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A novel of positively charged asymmetry membrane prepared from poly(2,6-dimethyl-1,4-phenylene oxide) by in situ amination Part III. Effect of benzyl and aryl bromination degrees of polymer on membrane performance and morphologies

Beibei Tang, Tongwen Xu *, Peijian Sun, Weihua Yang

Lab of Functional Membranes, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, PR China

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Abstract

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was brominated to different degrees of either benzyl or aryl position with simultaneous benzyl bromination degree around 80%. Membranes were prepared from the brominated PPO (BPPO) by adding the dimethylformamide (DMF) solution of trimethylamine (TMA) into the casting solution with phase inversion method. Membranes were characterized in terms of pure water flux, rejection to the cathodic electrodeposition paint, water content, ion exchange capacity (IEC) and SEM images. The results show that the membrane properties are significantly affected by the bromination processes. Benzyl-substitution enhances the pure water flux but reduces the rejection. The increase in water content of the membrane arises from the polarity of the bromination polymer while not from the charge density as proved by determining the water content of the membranes without adding TMA-DMF solution and the IEC values of the membranes. As for the aryl-substitution, it enhances the pure water permeability but has a negative effect on the rejection. The water content of the membrane increases and then reduces with an increase in the aryl bromination degree. The result is explained from the viewpoint of the polarity of the bromination polymer as well as the hydrophobicity of the bromine group and the charged density by determining IEC values. Furthermore, the SEM images are consistent well with the other measurements.

Keywords: Aryl bromination; Benzyl bromination; Positively charged membrane; PPO

1. Introduction

Membrane science and technology has been developing rapidly since the Loeb–Sourirajan phase inversion method was put forward. And now charged asymmetric membrane has been a research focus in the membrane field due to its high permeability and fine separation property [1]. Especially, positively charged membrane has been a hot topic because it has important applications such as the separation of bio macromolecules below the isoelectric point and recovering cathodic electrodeposition paint, etc. [2]. With the development of the industry, membranes with excellent performance are required. Thus, it is necessary to investigate the influence of the composition of the casting solution and the conditions of formation on membrane performance, which many researchers are devoting attention to. Modification of polymer that aims to produce materials with new and improved properties and investigate the effect of the condition of modification on membrane performance is the trend of this decade [3].

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a commonly utilized material for preparing membrane because it belongs to a class of thermally stable engineering plastics which possesses high transition temperature ($T_g = 212\,^{\circ}C$) and good thermal stability [4]. It has been used to prepare gas separation membranes, ion exchange membranes and pressure driven membranes, etc. by different modifications. For instance, Chowdhury et al. have studied the effects of simultaneous bromination and sulfonation of high molecular weight PPO on gas separation performance of membranes made from the resulting polymers [5]. Xu et al. have prepared a series of anion exchange mem-

* Corresponding author. Tel.: +86 551 360 1587; fax: +86 551 360 1592.
E-mail address: twxu@ustc.edu.cn (T. Xu).

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branes from PPO by conducting the processes of bromination and quaternary amination with different amines solutions [6–8]. Nogami et al. have prepared thin film composite membrane with sulfonated bromination PPO and tested their performance of nanofiltration applications [9]. However, it is rarely reported that the selection of PPO for use as ultrafiltration membrane material to study the influence of bromination degree and substitution position (benzyl or aryl) on membrane performance by phase inversion method.

In a previous project of our group, a novel positively charged ultrafiltration membranes have been obtained with a new route by which the dimethylformamide (DMF) solution of trimethylamine (TMA) is directly measured to the coating solution through the phase inversion technique to find multi-choice for preparing positively charged membranes [10]. And in the following work, the effects of the type of amine being added into the casting solution on the membrane performance and morphology have been investigated [11]. This work is to develop a positively charged membrane for the purpose of treating cathodic electrodeposition paint. In the paper, the effect of the degrees of bromination of PPO, including benzyl and aryl bromination, on membrane performance and morphologies prepared by phase inversion method will thus be investigated and their application in recovering cathodic electrodeposition paint will be concerned.

2. Experimental

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of intrinsic viscosity equal to $0.57 \times 10^{-3}\,m^3\,kg^{-1}$ (i.e. $0.57\,dL\,g^{-1}$) in chloroform at 25 °C was supplied by Institute of Chemical Engineering of Beijing (China); bromine supplied by Shanghai Chemical Reagent Co. was used for the preparation of bromination of PPO. Trimethylamine (TMA) was saturated aqueous solution and TMA-dimethylformamide (DMF) solution was prepared by evaporating TMA from its aqueous solution into DMF solvent as previous paper described [10]. Chlorobenzene and dimethylformamide (DMF) used as solvent, polyethylene glycol 400 (PEG 400) chosen as the additive of the membrane, and ethanol used for the coagulation bath, are all of analytical grade. Cathodic electrodeposition paint (EC3000 100#) kindly supplied by Dupont Company was used for solute rejection test. The composition of the cathodic electrodeposition paint whose dispersed particle size is between 0.001 and 0.1 μm is amino epoxy resin and it carries positive charge.

2.2. Bromination

The bromination of PPO with different substitution positions and degrees was achieved following a general procedure described by our previous papers [6,10,11]. PPO was dissolved in chlorobenzene to form an 8% solution and this solution was subjected to bromination by adding chlorobenzene-diluted bromine. The extent of bromination was controlled by the amount of bromine being added, while the substitution position (benzyl or aryl) was controlled by temperature. The final solution was precipitated with methanol, washed and dried at 80 °C for at least 20 h to get the brominated polymers. These polymers were conducted to ^{1}H NMR (unity plus 400) measurements for the precise determination of bromine contents in aryl and benzyl position, respectively.

2.3. Preparation of membranes

The brominated polymers with different substitution positions and degrees were dissolved in chlorobenzene to form about 23 wt.% solution. Then, identical volume of TMA-DMF solution and PEG 400 were added into the equal mass polymer solution to theoretically achieve identical value of the ion exchange capacity (IEC) for the membranes prepared from different brominated polymers. The casting solution was kept for a period, and then cast onto a clean glass plate. After evaporation about 90 s in atmosphere, the membrane was immersed into an ethanol solution to get membrane. It was then washed with de-ionized water repeatedly and wetly stored. The schematic diagram of the reaction between BPPO and TMA resulting in quaternary ammonium bromide was shown in Fig. 1.

2.4. Determination of coagulation value

Coagulation value can be used as a measure of thermodynamic stability of the casting solution [12]. The higher the coagulation value of the solution is, the higher the thermodynamic stability is. The coagulation value was determined by a titrimetric method. Pure non-solvent (ethanol) was slowly added into a 50 g of casting solution while being stirred intensively when the first appearance of turbidity (the coagulation of the polymeric solution) is visually observed and does not re-dissolve at temperature of 25 °C in 24 h. Then the coagulation value was calculated as the ratio of non-solvent (g) to polymer solution plus non-solvent (g).

2.5. Characterization of membranes

2.5.1. Pure water flux and rejection

Pure water flux and solute rejection test were conducted with a dead-end membrane module, which can offer a membrane area of 12.6 cm^2 and is made of stainless steel that can endure a pressure difference of 1.0 MPa. All the membranes were pretreated with higher pressure drop (0.6 MPa) for the same time (about 10 min) and then the pure water flux and solute rejection were measured at 0.3 MPa operation pressure difference. Water flux was achieved by measuring the volume of permeate that penetrated the unit area membrane per unit time and calculated as $F = V/At$, where V is the total volume of pure permeated during the experiment, A the membrane area, and t denotes the operation time. De-ionized water was used to measure the pure water flux of the membranes. The solute rejection rate was determined with aqueous solution of the cathodic electrodeposition paint. The feed was obtained from the diluted cathodic electrodeposition paint with de-ionized water, whose solid content is about 0.18%. The rejection rate (R) was calculated by $R = 1-(C_p/C_f)$, where C_p and C_f are the concentrations of the permeate and the