能和热稳定性较好;PIM-1 高分子链间距大、链堆积疏松、具有自具微孔特性;甲醇和水分子的分子动力学直径小于乙二醇,渗透汽化过程中扩散起主要作用;在水/乙二醇的分离过程中,增料液侧水的浓度有利于增大水通量、提高水的选择性,提高料液温度也同样可提高总通量和水的选择性;在甲醇/乙二醇的分离过程中,增加料液侧甲醇的浓度同样有利于提高通量和选择性,料液温度的提高导致通量增大、分离因子降低。

2) 通过腈基的羧基化反应制备了具有不同羧基化程度的羧基化 PIM-1 (CPIM-1)膜,主要考察了羧基化程度以及膜亲水性对渗透汽化分离水/乙二醇的影响规律。随着羧基化反应时间的延长,CPIM-1 的羧基化程度一直增大,当反应时间为 5 h 时,羧基化程度可达 94%;随着 CPIM-1 羧基化程度的增加,膜

的亲水性也有较大的提高，水/乙二醇的通量和分离因子均得到提高；当料液中水浓度从 5%变化至 25%时，总通量和水通量增大而乙二醇通量几乎不变，而水在膜上的吸附慢慢达到饱和状态，导致选择性下降。

本文合成的 PIM-1 纯度高，所制备 PIM-1 致密膜热稳定性和机械性能好，在渗透汽化纯化乙二醇过程中具有较高的渗透通量和适中的选择性，具有较高的科研价值和良好的工业应用前景。

关键词：渗透汽化；自具微孔高分子；膜分离技术；乙二醇纯化

Abstract

Ethylene glycol is an important chemical material, which is widely used as a nonvolatile antifreeze, coolant agent and also as an intermediate for producing different polymers like polyethylene glycol and polyester, and has become more crucial with increasing demand in various fields. Currently, ethylene glycol is mainly produced from two commercial routes: (i) direct oxidation of ethylene to ethylene oxide followed by hydrolysis of ethylene oxide, and (ii) direct synthesis from syngas. Excessive water or methanol will be produced as a by-product in the two routes respectively. Therefore, it is imperative to remove water and methanol from ethylene glycol solutions in order to obtain pure ethylene glycol product. Pervaporation is a novel separation technology that has been widely used in the separation of liquid solutions particularly azeotropes due to its simplicity, energy-saving efficiency and environmental friendliness.

A membrane with high separation performance is the most important in the pervaporation process. In this study, the PIM-1 membranes are prepared and applied to the purification of ethylene glycol. ¹H-NMR, XRD, FTIR, SEM, TGA and water contact angle were employed to characterize the physico-chemical properties and microstructure of the as-prepared membranes. And the relationship between membrane structure and performance was discussed thoroughly. The main results are presented as follows:

1) The polymer PIM-1 was synthesized according to the nuclear substitution reaction and its structure was characterized. The PIM-1 membrane was prepared and used to purification of ethylene glycol *via* pervaporation. The PIM-1 with high purity and molecular weight was obtained, which shows high mechanical property and thermostability. Since the kinetic diameter of water and methanol are smaller than that of ethylene glycol, diffusion process plays the main role in the pervaporation. In the separation of water/ethylene glycol, the water flux and separation factor increase

together with the water content and temperature of the feed. Comparably, the methanol flux and separation factor increase with the methanol content in the feed for separating of methanol/ethylene glycol, however, the former increases while the later decreases with increasing feed temperature.

2) The carboxylated PIM-1 (CPIM-1) with different carboxylation degree was prepared by the conversion of nitrile groups to carboxyl groups. The effect of carboxylation degree and hydrophilicity of the membrane on the pervaporation separation water/ethylene glycol was studied. The carboxylation degree increases with the reaction time and the carboxylation degree reaches to 94% by reacting for 5 h. As the carboxylation degree increases, the membrane hydrophilicity increases, the membrane flux and water selectivity also increases. The total flux and water flux almost remain the same as the water content increases from 5% to 25% in the feed, while the separation factor decreases due to the saturate sorption of water in membrane.

In summary, the PIM-1 membranes were prepared to remove methanol or water from ethylene glycol. The PIM-1 membranes have good thermostability and mechanical properties and show high permeability and moderate selectivity in the purification of ethylene glycol. The PIM-1 membranes should have a potential application in the industrial production of ethylene glycol.

Keywords: Pervaporation; Polymers of intrinsic microporosity; Membrane separation technology; Purification of ethylene glycol.

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