Sulfonated polyimides

as diffusion membrane materials and modifiers

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Acknowledgements

Abstract

Polyimides are one of the most promising polymers for the development and manufacturing of diffusion membranes, however, sulfonated polyimides remain under-explored in this role. Despite this, most research efforts are directed towards their application as proton-exchange membranes and meanwhile, their other diffusion transport applications remain poorly studied.

This work aims to investigate correlations between structural-morphological features of hydrolytically stable sulfonated polyimides and their influence on the realisation of their selective-transport properties with a focus on pervaporation and gas separation along with proton exchange applications.

For these purposes, a series of novel hydrolytically stable sulfonated polyimides based on 3,3',4,4'-(1,3-diphenoxy-benzene)tetracarboxylic dianhydride were synthesised and characterised in detail. Conformational aspects of the limitedly-flexible chain were established to play a key role in preventing film fragility. This allowed obtained polymers to form mechanically stable films by tuning their chemical structure to avoid undesirable structurisation. The relation between the chemical composition of the novel copolymers and their tendency to form films with micro-phase separated morphology was described by the application of the Flory-Huggins and Hansen solubility theories. The expansion of the solubility-theory approach on pervaporation and gas separation experiments allowed the development of a unique model for the prediction of real process selectivity values in terms of selective fixed-cite-carrier-facilitated transport observed for the studied systems. Based on discovered correlations, several high-performance pervaporation membranes were developed, including a first-of-its-kind asymmetric gradient-porous membrane with a defectless skin layer formed from a sulfonated polyimide.

The utilisation of the facilitated penetrant transfer effect allowed to create membranes with

high values of both flux and separation factors for the separation of various binary mixtures of methanol, including one reaching a separation factor of 147 with an overall flux of 1.01 $kg \cdot m^{-2} \cdot h^{-1}$ when separating methanol/methyl-tertbutyl ether mixture at 52 $°C$. The hydrolytic stability of obtained polymers allowed their prolonged utilisation as proton-exchange membranes in lab-scale membrane electrode assemblies reaching proton conductivity values as high as $1.2 \cdot 10^{-3}$ $S \cdot cm^{-1}$ at 25 $°C$. Discovered correlations allowed to increase the membranes' swelling, dimension and proton conductivity stability by incorporation of blocks inclined to form highly crystalline regions.

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Table 1. Structures of some monomers used to obtain sulfonated polyimides

1. Introduction

Diffusion membrane processes are increasingly finding their place as a highly efficient complement and analogue to other separation methods, such as distillation, extraction, adsorption, extractive distillation, freezing and others [1]. Low power consumption and ease of scalability of membrane separation processes make them attractive and have already made them a state-of-the-art technology in many industrial applications. The main factor determining the efficiency of such processes is the selective transport properties of the membrane material used [1, 2]. Materials that combine high productivity and high separation selectivity ensuring the efficiency of their application, are of major interest in the considered area. The development of membrane materials that make it possible to achieve high values of productivity and selectivity in relation to the separation of specific liquid and gaseous mixtures seems to be one of the most significant areas of research in the field of membrane technologies.

Polyimides are considered one of the most promising materials in the area of the diffusion membranes development. Strong interactions between macromolecules, caused by the presence of imide groups in the main chain of such polymers, provide high thermal, mechanical and chemical stability. The illustration of a general chemical structure of polyimide is presented in Figure 1. The main disadvantages of polyimides as materials for membrane applications, such as low permeability and low processability, are also associated with their supramolecular organization and the presence of intermolecular interactions [3,4]. As a result, many studies are aimed at increasing the values of free volume and obtaining thin selective layers from such polymers to obtain high-performance membranes with high selectivity characteristic of polyimides [4,5]. One of the most promising approaches to obtain of highly efficient membranes based on polyimides is the implementation of the possibility of selective facilitated transport of target low molecular weight penetrants, which is achieved by introducing carrier groups into polymer chains and organizing them into micro-heterogeneous structures.
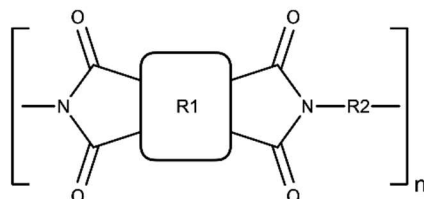
Figure 1. General chemical structure of polyimide.

In this regard, a key area of development is the synthesis of new materials for diffusion polymeric membranes based on polyimides, which combine high separation selectivity and high productivity values for the target component of the mixture. The study of the selective transport properties of microheterogeneous polyimides and composites based on them, which have sulfonic-acid and sulfonate groups in the main polymer chain as carriers of polar penetrants, as well as their relationship with the structural and morphological properties of such systems, make it possible to contribute to the solution of several important practical problems related to the development of highly efficient diffusion membranes.

The overall aim of this thesis was to develop and study new materials based on polyimides containing sulfonic-acid and sulfonate groups in the main chain, methods for their preparation and formation of highly efficient diffusion membranes from them for the separation of liquid and gaseous mixtures of components of different polarity, as well as developing proton exchange membranes.

1.1 The role of structural-morphological features and chemical structure in the realisation of selective-transport properties

1.1.1 Fundamentals of diffusion transport in polymers

The understanding of the mechanisms which regulate the diffusion of molecules through a polymer is one of the main conditions for establishing the relationship between the structural and morphological features of the polymer and its transport properties. Only the understanding of these mechanisms gives us the opportunity to purposefully influence the properties of the structures being developed in order to improve outcomes. Diffusion of small molecules, often called penetrants, through thin polymer films is most often described using the solution-diffusion model [2]. This approach makes it possible to rationalise the complex process of low molecular weight penetrants diffusion through a polymer matrix by conditionally dividing it into three main subprocesses:

1. Sorption of penetrant molecules onto the polymer surface from the side of the feed mixture.
2. Diffusion through the polymer under the action of a chemical potential gradient.
3. Desorption from the polymer surface into the permeate flow.
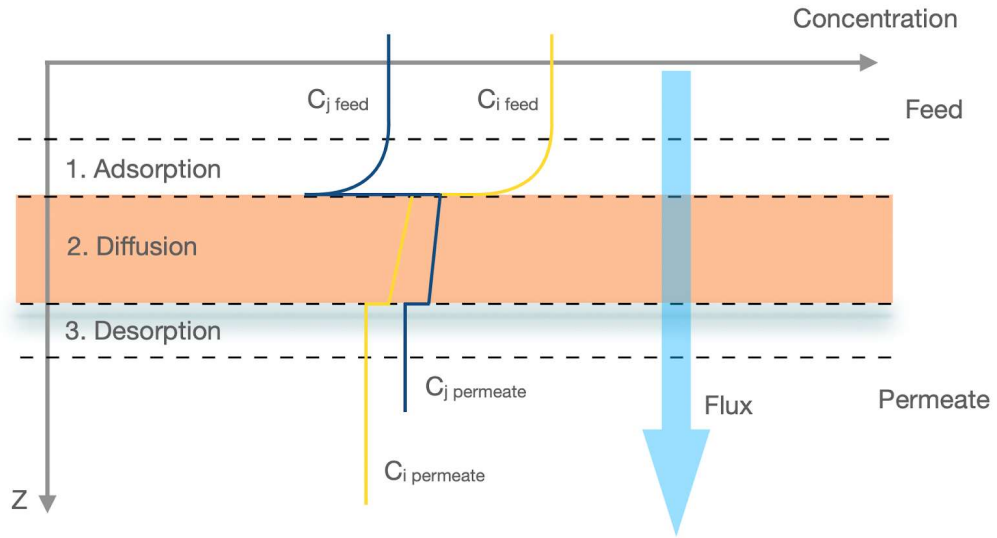
Figure 2. Schematic representation of transport according to the solution-diffusion model (adsorption, diffusion, desorption). The representation of each component concentration along the process z-axis is illustrated to demonstrate the separation mechanism.

The stages of sorption and desorption in the first approximation are in thermodynamic equilibrium with the feed mixture and permeate, respectively [1, 2]. The schematic representation of the solution-diffusion model is provided in Figure 2. When considering diffusion membrane processes from the equipment engineering and process scaling point of view, processes of turbulent and molecular diffusion of penetrant molecules into the near-membrane region that precedes the sorption stage and follows the desorption stage are also considered. The turbulent mass transfer into the laminar near-membrane layer is usually described by the application of criterial approaches and utilization of Reynolds, Sherwood and Schmidt Numbers [6] and is considered when it is vital to assess the influence of the flow regime on the membrane separation efficiency. The specifics of diffusion transport in the laminar boundary layer near the membrane surface usually lead to the local increase in the less-permeable penetrant activity near the membrane. This phenomenon is referred to as concentration polarization [2] and may cause a significant decrease in separation efficiency due to the increase in the less-permeable component transfer, caused by its increased activity near the membrane.

The rate-limiting step of mass transfer through the membrane is the diffusion of the penetrant through the thickness of the polymer [4]. There are many different approaches to the description of mass transfer processes through thin polymer films, however, models based on Fick's first law are the most common due to their simplicity and reasonable predictive ability [1]. Approaches based

on the interpretation of Fick's first law make it possible to represent, as a first-level assumption, the process of diffusion of a low molecular weight penetrant through a polymer matrix as a linear function of the chemical potential gradient of the transported substance. The expressions obtained within the framework of this model (1) can then be adapted to describe various processes of transport through diffusion-type membranes by taking into account the factors that determine the driving force within the particular considered process [1]. In the case of gaseous penetrants transport, the determining contribution to the value of the chemical potential of the penetrant is made by the value of its partial pressure in the mixture, while in the case of pervaporation, the determining factor is the value of the saturated vapor pressure of the penetrant under the process conditions. The specific productivity under the conditions of a stationary process, which is usually referred to as the flux (J, kg·m^{-2}·h^{-1}), taking into account all of the above, can be represented with the following expression:

$$J_i = \frac{P_i}{l}\left(p_{i feed} - p_{i perm}\right) \text{ (1)},$$

Where J_i -molar or mass flux, kg·m^{-2}·h^{-1} or mol·m^{-2}·s^{-1}. P_i - permeability coefficient, kg·μm·m^{-2}·h^{-1}·kPa^{-1} or mol·m·m^{-2}·s^{-1}·Pa^{-1}, which in terms of solution-diffusion is represented as a product of the corresponding diffusion and solubility coefficients; l - thickness, μm; $p_{i\ feed}$ and $p_{i\ perm}$ - partial (gas transport) or saturated vapor (pervaporation) pressure of the component in feed and permeate mixture correspondingly, Pa or kPa.

The ratio of permeability coefficients of a pair of penetrants is the selectivity of the material (S_{ij}) [6], which is used to characterize the ability of a material to the preferential transfer of the penetrant (i) under the conditions of the considered process (2)

$$S_i = \frac{P_i}{P_j} \text{ (2)}.$$

Assuming that the permeability coefficients depend only on the process temperature, one can determine the flux value, using the values of the permeability coefficients determined under the conditions of independent experiments on the transport of individual components. The value of the driving force for each component can be obtained from data on the composition of the initial mixture. For many diffusion processes, this assumption remains true - the values of the permeability coefficients depend only on the process temperature and can be determined experimentally on the transport of individual penetrants. The relationship between the values of the permeability

coefficients and the temperature of the process can usually be represented with sufficient accuracy with an Arrhenius-type relation (3)[1].

$$P_i(T_2) = P_i(T_1) \exp\left(-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right) (3),$$

Where T_i is process temperature in K, E_a is apparent activation energy of permeation, $J \cdot mol^{-1}$, R represents universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$.

The ratio of permeability coefficients determined in experiments on the diffusion of individual penetrants is referred to as ideal selectivity [6]. However, in many diffusion processes, the value of the permeability coefficient strongly depends on the composition of the separated mixture [7]. This is due to swelling and/or plasticization of the polymer in the feed mixture. The predominant affinity of the polymer for a particular component, which favourably affects the selectivity, often leads to excessive swelling of the polymer in the case of relatively high values of the thermodynamic activity of such penetrants. This is accompanied by an increase in the distances between macromolecules, which strongly affects the diffusion coefficients [1] and contributes to an increase in the fluxes of all components of the mixture, while the separation selectivity is significantly reduced. This phenomenon is known as the coupled transfer effect. In the case of gas separation, the additional assumption that the permeability coefficient remains constant at a given temperature remains justified for many systems. In the case of pervaporation separation however, this assumption is almost always invalid [7]. Due to the significant influence of the penetrants' interaction with the membrane material, real selectivity is used to adequately characterize the separation performance of a membrane in such cases. The real selectivity is the ratio of the permeability coefficients of a pair of penetrants, measured by separating their mixture of a given composition with a specific membrane, and can vary significantly over the entire range of compositions. In the case of pervaporation, the selectivity of the process is usually characterized by the separation factor (i/j) [8]:

$$\alpha_{i/j} = \frac{C_{ip}/C_{jp}}{C_{if}/C_{jf}} (4)$$

Where C_{ip} (C_{jp}) and C_{if} (C_{jf}) stand for concentration of the components i and j in permeate and feed mixtures correspondingly.

The requirement for a separation factor is due to the fact that the vapor-liquid equilibrium in most mixtures, the pervaporation separation of which is of interest, usually deviates from Henry's law.

Information about the molar composition of such non-ideal mixtures is not enough to determine the values of the saturation vapor pressure of the components. To determine the driving force of the pervaporation process in such cases, models such as NRTL, UNIQUAC and UNIFAC are successfully used [9].

The effect of polymer swelling on its selective transport properties has been the subject of study for several decades, but there is no complete universal model for predicting the real selectivity and flux values with suitable accuracy when separating a specific non-ideal mixture on a specific membrane. The extension of polymer solubility theories, such as the Flory-Huggins [10] and Flory-Rener [11] theories, to describe diffusion in swollen polymer systems leads to complex expressions and patterns that are difficult to use in applied problems of membrane technology. As a rule, the diffusion coefficient of a certain penetrant can be represented as a function of the penetrant's volume fraction in the polymer [12]. As the volume fraction of a particular penetrant in the polymer matrix increases, the value of the corresponding diffusion coefficient increases due to the increase in interchain distances caused by the presence of the penetrant. This also leads to an increase in the diffusion fluxes of all components - the effect of conjugated transfer or coupled transfer effect. The key to maintaining material selectivity along with high performance is to limit swelling to the extent that the interchain distances are large enough to facilitate the transfer of the selected component, but not sufficient to facilitate diffusion of the other components of the mixture. Numerous approaches have been described in the literature for the limitation of polymer swelling that can provide high diffusion selectivity. Cross-linking (covalent bonding) of matrix chains [1], and the introduction of nanoparticles that promote the supramolecular structure ordering [13] are among the most frequently used strategies. The formation of swellable regions within a swelling-resistant matrix is also one of the promising approaches that can be used to reduce the negative effects of coupled transfer. Such polymeric materials can be obtained using the ability of block copolymers to form micro-heterogeneous structures [14]. The morphology of these materials plays an important role in the implementation of their selective transport properties and their ability to facilitate the transport of a certain type of penetrants [15].

1.1.2 Peculiarities of diffusion transport through poly-electrolytes

Currently, one of the important tasks in the area of pervaporation membranes development is the separation of mixtures of organic components of different polarity [16]. In this direction, interest in the selective removal of polar components from mixtures with high values of their thermodynamic activity, such as azeotropic mixtures of methanol/toluene and ethanol/benzene, is high due to the necessity of separation processes in the pharmaceutical, oil, and chemical industries

[17]. Among all pervaporation membrane materials used for the selective isolation of polar components from nonpolar ones, polyvinyl alcohol [18], various polysaccharides [19], and composites thereof, for example, polyelectrolyte complexes [20], show excellent efficiency. The high hydrophilicity of the surface, which is experimentally characterized by low water contact angle values, high diffusion selectivity and the simplicity of crosslinking methods has made various polysaccharides, sulfoethylcellulose [19], polyvinyl alcohol, *etc.*, among the most commonly used in selective layers of such pervaporation membranes.

The transport of polar penetrants through such types of membranes, containing polar groups, such as hydroxy or sulfonic acid groups, occurs by the fixed site carrier facilitated transport mechanism [21]. However, excessive swelling of these types of membranes often limits their use in the separation of mixtures with a high content of [predominantly] transported penetrant [1].

One of the promising approaches to solving the problem of selectivity loss due to polymer swelling in the separation of the aforementioned systems is to obtain membranes in which separation occurs by mechanisms that ensure efficiency, even under conditions of high values of thermodynamic activity of the predominantly transported penetrant. For example, separation in terms of the selective fixed site carrier facilitated mechanism in the absence of a conjugated transfer effect. The facilitated transport model was first proposed by Mulder and used by Shao and Huang [21] to explain the dehydration of isopropyl alcohol on sulfonated polyether ether ketone membranes in terms of selective immobile-carrier-assisted selective transport. The authors suggest that the transfer of polar molecules occurs due to the filling of vacancies in the clusters of penetrants inside the polymer matrix, which are formed around the sulfonic acid groups. Within the framework of the proposed model, it should be noted that in the case of coupled transfer, not only the solubility of the components in the polymer but also the energy of interaction between penetrants plays an important role in the realisation of transport selectivity. If the A/B binary system is separated, then if A is hydrophilic and preferentially solvates strongly dissociating groups of the membrane and the A-A interaction energy is much higher than A-B, high separation efficiency can be achieved (Figure 3).
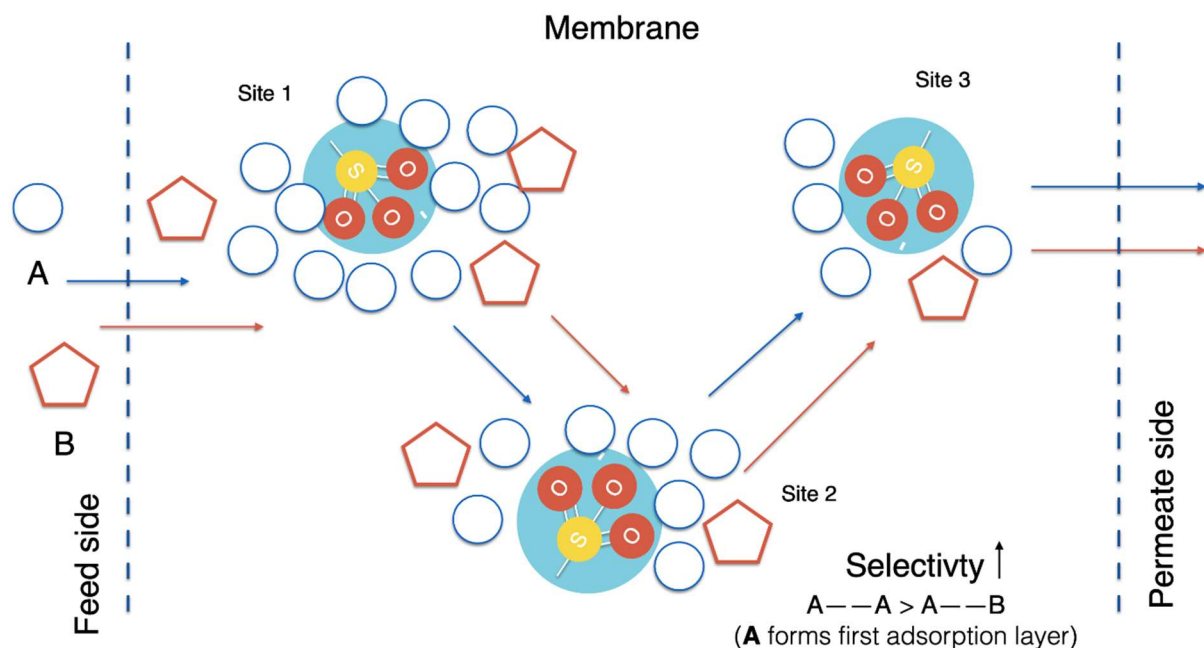
Figure 3. Schematic illustration of the influence of penetrants mutual affinity on transport selectivity in terms of coupled transport.

One of the earliest known examples of fixed-site carrier facilitated transport is the transport of water molecules through hydrophobic or moderately hydrophilic backbone polyelectrolytes containing highly polar dissociating side groups such as Nafion. Transport in such systems occurs through hydrophilic channels through which water clusters are transported, as was shown in a number of works [21, 22, 23]. This type of transport differs from the diffusion of single molecules of penetrants and can be indirectly detected by the nature of the swelling curves and the features of diffusion processes in pervaporation processes. Nafion membranes are widely used as materials for proton-conducting membranes due to their characteristic high values of proton conductivity, which are explained by the possibility of proton transfer by the "cluster" mechanism. The "cluster" transport mechanism is often defined as the possibility of proton transport through hydrophilic channels in intra water clusters [24].

The description of water molecules' transport mechanisms through hydrophilic channels in Nafion-type materials has heightened interest in polymers with highly polar groups in the field of membrane processes. A number of works [19, 23, 25] describe the selective transport properties of Nafion membranes during the dehydration of lower alcohols, and the separation of other liquid mixtures of components of different polarity. Due to low glass transition temperatures, irregular

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structure, and relatively large hydrophilic channels [26], Nafion-based membranes show high fluxes but low separation selectivities.

1.1.3 Microphase separation as a tool for control over selective transport properties

One approach used to make a polymer resistant to excessive swelling and plasticization, while still being able to facilitate the target component's transfer, is to introduce "carrier groups" into the swelling-resistant backbone of the polymer *via* a comonomer unit. Such systems can be formed from block copolymers, which could be designed to form micro-scale heterogeneous structures, where carriers with fixed centres are separated into a separate "phase", providing the presence of so-called "channels" of facilitated transport inside a matrix that is resistant to swelling [15]. The supramolecular chain packaging and the morphology of the block copolymer are among the most important factors that affect the selective transport properties of such systems. Tools for predicting and influencing the nature of the microheterogeneous structure can be used to obtain materials that are both resistant to swelling and capable of facilitating the transfer of polar penetrants.

The morphology of the copolymer, especially in the case of block copolymers, is mainly controlled by the overall degree of polymerization, the length and the mutual affinity of the blocks that make up the polymer [27]. Control over the phase separation and its appearance by changing these parameters allows one to influence the microphase separation and shape of the separated phases in particular for the synthesis of materials with unique properties. The tendency of the system to form distinguishable phases of a particular morphology can be assessed by the application of a number of theoretical approaches. However, to achieve acceptable accuracy, these estimates require a significant amount of experimental data as a basis [14]. When applied to block copolymer morphology, the term "phase" is often defined in the literature as the region of the material inside the polymer matrix, consisting mainly of blocks of a certain structure, having an interface with a distinctive border. At the same time, it should be clarified that due to the discrepancy with some criteria for a phase in the thermodynamic sense (there is no possibility of mechanical separation of the phase in the micro-heterogeneous structure of the block copolymer due to the presence of covalent bonds between the blocks), the term phase, which is used to describe the morphological features of block-copolymer films has a similar but not identical meaning. Nevertheless, such an approach is firmly established in the literature, is appropriate in the framework of existing theories, and also demonstrates predictive power [14, 27].

Hansen and Flory-Huggins solubility theories are the two main approaches most commonly used to describe the behaviour of polymer mixtures and solutions. They have proven to be valuable

tools for the theoretical description of the structural and morphological properties of block copolymers, as well as for the evaluation of their selective transport properties [14]. In terms of the Flory-Huggins lattice model, the Gibbs free energy of mixing components A and B can be represented by the following expression [28]:

$$\Delta G_m = RTV \left[\frac{\phi_A}{V_A N_A} ln\phi_A + \frac{\phi_B}{V_B N_B} ln\phi_B + \frac{\chi_{AB}}{V}(\phi_A \phi_B) \right] (5),$$

$$\chi_{AB} = \chi_H + \chi_S \ (6),$$

Where ϕ_A and ϕ_B volume fractions of components A and B in the mixture, N_A and number of monomers in the corresponding segments, V_A and V_B volumes of A and B segments, V arbitrary unit volume, χ_{AB} -Flory-Huggins interaction parameter, χ_H and χ_S - are enthalpic and entropic contributions respectively.

As was shown by Bates et $al.$ [14], the main indicator of the phase separation of a copolymer is the product of χ_{AB} and the total degree of polymerization (N). In the case of mixing phases of the copolymer: $\chi_{AB} \approx \chi_H$ - since the entropy of mixing per unit volume of dissimilar polymer segments is low. In this case, χ_H can be determined using the following expression [14, 27]:

$$\chi_H = \chi_{AB} = \frac{Z}{kT} [\varepsilon_{AB} - 1/2(\varepsilon_{AA} + \varepsilon_{BB})] \ (7),$$

χ_{AB} -intersegment Flory interaction parameter; Z a number of units in the unit cell, ε_{AB} interaction energy between A and B segments.

Using the relationship between the Hildebrand solubility parameter [29], the values of the molar volume and the interaction energy between two segments of different (AB) or similar (AA, BB) nature, we can obtain an equation for χ_{AB} in terms of the segments solubility parameters and their respective volume fractions [30]:

$$\chi_{AB} = \frac{V_{AB}}{RT} [\delta_A \phi_A - \delta_B \phi_B]^2 \ (8),$$

V_{AB} - arbitrary volume, $cm^3 \cdot mol^{-1}$; ϕ_A and ϕ_B - volume fractions of A and B segments, i-Hildebrand solubility parameter of the corresponding segment, $MPa^{1/2}$.

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The general solubility parameters of the segments ($\dot{i}$) can be obtained using the corresponding Hansen solubility parameters:

$$\delta_i = \left(\delta_{iD}^2 + \delta_{iP}^2 + \delta_{iH}^2\right)^{1/2} \text{ (9),}$$

Where, δ_i - Solubility parameter, MPa$^{1/2}$; indexes D, P and H correspond to dispersion, polar and hydrogen-bond parameters.

Hansen solubility parameters are widely used to describe the solubility and miscibility of various polymer-based systems and can be directly determined with acceptable accuracy using various experimental procedures [29, 31, 32].

Using the three Hansen solubility parameters, each compound can be represented as a point within the so-called Hansen space, where the unit values of the dispersion, polar, and hydrogen bond solubility parameters form a mutually orthogonal basis. The closer the points assigned to the compounds, the higher their affinity and ability to mix. Polymers are usually represented as a sphere (10) having a centre in coordinates identical to the set of polymer solubility parameters and a solubility radius that characterises the ability of the polymer to dissolve [33].

$$4(\delta_i - \delta_D)^2 + \left(\delta_j - \delta_P\right)^2 + (\delta_k - \delta_H)^2 = R_0^2 \text{ (10),}$$

The i, j, k represent indexes of unit vectors and R_0 stands for solubility radius, MPa$^{1/2}$.

If the distance between the solvent and the centre of the sphere is less than or equal to its solubility radius, the polymer dissolves in the given solvent (or demonstrates high swelling degrees). The term relative energy distance (RED = R_a/R_0, where R_a is the distance between the centre of the sphere and a given compound; R_0 is the solubility radius) is commonly used to characterize the affinity of a polymer for a given compound. If RED $\leq$ 1, then the polymer is soluble (or has a high degree of swelling) in the given solvent.

As in the case of the Hildebrand solubility parameter, the values of the Hansen solubility parameters of a mixture (dispersion, polar, and hydrogen bond parameters) can be determined as the sum of the products of the solubility parameter and the volume fraction of the corresponding component within the mixture:

$$\delta_{ij} = \delta_i \phi_i + \delta_j \phi_j \text{ (11),}$$

Where δ_i - parameter of the component (i/j) or the mixture (ij), MPa$^{1/2}$, φ_i - stands for volume fraction of the component i.

1.2 Synthesis of sulfonated polyimides
1.2.1 Specificity of polyimide-sulfonic acids

Polymers which have an imide fragment in the main chain are called polyimides. Strong non-covalent interactions between the imide units of the chain [34] determine the properties of polyimides: high thermal, radiative, and chemical stability, as well as high resistance to mechanical stress [35]. It is the features of the chemical structure of polyimides that determine the high values of the transition of their amorphous phase from the glassy to the visco-elastic state. Additionally, the presence of strong intermolecular interactions can cause the formation of ordered and highly crystalline regions, often having a melting temperature higher than the decomposition temperature of the main chain [34].

Often, polyimides are obtained by polycondensation of the corresponding dianhydrides and diamines [36] and less frequently, dianhydrides and diisocyanates [37]. Polyimide sulfonic acids and sulfonates are a subclass of polyimides characterised by the presence of sulfonic acid or sulfonate groups in the main or side chains.

In the literature, two main methods for the introduction of sulfonic acid groups into polyimides are most frequently encountered: (1) polymer sulfonation method (or post-sulfonation method) and (2) direct copolymerization of sulfonated monomers (monomer sulfonation method). At the same time, it should be noted that the synthesis of various aromatic polyimides from sulfonated monomers (mainly diamines) requires harsh conditions. In some cases, direct sulfonation is used, which has disadvantages such as: (a) lack of control over the degree of sulfonation, (b) inevitable side reactions, including crosslinking, (c) low reproducibility of the polymer microstructure, etc. The most promising is the introduction of sulfonic acid groups into monomers followed by their polymerization/polycondensation. This method avoids the degradation of polymer chains during sulfonation and facilitates the targeted introduction of sulfonic acid groups into certain regions of the polymer backbone. To date, sulfonated polyimides are most often obtained by co-polycondensation of sulfonated diamines, which makes it relatively easy to vary the polymer structure to achieve the desired properties. It should also be taken into account that there are works describing the introduction of sulfonic groups into the polymer structure through dianhydrides [38], but this approach is hindered through difficulties in synthesizing such monomers. Within the framework of the synthetic approach under discussion, it is possible to vary

the number of introduced sulfonic groups, and the number, size, and morphology of those regions. [39]

However, this method of sulfonic acid group introduction into polymer chains has its limitations. First, the number of commercially available sulfonated diamines is relatively small. In addition, most of these compounds have low reactivity due to the presence of sulfonic acid groups (a strong electron acceptor), which reduces the nucleophilicity of the diamine. This can lead to the formation of polymers with low molecular weight and poor film-forming properties, which are not suitable for practical use [40]. Due to the amphoteric nature of diamine sulfonic acids and their limited solubility, the synthesis of sulfonated polyimides is usually carried out in the presence of bases (triethylamine, sodium hydroxide, *etc.*). Alternatively, diamine sulfonic acids are introduced into the reaction mixture already in the form of the corresponding sulphonates. In this regard, most sulfonated polyimides are isolated from the reaction mixture in the form of the corresponding salts, which, if necessary, can be converted into a protonated form by treatment with acidic aqueous solutions [38].

1.2.2 Effect of chemical structure on the properties of films obtained from polyimide-sulfonic acids and their derivatives
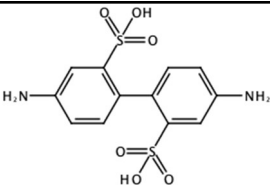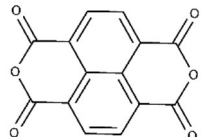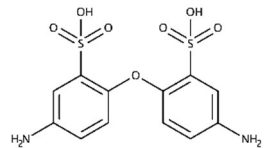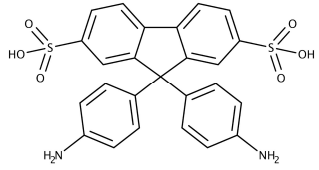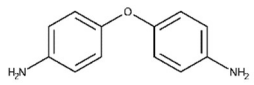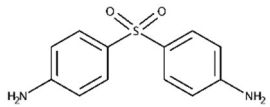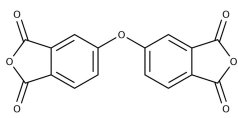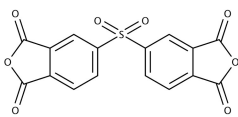
Recently, various sulfonated diamines have been synthesized and used to obtain sulfonated polyimides [41]. One of the most commonly used diamines is the commercially available 4,4-diaminobiphenyl-2,2-disulfonic acid (BDSA) [40]. However, sulfonated polyimides synthesized from BDSA generally exhibit relatively poor hydrolytic stability due to a shift in electron density to the sulfonic groups, which increases the electrophilicity of the carbonyls of the imide rings, making them more susceptible to hydrolysis.

Attempts have been made to improve the properties of BDSA-based sulfonated polyimides by introducing a six-membered naphthalene anhydride ring, which is considered to be more stable than five-membered imide rings. However, sulfonated polyimides based on naphthalene dianhydride (NTDA) have a number of disadvantages, mainly due to the rigid structure of BDSA-NTDA fragments [42].

Okamoto and colleagues described the synthesis of two sulfonated diamines: 4,4- diaminodiphenyl ester-2,2-disulfonic acid (ODADS) (with a flexible structure) and 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid (BAPFDS) (with a rigid and bulk structure) and polyimides based on them [43, 44]. The authors showed that sulfonated polyimides containing ODADS have much better hydrolytic stability compared to those based on BDSA due to the flexibility of the former. This

conclusion is confirmed by the fact that when flexible non-sulfonated diamines were replaced by rigid diamines, a decrease in the stability of polyimide sulfonic acids was observed. However, polymers with rigid BAPFDS fragments have shown the same hydrolytic stability as ODADS-based polyimides. The authors suggested that this stability is due to the high basicity of BAPFDS (which contributes to the stability of the imide ring). A selection of these monomers can be found in Table 1.

Table 1. Structures of some monomers used to obtain sulfonated polyimides

Name	Structure
4,4'-diamino[1,1'-biphenyl]-2,2'-disulfonic acid (BDSA)	
Dianhydride of naphthalene-1,4,5,8- tetracarboxylic acid (NTDA)	
4,4′-diaminodiphenylether-2,2′-disulfonic acid (ODADS)	
9,9′-bis(4-aminophenyl)fluorene-2,2'-disulfonic acid (BAPFDS)	
4,4′-diaminodiphenyl ether (ODA)	
4,4'-diaminodiohenylsulfone (DDS)	
3,3',4,4'-Diphenylether tetracarboxylic acid dianhydride (DPhEA)	
3,3',4,4'-Diphenylsulfone tetracarboxylic acid dianhydride (DPhSA)	

There are numerous examples in the literature of introducing angular or rigid rod-like bulk comonomers into the polymer structure to obtain efficient proton-conducting membranes with high chemical and mechanical stability [41, 43- 46].

The introduction of bulky or angular comonomers into macromolecules prevents the packaging of polymer chains; as a result, these sulfonated polyimides have relatively large free volumes and high interchain distances (as evidenced by the results of physical and structural studies [47, 48]). Large interchain distance values and free volumes (which can be occupied by water molecules and thus provide high degrees of swelling) give these membranes high conductivity under low humidity conditions, and also contribute to the high permeability coefficients of polar low molecular weight penetrants under conditions of diffusion transport.

Litt *et al.* [47, 49], Watanabe *et al.* [48-50], and others [50-53] studied polyimide sulfonic acids with bulky fluorene groups. Multiblock copolymers consisting of hydrophilic and hydrophobic blocks can form well-defined nanoscale water channels necessary for proton conduction, as shown by studies of the mechanisms of water transport through Nafion. The use of block copolymers as membrane materials makes it possible to reduce the dependence of their proton conductivity on humidity and temperature; in addition, it becomes possible to achieve an overall reduction in water absorption and dimensional changes (compared to random copolymers), as well as to reduce the negative impact of the effect of conjugate transfer in application to the development of diffusion membranes.

1.2.3 Structural and morphological features of sulfonated-block-copolyimides and their relation with selective-transport properties

Due to the presence of blocks of different polarity, block-copolyimide sulfonic acids are prone to the formation of microheterogeneous structures in films, provided that the conditions necessary for the implementation of phase separation are met. By varying the length of the blocks, the nature of the monomers forming them, as well as the general value of the degree of polycondensation, it is possible to control the morphology of the resulting systems.

The concept of clear phase separation in block copolymers as applied to sulfonated aromatic polyelectrolytes (such as sulfonated polyimides) has been extensively studied by McGrath and co-workers; they used sulfonated multiblock copolymers synthesized from various sulfonated monomers [42, 54, 55, 56]. Polymers based on sulfonated multiblock copolymers demonstrated a pronounced nano-phase separation (according to atomic force microscopy). The membranes from the studied copolymers had high proton conductivity even under conditions of low humidity (less than 40 %). A multiblock structure was obtained using sulfated poly(4-phenyl-2,5-benzophenone) as the hydrophilic block and poly(arylene ether sulfone) as the hydrophobic block [57]. The authors concluded that well-defined phase separation in multiblock copolymers leads to high proton conductivity. In this case, as the block length increased, the obtained copolymers passed to a

pronounced heterogeneous morphology, which improved their proton conductivity and water absorption [58, 59, 60]. In addition, multi-block copolymers based on sulfonated and non-sulfonated polyoligomers (*e.g.* poly(arylene ether sulfone) oligomers) exhibited anisotropic swelling (*i.e.* less in-plane swelling, but more swelling in the direction perpendicular to the plane of the membrane). This is important for real fuel cells since the proton conductivity of multiblock copolymers depends less on relative humidity and can be higher than that of membranes based on Nafion [61].

The formation of microheterogeneous structures from block copolymers, in particular from sulfonated block-copolyimides, is also of interest in diffusion separation membrane manufacture. This approach is one of the most promising while ensuring the structural integrity and resistance of the polymer to intensive swelling and plasticization. It allows the introduction of "carrier groups" into a swelling-resistant polymer matrix through a comonomer unit. Such systems can be formed by phase-separated block copolymers in which blocks containing immobile carriers will be separated into a distinct phase, providing the formation of so-called "channels" for facilitated transport within a stable matrix, limiting their excessive swelling or plasticization. [1]. Supramolecular chain packing and copolymer morphology are among the important factors influencing facilitated transport phenomena in such systems. In addition to morphology, the nature of the carrier undoubtedly plays a significant role in the selective transport properties of the material. It is known that various types of carriers provide selective facilitated transport of various compounds [62, 63, 64]. One of the possible types of carriers that could facilitate the penetration of polar components from the mixture being separated is the sulfonic acid group [65].

Several polyimide-based gas separation membranes are known [66, 67] in which transport facilitated by an immobile carrier is used to achieve high values of both selectivity and permeability. Among these materials, one of the promising types of polyimides capable of facilitated penetrant transport, in particular, are sulfonated polyimides. However, despite great interest in such systems as potential materials for proton-exchange [38], gas separation [68, 69], and pervaporation [70, 71] membranes, the effect of structural features, the nature of the counterion, and the morphology of such copolymers on their selective transport properties and the capacity for facilitated transport remain poorly understood.

1.3 Polyimide-sulfonic acids, their derivatives and composites as materials for diffusion membranes

1.3.1 Polyimide-sulfonic acids and their derivatives as materials for gas separation membranes

The performance of a polymer as a material for gas separation membranes is usually evaluated based on its position on the permeability vs selectivity plot. Originally suggested by Robeson [72] such plots demonstrate the statistical limit for the performance of the polymeric materials, which is referred to as Robeson's line [73]. Robeson's lines for a number of most commonly separated mixtures such as O_2/N_2, CO_2/CH_4 and others obtained on the basis of data for numerous polymers [74] are usually used for assessment of the obtained material performance in application to particular gas separation tasks.

Today's generation polyimides can be found near the limiting Robeson line for CO_2/CH_4 separation. Of the 16 polymers reported as "close to the existing boundary" in the Robeson analysis, 7 are polyimides [75]. Most of these polyimides are based on 6FDA anhydride and aromatic diamines containing bulky substituents preventing chain packing due to the steric hindrance they cause [5].

One of such bulky substituents is the sulfonic acid group [76]. In contrast to previously studied methyl and perforated substituents, sulfonic groups can form agglomerates within the polymer matrix, which, as discussed above, can act as areas of facilitated transport of polar penetrants, which, along with large free volume values, potentially provide high values of selectivity in the separation of mixtures of components of different polarity. The introduction of sulfonic acid groups into polyimides for subsequent use in gas separation dates back to the late 1990s [69]. Since then, this class of polymers has been shown to have high permeability and selectivity. To date, a number of topical patents are known [69, 77, 78], which describe highly efficient gas separation materials based on polyimides containing sulfonic and/or sulfonate groups, which shows their potential as efficient gas separation membranes. The position of some known sulfonated polyimides on the Robeson diagram for the O_2/N_2 gas pair is shown in Figure 4. However, the influence of the structure and morphology of sulfonated polyimides, as well as the transport features induced by the ability to facilitate the transfer of low molecular weight penetrants, remain under-investigated.
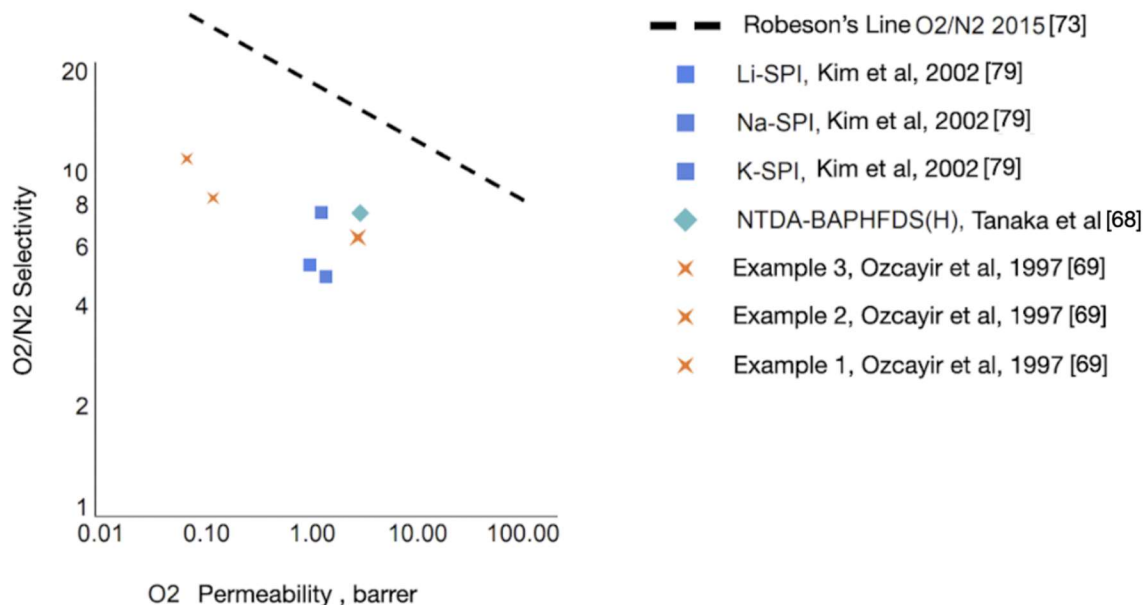
Figure 4. Selective-transport properties of some sulfonated polyimides represented as a Robeson diagram for O_2/N_2 separation.

1.3.2 Polyimide-sulfonic acids, their derivatives and composites as materials for pervaporation membranes

Due to the presence of strong interchain interactions, high glass transition temperatures, and high chemical resistance, along with the presence of strongly polar sulfonic acid groups, sulfonated polyimides are more suitable membrane materials than Nafion for effective pervaporation separation of mixtures of components of different polarity. Despite this, there are few studies on the selective transport properties of sulfonated polyimides under pervaporation conditions. Nevertheless, in the few works found, the excellent properties of some sulfonated polyimides in application to the pervaporation separation of mixtures of components of different polarity is demonstrated [70, 71]. The possibility of polar penetrants facilitated transfer, along with high surface hydrophilicity, high values of free volume due to the presence of bulky substituents in the main chain, and the presence of strong interchain interactions characteristic of polyimides, which help limit swelling, sulfonated polyimides seem to be promising materials for membrane technology.

The transport of water vapor through polyimide-sulfonic acids was studied in detail by F. Pirow and E. Epuchet *et al.* [80]. The authors showed that, as in the case of Nafion, the transport is carried out by the means of a "cluster" mechanism at values of the relative thermodynamic activity of water vapor greater than 0.6. At values below 0.6, the transport mechanism has a character closer to diffusion. Sulfonated polyimides exhibit good solubility in a large number of solvents [81], hydrophilicity provided by the presence of highly dissociative sulfonic acid groups, and high permeability values due to the implementation of transfer facilitated by a fixed carrier. These properties make sulfonated polyimides promising materials for the manufacture of highly efficient membranes for the pervaporation separation of mixtures of components of different polarities.

1.3.3 Polyimide-sulfonic acids as materials for proton exchange membranes

Polyelectrolyte membrane fuel cells (PEMFC) are divided into three types depending on their operating temperatures: above 120°C, from 70°C to 120°C and below 70°C - high-temperature, medium-temperature and low-temperature, respectively [42]. PEMFC systems have many practical advantages, in particular, their use in conjunction with compact cooling systems [81]. It should be noted that the limitations of the electrochemical characteristics of current high-temperature PEMFCs do not allow their use as power sources for vehicles; in addition, they are dangerous due to the possible thermal destruction of the components of the fuel cell and the membrane-electrode assembly. PEMFCs operating in low temperature/high humidity conditions have the necessary electrochemical characteristics; however, they require a highly refined CO_2-free fuel and a comparatively larger amount of water. For these reasons, PEMFCs operating at medium temperatures and low humidity are of great interest to researchers and the fuel cell industry [82].

Understanding the mechanism of proton transfer in polyelectrolyte membranes is one of the necessary conditions for selecting an effective membrane for specific conditions. As described above, one of the possible mechanisms of proton transfer is the cluster mechanism of transport. In this case, protons are transported by water molecules or their associates. The formed hydronium ions H_3O^+ or larger particles (such as $H_5O_2^+$ and $H_9O_4^+$) move inside the water-solvated channels. This transport mechanism is considered to be the dominant mechanism of proton transfer in low- or medium-temperature proton-exchange membranes at a high degree of their hydration. Another mechanism (the so-called Grotthuss mechanism) may also be present at low and moderate temperatures at low levels of hydration. In this case, water molecules or other molecules or their fragments capable of forming hydrogen bonds are considered as a transfer medium - a proton passes from a hydronium ion to a neighbouring molecule to form the next hydronium ion; thus, protons move through a network of hydrogen bonds [83]. This mechanism can also be present in low and

medium-temperature proton exchange rooms at high levels of hydration since water molecules can act as a proton acceptor medium [84]. To increase the efficiency of PEMFC, it is necessary to solve the problem of the decrease in proton conductivity at high temperatures and low humidity under the proton exchange conditions of such membranes, for example, those based on Nafion, used in DuPont low-temperature fuel cells [42, 85].

Sulfonated hydrocarbons (sulfonated polystyrene copolymers, sulfonated poly arylene polymers, *etc.*) are considered to be one of the promising materials for the development of proton-conducting membranes. Because many sulfonated hydrocarbons have high thermal and mechanical stability, they can retain their mechanical properties and high water absorption for long periods and over a wide temperature range. Sulfonated hydrocarbons also have significantly lower gas permeability than Nafion-like membranes [86].

However, membranes based on such polymers exhibit relatively low proton conductivity even at high ion exchange capacities and also tend to swell excessively in the presence of water (poor dimensional stability). In addition, sulfonated hydrocarbons generally exhibit lower chemical and oxidative stability compared to hydrocarbon polymers without sulfonic acid groups [46]. This behaviour is due to the susceptibility of the sulfonated polymer backbones to chemical attack, as well as the low molecular weight due to the low reactivity of the sulfonated monomers.

That is why the greatest attention in the literature is given to the study of sulfonated polyimides as materials for proton-conducting membranes. Currently, due to the need for more thermally and mechanically stable polymeric materials for proton exchange membranes [36], polyheteroarylenes with sulfonic acid groups in the main or side chains have become the object of intensive research. Polyimide-sulfonic acids are widely studied as potential materials for high-performance proton-exchange membranes in high- and medium-temperature hydrogen fuel cells. The characteristic features of polyimides, such as high thermal, chemical and thermal stability, make them the most attractive as promising materials for proton exchange membranes. A significant number of works are known [38, 52, 53, 54, 56, 61] establishing a relationship between the chemical structure and electrochemical properties of sulfonated polyimides. Due to significant advances in this field, it has been possible to obtain many polyimides with high values of proton conductivity; nevertheless, the stability of proton conductivity in a wide range of conditions, the dimensional stability upon swelling, and the hydrolytic stability of such polymers limit their wide application [87]. In this regard, a promising line of research is the preparation of hydrolytically stable polyimides showing stable values of proton conductivity and size in a wide range of temperatures and relative humidity values.

1.4 The Aim of the Study

The study is aimed at the development of synthetic approaches for the obtainment of novel sulfonated polyimides and investigation of correlations between their chemical structure, structural-morphological features and selective transport properties. The practical aspect of the work lies in the utilisation of such correlations for the development of high-performance diffusion membranes for various applications, including pervaporation, gas separation and proton exchange. In order to achieve the stated goal of the research project following objectives were set:

- Develop a method for the synthesis of film-forming hydrolytically and mechanically stable sulfonated polyimides based on 3,3',4,4'-(1,3-diphenoxybenzene)tetracarboxylic acid dianhydride

- Develop a method from the obtainment of asymmetric gradient porous membranes with defect less skin layer from synthesised sulfonated polyimides

- Study the microheterogeneus structure of films formed from obtained sulfonated polyimides and their composites with poly(4,4'-diphenyloxideamidon-N-phenylphtalimide) and describe them with application of Flory-Huggins and Hansen solubility theories

- Investigate selective transport properties of novel polymers and their composites in terms of separation various liquid and gaseous mixtures

- Optimize structural organization and morphology of membranes based on novel sulfonated copolymers synthesised from 4,4'-diamino-bisbiphenyl-2,2'-disulfonic, 4,4'-oxydianiline and 3,3',4,4'-(1,3-diphenoxybenzene)tetracarboxylic acid dianhydride for selective removal of methanol from binary mixtures with its predominant content

- Identify the optimal structure of composites based on novel sulfonated polyimides with poly(amide-imide) for separation of various methanol binary mixtures

- Develop mathematical models for estimation of developed membranes efficiency and prediction of real selectivity values in terms of pervaporation separation of methanol-containing mixtures.

- Study proton-conducting properties of the membranes based on a novel hydrolytically stable sulfonated copolyimide formed from 4,4'-diamino-bisbiphenyl-2,2'-disulfonic, 4,4'-oxydianiline and 3,3',4,4'-(1,3-diphenoxybenzene)tetracarboxylic acid dianhydride

- Study the influence of block-inclined to form areas of high crystallinity introduction into the copolyimide backbone on swelling resistance, dimension and proton conductivity stability

2. Preparation, structure, and pervaporation performance of poly(amide–imide)-sulfonated polyimide composites

2.1 Preface

The first paper of the thesis was published in the Journal of Applied Polymer Science on the 8th of July 2019 (doi: 10.1002/app.48197). The article emphasises the development of the synthetic route for the synthesis of novel hydrolytically stable homo-polyimide (SPI-1) based on 3,3',4,4'-(1,3-diphenoxy-benzene) tetracarboxylic dianhydride (DBTA) and 4,4'-bis-diphenyl-2,2'-disulfonic acid (BDSA); synthesis of poly(amide-imide) (PAI): SPI-1 composites and investigation of correlations between their structural-morphological and transport features. The article was featured on the cover of the issue in which it was published.

Hydrolytic stability is one of the important requirements for the materials of proton-exchange and other diffusion membranes. One of the most promising methods for ensuring hydrolytic stability is the usage of monomers that increase the electron density on the imide carbons of the polymer. These include 3,3',4,4'-(1,3-diphenoxybenzo)tetracarboxylic acid dianhydride (DBTA). Polymers based on DBTA have increased resistance to swelling and good hydrolytic stability [88] due to the presence of donor groups in mutual meta positions in its structure. It is because of these properties that DBTA was chosen as the main anhydride for the production of film-forming, hydrolytically stable sulfo-polyimides in the framework of the project.

Despite high weight-average molecular weight values, SPI-1 was lacking necessary mechanical properties and swelling stability to be used as a material for diffusion membranes unlike many known sulfonated polyimides [68, 69, 71]. In the course of X-ray phase studies, it was shown that along with an amorphous halo on the X-ray pattern of SPI-1, a characteristic reflection at $2\theta = 13°$ is present, which corresponds to an interplanar distance of 6.8 Å. On the basis of the X-ray diffraction data mechanical features of obtained polymer were suggested to be caused by the conformational features of its backbone. The ordering of the limitedly flexible fragments of a chain having an -O-Ph-O- fragment paired with the rigid *bis*-biphenyl fragment was suggested to cause the fragility of the films as well as poor swelling stability. To overcome these drawbacks self-supporting films were obtained from PAI:SPI-1 composites to study the influence of their structural-morphological features on transport properties, which later gave the basis for the synthesis of high-performance membranes for the separation of methanol / methyl-*tert*-butyl (MTBE) mixtures.

Novel polyimide, along with it's composites were characterised by NMR, TGA, DMA, DSC, FTIR spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) analysis. Self-standing films from PAI : SPI-1 composites with 7:3 and 6:4 SPI-1 weight ratios were studied in the process of the selective pervaporation of water/alcohol mixtures. The introduction of the sulfonated polyimide into the PAI matrix led to the formation of a new uniform polymer phase of the complex network structure.

The mixed-phase of PAI : SPI-1 showed increased thermal stability compared to the individual constituents. The fraction of SPI-1 introduced in PAI film was demonstrated to affect the transport properties of the composite. Due to the sulfonic acid groups presence in the SPI-1, an increase in the separation factor value of composites in comparison with the PAI film was expected, in the case of alcohol/water mixtures pervaporation. The methanol flux normalized to the membrane thickness increased with an increase of SPI-1 mass fraction in the composite, despite this, the permeability and separation factor of the material in the case of H_2O/EtOH azeotrope separation behaved in a more complex manner. The highest separation factor (23.2) was observed on the composite with 30 wt. % fraction of PI-S with equal thickness-normalized flux, compared with unmodified PAI film. In the case of the composite with 40 wt. %, the SPI-1 permeability value decreases to 0.425 kg·μm·m^{-2}·h^{-1} and a separation factor value (19.1) was between those for unmodified PAI and the composite containing 30 wt. % PI-S.

Unless the composite was identified as uniform, facilitated-transport channels on the interface of two polymer phases (which allow preliminary water transport) were detected. The concentration range corresponding to the compatibility of PAI and PI-S was defined to be the interval between 30 and 40 wt. % PI-S. The phase heterogeneity in the case of the 7:3 composite was confirmed by XRD, DSC, DMA, and SEM analysis. Both composites showed increased methanol permeability, and the thickness-normalized flux increased with increasing the PI-S mass fraction in the composite.

2.2 Author contribution

The applicant developed the synthetic procedure and obtained novel sulfonated polyimides, conducted pervaporation experiments, conceptualised the pervaporation section and participated in the analysis and interpretation of the data obtained in DSC, FTIR, NMR, TGA and XRD experiments. The applicant suggested that fragility of the SPI-1 films was caused by the conformational features of the -O-Ph-O- fragment paired with the rigid bis-biphenyl fragment.

Based on that hypothesis it was proposed to hinder the formation of ordered regions by incorporation of a flexible co-monomer into the sulfonated polyimide backbone.

2.3 Article

Kononova, S.V., Sapegin, D.A., Kruchinina, E.V., Gubanova, G.N., Romashkova, K.A., Didenko, A.L., Smirnova, V.E., Popova, E.N., Saprykina, N.N., Vlasova, E.N. & Svetlichnyi, V.M. (2019) Preparation, structure, and pervaporation performance of poly(amide–imide)-sulfonated polyimide composites. Journal of Applied Polymer Science.136 (45) p.48197.

https://doi.org/10.1002/app.48197

https://onlinelibrary.wiley.com/doi/abs/10.1002/app.48197

The article was featured on the cover of the Journal Issue:

https://onlinelibrary.wiley.com/toc/10974628/2019/136/45

3. Selective facilitated fixed-site carrier transport of methanol through sulfonated co-polyimide pervaporation membranes for the separation of methanol/toluene mixtures

3.1 Preface

The results of the first research iteration has led to the suggestion of conformation role in the realisation of the SPI-1 film mechanical characteristics. To hinder the ordering of the chains it was suggested to introduce 4,4'-oxydianiline (ODA) as a flexible co-diamine. As a result, properties of a series of copolyimides based on DBTA, BDSA and 4,4'-oxydianiline (ODA) obtained by a two-stage polycondensation process developed at the previous stage of the project were investigated. The article which describes the synthesis of copolymers, their thermal, structural and transport properties was published on 1st of April 2020 in the Separation and Purification Technology (doi:10.1016/j.seppur.2019.116274). The most prospective copolymer characterized with equimolar ratio of co-diamines (BDSA : ODA = 1:1 - SPI-2) was used to obtain a high performance asymmetric pervaporation membrane with defect-free selective layer, which was applied to the separation of methanol/toluene mixtures. As one of the practical results of the research project stage - the patent was obtained on the asymmetric membrane and its synthetic process [89].

Obtained polymers were characterized in terms of water / ethanol mixtures swelling and pervaporation for preliminary characterization of their selective-transport properties and potential as membrane materials. All obtained copolymers BDSA:ODA 6:4, 7:3 and 1:1 were capable of self-supporting film formation, which favoured the conformational features in the homopolyimide film fragility hypothesis. Preliminary characterization showed that among all obtained copolymers, the one comprised of equimolar parts of co-diamines was the most stable upon swelling, and was able to be protonated.

SPI-2 and its protonated form was characterised by the use of NMR spectroscopy, DSC, FTIR spectroscopy and TGA. The TGA curves of the obtained SPI-2 films illustrate the features characteristic of block copolymers. The uniqueness of glass transition temperature values on DSC curves for both protonated and unprotonated samples indicated the relatively short length of both blocks which co-operate during glass transition. Protonation of SPI-2 led to an increase in the value of glass transition temperature presumably because of hydrogen bond formation between sulfonic acid groups. The plasticization effect of $NH^+(Et)_3$ in SPI-2 provides necessary mechanical properties for the conduction of pervaporation experiments. A non-solvent induced phase

separation technique was successfully applied to form an asymmetric high-performance pervaporation membrane with a dense skin layer and sponge-like pore structure from SPI-2.

The behaviour of SPI-2 transport properties in the processes of H_2O/EtOH and methanol/toluene pervaporation separation witnessed the realization of the facilitated fixed-site carrier transport mechanism for polar penetrants in terms of their exceeding thermodynamic activity. Coupled transport of water and ethanol molecules through the facilitated fixed-site carrier transport mechanism was observed. The deviation of methanol transport during pervaporation of methanol/toluene mixtures of different compositions through SPI-2 films from the linear Fick's law pattern was explained by the realization of the facilitated fixed-site carrier transport mechanism. The implementation of cluster transport allowed reaching high separation factor values and fluxes for separation of methanol/toluene azeotropic mixture. The permeability coefficient (permeance value) of toluene in SPI-2 does not change significantly through the concentration range, whilst the high methanol content in feed mixtures greatly increases the methanol permeability coefficient (permeance value) and selectivity values. Those observations showed that the coupled transport of toluene molecules with methanol is unlikely to occur. The presence of the DBTA-ODA fragments was showed to ensure the limitation of membrane swelling [88] and provide diffusion selectivity for methanol/toluene mixture separation in terms of diffusion of single molecules and while transporting penetrants through clusters.

Obtained results allowed to established further research project goals:

- The peculiarities of polar / non-polar mixtures separation along with the data obtained by means of thermo-gravimetrical methods favoured the assumption of the block nature of the obtained copolymer and micro-heteregeneous character of its films. These observations formed the basis of the interest to morphological features of SPI-2 and their role in the realisation of its unique transport properties.
- Swelling resistance and hydrolytic stability of SPI-2 films during protonation proved its potential as a proton-exchange membrane material. This marked the interest in the studying of its proton-conductive performance and stability in a typical fuel-cell environment.
- The influence of the counter-ion on transport and other physical properties of SPI-2 films established the prospects for studying properties of sulfonated polyimides of the same backbone with different counter-ions.

3.2 Author contribution

The applicant authored the idea of incorporating a flexible co-monomer into sulfonated polyimide to obtain membranes with necessary mechanical and transport properties. All the polymers described in the article were synthesised by the applicant. The applicant conducted all the pervaporation experiments, developed a procedure for the synthesis of asymmetric membranes and suggested an explanation of the observed transport phenomena. The main conceptualisation, writing and revision of the article were conducted by the applicant. The analysis and interpretation of the experimental results using the state of the art theoretical approaches was conducted by the applicant.

3.3 Article

Sapegin, D.A., Kononova, S.V., Gubanova, G.N., Kruchinina, E.V., Saprykina, N.N., Popova, E.N. & Vlasova, E.N. (2020) Selective facilitated fixed-site carrier transport of methanol through sulfonated copolyimide pervaporation membranes for the separation of methanol/toluene mixtures. Separation and Purification Technology. 236 p.116274.

https://doi.org/10.1016/j.seppur.2019.116274

https://www.sciencedirect.com/science/article/abs/pii/S1383586619345174

4. On the structure, morphology and transport through limitedly flexible chain sulfonated co-polyimide

4.1 Preface

The data obtained on the previous stages of the project allowed to suggest the block-nature of obtained copolymers, their tendency to form micro-scale phase separated films and a great influence of the chain conformation of the polymer on mechanical properties of its films. The thorough study of structural, morphological, transport properties of obtained copolymers and their mutual influence was conducted. An explanation of the established patterns and relations was performed using the state-of-the-art theoretical and semi-empirical approaches was performed in the framework of the article published in the Polymer (doi:10.1016/j.polymer.2020.123142) on 6th January 2021.

The structural and morphological features of the limitedly flexible chain sulfonated co-polyimide and their influence on its transport properties were investigated and explained. The presence of the -O-Ph-O- fragments (which exhibited limited flexibility) in the copolymer backbone allows the realisation of a number of different chain conformations. Folded chain conformation formed by consequently realised *cis*-2 regions favours the fragility of the DBTA-BDSA based polymer films, which was confirmed with XRD and DSC analysis. It was suggested that the formation of *cis*-2 regions is more likely to be realized in the case of small counter-ions with high charge density due to the presence of intra-chain interactions between the neighbouring sulfonate groups and corresponding counter ions. The value of the copolymer's glass transition temperature rose with the decrease in the size and the increase in the value of charge density of the counter ion.

The block-type structure of the studied copolymer was confirmed with the detection of micro scale phase separation in the case of its triethylammonium salt form films with AFM in lateral force contrast mode. The Hansen solubility parameters of the studied copolymer were determined and used for the evaluation of its morphological features. The copolymer is well represented with two spheres in the Hansen space corresponding to polar and nonpolar blocks of the SPI-2. The protonation of the SPI-2 film favours the realisation of the disordered morphology due to the decrease in the value of the Flory interblock interaction parameter in terms of the constant polymerisation degree with the substitution of $NH^{+}(Et)_3$ to H^{+} ions. According to the obtained data SPI-2 block-copolymer has a lamellar-like morphology represented by the interconnected polar phase regions inside a nonpolar matrix. The normalised length of the polar block was estimated to

be between 0.37-0.41. The volume fraction of $NH^+(Et)_3$ ions localized inside the polar phase of the copolymer amounted to 0.3 on the basis of theoretical and experimental studies. The influence of $NH^+(Et)_3$ ions presence on the solubility behaviour of SPI-2 and its Hansen solubility parameters is established.

Morphological features of the copolymer were proven to be responsible for the realisation of the selective fixed-site carrier facilitated transport of methanol during pervaporation. The methanol is mainly transported through the polar regions of the copolymer, while the nonpolar regions assure the resistance to excessive swelling of the membrane. When separating a binary mixture with an excessive amount of methanol, the permeability coefficient of the second penetrant depends greatly on its distance to methanol in the Hansen space. The facilitation rate parameter is introduced to estimate the real separation selectivity value on the basis of the individual permeation experiments. The suppression of the coupled transport effect caused by morphological features of SPI-2 allowed reaching high values of separation selectivity along with the high flux values for the pervaporation separation of various industrially important methanol rich mixtures. Further studies of SPI-2 dense film and asymmetric membrane skin-layer surfaces with AFM showed, that the dense skin layer of the asymmetric membrane has a similar micro-phase separated morphology (Figure 5).
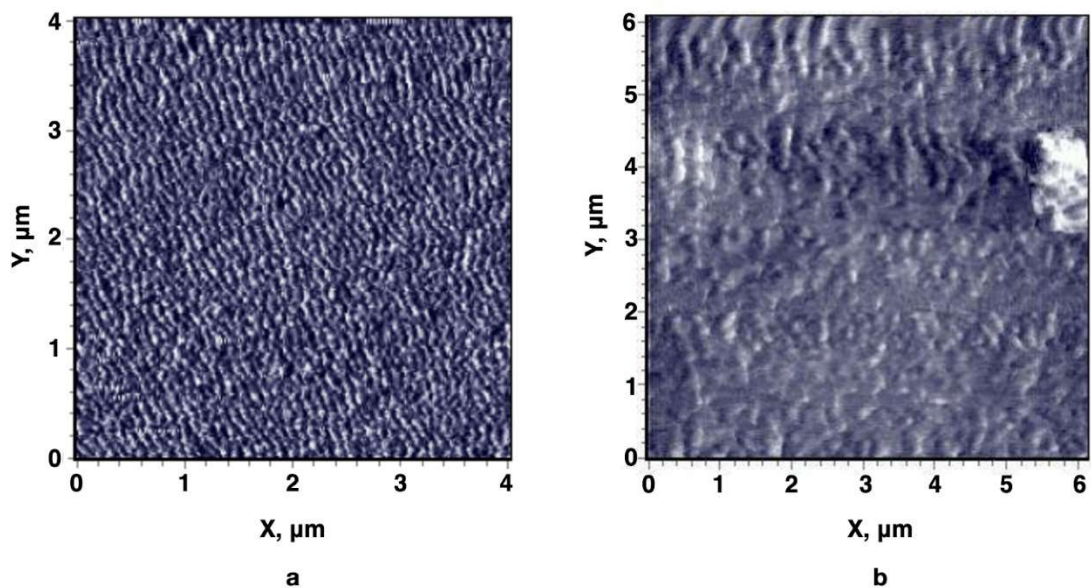

Figure 5. AFM lateral force contrast mode images of the top surfaces of SPI-2 dense film - a, skin layer of an asymmetric SPI-2 membrane obtained through non-solvent induced phase separation process.

The images presented in Figure 5 show the similarity between the morphological patterns of the samples, which along with the data on their selective-transport properties attests for the role of the sample morphology in the realisation of its transport properties. It should be noted that even in terms of the formation, through non-solvent induced phase separation process the skin-layer shows distinctive phase-separated morphology, however with a less pronounced pattern. This observation corresponds to the studies on mechanisms of the skin-layer formation in the processes of asymmetric diffusion membrane synthesis [90], and underlines the significance of the developed non-solvent induced phase separation process for obtaining asymmetric membranes with micro-scale phase separated skin layer.

According to the gas permeation experiments, similar to other polyimides, SPI-2 shows high values of separation selectivity along with low permeability values. The introduction of water as a carrier agent into the polar phase regions of the copolymer allows increasing permeability and separation selectivity of the CO_2/CH_4 penetrant pair. As in the case of PV, the rate of transport facilitation correlates with the distance between the penetrant and the carrier in the Hansen space. The similarity of real and ideal CO_2/CH_4 selectivity values attests to the resistance of SPI-2 to the CO_2-induced plasticisation. The morphological and structural features of SPI-2 make it perspective in application to the development of the fixed-site carrier facilitated membranes as a matrix material providing localized interconnected sites for carriers inside the nonpolar stable matrix.

4.2 Author Contribution

The article represents a thorough review and interpretation of the experimental data obtained during previous steps of research. The applicant designed and conducted all the synthetic procedures for the synthesis of the studied polymers. The theoretical calculation and design of all models based on the Hansen Solubility Parameters application approach were authored and conducted (including corresponding experiments) by the applicant. The interpretation of structural and morphological data with the usage of computational chemistry instruments and state of the art theoretical approaches was authored and conducted by the applicant. All the pervaporation experiments were conducted by the applicant. The applicant conceptualised, wrote and revised the text of the article.

4.3 Article

Sapegin, D.A., Gubanova, G.N., Kruchinina, E.V., Volkov, A.Y., Popova, E.N., Vylegzhanina, M.E., Setnickova, K. & Kononova, S.V. (2021) On the structure, morphology and transport through

limitedly flexible chain sulfonated co-polyimide. Polymer.212 p.123142. https://doi.org/10.1016/j.polymer.2020.123142

https://www.sciencedirect.com/science/article/abs/pii/S0032386120309678

The article was nominated for the Andrew Keller award for the best European paper, and featured in the special issue of the journal: https://www.sciencedirect.com/journal/polymer/special-issue/10F66N9350W

5. Increasing the performance of asymmetric pervaporation membranes for the separation of methanol/methyl-*tert*-butyl ether mixtures by the introduction of sulfonated polyimide into the poly(amide-imide) matrix

5.1 Preface

The relationship between structural and morphological features of the PAI : SPI-1 composites with their selective-transport properties established on the previous stages of the project were used to obtain high-performance asymmetric pervaporation membranes for separation of methanol/MTBE mixtures. The synthesis, characterisation and modelling of obtained membranes' performance was described in an article published in the Journal of Applied Polymer Science on 1st October 2020 (doi:10.1002/app.49982).

The main challenge within the framework of the research project stage was to introduce the amount of SPI-1 as a modifier into PAI matrix which is sufficient for methanol transport facilitation, but insufficient for drastic reduction of the adsorption selectivity characteristic to unmodified PAI membranes. The phase heterogeneity between PAI and SPI phases inside the composites was detected by the means of DSC.

The negative value of MTBE permeation activation energy for PAI and 1 wt.% SPI membranes leads to an increase in PV selectivity with the rise of the process temperature. The incorporation of SPI into the PAI matrix was showed to cause a significant increase in permeability of both components inducing a loss in separation selectivity. The increase in permeability values was attributed to the formation of the facilitated transport areas on the interface of the polymer. The decrease in selectivity values was attributed to the influence of SPI-1 introduction on PAI adsorption selectivity. Modification of PAI by the introduction of 1 wt.% SPI allowed to achieve an improved PSI value induced by the rise of membrane flux accompanied by a slight decrease in the selectivity of the separation.

Due to the high values of both flux and selectivity while separating methanol poor mixtures, (< 5 wt.% methanol) 1 wt. % SPI membranes are considered highly promising for hybrid methanol/MTBE separation process. A semi-empirical mathematical model for the prediction of membrane transport properties and membrane node performance was developed on the basis of the obtained data. The key parameters of the 1 wt.% SPI membrane node in a typical hybrid separation unit were determined.

5.2 Author Contribution

The applicant authored the idea of incorporating a small amount of SPI-1 homopolyimide to increase the efficiency of poly(amide-imide) asymmetric membranes. The data obtained on previous stages of the research project along with the results reported by other researchers was used to determine the preliminary composition range of the composites. All the polymers and membranes described in the article were obtained by the applicant. The applicant also conducted all the pervaporation experiments, developed the mathematical model for the prediction of transport properties and interpreted all the experimental results. The article was conceptualised, written and revised by the applicant.

5.3 Article

Sapegin, D.A., Gubanova, G.N., Popova, E.N. & Kononova, S.V. (2020) Increasing the performance of asymmetric pervaporation membranes for the separation of methanol/methyl-tert-butyl ether mixtures by the introduction of sulfonated polyimide into the poly(amide-imide) matrix. Journal of Applied Polymer Science.138 (10) p.49982. https://doi.org/10.1002/app.49982

https://onlinelibrary.wiley.com/doi/abs/10.1002/app.49982

6. Introduction of a crystalline block as a strategy to increase swelling resistance and dimensional stability of sulfonated copolyimide

6.1 Preface

The block nature of the obtained sulfonated copolyimides along with relative ease of their synthesis formed the basis for their further modification. Based on the data obtained on the previous stages of the project it was proposed that it is possible to influence the swelling and dimensional stability of considered sulfonated copolyimides by an introduction of a block inclined to form highly crystalline structures. The evaluation of proton conductivity of previously obtained SPI-2 along with a novel highly crystalline sulfonated copolyimide was reported in the article published on 23d March 2022 in the Journal of Applied Polymer Science (doi:10.1002/app.52373)

As was stated on the previous research project steps - the investigation of transport properties of the developed highly hydrolitically stable sulfonated copolyimides in application to proton exchange membranes development was of great interest. Accounting for major problems reported in the designated area, it was proposed to study the effect of the crystalline phase introduction on swelling and dimensional stability along with proton exchange performance of the materials. During the research, a new method for obtainment of protonated films from sulfonated polyimides leading to defect-free protonated films was established, and later published here [91].

The properties of the obtained crystalline sulfonated copolymer were compared to the ones of the similar amorphous polyimide (SPI-2). The studied crystalline copolymer showed constancy of the proton conductivity values in the broad range of temperatures (20–120 °C, RMSD of 0.23 %) and relative humidity values. Relative humidity is often used to characterise the relative activity of water vapour in the system and is defined as a ratio of the water vapour pressure to the saturated vapour pressure under given conditions. The results of AFM and XRD analysis along with data obtained with DSC and TGA revealed the presence of highly crystalline areas, most probably formed by DBTA-BAPB blocks of the polymer. Obtained copolymer showed acceptable mechanical stability which allowed to conduct pervaporation and direct proton conductance experiments.

The introduction of the block inclined to form crystalline areas in the matrix of the polymer allowed to obtain a copolymer with enhanced swelling resistance and dimensional stability. The decrease in chain mobility induced by the presence of highly ordered areas led to the constancy of the proton conductivity values in the middle-temperature range, while it did not induce a significant

decrease of the proton conductivity values in the low humidity conditions. The suggested approach seems promising for the obtainment of mechanically and dimensionally stable materials with high swelling resistance and reliable performance in a broad range of temperatures and relative humidity values.

The preliminary characterisation of SPI-2 as a potential proton exchange membrane material led to further investigation of its stability and proton-conductive properties in the environment of a fuel-cell [91]. Relatively high values of SPI-2 proton conductivity ($1.2 \cdot 10^{-3}$ S·cm^{-1}) along with its stability during the laboratory fuel-cell runs allowed to demonstrate its high potential as a material for medium-temperature fuel cells.

6.2 Author Contribution

The applicant authored the idea of incorporating a highly crystalline block into sulfonated copolyimides to increase its dimensional stability. All the polymers described in the article were synthesised by the applicant. The applicant also conducted all the pervaporation experiments, interpreted the experimental results, conceptualised, wrote and revised the text of the article.

6.3 Article

Sapegin, D.A., Gubanova, G.N., Vlasova, E.N., Zaharova, N.V., Afanas'eva, N.V., Popova, E.N., Sokolova, M.P., Lavrentyev, V.K., Primachenko, O.N. & Kononova, S.V. (2022) Introduction of a crystalline block as a strategy to increase swelling resistance and dimensional stability of sulfonated copolyimide. Journal of Applied Polymer Science.139 (24) p.52373.

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https://onlinelibrary.wiley.com/doi/abs/10.1002/app.52373

7. Conclusion

To achieve the proposed goal of the study a method for the synthesis of film-forming chemically resistant polyimides based on 3,3',4,4'-(1,3-diphenoxybenzo)tetracarboxylic acid dianhydride containing sulfonic-acid groups in the main chain was developed. Micro-heterogeneous structure of the obtained polyimides and their composites with poly(4,4'-diphenyloxidamido-*N*-phenylphthalimide) was detected and studied in detail. Selective transport properties of new polyimides and composites based on them in relation to the separation of various liquid and gaseous mixtures were investigated. The relationship between structural-morphological features of the studied materials allowed to obtain highly promising pervaporation and proton exchange membranes. Structural organization in membranes based on copolymers of 4,4'-bisbiphenyl-2,2'-disulfonic acid, 4,4'-diaminodiphenyl oxide and 3,3',4,4'-(1,3-diphenoxybenzo)tetracarboxylic acid dianhydride was optimized for selective pervaporation separation of methanol from its liquid mixtures with a number of organic components in broad compositions range. A method for the preparation of asymmetric gradient-porous membranes with a defect-free diffusion layer from new sulfonated polyimides was developed. Based on the theoretical studies on the morphological behaviour of obtained sulfonated-block-copolyimides a mathematical model for prediction of the efficiency of the developed membranes in the processes of pervaporation separation of various methanol-containing mixtures was proposed. The hydrolytic stability of the copolymer based on 4,4'-bisbiphenyl-2,2'-disulfonic acid, 4,4'-diaminodiphenyl oxide (1:1) and 3,3',4,4'-(1,3-diphenoxybenzo)tetracarboxylic acid dianhydride (SPI-2) was illustrated, and a method for the obtainment of defectless protonated films from sulfonated polyimides was proposed. Proton-exchange properties of SPI-2 based membranes were investigated. Based on the morphological studies an approach for increasing dimension and swelling stability by introduction of blocks prone to crystallization was proposed. Such blocks were introduced into the structure of the copolymer based on 4,4'-bisbiphenyl-2,2'-disulfonic acid and dianhydride 3,3',4,4'-(1,3-diphenoxybenzo)tetracarboxylic acid and induced an increase in the stability of swelling, dimensions and proton conductivity of the membrane in a broad temperature and relative humidity ranges.

During the research project several significant results demonstrating the scientific novelty of the work were achieved. Polyimides based on the monomeric system: 4,4'-bisbiphenyl-2,2'-disulfonic acid, 4,4'-diaminodiphenyl oxide and 3,3',4,4'-(1,3-diphenoxybenzo)tetracarboxylic acid dianhydride were synthesized and characterised for the first time. The microheterogeneous nature of the structure of copolymers based on the studied monomer system and its role in the realisation of their selective transport properties are demonstrated. Several methods have been developed for

influencing the micro-heterogeneous structure of films of copolymers and their composites with poly(amide-imides) to control their selective transport properties. The effect of selective facilitated transfer of polar low molecular weight penetrants through membranes based on the developed sulfonated polyimides was discovered and utilised. For the first time, a technique was developed for the obtainment of asymmetric gradient-porous membranes with a defect-free micro-scale phase separated diffusion layer based on sulfonated polyimides. The influence of the counterion on the micro-heterogeneous structure of the copolymer of the optimal structure was established. Based on the solution-diffusion transport model and the solubility theories of Hansen and Flory-Huggins, a mathematical model has been developed to predict the real values of selectivity in the pervaporation separation of binary methanol mixtures with membranes from the sulfonated-block-co-polyimide of optimal structure. The efficiency of the proposed strategy of crystallizing blocks introduction into the main chain of sulfonated-polyimide to increase swelling resistance and stabilize proton conductivity values in a wide range of temperatures and relative humidity values was demonstrated.

Several materials and approaches with high practical significance were developed within the framework of the project. Highly efficient pervaporation membranes based on new sulfonated polyimides and their composites with poly(amide-imides) were developed and proved to demonstrate high performance and selectivity with respect to methanol in the separation of its binary mixtures in a wide range of concentrations. Obtained membranes were illustrated to be very promising for use in the chemical and oil industries in application to separation of methanol mixtures with lower aromatic hydrocarbons, dimethyl carbonate, dimethoxyethane, methyl-*tert*-butyl ether, as well as in the desalination of aqueous solutions, including those with high salinity. Gas separation membranes with high selectivity in relation to the selective separation of O_2/N_2, CO_2/CH_4, and CO_2/N_2 mixtures, based on sulfonated-block-*co*-polyimide were developed. The membranes demonstrated high potential for use in the chemical industry in application to the separation of gaseous mixtures and mechanical engineering to obtain technical gases of a given purity. A novel method was proposed for the prediction of real selectivity values in the pervaporation separation of binary methanol mixtures based on experimental data on the individual transport of penetrants. High-performance proton-exchange membranes based on the studied sulfonated polyimides with high proton conductivity values were obtained. An approach for stabilization of the proton conductivity values over a wide range of temperatures and relative humidity values, by the introduction of a block prone to crystallization into the polymer structure, showed exceptional promise.

8. Recommendations for future work

A number of interesting discoveries made during the research project, allowed to establish correlations between chemical structure, structural-morphological features, and mechanical and selective-transport properties of studied systems making it possible to develop high-performance membrane materials. The established correlations along with recent developments in the field of membrane and polymer science indicate that the variation of the copolymer system, in terms of both sulfonated and non-sulfonated diamines shows tremendous promise as a research topic. Being able to form hydrolytically stable sulfonated polyimides, 3,3',4,4'-(1,3-diphenoxy-benzene)tetracarboxylic dianhydride can be used to obtain high-performance polymers for a variety of diffusion transport applications. In terms of increasing the proton conductivity other sulfonated diamines with more flexible structures, or having sulfonic acid group terminated side-chains may be considered to alter the morphology and transport features of polar channels. The variation of non-sulfonated diamine fragments for structures with higher free volume values could potentially allow for high values of gas permeability while retaining high selectivity values. Since only diblock-like copolymers were considered in the framework of the present research project the study on terpolymers comprised of 4,4'-oxydianiline, 4,4'-Bis(4-aminophenoxy)biphenyl and 4,4'-diamino-bisbiphenyl-2,2'-disulfonic acid may lead to methods for controlled synthesis of sulfonated polyimides with desired crystallinity degree, and improved proton conductivity performance.

The extension of the proposed solubility-theories application approach for the description of real pervaporation performance in two ways:

- Expansion of the range of studied mixtures for described systems
- Application of the approach for other membranes

These are extremely promising due to the lack of comprehensive universal pervaporation transport models. Based on the comparison of selective-transport properties of developed membranes to state-of-the-art performance, one of the most promising paths to follow is the development of high-performance membranes based on sulfonated polyimide : poly(amide-imide) composites for the separation of methanol from its industrially important liquid mixtures, such as those with dimethyl carbonate and dimethoxyethane. The utilisation of selective fixed-site-carrier-facilitated transfer of small polar molecules observed for a number of obtained copolymers allows considering their application to the separation of azeotropic mixtures with high polar component content and water desalination.

Last but not least, the development and characterisation of thin-film composite membranes with selective layers from studied sulfonated copolyimides may provide opportunities for additional

selective layer swelling control by means of the usage of different nano/ultra-porous support materials. Due to the relatively high costs of sulfonated polyimides' production development of high-performance, thin-film composite membranes based on the nano/ultra-porous supports fabricated from commercially available polymers, such as Torlon and P84, may drastically reduce the overall cost of the membrane and by so making it competitive in the modern market.

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