Journal of Membrane Science 480 (2015) 47–63

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Prediction of gas permeability coefficients of copolyimides by group contribution methods

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ARTICLE INFO

Article history:
Received 31 July 2014
Received in revised form
23 December 2014
Accepted 9 January 2015
Available online 21 January 2015

Keywords:
Copolyimide
Membrane based gas separation
Group contribution method
Permeability
Structure–property relationship

ABSTRACT

Group contribution methods have been tested for several polyimide structures to calculate their gas permeability coefficients, but predictive studies on copolyimides have not been reported to date. The aim of this work is to design novel copolyimide structures with better separation properties than the upper bound performance of currently available polymers. For this purpose, the group contribution methods of Park and Paul and Alentiev et al. were used to predict the permeability coefficients for 30 different copolyimides that had been prepared and had gas permeability data available in the literature. The results have shown that the method of Alentiev et al. give better predictions for copolyimides. Next, the method of Alentiev et al. was used to predict the permeability coefficients of H_2, O_2, N_2, CO_2, and CH_4 gases at 35 °C for more than 2200 copolyimide structures. The diamine/diamine or dianhydride/dianhydride ratios were also varied as 50/50, 25/75, and 75/25. The ideal selectivity values were calculated for O_2/N_2, CO_2/CH_4, CO_2/N_2 and H_2/CO_2 separation applications and the results were evaluated in terms of the permeability-selectivity plots to propose copolyimide structures with enhanced separation properties. A unique feature of most of the outstanding structures emerged in this study is the sulphone containing diamines such as p-BAPS and pDDS.

1. Introduction

Membrane based gas separation processes are getting attention in separation of many commercially important gas pairs. Aromatic engineering polymers such as polysulfones and polycarbonates are widely used as membrane materials. Another class of aromatic polymers is polyimides. Polyimides are attractive due to their outstanding thermal and chemical stability, and good mechanical properties. They also exhibit attractive separation properties and some of them have found commercial application. However, the gas separation industry is in need of the development of novel membrane materials in order for membrane based gas separation to compete with the traditional separation technologies. Considering the excessive number of possible monomer structures which may be used to build polyimides, a search for new membrane polymers requires a comprehensive analysis which could show what can be and what cannot be achieved from polyimides. This requirement becomes overwhelming when the possibility of building copolyimide structures in addition to homopolyimides is recognized.

Polyimides are synthesized by the reaction of two monomers (dianhydride and diamine) in a solvent and by dehydration of this solution (polyamic acid) by thermal or chemical imidization. If this procedure is carried out with three monomers instead of two then copolyimides are synthesized. There are a large number of studies reported in the literature on the synthesis of polyimides with limited separation performance for commercial applications [1,2]. Copolyimides allow us to optimize the separation properties by using two different polyimides which have different permeability and selectivity properties, such as one having high permeability-low selectivity and the other having low permeability-high selectivity. Apart from tailoring the separation properties of two homopolyimides by combining them with a defined ratio, copolyimides also give an opportunity to synthesize plasticization resistant, robust membrane materials with the judicious selection of the monomers such as using a cross-linkable diamine. While plasticization effect can be minimized by the help of cross-linking, separation properties can be optimized with the use of suitable homopolyimides. Plasticization is a serious concern limiting the use of PIs as membrane material for gas separation involving CO_2, H_2S and condensable hydrocarbons such as propylene and propane.

The thermal, mechanical and separation properties of polyimides strongly depend on their chemical structure, i.e. a slight modification on their chemical structure may often result in a significant change in properties. Thus, development of structure-property relationships for polyimides may provide a guideline for designing polyimides and copolyimides having desirable end-use properties. There are detailed experimental studies in the literature focusing on the effect of

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http://dx.doi.org/10.1016/j.memsci.2015.01.012
0376-7388/

polymer chemical structures on transport properties resulting in a large amount of data on the gas permeation parameters [1,2]. This data can be used to develop relationships which will be then used to predict the permeation parameters of polymers that have not been investigated or prepared yet. This provides an opportunity for the synthesis of novel polymers with desired properties.

There are group contribution methods in the literature, such as the methods of Robeson et al. [3] and Park and Paul [4], developed for predicting the gas permeability coefficients of glassy polymers based on the experimental data for 65 and 105 glassy polymers prepared from 24 and 41 structural subunits, respectively. There is also the group contribution method of Alentiev et al. [5] developed specifically to predict the permeability coefficients of polyimides using a database including about 120 polyimides prepared from 9 dianhydrides and 70 diamines. These methods have been tested for several polyimide structures, but no predictive studies for copolyimides have been reported. Considering the structural complexity of copolyimides, predicting their permeation parameters is a more difficult task. Moreover, there are other factors that influence the permeability values such as polymer synthesis, film formation procedure, solvent type, annealing conditions, etc. which are all reflected to the conformation of the polymer chain. For example, the effect of solvent type on the gas permeability values has been investigated in the last decade [6,7]. In light of foregoing findings, the prediction of structure–property relationship of copolyimides is hard but important for designing new membrane materials.

The objective of this study is to design copolyimides with better separation properties than the upper bound performance of currently available polymers. Thousands of different copolyimide structures can be proposed, however, the experimental analysis of the separation properties of all these structures is a tedious and time-consuming task. The group contribution methods can predict the permeability coefficients and ideal separation factors for the proposed structures. In this study, the group contribution methods of Park and Paul and Alentiev et al. first will be used to predict the permeability coefficients for 30 different copolyimides that have been synthesized in the literature and have gas permeability data available. After it is shown that the group contribution methods can be applied to predict the permeability and selectivity values of copolyimides within reasonable error for the available data, one of these methods will be used to predict the permeability coefficients of H_2, O_2, He, CO_2, N_2, and CH_4 gases at 35 °C for more than 2200 proposed copolyimide structures whose subunit increments are commercially available. The value of 35 °C is chosen due to the fact that the majority of the available data in the literature have been reported at this temperature. The diamine/diamine or dianhydride/dianhydride ratios are also varied as 50/50, 25/75, and 75/25. The ideal selectivity values are calculated for O_2/N_2, CO_2/CH_4, H_2/CO_2, H_2/N_2, and CO_2/N_2 separation applications and the results are evaluated in terms of the permeability-selectivity plots to propose copolyimide structures with separation properties better than the upper bound performance of current polymers. However, it should also be noted that we can only propose copolyimide structures whose monomer data is available in the database.

This study is the first to use group contribution methods as a predictive tool to screen the separation properties of a large number of copolyimide structures and propose possible copolymides which may show near or above the current polymer upper bound performance. Apart from the work of Alentiev et al. [5] which estimates the transport properties of about 500 different homopolyimides, we have not found any other study that uses group contribution methods for screening of homopolyimides.

2. Group contribution methods

Group contribution methods are based on several assumptions. First, polymer structure is assumed to be represented as a sum of several subunits which have a certain increment into the property in question; second, the increments are assumed to be constant for the whole set of complex structures, and third, the properties of complex molecules are assumed to be represented as sums of the corresponding increments after accounting for weight factors [8].

There are many group contribution methods developed to predict numerous properties of polymers such as glass transition temperature, melting point, cohesion energy, heat capacity, etc. [9,10]. Besides the prediction of characteristic properties, group contribution methods also have been used to predict the transport properties of polymers. Salame [11] was the first to use the group contribution method to predict the permeability coefficients of polymers based on cohesive energy density and FFV assigning parameter values based on the polymer repeat units. Later on, Park and Paul applied the group contribution method to predict permeability coefficients of aromatic polymers [4]. The empirical factors for 41 different structural units were determined from a permeability database of 102 polymers. At the same time period, Robeson et al. [12,13] proposed a group contribution method based on solving a least squares fit of a large data base of polymers containing aromatic units in the main chain. They assumed that the permeability of copolymers followed a logarithmic relationship with the permeability of the homopolymers. Different normalization parameters, such as molecular mass, van der Waals volume, molecular volume, etc. were used in these studies. For instance, Robeson et al. [12,13] used volume fraction of comonomers or homopolymer comprising the copolymer in their permeability predictions of aromatic polymers, such as polycarbonates, polyarylates, polysulfones, polyimides, aromatic polyamides, poly(aryl ketones), poly(aryl ethers). Another method was proposed by Yampolskii et al. [14] in which the polymer structure was subdivided into a number of groups (building blocks) and predictions were based on the chemical structure of the repeat units with the groups chosen to be specific atoms and their bond configurations. In a subsequent study, Alentiev et al. applied group contribution method to polyimides considering a polyimide as an alternating copolymer of a dianhydride and a diamine [5] and calculated permeability values for dianhydrides and diamines using a basic set of 120 homopolyimide structures and multiple linear regression method. A different method was developed by Meares [15] which gives the relationship between the activation energy of diffusion and cohesive energy times the square of the gas diameter. Meares [15] used this predicted activation energy to calculate the diffusivity and permeability coefficients of polymers.

In this paper, two of the above mentioned group contribution methods are used for prediction of permeability coefficients and ideal selectivities of copolyimides. Method of Park and Paul [4] is developed for polymers generally and used to predict permeability coefficients of different polymer types, i.e. polycarbonates, polysulfones, polyesters, polyether ketones, polyimides, etc., whereas method of Alentiev et al. [5] is specifically developed for polyimides.

2.1. Method of Park and Paul

This method involves an empirical modification of a free volume scheme that has been used by Bondi [16]. The group contribution correlations were developed using a database of over 105 glassy polymer structures whose specific volume (at 30 °C) and permeability to various gases (at 35 °C) are believed to be known very well. Park and Paul [4] assumed that permeability coefficient (P) depends on the fractional free volume of the polymer and the fractional free volume changes with the gas type [4].

$$P = A_m \exp\left(\frac{-B_m}{\mathrm{FFV}}\right) \tag{1}$$

A_m and B_m are constants for a particular gas in Eq. (1) and fractional free volume, FFV, is defined as

$$(\mathrm{FFV})_m = \left[V - (V_0)_m\right]/V \tag{2}$$