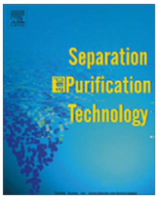
Separation and Purification Technology 93 (2012) 15–24

Contents lists available at SciVerse ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



Polyphosphazene membrane for desulfurization: Selecting poly[bis(trifluoroethoxy) phosphazene] for pervaporative removal of thiophene

Zhengjin Yang, Weiyu Zhang, Jiding Li *, Jinxun Chen

The State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China

ARTICLE INFO

Article history:
Received 9 January 2012
Received in revised form 13 March 2012
Accepted 14 March 2012
Available online 23 March 2012

Keywords:
Desulfurization
Pervaporation
Polyphosphazene
Solubility parameter
Group contribution

ABSTRACT

Concerning the standstill state of pervaporation desulfurization, development of new pervaporation desulfurization membranes is vital. The polymer selection can be based on solubility parameter theory. Using group contribution method, the solubility parameter of poly[bis(trifluoroethoxy) phosphazene] (PTFEP) was calculated. The differences in solubility parameters between thiophene and polymers including PTFEP were calculated and investigated for their potential application as pervaporation desulfurization membranes. PTFEP had the most similar solubility parameter to thiophene among the polymers calculated in this work. The results indicated superior possibility for its application in pervaporation desulfurization. PTFEP was thus synthesized and characterized by DSC, GPC, XPS, ^{1}H-NMR and ^{31}P-NMR. The PTFEP composite membrane was fabricated and utilized in pervaporation removal of thiophene. A pretty high sulfur enrichment factor of 15.69 was obtained which confirmed the results suggested by the solubility parameter theory. Compared with literatures, we positively believe that an increase in solubility parameter differences causes a decrease in sulfur enrichment factor. Meanwhile, the swelling behavior and morphology of the membrane, the effect of feed temperature, and the effect of feed sulfur concentration were also investigated.

1. Introduction

Gasoline plays an important role in modern society, providing raw materials for petrochemical industry and fueling the world. Nevertheless, the combustion of organo-sulfur leads to the emission of SO_x which causes acid rain. As the requirements for friendlier environment increases, stringent regulations are made to limit sulfur content in transportation fuels, especially in gasoline. The United States, Canada and the Europe Union have established regulations requiring sulfur content in transportation fuels to be less than 50 ppm [1]. Recent standard in China requires sulfur content in gasoline to be within 500 ppm. Concerning this urgent demanding, desulfurization of gasoline becomes critical, especially in China.

To date, various methods are attempted for desulfurization of gasoline, such as hydro-desulfurization (HDS) [2], adsorption desulfurization [3], extraction desulfurization [4], oxidative desulfurization and so on. However, the HDS process suffers from high cost and apparent octane number loss; while extraction desulfurization and oxidative desulfurization needs valid absorbents and catalysts and the absorbents regeneration remains tough. As a newly emerged unit operation, pervaporation (PV) is potential in both academic and industrial aspects for its low cost, easy manipulation, low energy consumption, high efficiency and easy scale-up. Currently, PV dominates the field of deep desulfurization for gasoline.

Compared with the application in aqueous solutions, PV membranes are strictly required in stability and great efforts have been made to obtain satisfactory membrane materials with high stability in organic systems. Hydroxyethyl cellulose (HEC), polyimides (PI) [5], hydroxyl-terminated polybutadiene acrylonitrile (HTBN) [6] and polyethersulfone (PES) [7] are investigated in desulfurization of gasoline. To enhance the PV performance in desulfurization of gasoline, chemical modification of available materials is an important aspect. For examples, polydimethylsiloxane (PDMS) and polyethylene glycol (PEG) are well researched polymers for PV desulfurization [8–15] and their capacities for the removal of thiophene were verified by solubility parameter theory [9]. To further improve its pervaporation performance in organic systems,

---

Abbreviations: PTFEP, poly[bis(trifluroethoxy) phosphazene]; PVDF, poly(vinylidene fluoride); PU, polyurethane; PE, polyethylene; PP, polypropylene; CA, cellulose acetate; LDPE, low-density polyethylene; PSf, polysulfone; PAN, poly(acrylonitrile); PS, polystyrene; HDPE, high-density polyethylene; CTA, cellulose triacetate; PVC, polyvinylchloride; HTBN, hydroxyl terminated butadiene acrylonitrile; PI, polyimide; PDMS, poly(dimethylsiloxane); PVP, polyvinyl pyrrolidone; PVAC, polyvinyl acetate; PEA, poly(ethyl acrylate); PES, polyester; PMMA, polymethyl methacrylate; PC, polycarbonate; PEG, poly(ethyl glycol); PEI, polyetherimide; PTFE, poly(tetrafluoroethylene).

* Corresponding author. Tel./fax: +86 10 62782432.
E-mail address: lijiding@mail.tsinghua.edu.cn (J. Li).

1383-5866/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.seppur.2012.03.015

Nomenclature

δ	solubility parameter	U_h	hydrogen bond contribution to cohesion energy
δ_d	dispersion component of solubility parameter	V	molar volume of specific groups
δ_p	polarity component of solubility parameter	J	pervaporation flux
δ_h	hydrogen bond component of solubility parameter	β	sulfur enrichment factor
δ_v	integration of δ_p and δ_d	R	molar gas constant
$\Delta\delta_v$	solubility parameter difference	E_a	activation energy
δ_{vm}	δ_v of membrane	c_p	sulfur contents of the permeate samples
δ_{hm}	δ_h of membrane	c_f	sulfur contents of the feed mixture
δ_{vs}	δ_v of solvents	DS	degree of swelling
δ_{hs}	δ_h of solvents	M_d	mass of the dry membrane
F_d	dispersion contribution to cohesion energy	M_s	mass of the swelled membrane
F_p	polarity contribution to cohesion energy	Mn	numeric molecular weight

the PDMS composite membrane was cross-linked and the interfacial stability and solvent resistance were enhanced by introducing an anchor [16]. PEG was also selected and cross-linked for desulfurization of gasoline [14,17]. Unfortunately, to our best knowledge two major problems have not been well addressed. The high deformational and rotational property of PEG backbone and PDMS backbone limited their full expansion of desulfurization property because of the relatively high degree of swelling. The other is the comparatively inert chemical nature of the backbones in these two polymers which limits their chemical modification and thus confines their desulfurization capacities. Starting polymers with both high flexibility and easy chemical modification will be highly expected in pervaporation desulfurization.

Polyphosphazene (POP) and its derivatives are well investigated since its successful synthesis by Allcock et al. [18,19]. The POP polymer matrix is comprised of alternating phosphorous and nitrogen atoms. It can be easily modified by substituting the pendent chlorine atoms with nucleophiles. Low rotation energy of P–N bond and no conjugate effect endow the polymer chain with high flexibility. The feasibility of organic substitution [20,21] gives these inorganic–organic hybrid polymers amazing capacity for pervaporation [22–24]. Poly[bis(trifluroethoxy) phosphazene] (PTFEP) is one of this polymer family that is synthesized by substituting the chlorine with sodium trifluoroethyloxide. In this work, PTFEP was selected, synthesized and investigated for PV desulfurization according to the results of solubility parameter theory. The synthesized PTFEP was characterized by differential scanning calorimetry (DSC), gel permeation chromatography (GPC), X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance (NMR). PTFEP composite membrane with PVDF as support was prepared and investigated for the removal of thiophene. The swelling behavior and the morphology of the PTFEP membrane, the effect of feed temperature and the effect of feed sulfur concentration were also investigated. Interestingly, we found that an increase in solubility parameter differences caused a decrease in sulfur enrichment factor.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (HCCP) was purchased from Tianhu Chem. Co., Ltd. (Hubei, China). It was recrystallized twice in heptane and sublimed at 50 °C before use. Trifluoroethanol was purchased from Alfa Aesar (Tianjin, China) and stored at 5 °C in refrigerator. Benzene and tetrahydrofuran used for dissolving poly(dichlorophosphazene) (PDCP) and as solvents for chlorine substitution reaction were dried by calcium hydride over 48 h, and then distilled. Heptane, ethyl acetate, acetone and sodium were purchased from FuChen Chemicals (Tianjin, China) and were used as received. PVDF (PVDF-1015, Mw ~ 2.38 × 10^5 g/mol) porous support was prepared in our laboratory using non-solvent induced phase separation (NIPS) method by dissolving PVDF in TEP to form a 15 wt.% dope solution, which was then cast onto the non-woven fabrics and immersed into water to induce polymer precipitation.

2.2. Synthesis of PTFEP

PDCP and PTFEP were synthesized by the ring opening polymerization of the HCCP under vacuum and the following nucleophilic substitution of chlorine with sodium trifluoroethoxide. The typical polymerization procedure was reported in literatures [19,25–27] and modified as follows. The overall schematic representation was shown in Fig. 1.

For synthesis of PDCP, 20 g of HCCP was placed in a glass tube. The tube was evacuated for 30 min at a pressure of less than 133 Pa. Then tube was sealed under vacuum and heated at 260 °C for 25 h. After cooling down to 25 °C, PDCP was obtained by dissolving with benzene and then precipitating with heptane. It should be noted that the PDCP benzene solution would suffer from gel formation for long time storage and PDCP would be cross-linked in air slowly. Additionally, the PDCP would suffer from cross-linking at longer reaction time or higher reaction temperature. However, shorter reaction time or lower reaction temperature will reduce percent conversion of the monomer. We have conducted several groups of polymerization and a balance between percent conversion and cross-linking was obtained in the above mentioned reaction condition.

For the synthesis of PTFEP, the above obtained PDCP was substituted at 60 °C for 24 h with sodium trifluoroethoxide which was prepared by reacting trifluoroethanol with sodium (1:1.2) in THF at 0 °C. Noting that higher reaction temperature or longer reaction time may break the PDCP polymer chain and shorter reaction time or lower reaction temperature cannot lead to the fully substitution of PDCP. PTFEP was obtained by neutralizing with concentrated hydrochloric acid at 25 °C. The crude PTFEP product was filtered off and dissolved in THF which was then evaporated under vacuum. Similar procedure was repeated using ethyl acetate. Finally, purified PTFEP product was obtained by repeated precipitation

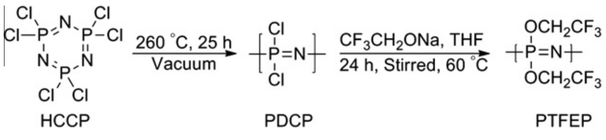


Fig. 1. Schematic representation for the synthesis of PDCP and PTFEP.