Phase segregation and gas permeation properties of poly(urethane urea) bi-soft segment membranes

Monica Faria [*], Maria Norberta de Pinho

CeFEMA/Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, Lisboa 1049-001, Portugal

A B S T R A C T

Segmented poly (urethane urea) membranes, containing two soft segments, poly(propylene oxide) and poly(caprolactone), were prepared by extending a poly(propylene oxide) based tri-isocyanated prepolymer with poly(caprolactone) diol. The membranes synthesized with poly(caprolactone) diol content ranging from 0 wt.% to 15 wt.% were characterized by infrared spectroscopy (ATR-FTIR). It was concluded that the urethane groups form hard segment aggregates dispersed in the soft segment phase and that this aggregation increases with the increase of poly(caprolactone) content. Gas permeation experiments performed by a photoacoustic system led to the conclusion that permeabilities of CO_2 increased from 188 Barrer to 337 Barrer when the poly(caprolactone) membrane content increased from 0 wt.% to 10 wt.% and was lowest, 113 Barrer, for the membrane containing 15 wt.% of PCL. The permeability of O_2 through the membranes was independent of poly(caprolactone) content and was between 10 and 11 Barrer. The membrane with the highest CO_2 permeability contains 10 wt.% of poly(caprolactone) and is characterized by the highest contribution of hydrogen bonding between urethane and urea hard segments.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Polyurethanes generally exhibit a two-phase structure in which hard segment (HS) enriched domains, composed mainly of the diisocyanate and/or the chain extenders, are dispersed in a matrix of soft segments (SS) composed of a sequence of polyol moieties. The hard-to-soft segment ratio can be changed by controlling the synthesis parameters in order to get tailored polyurethane membranes with improved bulk properties responsible for the final mass transfer properties [1–3] and surface properties that affect bio- and hemocompatibility [4,5] making them good candidates for biomedical applications.

The versatility of the structure design of polyurethane membranes can be further increased by the introduction of a second SS and was first reported in our group by Zhao and de Pinho [6]. In these polymers the phase segregation that occurs between SS's and HS's may be accompanied by different extents of phase separation between the two SS's opening up new possibilities for tuning bulk and surface membrane properties [7,8].

With the aim of developing novel membranes for blood contacting devices, namely membrane blood oxygenators, our group has focused on the synthesis of highly versatile bi-soft segment poly(urethane urea) (PUU) membranes that ultimately fulfil a twofold goal: exhibit enhanced hemocompatibility and have suitable gas permeation rates. Achievements relative to these two points led to the synthesis of three groups of symmetric PUU membranes containing poly(propylene oxide) (PPO) as the first SS and different second SS's: poly(butadienediol) (PBDO) defined as PU/PBDO membranes [6,9–11],

* Corresponding author.
   E-mail address: monicafaria007@gmail.com (M. Faria).

poly(dimethylsiloxane) (PDMS) defined as PU/PDMS membranes [7] and polycaprolactone (PCL) defined as PU/PCL membranes [12,13]. Comparison of the hemocompatibility properties of the three groups of symmetric bi-soft segment PUU revealed that the introduction of PCL as a second SS proved to be a major contribution to the hemocompatibility improvement [12–14]. Our past studies also reveal that the type and content of the second SS strongly influence the structural features of the symmetric bi-soft segment PUU membranes that in turn have a crucial effect on the gas permeation properties. For the PU/PBDO membranes phase segregation studies showed the existence of hydrogen bonded HS's with formation of urethane/urea aggregates. By increasing the PBDO content in the membranes a higher percentage of mixing between the two SS's was verified as well as a decrease of the urethane/urea aggregation [10]. We also found that the CO_2 permeability of the membranes was dependent on the ratio of PU to PBDO. Membranes containing 20 wt.% and 67 wt.% of PBDO had CO_2 permeability of 150 Barrer and 90 Barrer, respectively. In this case larger quantities of the second SS led to higher degrees of mixing between microphases which in turn resulted in lower CO_2 permeabilities [9]. With regard to the PU/PDMS membranes containing 25 wt.% to 75 wt.% of PDMS results showed evidence of phase separation between the two SS's. The structures analysis of the membranes containing lower amounts of PDMS showed that the HS's formed aggregates and that these decreased with the increase of PDMS content. Membranes containing 25 wt.% and 75 wt.% of PDMS had CO_2 permeability of 200 Barrer and 800 Barrer, respectively and O_2 permeability of 30 Barrer and 120 Barrer, respectively. The CO_2 and O_2 permeability of the membranes rose with the increase of PDMS. The high permeability of the 75 wt.% PDMS membrane was attributed to the higher content of siloxane groups, lower degree of cross-linking and lower aggregation of urethane/urea groups [7]. The PU/PCL membranes exhibited very low permeation fluxes both towards O_2 and CO_2 that made it difficult to accurately measure them with the conventional constant pressure apparatus used in the studies of the PU/PBDO and PU/PDMS membranes. Because the introduction of PCL as a second SS had proved to be an essential asset to the enhancement of hemocompatibility (compared to the PU/PBDO and PU/PDMS membranes) it is of great importance to determine the gas permeation properties of these membranes in order to design PU/PCL membranes with structures that will fulfil the twofold goal of combining a blood contacting hemocompatible dense surface and membrane cross-sections that introduce minimal resistance to CO_2 and O_2 flow.

The present work addresses the synthesis of symmetric PUU bi-soft segment membranes containing varying quantities of PCL as second SS's. O_2 and CO_2 gas permeability rates were measured by a highly sensitive photoacoustic gas detection system [15]. The membrane structures in terms of microphase segregation were studied by Attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR) and were correlated to the gas permeation properties.

1.1. Theory

The permeation of a single gas through a dense polymer membrane is classically described by the solution-diffusion model [16]. Under this model it is assumed that:

(a) At the membrane/fluid interfaces, the partition of a solute, *A,* between the fluid mixture and the membrane phase is given by a solubility coefficient, S_A.
(b) The steady-state unidimensional transport of solute *A* across the dense layer of the membrane (y-direction) is expressed by Fick's 1st law of diffusion:

$$J_{Ay} = -D_{Am} \frac{dC_A}{dy} \tag{1}$$

where J_{Ay} is the flux of the solute *A* (cm^3(STP) of A/cm^2/s), D_{Am} is the diffusion coefficient (cm^2/s) and $\frac{dC_A}{dy}$ is the gradient of the volumetric concentration of solute *A* in the membrane phase (cm^3(STP) of A/cm^4). Fick's 1st law of diffusion describes the linear variation of the diffusion fluxes of solute *A* with the concentration gradient of *A* in the membrane phase.

Integrating Eq. (1) over the thickness, *l*, of the dense membrane,

$$J_{Ay} \int_0^l dy = D_{Am} \int_{C_{A0m}}^{C_{Alm}} dC_A = D_{Am}(C_{A0m} - C_{Alm}) \tag{2}$$

where 0 and *l* represent the positions of the feed and permeate interfaces, respectively, and *m* represents the membrane phase. C_{A0m} and C_{Alm} represent the concentration of solute *A* in the membrane at the feed and permeate interfaces, respectively.

For dilute solutions, according to Henry's law of solubility, a solubility coefficient, S_A, which is characteristic of a particular solute, *A*, and a particular membrane, relates the concentration of *A* at each membrane surface, C_{Am}, to the partial pressure of *A*, p_A, in the adjacent gas, $S_{Aom} = S_{Alm} = S_A$, thus

$$S_A = \frac{C_{A0m}}{p_{A0}} = \frac{C_{Alm}}{p_{Al}} \tag{3}$$

Under steady state conditions, and assuming diffusion and solubility coefficients to be independent of concentration, the gas permeation flux can be expressed by combining Eqs. (2) and (3)