SOLUBILITY STUDY OF LADDER-LIKE POLYPHENYLSILSESQUIOXANES (L-PPSQ) FOR MEMBRANE APPLICATION

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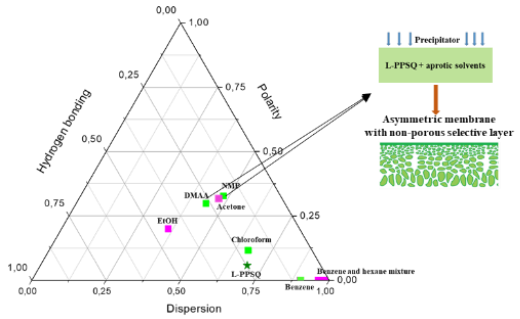
Abstract

In this work, the solubility of a high-molecular-weight homopolymer, ladder polyphenylsilsesquioxane (L-PPSQ), was studied in various classes of solvents: alcohols, aprotic solvents, ketones, alkanes, and aromatic hydrocarbons. The Hansen parameters and the parameter of remote interaction between the polymer and its solvent are analyzed. The insolubility of L-PPSQ in a wide range of solvents allows us to expect that the properties of a membrane would be stabile when the latter is operated in these media. At the same time, aprotic solvents are well suited for the preparation of membranes based on L-PPSQ by the solution phase inversion method.



Key words: polypheylsilsesquioxanes, solubility, Hansen parameters, membranes

Introduction

For CO_2 separation and aromatic/aliphatic hydrocarbon separation, membrane separation processes are promising. Membrane technologies can significantly reduce separation costs due to compactness, modularity, greater separation efficiency and reduced energy costs compared to traditional processes. High permeability, selectivity, and stability at elevated temperatures are key when choosing membrane materials and developing membranes based on them.

A special place among polymers is occupied by ladder polyphenylsilsesquioxanes (L-PPSQ) - glassy polymers with high thermal stability (decomposition onset temperature 495°C) even in the presence of water vapor. The recently developed original method for the synthesis of L-PPSQ [1] made it possible to obtain a polymer with a high molecular weight (1,000,000 g/mol), and, as a consequence, good mechanical (tensile strength 39 MPa and elongation at break 9%) and film-forming properties. The high thermal stability of L-PPSQ (T(glass)>T(decomposition)>490°C), (even in the presence of water vapor) and high mechanical characteristics make this polymer unique among existing membrane materials.

Despite the widespread use of L-PPSQ block copolymers in membrane science and technology, the solubility, mechanical and transport properties of L-PPSQ homopolymer have been largely unexplored. There is one publication in the literature from the early 90s, where the gas permeability of l-PFSS was studied [2]. However, in this work, the structure of the polymer was practically not studied. Thus, in this work, the solubility of the homopolymer in a number of organic solvents was first studied. This is necessary to understand the solvent used to prepare the membranes, as well as their application.

Results and discussion

At the first stage of the work, the solubility of L-PPSQ in 7 organic solvents of various natures (chloroform, benzene, n-methylpyrrolidone, dimethylacetamide, hexane, acetone, ethanol) and two organic mixtures (benzene/ethanol of various compositions) was studied and their Hansen solubility parameters were analyzed [3] (Figure 1). The studied L-PPSQ has the following molecular weight characteristics: *Mw* = 1057 kg/mol, *Mp* = 1731 kg/mol, *Mn* = 344 kg/mol. Solubility parameters (δ)

were calculated taking into account group contributions using equations (1-3):

$$\delta = \left(\frac{\sum_i E_{coh}^i}{\sum_i V_m^i}\right)^{1/2} \quad (1)$$

$$E_{coh} = E_d + E_p + E_h \quad (2)$$

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

where E_{coh} is the cohesion energy, V_m is the molar volume of the *i*-th functional group of the molecule, E_d is the dispersion component of energy, E_p is the polar component of energy, E_h is the energy of hydrogen bonds, δ_d is the contribution of dispersion interaction, δ_p is the contribution of polar interaction, and δ_h is the contribution of the interaction of hydrogen bonds.

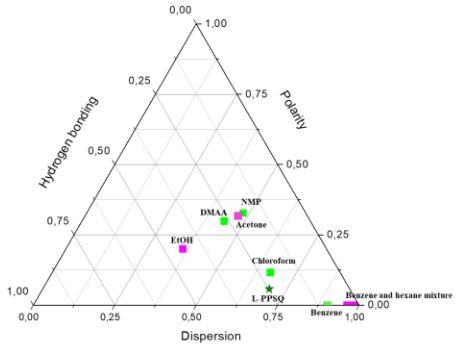


Figure 1. Comparison of Hansen solubility parameters for L -PPSQ and its solvents.

In Figure 1, the solvents (chloroform, benzene and polar aprotic amide solvents: NMP and DMAA) for L-PPSQ are highlighted in green. Solvents (hexane, acetone and ethanol and mixtures of hexane and benzene) in which L-PPSQ is insoluble are highlighted in purple. This behavior is characteristic of PPSQ. Various groups of researchers noted the solubility of materials of this class in benzene, chloroform and aprotic solvents (THF, DMF) and their insolubility in ketones, alcohols, simple ether, and in saturated cyclic and aliphatic hydrocarbons [4]. The insolubility of L-PPSQ in a wide range of solvents allows us to expect that the properties of a membrane would be stabile when the latter is operated in these media. Apparently, an undoubted advantage of L-PPSQ is that it is soluble in solvents with various viscosities, which would allow the development of membranes with good performance characteristics on its basis.

One of the ways to predict the sorption affinity of a polymer material and a solvent is to determine the parameter of their long-range interaction. To estimate such interaction, the difference in the solubility parameters of the polymer and the solvent is used taking into account the contributions of polar and dispersion interaction as well as hydrogen bonds [5].

The smaller the difference between the solubility parameters of the polymer and the solvent, the higher the affinity between them, hence one should expect large values of solvent sorption in the polymer material [6]. The affinity of the *i*-th solvent (*s*) to the polymer material (*p*) can be estimated by the long-range parameter Δ_{s-p} (formula 4): the lower the long-range parameter, the stronger the solvent-polymer interaction [3].

$$\Delta_{s-p} = \sqrt{\left(\delta_{d,s} - \delta_{d,p}\right)^2 + \left(\delta_{p,s} - \delta_{p,p}\right)^2 + \left(\delta_{h,s} - \delta_{h,p}\right)^2} \quad (4)$$

Table 1

Estimation of the long-range interaction of the polymer and solvents of various nature

Compound	Δ_{s-p}
L-PPSQ	**-**
Chloroform	**3.11**
Benzene	**6.0**
NMP	**10.6**
DMAA	**10.5**
Hexane	**9.3**
Acetone	**9.7**
Ethanol	**14.5**
Benzene/ Hexane 10/90	**11.3**
Benzene/ Hexane 30/70	**10.5**

Based on the values of the long-range interaction parameter obtained, we can say that benzene and chloroform are the best solvents for L-PPSQ in the series studied. The interaction of L-PPSQ with MP and DMAA solvents appears to occur at the boundary of the region of "good" solvents in terms of the long-range parameter value (MF: 10.6 $MPa^{1/2}$; DMAA: 10.5 $MPa^{1/2}$). In the 30 wt.% benzene/ 70 wt.% n-hexane mixture, L-PPSQ swells strongly but does not dissolve. L-PPSQ is insoluble in pure hexane, acetone and ethanol. Moreover, this polymer does not swell at all in ethanol and hexane, while its behavior in acetone requires further study. Thus, it can be assumed that a long-distance parameter value above 10.5-10.6 delineates the region of "bad" solvents.

Conclusions

In the present work, the solubility of L -PPSQ in various organic solvents was investigated and their Hansen solubility parameters were analyzed. Thanks to the calculation of the long-range Δ_{s-p}, it was found that organic solvents with a parameter of up to 10.6 dissolve L-PPSQ. Organic solvents exceeding this value are not solvents for L-PPSQ.

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