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Preparation of poly(phthalazinone ether sulfone ketone) asymmetric ultrafiltration membrane

II. The gelation process

Peiyong Qin[a], Cuixian Chen[a,*], Binbing Han[b], Shintani Takuji[c], Jiding Li[a], Benhui Sun[d]

[a] *Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China*
[b] *Department of Chemical Engineering, Colorado State University, Fort Collins, CO 80523, USA*
[c] *Core Technology Center, Nitto Denko Corporation, Osaka 5678680, Japan*
[d] *Institute of Polymer Material, Beijing University of Chemical Technology, Beijing 100029, PR China*

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Abstract

Formation kinetics of the poly(phthalazinone ether sulfone ketone) (PPESK) asymmetric membrane via wet phase-inversion process has been studied experimentally. The membrane morphology has been observed using an online optical microscope–CCD camera experimental system. The precipitation front movement, X, has been measured. Three different linear correlations between the value of X^2 and the gelation time, t, have been identified. This observation is different from a commonly accepted conclusion which assumed a single linear correlation between X^2 and t for the whole gelation process. Compared to the morphology evolution of the membrane, it is realized that these three correlations correspond to the three consecutive gelation steps: formation of the top layer, formation of the transition layer and formation of the support layer. The effect of two additives, PEG1000 and Tween80, on the formation kinetics as well as the membrane flux has also been studied. The results present here may provide better understanding of the asymmetric membrane formation process.

Keywords: Poly(phthalazinone ether sulfone ketone); Gelation kinetics; Additive; Phase-inversion; Asymmetric membrane

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1. Introduction

Since the initial development by Loeb and Sourirajan [1], asymmetric membranes have been widely used in numerous applications, such as in food and pharmaceutical processing, chemical separation, waste water handling, drug delivery, artificial organs, and so on. Although many polymer materials have been synthesized and used in asymmetric membrane preparation, there still is a large need to develop new polymeric materials with high temperature resistance and chemical stability. As we shown in our previous paper, poly(phthalazinone ether sulfone ketone) (PPESK) is a novel developed copolymer with a very high glass transition temperature being of around 280 °C [2]. Fig. 1 shows the chemical structure of this copolymer. It contains different component ratios of bis(4-fluorodiphenyl)ketone and bis(4-chlorodiphenyl)sulfone with respect to a certain amount of 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one. This polymeric material shows an excellent tolerance to commonly used acids, bases and oxidants. By introducing other groups on to its polymer chain, the hydrophilicity and charging characteristics of this polymer can be altered. Several attempts have been conducted to use this novel polymer in membrane applications, including the gas separation membrane, electron transport membrane, ultrafiltration membrane and nanofiltration membrane [3–9]. However, up to now, details on the membrane formation process with this copolymer have not been reported yet. Better understanding of the membrane formation process can provide insight into the

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[*] Corresponding author. Tel.: +86 10 62782432; fax: +86 10 62770304.
E-mail address: cxchen@mail.tsinghua.edu.cn (C. Chen).

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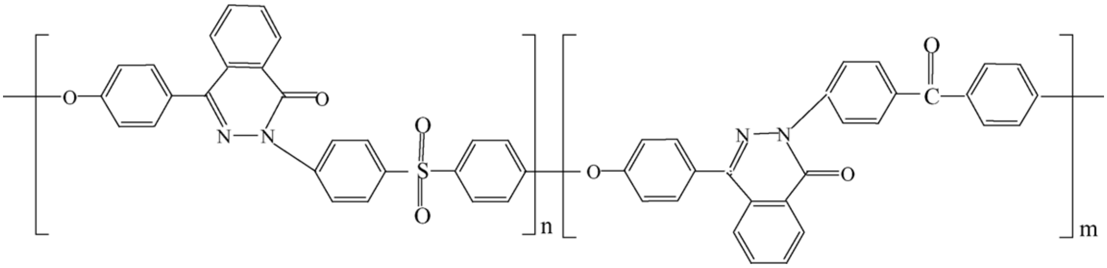

Fig. 1. Chemical structure of PPESK.

relationship between the membrane material, the membrane formation condition, and the membrane performance.

Asymmetric membranes are prepared by phase-inversion, which involves a phase separation of an initially homogeneous polymer solution into two phases, i.e., a polymer poor liquid phase which forms the membrane pores and a polymer rich solid phase which forms the membrane structure.

Numerous research studies have been conducted to rationalize the asymmetric membrane preparation procedure. A ternary phase diagram for a polymer–solvent–nonsolvent (precipitant) system is usually used to describe the precipitation pathway of the casting polymer solution during a membrane formation process [10–14]. Young and Chen [12] proposed a two-step mechanism to describe a diffusion-controlled asymmetric membrane formation process. According to their model, an asymmetric membrane can be divided into two layers, top layer and sub layer. When a casting polymer solution is immersed into a coagulation bath, the top layer is first formed at the polymer–nonsolvent interface. Depending on the interactions between solvent and nonsolvent, solvent and polymer, and nonsolvent and polymer, a dense top layer or a porous top layer may form. Following that, a sub layer forms, which is strongly affected by the formed top layer and all the three interactions mentioned above.

Several research studies measured the rate of precipitation of asymmetric membrane solutions [10,12]. According to Strathmann and Kock [10], a plot of the square value of the movement of the precipitation front, X^2, against the time t, should give a straight line. This prediction has been supported by several other investigations [12,13,15].

Since an asymmetric membrane is not homogeneous in structure, it may not be reasonable to use the same equation to describe the whole membrane formation process. The top layer is the most important part for an asymmetric membrane. Usually the top layer is very thin, only several microns or even >1 μm. Thus, the formation of the top layer is very fast, within several seconds or even >1 s. Therefore, observation of the evolution of a top layer is usually very difficult. For example, the first picture Kang et al. captured during their research studies has been over 20 s [13] while that for Strathmann and Kock was 12 s [10]. However, at these points the membrane formation process may already be in the sub layer formation step.

In this study, an attempt has been made to elucidate the evolution of an asymmetric membrane formation, especially in the very early stage, by using a recently developed optical microscope/CCD camera experimental system. The results presented here may provide better understanding of the formation mechanism of asymmetric membranes.

2. Experimental

2.1. Materials

Poly(phthalazinone ether sulfone ketone) (PPESK) was obtained from Dalian Polymer New Material Co. Ltd., Liaoning Province, PR China. The measured molecular weight of PPESK is 218,900 and the glass transition temperature is 279 °C. *N*-methyl pyrrolidone (NMP) was obtained from Beijing Yili Fine Chemicals Co. Ltd., Beijing, PR China and was used as a solvent. Tween80 (Tianjin Tiantai Fine Chemicals Co. Ltd., Tianjin, PR China) and PEG1000 (Beijing Yili Fine Chemicals Co. Ltd., Beijing, PR China) were used as nonsolvent additives.

2.2. Observation of the gelation process

The gelation process of a casting solution was visually observed using an online optical microscope–CCD camera experimental system (OM–CC system). Fig. 2 shows this system. It contains an Olympus IX71 optical microscope (Olympus, Japan), a Basler A101f CCD camera (Basler AG, Ahrensburg, Germany), a personal computer and two specially designed microscope slides. Twelve frames of images can be captured by using this system per second. This allows people to clearly look at the gelation process, especially in the very early stage. The magnification can be changed from 120× to 2000×. During the test, 10 μL casting solution for membrane formation was placed in a compartment which is formed by the two specially designed microscope accessories mentioned above (see Fig. 2). Then 1 mL DI water was carefully injected into this compartment using a syringe. The casting solution was either a PPESK/NMP or PPESK/additive/NMP solution. The DI water was used as the precipitant. The images were automatically captured by the camera and stored in a computer using a high speed