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Invited paper

Yuri Yampolskii in Membrane Materials Science

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Highlights

- Yu. P. Yampolskii's role in membrane material science
- Novel polymeric materials
- Inverse gas chromatography for permeable glassy polymers
- Compiling of TIPS Database
- Prediction of gas transport properties of polymers

Graphical abstract

Abstract

The article aims to pay respects to the excellent scientist and good friend Yuri Pavlovich Yampolskii. This article describes several scientific areas that Yampolskii was actively engaged in, and is divided accordingly into three chapters. The first chapter contains information about the main group of polymers (polyvinyl-trimethyl silane, polynorbornenes, PIM-family polymers, perfluorinated polymers, etc) that Yampolskii investigated in the framework of membrane gas separation. The second chapter considers the application of the inverse gas chromatography technique for the characterization of penetrant sorption in polymeric membrane materials (highly permeable glassy polymers) that was mainly developed by Yampolskii's group. The third chapter describes the work of Yampolskii's group on computational chemistry, compiling gas transport data into the TIPS RAS Database, its capabilities in correlation analysis, and "structure-property" predictions. We will miss our beloved teacher and colleague and hope this article will, to some extent, tell a story of his eventful and energetic life in the scientific world.

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1. Introduction

Yuri Pavlovich Yampolskii (Yu.P. Yampolskii) is the founder of a whole area in Russian science - membrane materials science. His work shifted in this direction in the late 1970s - early 1980s of the last century and began from the study of the gas transport properties of polyvinyl-trimethyl silane (PVTMS), its derivatives, and copolymers [1–4]. This was associated with the advent of gas separation PVTMS membrane, its introduction into industrial processes, and the development of membrane technology in the USSR. However, even then the scientific interests of Yuri Pavlovich were not limited to the materials based on the PVTMS: the study of other polymers started [5–7], the search for the correlation between transport parameters, the structure of polymers, and their physicochemical characteristics, measured by different methods, was also initiated [8]. In the mid-1980s, Yampolskii became the initiator of work related to probe methods for studying the free volume of polymers. The first study was collaborative work with the Institute of Chemical Physics of the USSR Academy of Sciences on the annihilation of positrons [9]; the continuation of this work resulted in a series of publications [10–14]. Since the beginning of the 1990s of the last century, Yuri Pavlovich was invited to write and edit monographs in the area of membrane science [10,15–19]. The connection of transport properties with data of various probe methods has become the most important achievement of modern membrane materials science. The relationship between the chemical structure of polymers and their transport characteristics, not only qualitative but also quantitative [20], is the most important contribution of Yampolskii to the area designated by him "membrane materials science". The series of lectures with the same name, founded by Yampolskii, is taught today by his students and acolytes in the Moscow State University and the A.V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences. Finally, the thermodynamics of the interaction of polymers and sorbates (including gases) was combined by Yampolskii with data from membrane studies, which determined the principal connection of fundamental science with practical applications. This article is divided into three chapters devoted to three scientific areas, to which Yampolskii contributed greatly.

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2. Polymers for membrane gas separation

Yampolskii is well known as one of the pioneers in membrane materials science. He studied polymers as membrane materials starting from the 1970s and managed to investigate a wide range of polymer types throughout his career. He published many works compiling his findings and reviewing some general trends regarding different polymers' place in membrane science [17,21–24]. Some of his works were dedicated to rubbery polymers [4,6,7,25–29], polystyrenes [25,30], polyimides [31–36], polyarylenes [37–39].

This chapter aims to provide some resumes on the polymers studied by Yampolskii (Fig. 1), though it is hard to cover all of the research fields he had an impact on.

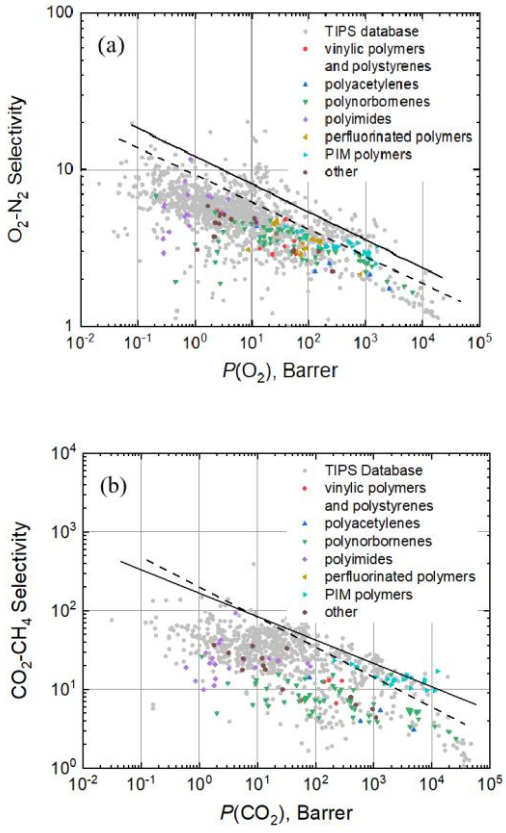


Fig. 1. Location of the polymers studied by the group of Yampolskii in the Robeson diagrams for O_2-N_2 pair (a) and CO_2-CH_4 pair (b). Solid and dashed lines correspond to Robeson's upper bounds of 1991 [40] and 2008 [41].

2.1. Poly(vinyl trimethylsilane)

Poly(vinyl trimethylsilane) (PVTMS) was for the first time synthesized in A.V. Topchiev Institute of Petrochemical Synthesis (TIPS RAS) in the middle of the 1960s by the team of Durgaryan and Nametkin (Fig. 2) [42].

PVTMS had an impressive gas permeability and selectivity combination at the time of its first appearance and soon it was scaled to the production level, an asymmetric membrane was prepared. Yampolskii had actively participated in the investigation of gases and vapors' permeability, diffusion, and solubility in PVTMS [1,3,7,25]. As it was obvious already that the chemical structure of polymers affects their properties and gas transport parameters, some works on chemical modification of PVTMS were performed [2]. However, the performed modification did not lead to an improvement of gas separation properties and thus PVTMS remained the model polymer for further investigations of the physicochemical behavior of polymers [26,43,44].

In the 1980s-1990s new polymers appeared that stirred the interest of the membrane science society, and PVTMS started to slowly lose its position. However, it is worth mentioning that well-investigated and stable PVTMS is still used by researchers to calibrate novel methods and study some polymer properties and modification types.

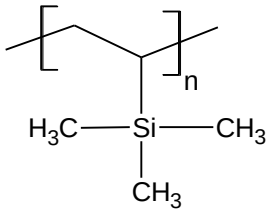


Fig. 2. PVTMS structure.

2.2. Polyacetylenes

From the first publication about the synthesis and gas permeability of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) [45], this polymer was investigated numerous times by different scientific teams and it was very popular, to say the least (Fig. 3). The reason for this commotion is the anomalously high free volume and gas permeability of PTMSP, though it was found later that this polymer is susceptible to physical aging [46,47].

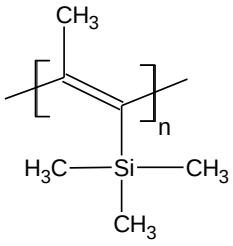


Fig. 3. PTMSP structure.

Yampolskii had joined this global trend to study PTMSP in the late 1980s [7, 48]. He investigated this polymer from different points of view as it was important to deeper understand PTMSP structure and Physico-chemical properties peculiarities. Yampolskii and his colleagues studied the process of physical aging of PTMSP [49], used different methods to investigate its free volume [50].

PTMSP made it clear that the rigid polymer backbone of polyacetylenes with a double -C=C- bond leads to high gas permeability and diffusivity. It made Yampolskii quite interested in the polyacetylenes group overall. And, though this polymer class variety is limited by the side-groups in a repeat unit, Yampolskii with his Russian and foreign colleagues performed studies of a series of substituted polyacetylenes, that have confirmed polyacetylenes to be, in general, highly permeable polymers [51–53].

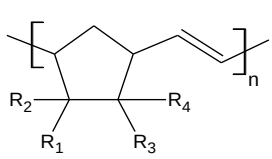
2.3. Polynorbornenes

Polynorbornenes is the polymer class (Fig. 4), which representatives are actively synthesized in TIPS RAS. Finkelshtein and Gringolt's teams work on the synthesis of such polymers since the 1990s [54,55]. One of the important characteristics of this group is the possibility of two types of synthesis: metathesis and addition polymerization.

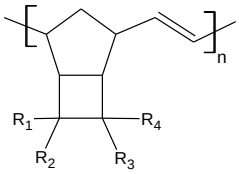
Yampolskii had a long and fruitful collaboration with Finkelshtein and Gringolts teams. It can be seen by an astonishing number of publications they prepared together [56–78].

Among other things, the studies they performed were dedicated to the difference between addition and metathesis polymers [67]. Two types of synthesis lead to the formation of dramatically different isomers. They differ in such properties as glass transition temperature (T_g), density and free volume, gas separation parameters. Therefore, this polymer class may be useful for a wide range of tasks.

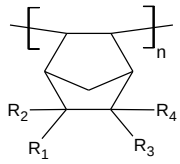
While the metathesis synthesis is easier than the additional one, the resulting polymers have lower T_g, lower gas permeability, and lower chemical stability. On the other hand, addition polymerization leads to the formation of mechanically stable films with higher T_g and gas permeability, but the additive synthesis is more troublesome.



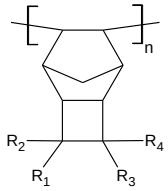
Metathesis polynorbornene structure



Metathesis polytricyclononene structure



Additive polynorbornene structure



Additive polytricyclononene structure

Fig. 4. Polynorbornenes class structures. R_1, R_2, R_3, R_4 – substituents.

It is worth noting, that during the period of collaboration of Yampolskii with Finkelshtein and Gringolts polynorbornenes with (i) $–Si(CH_3)_3$ and $–Ge(CH_3)_3$ substituents [67,69], (ii) Si-O-Si fragments [68,72,77], as well as (iii) fluorine-containing [58] and halogen-containing [56] polynorbornenes were characterized. Such features of polynorbornenes as cis/trans isomers content [59,60], position and number of substituents [63,66], and stereoisomerism [74] were investigated.

2.4. Polymers of intrinsic microporosity

Polymers of intrinsic microporosity (PIM) are characterized by relatively high gas permeability, large inner surface area, and free volume, as well as great sorption capacity (Fig. 5). These properties place this group close to many polyacetylenes, yet they have a completely different structure. The first member of the group, PIM-1, was first reported about 15 years ago by P.M. Budd et al. [79]. Yampolskii immediately realized the importance and potential of such polymers and began the investigation in this area. In 2008, in a team of authors, including the discoverers of PIM-1, he published an article on the gas permeation and physicochemical properties of PIM-1 [80]. The further collaboration lead to the discovery of a novel group of PIM-based polyimides, called PIM-PIs; eight members of this group were characterized in detail in 2009 [81] and three more in 2013 [82]. Although, in general, polyimides have medium gas separation properties, the works of Yampolskii with co-authors demonstrated extremely high gas solubilities and gas permeation properties of PIM-PIs due to the introduction of PIM units into the structure of the polyimides.

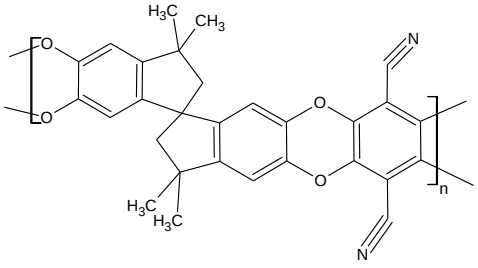


Fig. 5. PIM-1 Structure.

The idea of increasing the rigidity of the backbone, coupled with the concept of PIMs, lead to further development of PIM-derived materials, including polymers with ethanoanthracene units, which became an actively investigated area. A substantial part of Yampolskii's work was dedicated to the investigation of the properties of PIM copolymers containing ethanoanthracene and, later, other anthracene-based moieties [83–85]. Some of the developed polymers exhibited excellent properties, significantly surpassing the upper bound of the Robeson 2008 diagram [41].

The investigation of PIM-1 material continues even now, with the direction shifted to the development of new methods of PIM-1 synthesis, for example, using polycondensation reaction in dimethylsulfoxide [86] and to the detailed description of PIM-1 treated by different methods [87].

2.5. Perfluorinated polymers

Since the invention of polytetrafluoroethylene (in 1938th) researchers pay attention to perfluorinated polymers due to a unique combination of their physicochemical properties (excellent chemical and thermal resistance, low cohesive energy, flame, and oxidative stability, etc). However, an intensive investigation of the group of the polymers started in the 1990s since novel perfluorinated glassy non-crystalline polymers (amorphous Teflon AF and Hyflons AD, Cytop, homo- and copolymers of hexafluoropropylene, poly(perfluoro-2-methyl-2-ethyl dioxole-1,3), poly(perfluoro propyl vinyl ether)) began to be tested on gas permeability often in collaboration with Yampolskii group [88–95]. The perfluorinated polymers showed unusual selectivities for methane- and hydrogen-containing gas pairs and are of interest for separation of bio-hydrogen, biogas, enrichment of helium and nitrogen from natural gas. The perfluorinated polymers often overcome Robeson's upper bounds in 1991 and 2008 for N_2-CH_4, He-CH_4, He-CO_2, etc. The peculiarities and nature of gas sorption, diffusion, and permeation in the perfluorinated polymers were summarized and thoroughly discussed in his review [24].

3. Inverse gas chromatography

Inverse gas chromatography (IGC) is a variety of gas-liquid chromatography and is widely applied for the estimation of physicochemical parameters of sorption, phase, and relaxation transitions of various non-volatile low molecular compounds and polymers [96,97]. A set of compounds investigated as stationary phases includes low molecular compounds with molecular masses up to one thousand Daltons (higher n-alkanes [98–102], asphaltenes [103], oligomers of polyethylene oxides [104], phosphates [101,105], ionic liquids [106–109], liquid-crystalline compounds [110–112], etc) and high molecular compounds. Intensive exploration of the polymers as the stationary phases began after a pioneer work of Smidsrod and Guillet with N-isopropyl acrylamide [113]. Until now, a huge number of polymers have been investigated. And, one can divide them into two groups: polymers investigated (i) above the glass transition temperature (regions DC and IJ in Figs. 6a and b respectively) and melting point (region GF in Fig. 6a) and (ii) below the temperature (less numerous group, regions AB and HI in Figs. 6a and b respectively). A major part of thermodynamic parameters of sorption in high molecular compounds has been studied at temperatures of 5-40 °C above glass transition temperature (or melting point) when the polymers are in rubbery-like or molten states. Here, one distinguishes polyolefins, polysiloxanes, polyethers, polyesters, polyurethanes, polysulfones, polyetherimides, poly alkyl acrylates, and –methacrylates and their copolymers, polystyrenes, polyvinyl acetates, and its copolymers, etc [114–116,116,117].

The application of IGC for testing glassy polymers is distinguished by some peculiarities requiring additional consideration. The equilibrium retention below and above the glass transition temperature is limited by the rate of sorbate diffusion in the polymer film covering solid support. If a condition $(Dtl^{-2})^{0.5} < 1$ (where D is the diffusion coefficient of the solute in the polymer, l is the thickness of the film, and t is the retention time of the solute in the chromatographic column with the polymer stationary phase) is met the retention diagram in passing through T_g becomes Z-shaped (Fig. 6a) and line AB corresponds to adsorption of the solute onto the surface of the polymer stationary phase. In the case of $(Dtl^{-2})^{0.5} >> 1$, an equilibrium absorption regime is attained. This condition can be satisfied (i) by a decrease in the thickness of the polymeric stationary phase that may result in undesirable effects (an increase of the influence of surface adsorption on the total specific retention volume) and (ii) by investigation of polymeric materials with higher diffusion coefficients of solutes. The first polymer satisfying the second requirement, PVTMS, was studied by the group of Yampolskii in the middle of the 1980s [118,119]. Meanwhile, drawing attention to the chronology, it is worth noting that the first IGC investigation of polymers above glass transition temperature was performed by Tait and Abushihada [120,121] in 1977th. The authors investigated the absorption behavior of poly(vinyl chloride), polystyrene, poly(methyl methacrylate) below and above their glass transition temperature. However, the regimes of elution of solutes during the experiments for the glassy state of the polymers corresponded to those for the

investigation of adsorption behavior of the same stationary phases [122]. The same doubts can be referred to a relatively early IGC investigation (1980th) of polysulfone by Danganyach and Bonner [123]. Later on, highly permeable (at that time) polymers were analyzed by group of Yampolskii: poly(2,6-dimethyl phenylene oxide-1,4) [124] (PPO), perfluorinated copolymers of tetrafluoroethylene and perfluorodioxoles (amorphous Teflon AF1600 and AF2400) [125–127], Hyflons AD [128,129]), metathesis type poly(5,6-bis(trimethylsilyl norbornene)) [130], PTMSP [131], additive poly(5-trimethylsilyl norbornene) [62], PIM-1 [80], poly(perfluoro-2-methyl-2-ethyl-dioxole-1,3) [95]. A peculiarity of the retention diagrams of solutes for those polymers is their linear behavior above and below glass transition temperature that is attained by higher diffusion coefficients of the solutes in the rubbery and glassy states of the polymers (Fig. 7a). Meanwhile, further investigations of the perfluorinated amorphous Teflon AF by IGC were differed by the two linear branches [126,127] as the retention diagram in Fig. 6b demonstrates.

Different slopes of the retention diagrams reflect different heats of sorption of solutes in the rubbery and glassy polymers. Indeed, the sorption of solutes in the rubbery-like polymers (excess partial molar enthalpy or partial enthalpy of mixing ΔH_m) characterizes intermolecular interactions between solute and polymer. And, ΔH_m can be slightly negative for favorable solute-polymer systems with similar chemical structures (for instance, hydrocarbon solutes in hydrocarbon-based polymers [29], fluorocarbon solutes in fluorocarbon-based polymers [132]) and positive for unfavorable interactions in the unlike systems (hydrocarbon-fluorocarbon and vice versa) [29,132]. Nonetheless, the amounts of the excess enthalpies (as well as excess entropies) for the solute-rubber systems yet remain close to zero (Fig. 7b). On the contrary, the sorption of solutes in the glassy polymers differ by a significant thermal effect that is expressed in higher excess partial molar parameters of enthalpy and entropy (Fig. 7b) due to the presence of non-equilibrium free volume in the structure of glassy polymers (see more detailed discussion of the phenomena and thermodynamic models of sorption in glassy polymers elsewhere [116,126,127]).

Another unique application of the IGC technique proposed by Yampolskii is the characterization of cavities of free volume. The solute molecules were supposed to monitor the free volume elements and the more negative partial molar enthalpy of mixing is the more comparable sizes are for the solute molecule and the cavities of free volume. A good example of the applicability of the approach is a comparison of different probe techniques for the perfluorinated copolymer Hyflon AD [129]. The results of various techniques (photochromic probes, positron annihilation lifetime spectroscopy, ^{129}Xe NMR, IGC, and molecular dynamics simulation) showed a good agreement in the estimation of a mean value of free volume element [129]. The experimental data for other polymers are also presented in Fig. 8 However, further testing of the perfluorinated polymers AF1600 and AF2400 revealed another dependency of ΔH_m vs. V_c [126,127] that did not repeat the previous ones. It might be associated with the difficulties of measurements of the equilibrium sorption parameters for the higher alkanes at temperatures close to the glass transition temperature. Despite the dissonances, inverse gas chromatography can be considered an effective instrument for the determination of the high-temperature sorption parameters for the polymers with higher free volume.

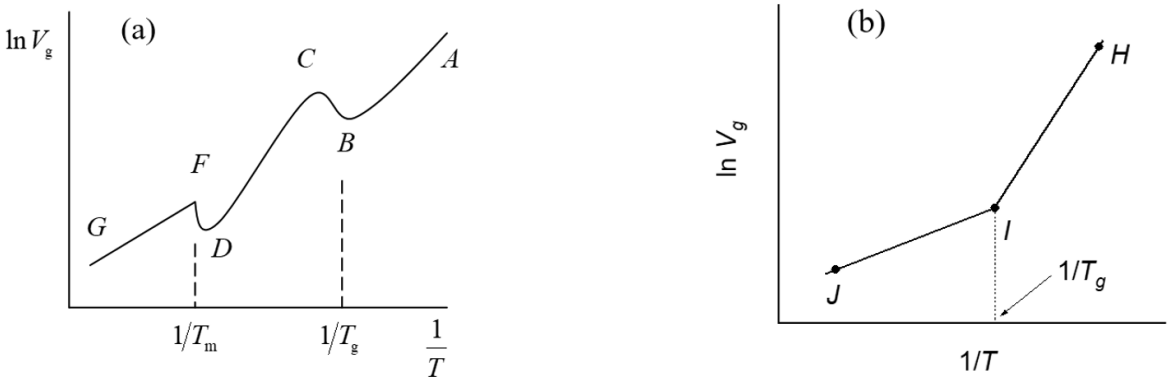


Fig. 6. A schematic representation of retention diagrams (a dependence of specific retention volume on temperature) in van Hoff coordinates in passing through glass transition and melting temperatures for regimes of non-equilibrium (a) and quasi-equilibrium (b) absorption in a polymer stationary phase. Explanations in the text.

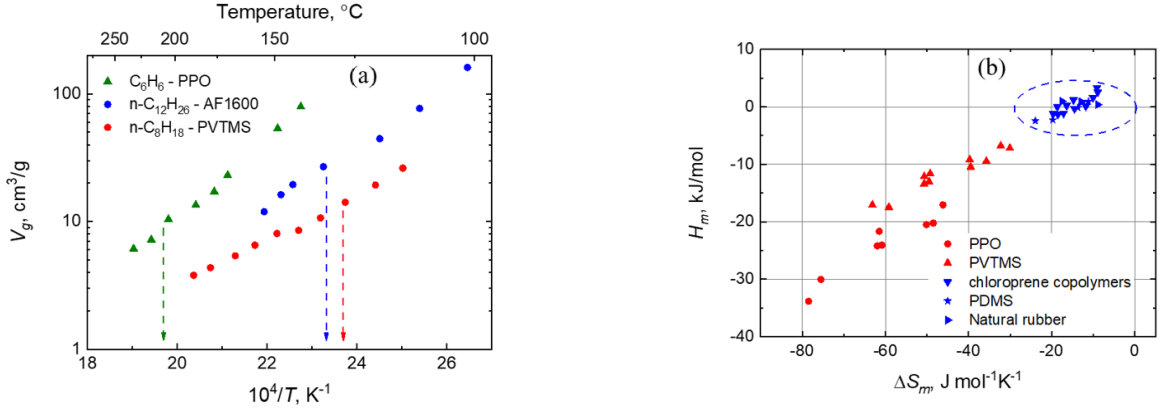


Fig. 7. (a) Retention diagrams of benzene-PPO, n-dodecane-AF1600, and n-octane-PVTMS systems in passing through glass transition temperature (T_g denoted by arrows); (b) diagram of partial molar enthalpy of mixing versus partial molar entropy of mixing for different solutes in glassy (red symbols) and rubbery (blue symbols) polymers

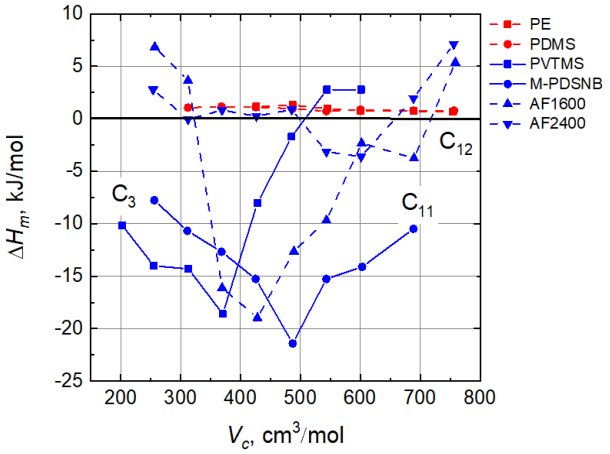


Fig. 8. A dependence of partial molar enthalpy of mixing ΔH_m on critical volume V_c of the n-alkane solutes.

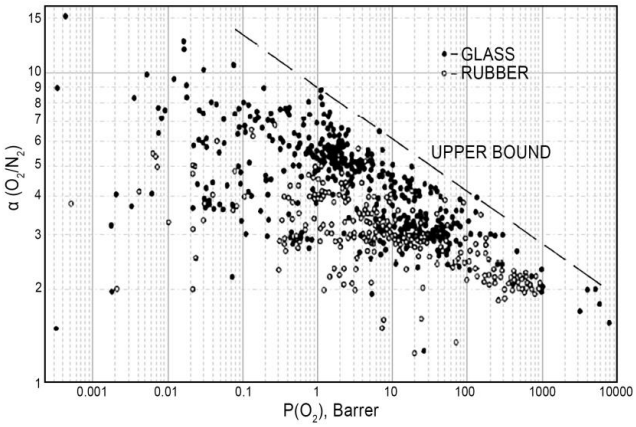


Fig. 9. Robeson diagram for O_2-N_2 gas pair [40].

4. The 'Gas separation properties of glassy polymers' Database and membrane gas transport properties predictions

The most known work on the systematization of numerous permeability (P) and selectivity (α) data for polymers was performed by Robeson in 1991 [40]. This work contained correlations of selectivity versus permeability of polymer membranes (so-called, Robeson diagrams), and laid the foundations of permeability/selectivity trade-off investigation [133]. Robeson diagrams were plotted using data from over 300 references, and an example of such a diagram is provided in Fig. 9.

As shown in Fig. 1a data cloud is limited by the upper bound. The upper bound sets an aim for the researchers as the area above it represents the most promising polymers for membrane gas separation. Robeson's work became highly cited soon and was developed further by Robeson [41] and other researchers [134,135] to establish up-to-date upper bounds.

Membrane gas separation studying is quite well developed at A.V. Topchiev Institute of Petrochemical Synthesis, RAS (TIPS RAS). It can't be argued that Yuri Pavlovich Yampolskii had a great deal in the popularization of this research field in Russia and globally. Yampolskii started to accumulate literature on the gas transport properties of polymers in the 1980s. This literature included data collected in TIPS RAS and also data published by international research groups. Robeson's work, mentioned above, made a great impression on Yampolskii, and it became obvious that the dataset collected by him can be further expanded and used as a tool to study property-property and structure-property relationships on a big range of different polymers. Yampolskii gathered a team that was supposed to work on the Database with him. This team included Shishatskii, Ishunina, and Alentiev. The decision was made that the future Database will contain information about glassy amorphous polymers, and in the middle 1990s, thanks to the collective work of Yampolskii's group, the Database [136] consisted of 311 polymers already. This dataset was considered sufficient to initiate the first attempts to predict gas transport properties of polymers by their chemical structure.

Different methods used to predict the properties of various substances are the following: group contribution methods [137–140], graph theory [141–143], artificial neural networks [144–146], and computer modeling [147–153]. First attempts to predict the Physico-chemical properties of different low molecular weight organic substances were made in the 1930s-1940s [154,155]. A group contribution method was later used to predict a wide range of hydrocarbons properties [156]. These methods were further applied in the scope of chemical kinetics [157–159] and developed by international researchers [160–164].

It was very tempting to start predicting polymer properties by group contribution methods, though there were always difficulties in the transition from low molecular weight to high molecular weight compounds. Nevertheless, examples of attempts to predict polymer properties can be found in [165–168]. A huge influence on the development of group contribution methods had Van Krevelen's book [137]. It systematically considered the possibilities of calculation and prediction of various properties of polymers, including density, coefficient of thermal expansion, heat capacity, mechanical properties, and even some sorption and mass transfer processes parameters. Van Krevelen had noted that it is possible to perform predictions using different additive methods, i.e. by atomic, group, or bond contributions, however, he had chosen to split the structure by groups as a preferable method. These groups may be both by individual atoms (e.g., -O-, -Cl-) and bigger fragments (e.g., $-CH_3$, $-C_6H_4-$). Van Krevelen method is widely accepted and applied to calculate unknown properties of new polymers.

A series of independent methods were also developed for polymer properties prediction. Bicerano [169] proposed to use topological indices of connectivity, based on graph theory to represent the polymer structure and predict its properties. This method is hard to comprehend as the formulas used for calculations include correction factors of an unknown origin.

Askadskii's semi-empirical methods complex [138,170] seems quite reliable. It is based on calibration using well-known model polymers as standards. Calculation of polymer properties takes into account the basic concepts of solid-state physics. The van-der-Waals volume of the atoms constituting a repeat unit of a polymer serves as a fundamental characteristic. A repeat unit was presented as a set of anharmonic oscillators, composed of atom pairs of the repeat unit. The energy of intermolecular interaction is considered in some cases, for example, for coefficients of thermal expansion or glass transition temperature calculation.

One can see that quite an impressive foundation was built to start implementing classical prediction methods to calculate gas transport properties of membrane polymer materials. In Salame's works [171–173] new concept of the Permachor (π) parameter is proposed. This parameter characterizes each group of the repeat unit, and gas permeability was calculated by the formula $P=A\cdot\exp(-s\cdot\pi)$. This method contained some debatable moments. First of all, the calculation was performed for the polymers of glassy, semi-crystalline, and rubber polymers collectively, so the same group could have had different values depending on, for example, the degree of crystallinity. In addition, different polymers with the same permeability value should have had the same selectivity level.

The first reliable predictions by group contribution methods were performed in [139,140,174] at the end of the 1990s. These studies were based on splitting the polymer structures into relatively big structural fragments. The accuracy of these predictions was very high, however, it was later noted in [175] that this accuracy could've been associated with the preliminary selection of the data and omitting the results that could add to the dispersion.

At approximately that time, the team of Yampolskii with the help of its new member, young student Kirill Loza, started to publish a series of articles on gas transport properties prediction. In the framework of the first work performed by the Yampolskii team [20], ~300 polymers from the Database [136] were split into the following groups: H, C(sp^3), C(sp^2), C(aromatic–sp^2), O=, -O-, Si, Cl, Br, F, -N<, =S=, -S-. The calculations were performed for six main gases important for membrane gas separation: H_2, He, O_2, N_2, CO_2, and CH_4. The best results were achieved when groups were attributed to the polymer backbone or side group separately. This method was called the modified atomic contributions method. The need to bring all data points to the same temperature prompted the study of the correlation of permeability with an apparent activation energy of permeation (E_P) [176]. The results of this work are still used by the Membrane Gas Separation Laboratory of TIPS RAS

to estimate E_P for the polymers, for which no temperature dependences of gas transport parameters were measured. Good accuracy of predictions was shown in [20] for polyimides and polynorbornenes. However, the group contribution methods were further developed for polyimides: in [177] polyimides gas transport parameters were predicted using the presentation of this vast class of condensation polymers as alternating copolymers of dianhydrides and diamines. So, each dianhydride and diamine acted as a whole fragment, which has its contributes to the gas permeability or diffusivity. It should be noted, that this work was inspirational for other investigators. For example, in 2015 Velioglu and Tantekin-Ersolmaz published their work [178] on the prediction of copolyimides gas permeability that provided great results and accuracy.

There are different possible uses of the Database. For example, it can be used to select membrane materials for specific purposes [179]. It is also applicable for the investigation of the dependencies between transport characteristics and physicochemical parameters of polymers within the framework of well-known theoretical models on a representative dataset. For example, the theory of free volume describes well the correlation of diffusion and permeability coefficients with the inverse free volume for polymers of a similar structure. However, for a large dataset (even, for example, for polyimides with similar structure [180]) these correlations become mediocre at best because of large uncertainties in the quantitative determination of the free volume. Removing this uncertainty by solving the system of equations for a pair of gases lead to the development of the so-called "paired correlations" method, which determines the relationship between permeability and diffusion coefficients for various gas pairs with high accuracy [181] and which shows the dependencies of these correlations on the penetrant parameters (Fig. 10).

A year earlier, B.D. Freeman published similar dependencies based on the theory of activated diffusion [133], and later this was confirmed independently by Robeson [182] and Teplyakov [183]. The use of the Database as a source of interconnected information made it possible to identify the relationship of the free volume with the diffusion activation energy [184], the connection of the solubility with the surface area of the penetrant molecule [185], the connection of transport parameters with the size of the elements of the free volume [186], the effect of temperature on the transport characteristics of polymers [187], and many more.

The work on the Database was continued in the Yampolskii Laboratory, and in the 2000s this base has already contained information for about 650 homopolymers. In the 2010s the theoretical work on Database and properties prediction had a new start with the development of the bond contribution method [188–190]. With the careful supervision of Yampolskii his student, V. Ryzhikh, started to work in this computer-based theoretical field. To date, the Database contains information on gas transport parameters of about 1400 polymer materials.

Other databases of polymer properties are also available [191,192]. There are some differences regarding their features (and, consequently, functions) and contents. The comparison between the three databases is presented below in Table 1. It should be mentioned that at some point the Database of TIPS RAS was expanded by the addition of data on gas solubility coefficient. An important source to perform this work was the handbook [193] that Yampolskii worked on. It contained a set of solubility coefficient data for various polymers and served as a starting point for the expansion of the Database. These data were helpful when a new direction was taken to a more physically meaningful representation of polymers: a presentation as a set of oligomer conformations. At that time new gas solubility predictions method based on oligomeric molecule geometry was developed in collaboration with M.V. Goubko's team [194–197].

Yampolskii always had an interest in so-called 'computer chemistry', thus, when in the 1990s-2000s compute power improved drastically and molecular dynamics of polymers became quite popular, Yampolskii decided to take part in studies of this sort. Yampolskii had a fruitful collaboration with the D. Hofmann team. They studied a polymer structure and quantitatively assessed free volume value and distribution [149,150,198,199]. Some attempts were also made in the prediction of gas transport parameters both by Hofmann [200] and Economou [201] teams. Later new collaboration occurred with Mazo and Balabaev. This partnership is active to date and a series of works on the investigation of free volume, its morphology, and composition has been published recently [202,203].

Table 1
Comparison of databases including gas transport properties of polymers and polymer-containing membranes

Features	TIPS Database [136]	Poly Info [191]	Polymer Gas Separation Membrane Database (Membrane Society of Australasia) [192]
Structure representation	Computer-recognized	Computer-recognized	No information on a structure
Structure search	Yes	Yes	No
The ability for a user to retrieve data	Yes, for an authorized user. No open access currently	Possible	Yes, a downloadable MS Excel file is present
Functions	-Reference data -Polymer structure-property relationship determination -Properties prediction using group contribution method -Machine learning	-Reference data -Machine learning	-Reference data -The Robeson diagram is plotted online -Machine learning disregarding the structure
Contents			
The overall number of polymer materials	~1400	~20000 (~1200 for transport properties)	~1500
Types of objects	Glassy homopolymers, glassy copolymers Rubbery, semi-crystalline, hyperbranched polymers are being added currently	Glassy and rubbery homo- and copolymers, semi-crystalline polymers, polymer blends, polymer composites	Glassy and rubbery homo- and copolymers, semi-crystalline polymers, polymer composites, doped polymers, carbon molecular sieves
Gas permeability	Yes	Yes	Yes
Gas diffusion	Yes	Yes	No
Gas sorption	Yes	Yes	No
Activation energies of gas transport properties	Yes	No	No
Physicochemical properties	Yes	Yes	No
Mechanical properties	No	Yes	No
Electrical properties	No	Yes	No
Optical properties	No	Yes	No

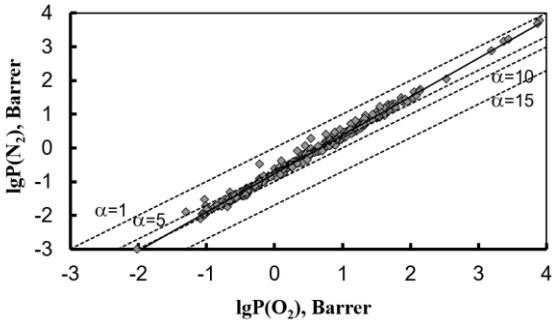


Fig. 10. Correlation of permeability coefficients for O_2/N_2 gas pair.

Conclusions

In retrospect, his influence on the development of membrane science in the USSR, Russian Federation, and the whole world was substantial and is difficult to estimate as of yet. In this short review, we tried to collect, observe and describe the main fields that Yuri Pavlovich Yampolskii was working on. His ability to spark one's interest at tet-a-tet conversations in the laboratory, during the conferences and patience always motivated him to begin novel experiments, explore novel types of polymers, and discover novel techniques. Yampolskii was also an excellent educator, and his students now proceed with their membrane-related projects over the world.

References

[1] Yu. P. Yampolskii, E. G. Novitskiy, S. G. Durgarjan, N. S. Nametkin, Permeability and diffusion of hydrocarbons through polyvinyl trimethyl silane, Vysokomol. Soedin. B, 20 (1978) 632–635.

[2] Yu. P. Yampol'skii, L. B. Krentsel, A. A. Azizov, S. G. Durgar'yan, A. D. Litmanovich, Gas permeability of chlorinated polyvinyl trimethyl silane, Polym. Sci. USSR, 22 (1980) 506–511 doi: 10.1016/0032-3950(80)90032-5.

[3] Yu. P. Yampol'skii, V. V. Volkov, N. E. Kalyuzhnyi, S. G. Durgar'yan, Permeability, diffusion and sorption of SO2 in polyvinyltrimethyl silane membranes, Polym. Sci. USSR, 26(8) (1984) 1832–1840 doi: 10.1016/0032-3950(84)90360-5.

[4] Yu. P. Yampol'skii, N. K. Gladkova, V. G. Filippova, S. G. Durgar'yan, Permeability of silane-siloxane block-copolymers to hydrocarbons, Polym. Sci. USSR, 27 (1985) 2155–2164 doi: 10.1016/0032-3950(85)90500-3.

[5] Yu. P. Yampolskii, S. G. Durgarjan, N. S. Nametkin, Permeability, diffusion and solubility of n-alkanes in polymers, Vysokomol. Soedin. B, 21(8) (1979) 616–621.

[6] N. A. Plate, S. G. Durgarjan, V. S. Khotimskii, V. V. Teplyakov, Yu. P. Yampol'skii, Novel poly(silicon olefins) for gas separations, J. Membr. Sci., 52 (1990) 289–304 doi: 10.1016/S0376-7388(00)85133-9.

[7] S. G. Durgar'yan, Y. P. Yampol'skii, N. A. Plate, Selectively Permeable Polymers and Gas-separation Membranes: Structure and Transport Properties, Russ. Chem. Rev., 57 (1988) 549–558 doi: 10.1070/RC1988v057n06ABEH003371.

[8] Yu. P. Yampol'skii, S. G. Durgan'yan, N. S. Nametkin, Coefficients of translational and rotational diffusion of low-molecular compounds in polymers with various glass transition temperatures, Polym. Sci. USSR, 24 (1982) 592–598 doi: 10.1016/0032-3950(82)90048-X.

[9] V. V. Volkov, A. V. Gol'danskii, S. G. Durgar'yan, V. A. Onishchuk, V. P. Shantorovich, Yu. P. Yampol'skii, A positron annihilation method of studying the microstructure of polymers in relation to their diffusional properties, Polym. Sci. USSR, 29 (1987) 217–224 doi: 10.1016/0032-3950(87)90104-3.

[10] Yu. P. Yampolskii, V. P. Shantarovich, Chemical structure and free volume of polymers in prediction of their membrane properties, Vysokomol. Soedin. C, 43 (2001) 2329–2349.

[11] V. P. Shantarovich, T. Suzuki, Y. Ito, K. Kondo, R. S. Yu, P. M. Budd, Y. P. Yampolskii, S. S. Berdonosov, A. A. Eliseev, Structural heterogeneity in glassy polymeric materials revealed by positron annihilation and other supplementary techniques, Phys. Status Solidi C, 4 (2007) 3776–3779 doi: 10.1002/pssc.200675852.

[12] V. P. Shantarovich, I. B. Kevdina, Yu. P. Yampolskii, A. Yu. Alentiev, Positron Annihilation Lifetime Study of High and Low Free Volume Glassy Polymers: Effects of Free Volume Sizes on the Permeability and Permselectivity, Macromolecules, 33 (2000) 7453–7466 doi: 10.1021/ma000551+.

[13] V. P. Shantarovich, Z. K. Azamatova, Y. A. Novikov, Y. P. Yampolskii, Free-Volume Distribution of High Permeability Membrane Materials Probed by Positron Annihilation, Macromolecules, 31 (1998) 3963–3966 doi: 10.1021/ma971128c.

[14] Y. Yampolskii, V. Shantarovich, Positron Annihilation Lifetime Spectroscopy and Other Methods for Free Volume Evaluation in Polymers, in: Y. Yampolskii, I. Pinnau, B. Freeman (Eds.), Materials Science of Membranes for Gas and Vapor Separation, John Wiley & Sons, Ltd, Chichester, UK, 2006, 191–210, doi: 10.1002/047002903X.ch6.

[15] Y. Yampolskii, Polymeric Gas Separation Membranes, Macromolecules, 45 (2012) 3298–3311 doi: 10.1021/ma300213b.

[16] Yu. P. Yampol'skii, N. A. Belov, A. Yu. Alentiev, Nanostructure of gas separation membrane materials, in: A. B. Yaroslavtsev (Ed.), Nanomaterials: Properties and Prospective Applications, Scientific World, Moscow, (2014) 114–145.

[17] Y. Yampolskii, I. Pinnau, B. Freeman, Eds., Materials Science of Membranes for Gas and Vapor Separation: Freeman/Materials Science of Membranes for Gas and Vapor Separation. John Wiley & Sons, Ltd, Chichester, UK, 2006.

[18] Y. Yampolskii, E. Finkelshtein, Eds., Membrane Materials for Gas and Vapor Separation: Synthesis and Application of Silicon-Containing Polymers. John Wiley & Sons, Ltd, Chichester, UK, (2017).

[19] D. R. Paul, Y. P. Yampolskii, Eds., Polymeric gas separation membranes. CRC Press, Boca Raton, 1994.

[20] Yu. Yampolskii, S. Shishatskii, A. Alentiev, K. Loza, Group contribution method for transport property predictions of glassy polymers: focus on polyimides and polynorbornenes, J. Membr. Sci., 149 (1998) 203–220 doi: 10.1016/S0376-7388(98)00152-5.

[21] Yu. P. Yampol'skii, V. V. Volkov, Studies in gas permeability and membrane gas separation in the Soviet Union, J. Membr. Sci., 64 (1991) 191–228 doi: 10.1016/0376-7388(91)80092-K.

[22] D. R. Paul, Yu. P. Yampol′skii, Polymeric gas separation membranes. 2018.

[23] Y. P. Yampolskii, N. A. Belov, A. Y. Alentiev, Fluorine in the structure of polymers: influence on the gas separation properties, Russ. Chem. Rev., 88 (2019) 387–405 doi: 10.1070/RCR4861.

[24] Yu. Yampolskii, N. Belov, A. Alentiev, Perfluorinated polymers as materials of membranes for gas and vapor separation, J. Membr. Sci., 598 (2020) 117779 doi: 10.1016/j.memsci.2019.117779.

[25] Yu. P. Yampolskii, S. G. Durgarjan, N. S. Nametkin, Permeability, diffusion and solubility of n-alkanes in polymers, Vysokomol. Soedin. B, 21 (1979) 616–621.

[26] Yu. P. Yampol'skii, N. E. Kalyuzhnyi, Excess mixing functions in polymers and low-molecular-weight solvents, Polym. Sci. USSR, 29 (1987) 2418–2423 doi: 10.1016/0032-3950(87)90176-6.

[27] M. B. Davydova, Yu. P. Yampol'skii, S. G. Durgar'yan, Sorption of hydrocarbons in polyvinyl trimethyl silane and polydimethylsiloxane with nickel acetylacetonate additives, Polym. Sci. USSR, 30 (1988) 1501–1507 doi: 10.1016/0032-3950(88)90437-6.

[28] E. Sh. Finkelshtein, N. V. Ushakov, E. G. Krasheninnikov, Yu. P. Yampolskii, New polysilalkylenes: synthesis and gas-separation properties, Russ. Chem. Bull., 53 (2004) 2604–2610 doi: 10.1007/s11172-005-0161-3.

[29] L. E. Starannikova, N. A. Belov, V. P. Shantorovich, T. Suzuki, T. G. Golenko, K. L. Makovetskii, Yu. P. Yampol'skii, Transport and physicochemical parameters of polypentenamer, Polym. Sci. Ser. A, 49 (2007) 509–516 doi: 10.1134/S0965545X07050045.

[30] V. S. Khotimskii, V. G. Filippova, I. S. Bryantseva, V. I. Bondar, V. P. Shantarovich, Y. P. Yampolskii, Synthesis, transport, and sorption properties and free volume of polystyrene derivatives containing Si and F, J. Appl. Polym. Sci., 78 (2000) 1612–1620 doi: 10.1002/1097-4628(20001128)78:9<1612::aid-app60>3.0.co;2-t.

[31] A. Y. Alent'ev, Yu. P. Yampol'skii, A. L. Rusanov, D. Likhatchev, G. V. Kazakova, L. Komarova, M. P. Prigozhina, Transport Properties of Poly(ether imides), Polym. Sci. - Ser. A, 45 (2003) 933–939.

[32] N. Belov, R. Chatterjee, R. Nikiforov, V. Ryzhikh, S. Bisoi, A. G. Kumar, S. Banerjee, Yu. Yampolskii, New poly(ether imide)s with pendant di-tert-butyl groups: Synthesis, characterization and gas

transport properties, Sep. Purif. Technol., 217 (2019) 183–194 doi: 10.1016/j.seppur.2019.02.017.

[33] R. Chatterjee, A. G. Kumar, R. Nikiforov, V. Ryzhikh, N. Belov, V. Padmanabhan, Y. Yampolskii, S. Banerjee, Novel semi-fluorinated poly(ether imide)s with benzyl ether side groups: Synthesis, physicochemical characterization, gas transport properties and simulation, Eur. Polym. J., 135 (2020) doi: 10.1016/j.eurpolymj.2020.109879.

[34] Yu. P. Y. E .G. Bulycheva L. B. Elshina, A. L. Rusanov, A. Yu. Alentiev, Yu. G. Ishunina, Transport properties of polynaphtylimides, Polym. Sci. - Ser. B, 39 (1997) 390.

[35] Y. Y. A. Korikov Ya. S. Vygodskii, Transport properties of cardo poly(imides): homo- and copolymers, Polym. Sci. Ser. A, 43(6) (2001) 638–646.

[36] V. P. Shantarovich, T. Suzuki, C. He, Y. Ito, Y. P. Yampolskii, A. Y. Alentiev, Positron annihilation in PI189 and PI304 polyimides, Radiat. Phys. Chem., 73 (2005) 45–53 doi: 10.1016/j.radphyschem.2004.06.005.

[37] A. Alentiev, E. Drioli, M. Gokzhaev, G. Golemme, O. Ilinich, A. Lapkin, V. Volkov, Y. Yampolskii, Gas permeation properties of phenylene oxide polymers, J. Membr. Sci., 138 (1998) 99–107 doi: 10.1016/s0376-7388(97)00219-6.

[38] A. Y. Alentiev, I. S. Levin, M. I. Buzin, N. A. Belov, R. Y. Nikiforov, S. V. Chirkov, I. V. Blagodatskikh, A. S. Kechekyan, P. A. Kechekyan, V. G. Bekeshev, V. E. Ryzhikh, Yu. P. Yampolskii, Gas transport parameters, density and free volume of nanocrystalline poly-2,6-dimethylphenylene oxide, Polymer, 226 (2021) 123804 doi: 10.1016/j.polymer.2021.123804.

[39] I. M. Tkachenko, N. A. Belov, Y. V. Yakovlev, P. V. Vakuliuk, O. V. Shekera, Y. P. Yampolskii, V. V. Shevchenko, Synthesis, gas transport and dielectric properties of fluorinated poly(arylene ether)s based on decafluorobiphenyl, Mater. Chem. Phys., 183 (2016) 279–287 doi: 10.1016/j.matchemphys.2016.08.028.

[40] L. M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, J. Membr. Sci., 62 (1991) 165–185 doi: 10.1016/0376-7388(91)80060-J.

[41] L. M. Robeson, The upper bound revisited, J. Membr. Sci., 320 (2008) 390–400 doi: 10.1016/j.memsci.2008.04.030.

[42] N. S. Nametkin, V. S. Khotimskii, S. G. Durgar'yan, Synthesis of high molecular weight poly(vinyl trimethylsilane) and some of its properties, Dokl. Akad. Nauk SSSR, 166 (1966) 1118–1120.

[43] N. E. Kalyuzhnyi, Yu. P. Yampol'skii, Chromatographic determination of the Flory-Huggins parameter and solubility parameter of polyvinyl trimethyl silane, Polym. Sci. USSR, 31 (1989) 1883–1888 doi: 10.1016/0032-3950(89)90024-5.

[44] A. M. Shishatskii, Yu. P. Yampol'skii, K.-V. Peinemann, Effects of film thickness on density and gas permeation parameters of glassy polymers, J. Membr. Sci., 112 (1996) 275–285 doi: 10.1016/0376-7388(95)00301-0.

[45] T. Masuda, E. Isobe, T. Higashimura, K. Takada, Poly[1-(trimethylsilyl)-1-propyne]: a new high polymer synthesized with transition-metal catalysts and characterized by extremely high gas permeability, J. Am. Chem. Soc., 105 (1983) 7473–7474 doi: 10.1021/ja00363a061.

[46] T. Masuda, B. Z. Tang, T. Higashimura, H. Yamaoka, Thermal degradation of polyacetylenes carrying substituents, Macromolecules, 18(12) (1985) 2369–2373 doi: 10.1021/ma00154a006.

[47] Shimomura H., Nakanishi K., Odani H., Kurata M., Masuda T., Higashimura T., Permeation of gases in poly(1-(trimethylsilyl)-1-propyne), Kobunshi Ronbunshu, 43 (1986) 747–753 doi: 10.1295/koron.43.747.

[48] N. A. Platé, A. K. Bokarev, N. E. Kaliuzhnyi, E. G. Litvinova, V. S. Khotimskii, V. V. Volkov, Y. P. Yampolskii, Gas and vapor permeation and sorption in poly (trimetylsilylpropyne), J. Membr. Sci., 60 (1991) 13–24 doi: 10.1016/s0376-7388(00)80321-x.

[49] Y. P. Yampol'skii, S. M. Shishatskii, V. P. Shantorovich, E. M. Antipov, N. N. Kuzmin, S. V. Rykov, V. L. Khodjaeva, N. A. Platé, Transport characteristics and other physicochemical properties of aged poly(1-(trimethylsilyl)-1-propyne), J. Appl. Polym. Sci., 48 (1993) 1935–1944 doi: 10.1002/app.1993.070481107.

[50] Yu. P. Yampol'skii, V. P. Shantorovich, F. P. Chernyakovskii, A. I. Kornilov, N. A. Plate, Estimation of free volume in poly(trimethylsilyl propyne) by positron annihilation and electrochromism methods, J. Appl. Polym. Sci., 47 (1993) 85–92 doi: 10.1002/app.1993.070470111.

[51] V. Bondar, A. Alentiev, T. Masuda, Y. Yampolskii, Gas sorption in substituted polyacetylenes, Macromol. Chem. Phys., 198 (1997) 1701–1708 doi: 10.1002/macp.1997.021980601.

[52] L. G. Toy, K. Nagai, B. D. Freeman, I. Pinnau, Z. He, T. Masuda, M. Teraguchi, Y. P. Yampolskii, Pure-Gas and Vapor Permeation and Sorption Properties of Poly[1-phenyl-2-[p-(trimethylsilyl)phenyl]acetylene] (PTMSDPA), Macromolecules, 33 (2000) 2516–2524 doi: 10.1021/ma991566e.

[53] Y. P. Yampolskii, A. P. Korikov, V. P. Shantarovich, K. Nagai, B. D. Freeman, T. Masuda, M. Teraguchi, G. Kwak, Gas Permeability and Free Volume of Highly Branched Substituted Acetylene Polymers, Macromolecules, 34 (2001) 1788–1796 doi: 10.1021/ma000628u.

[54] E. S. Finkelshtein, K. L. Makovetskii, Y. P. Yampolskii, E. B. Portnykh, I. Y. Ostrovskaya, N. E. Kaliuzhnyi, N. A. Pritula, A. I. Golberg, M. S. Yatsenko, N. A. Platé, Ring-opening metathesis polymerization of norbornenes with organosilicon substituents. Gas permeability of polymers obtained, Makromol. Chem., 192 (1991) 1–9 doi: 10.1002/macp.1991.021920101.

[55] E. Sh. Finkel'shtein, E. B. Portnykh, K. L. Makovetskii, I. Ya. Ostrovskaya, M. L. Gringol'ts, U. M. Dzhemilev, A. I. Goldberg, Metathesis of spirocyclo[2.2.1]hept-2-ene-7,1'-cyclopropane, Russ. Chem. Bull., 42 (1993) 124–125 doi: 10.1007/BF00699991.

[56] E. Sh. Finkel'shtein, N. B. Bespalova, E. B. Portnykh, K. L. Makovetskii, I. Y. Ostrovskaya, S. M. Shishatskii, Yu. P. Yampolskii, N. A. Plate, N. E. Kaliuzhniy, Synthesis and gas permeability of halogen derivatives of norbornene polymers, Polym. Sci. - Ser. A, (1993).

[57] V. I. Bondar, Yu. M. Kukharskii, Yu. P. Yampol'skii, E. Sh. Finkelshtein, K. L. Makovetskii, Permeation and sorption in polynorbornenes with organosilicon substituents, J. Polym. Sci. Part B Polym. Phys., 31 (1993) 1273–1283 doi: 10.1002/polb.1993.090311002.

[58] Y. P. Yampol'skii, N. B. Bespalova, E. S. Finkelshtein, V. I. Bondar, A. V. Popov, Synthesis, Gas Permeability, and Gas Sorption Properties of Fluorine-Containing Norbornene Polymers, Macromolecules, 27 (1994) 2872–2878 doi: 10.1021/ma00088a030.

[59] Yu. P. Yampol'skii, E. Sh. Finkelshtein, K. L. Makovetskii, I. Y. Ostrovskaya, E. B. Portnykh, M. L. Gringolts, Yu. G. Ishunina, I. B. Kevdina, V. P. Shantarovich, Synthesis and transport properties of polynorbornene with different content of cis-trans units, Polym. Sci. - Ser. A, 38 (1996) 959–963.

[60] Y. P. Yampolskii, E. S. Finkelshtein, K. L. Makovetskii, V. I. Bondar, V. P. Shantarovich, Effects of cis-trans-configurations of the main chains of poly(trimethylsilyl norbornene) on its transport and sorption properties as well as free volume, J. Appl. Polym. Sci., 62 (1996) 349–357 doi: 10.1002/(sici)1097-4628(19961010)62:2<349::aid-app9>3.0.co;2-x.

[61] E. S. Finkelshtein, K. L. Makovetskii, M. L. Gringolts, Y. V. Rogan, T. G. Golenko, L. E. Starannikova, Y. P. Yampolskii, V. P. Shantarovich, T. Suzuki, Addition-Type Polynorbornenes with $Si(CH_3)_3$ Side Groups: Synthesis, Gas Permeability, and Free Volume, Macromolecules, 39 (2006) 7022–7029 doi: 10.1021/ma061215h.

[62] L. Starannikova, M. Pilipenko, N. Belov, Y. Yampolskii, M. Gringolts, E. Finkelshtein, Addition-type polynorbornene with $Si(CH_3)_3$ side groups: Detailed study of gas permeation and thermodynamic properties, J. Membr. Sci., 323 (2008) 134–143 doi: 10.1016/j.memsci.2008.06.009.

[63] M. L. Gringolts, M. V. Bermeshev, L. E. Starannikova, Y. V. Rogan, Y. P. Yampol'skii, E. S. Finkel'shtein, Synthesis and gas separation properties of metathesis polynorbornenes with different positions of one or two $SiMe_3$ groups in a monomer unit, Polym. Sci. Ser. A, 51 (2009) 1233–1240 doi: 10.1134/s0965545x0911008x.

[64] M. Gringolts, M. Bermeshev, Y. Yampolskii, L. Starannikova, V. Shantarovich, E. Finkelshtein, New High Permeable Addition Poly(tricyclononenes) with $Si(CH_3)_3$ Side Groups. Synthesis, Gas Permeation Parameters, and Free Volume, Macromolecules, 43 (2010) 7165–7172 doi: 10.1021/ma100656e.

[65] M. V. Bermeshev, A. V. Syromolotov, M. L. Gringolts, L. E. Starannikova, Y. P. Yampolskii, E. S. Finkelshtein, Synthesis of High Molecular Weight Poly[3-{tris(trimethylsiloxy)silyl}tricyclononenes-7] and Their Gas Permeation Properties, Macromolecules, 44 (2011) 6637–6640 doi: 10.1021/ma201486d.

[66] E. S. Finkelshtein, M. V. Bermeshev, M. L. Gringolts, L. E. Starannikova, Y. P. Yampolskii, Substituted polynorbornenes as

promising materials for gas separation membranes, Russ. Chem. Rev., 80 (2011) 341–361 doi: 10.1070/rc2011v080n04abeh004203.

[67] M. Bermeshev, B. Bulgakov, D. Demchuk, M. Filatova, L. Starannikova, E. Finkelshtein, Metathesis and addition polymerization of novel Me_3Si- and Me_3Ge-substituted tricyclononenes, Polym. J., 45 (2012) 718–726 doi: 10.1038/pj.2012.211.

[68] M. V. Bermeshev, A. V. Syromolotov, L. E. Starannikova, M. L. Gringolts, V. G. Lakhtin, Y. P. Yampolskii, E. S. Finkelshtein, Glassy Polynorbornenes with Si–O–Si Containing Side Groups. Novel Materials for Hydrocarbon Membrane Separation, Macromolecules, 46 (2013) 8973–8979 doi: 10.1021/ma4021278.

[69] M. Bermeshev, B. Bulgakov, L. Starannikova, G. Dibrov, P. Chapala, D. Demchuk, Y. Yampolskii, E. Finkelshtein, Synthesis and gas permeation parameters of metathesis polytricyclononenes with pendant Me_3E-groups (E=C, Si, Ge), J. Appl. Polym. Sci., 132 (2014) 41395 doi: 10.1002/app.41395.

[70] N. Belov, Yu. Nizhegorodova, M. Bermeshev, Yu. Yampolskii, Detailed study of the gas permeation parameters of a glassy poly(tricyclononene) with Si–O–Si side groups, J. Membr. Sci., 483 (2015) 136–143 doi: 10.1016/j.memsci.2015.02.040.

[71] M. V. Bermeshev, L. E. Starannikova, S. R. Sterlin, A. A. Tyutyunov, A. N. Tavtorkin, Yu. P. Yampolskii, E. Sh. Finkelshtein, Synthesis and gas-separation properties of metathesis poly(3-fluoro-3-pentafluoroethyl-4,4-bis(trifluoromethyl)tricyclonene-7), Pet. Chem., 55 (2015) 753–758 doi: 10.1134/S0965544115050035.

[72] P. P. Chapala, M. V. Bermeshev, L. E. Starannikova, N. A. Belov, V. E. Ryzhikh, V. P. Shantarovich, V. G. Lakhtin, N. N. Gavrilova, Y. P. Yampolskii, E. S. Finkelshtein, A Novel, Highly Gas-Permeable Polymer Representing a New Class of Silicon-Containing Polynorbornens As Efficient Membrane Materials, Macromolecules, 48 (2015) 8055–8061 doi: 10.1021/acs.macromol.5b02087.

[73] N. A. Belov, M. L. Gringolts, A. A. Morontsev, L. E. Starannikova, Y. P. Yampolskii, E. S. Finkelstein, Gas-transport properties of epoxidated metathesis polynorbornenes, Polym. Sci. Ser. B, 5(5) (2017) 560–569 doi: 10.1134/s1560090417050025.

[74] D. A. Alentiev, M. V. Bermeshev, L. E. Starannikova, E. V. Bermesheva, V. P. Shantarovich, V. G. Bekeshev, Y. P. Yampolskii, E. Sh. Finkelshtein, Stereoselective synthesis and polymerization of Exo-5-trimethylsilylnorbornene, J. Polym. Sci. Part Polym. Chem., 56 (2018) 1234–1248 doi: 10.1002/pola.29003.

[75] D. A. Alentiev, E. S. Egorova, M. V. Bermeshev, L. E. Starannikova, M. A. Topchiy, A. F. Asachenko, P. S. Gribanov, M. S. Nechaev, Y. P. Yampolskii, E. Sh. Finkelshtein, Janus tricyclononene polymers bearing tri(n-alkoxy)silyl side groups for membrane gas separation, J. Mater. Chem. A, 6 (2018) 19393–19408 doi: 10.1039/C8TA06034G.

[76] A. A. Morontsev, V. A. Zhigarev, R. Y. Nikiforov, N. A. Belov, M. L. Gringolts, E. S. Finkelshtein, Y. P. Yampolskii, A new approach to improvement of gas permeation properties of olefin metathesis derived poly(norbornenes): gem-difluorocyclopropanation of backbone double bonds, Eur. Polym. J., 99 (2018) 340–349 doi: 10.1016/j.eurpolymj.2017.12.020.

[77] D. A. Alentiev, D. M. Dzhaparidze, M. V. Bermeshev, L. E. Starannikova, M. P. Filatova, Yu. P. Yampolskii, E. Sh. Finkelshtein, Addition Copolymerization of Silicon-Containing Tricyclononene with 2,5-Norbornadiene Dimer, Polym. Sci. Ser. B, 61 (2019) 812–816 doi: 10.1134/S1560090419060022.

[78] D. A. Alentiev, E. S. Egorova, M. V. Bermeshev, L. E. Starannikova, Y. P. Yampolskii, E. Sh. Finkelshtein, Crosslinking of addition copolymers from tricyclononenes bearing $(CH_3)_3Si$- and $(C_2H_5O)_3$ Si-groups as a modification of membrane gas separation materials, Polym. Eng. Sci., 59 (2019) 2502–2507 doi: 10.1002/pen.25128.

[79] P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib, C. E. Tattershall, Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials, Chem. Commun. 339 (2004) 230 doi: 10.1039/b311764b.

[80] P. Budd, N. McKeown, B. Ghanem, K. Msayib, D. Fritsch, L. Starannikova, N. Belov, O. Sanfirova, Y. Yampolskii, V. Shantarovich, Gas permeation parameters and other physicochemical properties of a polymer of intrinsic microporosity: Polybenzodioxane PIM-1, J. Membr. Sci., 325 (2008) 851–860 doi: 10.1016/j.memsci.2008.09.010.

[81] B. S. Ghanem, N. B. McKeown, P. M. Budd, N. M. Al-Harbi, D. Fritsch, K. Heinrich, L. Starannikova, A. Tokarev, Y. Yampolskii, Synthesis, Characterization, and Gas Permeation Properties of a Novel Group of Polymers with Intrinsic Microporosity: PIM-Polyimides, Macromolecules, 42 (2009) 7881–7888 doi: 10.1021/ma901430q.

[82] Y. Rogan, L. Starannikova, V. Ryzhikh, Y. Yampolskii, P. Bernardo, F. Bazzarelli, J. C. Jansen, N. B. McKeown, Synthesis and gas permeation properties of novel spirobisindane-based polyimides of intrinsic microporosity, Polym. Chem., 4 (2013) 3813–3820 doi: 10.1039/c3py00451a.

[83] E. Tocci, L. D. Lorenzo, P. Bernardo, G. Clarizia, F. Bazzarelli, N. B. Mckeown, M. Carta, R. Malpass-Evans, K. Friess, K. Pilnáček, M. Lanč, Y. P. Yampolskii, L. Straarannikova, V. Shantarovich, M. Mauri, J. C. Jansen, Molecular Modeling and Gas Permeation Properties of a Polymer of Intrinsic Microporosity Composed of Ethanoanthracene and Tröger's Base Units, Macromolecules, 47 (2014) 7900–7916 doi: 10.1021/ma501469m.

[84] L. Starannikova, N. Belov, V. Shantarovich, J. Zhang, J. Jin, Y. Yampolskii, Effective increase in permeability and free volume of PIM copolymers containing ethanoanthracene unit and comparison between the alternating and random copolymers, J. Membr. Sci., 548 (2018) 593–597 doi: 10.1016/j.memsci.2017.11.049.

[85] I. I. Ponomarev, K. M. Skupov, K. A. Lyssenko, I. V. Blagodatskikh, A. V. Muranov, Y. A. Volkova, D. Yu. Razorenov, I. I. Ponomarev, L. E. Starannikova, D. A. Bezgin, A. Yu. Alentiev, Y. P. Yampolskii, New PIM-1 copolymers containing 2,3,6,7-anthracenetetrayl moiety and their use as gas separation membranes, Mendeleev Commun., 30 (2020) 734–737 doi: 10.1016/j.mencom.2020.11.015.

[86] I. I. Ponomarev, D. Yu. Razorenov, I. V. Blagodatskikh, A. V. Muranov, L. E. Starannikova, A. Yu. Alent'ev, R. Yu. Nikiforov, Yu. P. Yampol'skii, Polymer with Intrinsic Microporosity PIM-1: New Methods of Synthesis and Gas Transport Properties, Polym. Sci. Ser. B, 61 (2019) 605–612 doi: 10.1134/S1560090419050142.

[87] L. E. Starannikova, A. Yu. Alentiev, R. Yu. Nikiforov, I. I. Ponomarev, I. V. Blagodatskikh, A. Yu. Nikolaev, V. P. Shantarovich, Yu. P. Yampolskii, Effects of different treatments of films of PIM-1 on its gas permeation parameters and free volume, Polymer, 212 (2021) 123271 doi: 10.1016/j.polymer.2020.123271.

[88] A. Yu. Alentiev, Yu. P. Yampolskii, V. P. Shantarovich, S. M. Nemser, N. A. Platé, High transport parameters and free volume of perfluorodioxole copolymers, J. Membr. Sci., 126 (1997) 123–132 doi: 10.1016/S0376-7388(96)00272-4.

[89] V. I. Bondar, B. D. Freeman, Yu. P. Yampolskii, Sorption of Gases and Vapors in an Amorphous Glassy Perfluorodioxole Copolymer, Macromolecules, 32 (1999) 6163–6171 doi: 10.1021/ma9817222.

[90] T. C. Merkel, V. Bondar, K. Nagai, B. D. Freeman, Yu. P. Yampolskii, Gas Sorption, Diffusion, and Permeation in Poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole-*co*-tetrafluoroethylene), Macromolecules, 32 (1999) 8427–8440 doi: 10.1021/ma990685r.

[91] A. Yu. Alentiev, V. P. Shantarovich, T. C. Merkel, V. I. Bondar, B. D. Freeman, Yu. P. Yampolskii, Gas and Vapor Sorption, Permeation, and Diffusion in Glassy Amorphous Teflon AF1600, Macromolecules, 35 (2002) 9513–9522 doi: 10.1021/ma020494f.

[92] N. A. Belov, A. A. Zharov, A. V. Shashkin, M. Q. Shaikh, K. Raetzke, Yu. P. Yampolskii, Gas transport and free volume in hexafluoropropylene polymers, J. Membr. Sci., 383 (2011) 70–77 doi: 10.1016/j.memsci.2011.08.029.

[93] N. Belov, Yu. Nizhegorodova, A. Zharov, I. Konovalova, V. Shantarovich, Yu. Yampolskii, A new polymer, poly(perfluoropropylvinyl ether) and its comparison with other perfluorinated membrane materials, J. Membr. Sci., 495 (2015) 431–438 doi: 10.1016/j.memsci.2015.08.037.

[94] R. Nikiforov, N. Belov, A. Zharov, I. Konovalova, B. Shklyaruk, Yu. Yampolskii, Gas permeation and diffusion in copolymers of tetrafluoroethylene and hexafluoropropylene: Effect of annealing, J. Membr. Sci., 540 (2017) 129–135 doi: 10.1016/j.memsci.2017.06.006.

[95] N. Belov, R. Nikiforov, E. Polunin, Yu. Pogodina, I. Zavarzin, V. Shantarovich, Yu. Yampolskii, Gas permeation, diffusion, sorption and free volume of poly(2-trifluoromethyl-2-pentafluoroethyl-1,3-perfluorodioxole), J. Membr. Sci., 565 (2018) 112–118 doi: 10.1016/j.memsci.2018.07.077.

[96] J.-M. Braun, J. E. Guillet, Study of polymers by inverse gas chromatography, in: Mechanisms of Polyreactions-Polymer Characterization, 21, Springer Berlin Heidelberg, Berlin, Heidelberg, 1976, 107–145, doi: 10.1007/3-540-07727-8_5.

[97] A. Voelkel, Physicochemical measurements (inverse gas chromatography), in: Gas Chromatography, Elsevier, 2021, 561–579, doi: 10.1016/B978-0-12-820675-1.00013-7.

[98] S. Ng, H. G. Harris, Henry's constants for methane, ethane, ethylene, propane, and propylene in octadecane, eicosane, and docosane, J. Chem. Eng. Data, 14 (1969) 482–483 doi: 10.1021/je60043a014.
[99] Q. Du, P. Hattam, P. Munk, Inverse gas chromatography. 7. Polymer-solvent interactions of hydrocarbon polymers, J. Chem. Eng. Data, 35 (1990) 367–371 doi: 10.1021/je00061a039.
[100] C. L. Young, Activity coefficients of solutions of C_4—C_8 hydrocarbons in n-tetracosane and n-dotriacontane, Trans Faraday Soc, 64 (1968) 1537–1546 doi: 10.1039/TF9686401537.
[101] S. H. Langer, R. J. Sheehan, J. C. Huang, Gas-chromatographic study of the solution thermodynamics of hydroxylic derivatives and related compounds, J. Phys. Chem., 86 (1982) 4605–4618 doi: 10.1021/j100220a029.
[102] R. J. Sheehan, S. H. Langer, Determination of Liquid-Liquid Distribution Coefficients by Gas-Liquid Chromatography, Ind. Eng. Chem. Process Des. Dev., 10 (1971) 44–47 doi: 10.1021/i260037a008.
[103] E. W. Funk, Study of Heavy Hydrocarbons by Inverse-Phase Chromatography, Prod. RD, 16 (1977) 115–120 doi: 10.1021/i360062a002.
[104] M. Schiller, J. Gmehling, Measurement of activity coefficients at infinite dilution using gas-liquid chromatography. 4. Results for alkylene glycol dialkyl ethers as stationary phases, J. Chem. Eng. Data, 37 (1992) 503–508 doi: 10.1021/je00008a030.
[105] P. Alessi, I. Kikic, A. Papo, G. Torriano, Gas chromatographic characterization of phosphate esters, J. Chem. Eng. Data, 23 (1978) 29–33 doi: 10.1021/je60076a001.
[106] F. Mutelet, V. Butet, J.-N. Jaubert, Application of Inverse Gas Chromatography and Regular Solution Theory for Characterization of Ionic Liquids, Ind. Eng. Chem. Res., 44 (2005) 4120–4127 doi: 10.1021/ie048806l.
[107] F. Mutelet, J.-N. Jaubert, Accurate measurements of thermodynamic properties of solutes in ionic liquids using inverse gas chromatography, J. Chromatogr. A, 1102 (2006) 256–267 doi: 10.1016/j.chroma.2005.10.046.
[108] C. Yao, J. L. Anderson, Retention characteristics of organic compounds on molten salt and ionic liquid-based gas chromatography stationary phases, J. Chromatogr. A, 1216 (2009) 1658–1712 doi: 10.1016/j.chroma.2008.12.001.
[109] C. F. Poole, S. K. Poole, Ionic liquid stationary phases for gas chromatography: Gas Chromatography, J. Sep. Sci., 34 (2011) 888–900 doi: 10.1002/jssc.201000724.
[110] Z. Witkiewicz, J. Oszczudłowski, M. Repelewicz, Liquid-crystalline stationary phases for gas chromatography, J. Chromatogr. A, 1062 (2005) 155–174 doi: 10.1016/j.chroma.2004.11.042.
[111] E. Ghanem, S. Al-Hariri, Separation of Isomers on Nematic Liquid Crystal Stationary Phases in Gas Chromatography: A Review, Chromatographia, 77 (2014) 653–662 doi: 10.1007/s10337-014-2675-z.
[112] H. Grajek, Z. Witkiewicz, M. Purchała, W. Drzewiński, Liquid Crystals as Stationary Phases in Chromatography, Chromatographia, 79 (2016) 1217–1245 doi: 10.1007/s10337-016-3154-5.
[113] O. Smidsrød, J. E. Guillet, Study of Polymer-Solute Interactions by Gas Chromatography, Macromolecules, 2 (1969) 272–277 doi: 10.1021/ma60009a012.
[114] S. Mohammadi-Jam, K. E. Waters, Inverse gas chromatography applications: A review, Adv. Colloid Interface Sci., 212 (2014) 21–44 doi: 10.1016/j.cis.2014.07.002.
[115] A. Voelkel, B. Strzemiecka, K. Adamska, K. Milczewska, Inverse gas chromatography as a source of physiochemical data, J. Chromatogr. A, 1216 (2009) 1551–1566 doi: 10.1016/j.chroma.2008.10.096.
[116] N. A. Belov, A. P. Safronov, Yu. P. Yampolskii, Inverse-gas chromatography and the thermodynamics of sorption in polymers, Polym. Sci. Ser. A, 54 (2012) Art. no. 11 doi: 10.1134/S0965545X1210001X.
[117] J. M. R. C. A. Santos, J. T. Guthrie, Analysis of interactions in multicomponent polymeric systems: The key-role of inverse gas chromatography, Mater. Sci. Eng. R Rep., 50(3) (2005) 79–107 doi: 10.1016/j.mser.2005.07.003.
[118] Yu. P. Yampolskii, S. G. Durgarjan, N. E. Kaliuzhnyi, Sorption of n-alkanes in poly(vinyltrimethylsilane) studied by inverse gas chromatography, J. Chromatogr. A, 286 (1984) 97–105 doi: 10.1016/S0021-9673(01)99176-9.
[119] Yu. P. Yampolskii, N. E. Kaliuzhnyi, S. G. Durgar'yan, Thermodynamics of sorption in glassy poly(vinyltrimethylsilane), Macromolecules, 19 (1986) 846–850 doi: 10.1021/ma00157a062.
[120] P. J. T. Tait, A. M. Abushihada, Comparative studies on the use of gas chromatographic and vapour pressure techniques for the determination of the interaction energy parameter, Polymer, 18 (1977) 810–816 doi: 10.1016/0032-3861(77)90186-0.
[121] P. J. T. Tait, A. M. Abushihada, Use of a Gas Chromatographic Technique for the Study of the Variation of the Interaction Energy Parameter with Temperature, Macromolecules, 11 (1978) 918–922 doi: 10.1021/ma60065a015.
[122] A. S. Glass, J. W. Larsen, Inverse gas chromatography of glassy polymer surfaces, Macromolecules, 26 (1993) 6354–6358 doi: 10.1021/ma00076a009.
[123] K. C. B. Dangayach, D. C. Bonner, Solvent interactions with polysulfone, Polym. Eng. Sci., 20 (1980) 59–64 doi: 10.1002/pen.760200110.
[124] M. B. Davydova, Yu. P. Yampolskii, An inverse gas chromatography study of sorption in polyphenylene oxide, Polym. Sci. USSR, 33 (1991) 495–501 doi: 10.1016/0032-3950(91)90249-P.
[125] Yu. P. Yampolskii, V. G. Berezkin, T. V. Popova, A. P. Korikov, B. D. Freeman, V. I. Bondar, T. C. Merkel, Thermodynamics of gas and vapor sorption by amorphous glassy AF Teflons, Polymer Science, 42 (2000) 1033–1034.
[126] N. A. Belov, A. P. Safronov, Yu. P. Yampolskii, Thermodynamics of Sorption in an Amorphous Perfluorinated Copolymer AF1600 Studied by Inverse Gas Chromatography, Macromolecules, 44 (2011) 902–912 doi: 10.1021/ma1025658.
[127] Y. Yampolskii, N. Belov, Investigation of Polymers by Inverse Gas Chromatography, Macromolecules, 48 (2015) Art. no. 19 doi: 10.1021/acs.macromol.5b00895.
[128] N. A. Belov, O. Yu. Sanfirova, Yu. P. Yampol'skii, J. C. Jansen, Study of the Hyflon AD80 perfluorinated copolymer by inverse gas chromatography, Polym. Sci. Ser. A, 52 (2010) 781–786 doi: 10.1134/S0965545X1008002X.
[129] J. C. Jansen, M. Macchione, E. Tocci, L. De Lorenzo, Y. P. Yampolskii, O. Sanfirova, V. P. Shantarovich, M. Heuchel, D. Hofmann, E. Drioli, Comparative Study of Different Probing Techniques for the Analysis of the Free Volume Distribution in Amorphous Glassy Perfluoropolymers, Macromolecules, 42 (2009) 7589–7604 doi: 10.1021/ma901244d.
[130] Yu. P. Yampolskii, S. A. Soloviev, M. L. Gringolts, Thermodynamics of sorption in and free volume of poly(5,6-bis(trimethylsilyl)norbornene), Polymer, 45 (2004) 6945–6952 doi: 10.1016/j.polymer.2004.08.004.
[131] V. G. Berezkin, A. A. Korolev, I. V. Malyukova, R. G. Mardanov, V. S. Khotimskii, Yu. P. Yampol"skii, Influence of the carrier gas on retention factors of gaseous hydrocarbons on poly trimethylsilyl propyne using capillary gas chromatography, Russ. Chem. Bull., 50 (2001) 1228–1232 doi: 10.1023/A:1014002722839.
[132] N. Belov, Y. Yampolskii, M. C. Coughlin, Thermodynamics of Sorption in an Amorphous Perfluorinated Rubber Studied by Inverse Gas Chromatography, Macromolecules, 39 (2006) 1797–1804 doi: 10.1021/ma052428u.
[133] B. D. Freeman, Basis of Permeability/Selectivity Tradeoff Relations in Polymeric Gas Separation Membranes, Macromolecules, 32 (1999) 375–380 doi: 10.1021/ma9814548.
[134] B. Comesaña-Gándara, J. Chen, C. G. Bezzu, M. Carta, I. Rose, M.-C. Ferrari, E. Esposito, A. Fuoco, J. C. Jansen, N. B. McKeown, Redefining the Robeson upper bounds for CO_2/CH_4 and CO_2/N_2 separations using a series of ultra permeable benzotriptycene-based polymers of intrinsic microporosity, Energy Environ. Sci., 12 (2019) 2733–2740 doi: 10.1039/C9EE01384A.
[135] A. X. Wu, J. A. Drayton, Z. P. Smith, The perfluoro polymer upper bound, AIChE J., 65 (2019) doi: 10.1002/aic.16700.
[136] TIPS RAS, Database "Gas Separation Parameters of Glassy Polymers," 1998. Available: http://www.ips.ac.ru/index.php?option=com_content&task=view&lang=en&id=853
[137] D. W. Van Krevelen, K. Te Nijenhuis, Properties of Polymers Their Correlation with Chemical Structure ; their Numerical Estimation and Prediction from Additive Group Contributions. Elsevier Science & Technology Books, Amsterdam, Nederlands, 1990.
[138] A. A. Askadskij, Computational materials science of polymers. Cambridge International Science Publ, Cambridge, 2003.
[139] L. Robeson, A group contribution approach to predict permeability and permselectivity of aromatic polymers, J. Membr. Sci., 132 (1997) 33–54 doi: 10.1016/S0376-7388(97)00031-8.

[140] D. V. Laciak, L. M. Robeson, C. D. Smith, Group contribution modeling of gas transport in polymeric membranes, in: B. D. Freeman, I. Pinnau (Eds.), Polymer Membranes for Gas and Vapor Separation: Chemistry and Materials Science, 733, American Chemical Society, Washington, DC, 1999, doi: 10.1021/bk-1999-0733.
[141] M. R. Surgi, A. J. Polak, R. C. Sundahl, Description of oxygen permeability in various high polymers using a graph-theoretical approach, J. Polym. Sci. Part Polym. Chem., 27 (1989) 2761–2776 doi: 10.1002/pola.1989.080270821.
[142] L. Kier, L. H. Hall, Molecular Connectivity In Chemistry And Drug Research. Elsevier Science, Saint Louis, 2014.
[143] M. Randic, Characterization of molecular branching, J. Am. Chem. Soc., 97 (1975) 6609–6615 doi: 10.1021/ja00856a001.
[144] M. Wessling, Relaxation phenomena in dense gas separation membranes, Ph.D. Thesis, University of Twente, Twente, 1993.
[145] J. W. Barnett, C. R. Bilchak, Y. Wang, B. C. Benicewicz, L. A. Murdock, T. Bereau, S. K. Kumar, Designing exceptional gas-separation polymer membranes using machine learning, Sci. Adv., 6 (2020) eaaz4301 doi: 10.1126/sciadv.aaz4301.
[146] H. Doan Tran, C. Kim, L. Chen, A. Chandrasekaran, R. Batra, S. Venkatram, D. Kamal, J. P. Lightstone, R. Gurnani, P. Shetty, M. Ramprasad, J. Laws, M. Shelton, R. Ramprasad, Machine-learning predictions of polymer properties with Polymer Genome, J. Appl. Phys., 128 (2020) 171104 doi: 10.1063/5.0023759.
[147] A. A. Gusev, U. W. Suter, Dynamics of small molecules in dense polymers subject to thermal motion, J. Chem. Phys., 993) (1993) 2228–2234 doi: 10.1063/1.466198.
[148] D. Hofmann, L. Fritz, J. Ulbrich, C. Schepers, M. Böhning, Detailed-atomistic molecular modeling of small molecule diffusion and solution processes in polymeric membrane materials, Macromol. Theory Simul., 9 (2000) 293–327 doi: 10.1002/1521-3919(20000701)9:6<293::AID-MATS293>3.0.CO;2-1.
[149] D. Hofmann, M. Heuchel, Yu. Yampolskii, V. Khotimskii, V. Shantarovich, Free Volume Distributions in Ultrahigh and Lower Free Volume Polymers: Comparison between Molecular Modeling and Positron Lifetime Studies, Macromolecules, 35 (2002) 2129–2140 doi: 10.1021/ma011360p.
[150] D. Hofmann, M. Entrialgo-Castano, A. Lerbret, M. Heuchel, Y. Yampolskii, Molecular Modeling Investigation of Free Volume Distributions in Stiff Chain Polymers with Conventional and Ultrahigh Free Volume: Comparison between Molecular Modeling and Positron Lifetime Studies, Macromolecules, 36 (2003) 8528–8538 doi: 10.1021/ma034971l.
[151] D. N. Theodorou, Principles of Molecular Simulation of Gas Transport in Polymers, in: Y. Yampolskii, I. Pinnau, B. Freeman (Eds.), Materials Science of Membranes for Gas and Vapor Separation, John Wiley & Sons, Ltd, Chichester, UK, 2006, 49–94, doi: 10.1002/047002903X.ch2.
[152] A. Gooneie, S. Schuschnigg, C. Holzer, A Review of Multiscale Computational Methods in Polymeric Materials, Polymers, 9 (2017) 16 doi: 10.3390/polym9010016.
[153] T. E. Gartner, A. Jayaraman, Modeling and Simulations of Polymers: A Roadmap, Macromolecules, 52 (2019) 755–786 doi: 10.1021/acs.macromol.8b01836.
[154] F. D. Rossini, Symposium on Fundamental Chemical Thermodynamics of Hydrocarbons and their Derivatives: Heat of Formation of Gaseous Hydrocarbons., Chem. Rev., 27 (1940) 1–16 doi: 10.1021/cr60086a001.
[155] R. H. Ewell, Thermodynamic Properties of Paraffins and Olefins, Ind. Eng. Chem., 32 (1940) 778–783 doi: 10.1021/ie50366a010.
[156] V. M. Tatevskiy, The physico-chemical properties of paraffin hydrocarbons relationships and calculation methods. Gostoptechizdat, Moscow, 1960.
[157] S. W. Benson, J. H. Buss, Additivity Rules for the Estimation of Molecular Properties. Thermodynamic Properties, J. Chem. Phys., 29 (1958) 546–572 doi: 10.1063/1.1744539.
[158] S. W. Benson, Thermochemical kinetics: methods for the estimation of thermochemical data and rate parameters. Wiley, New York, 1968.
[159] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, R. Walsh, Additivity rules for the estimation of thermochemical properties, Chem. Rev., 69 (1969) 279–324 doi: 10.1021/cr60259a002.
[160] N. Cohen, S. W. Benson, Estimation of heats of formation of organic compounds by additivity methods, Chem. Rev., 93 (1993) 2419–2438 doi: 10.1021/cr00023a005.
[161] S. E. Stein, D. M. Golden, S. W. Benson, Predictive scheme for thermochemical properties of polycyclic aromatic hydrocarbons, J. Phys. Chem., 81 (1977) 314–317 doi: 10.1021/j100519a007.
[162] S. P. Verevkin, Improved Benson Increments for the Estimation of Standard Enthalpies of Formation and Enthalpies of Vaporization of Alkyl Ethers, Acetals, Ketals, and Ortho Esters, J. Chem. Eng. Data, 47 (2002) 1071–1097 doi: 10.1021/je020023o.
[163] O. V. Dorofeeva, V. S. Yungman, P. Saks, Enthalpies of Formation for Gaseous Polychlorinated Biphenyls: A Modified Group Additivity Scheme, J. Phys. Chem. A, 105 (2001) 6621–6629 doi: 10.1021/jp010082t.
[164] O. V. Dorofeeva, O. N. Ryzhova, N. F. Moiseeva, The quantum-chemical determination of group contributions to the thermodynamic properties of organophosphorus compounds, Russ. J. Phys. Chem. A, 82 (2008) 933–937 doi: 10.1134/S0036024408060113.
[165] R. E. Robertson, The Configurational Entropy of Polyethylene at the Melting Point, Macromolecules, 2 (1969) 250–254 doi: 10.1021/ma60009a008.
[166] R. Simha, S. T. Hadden, Application of Cell Theory to Liquid Hydrocarbons, J. Chem. Phys., 25 (1956) 702–709 doi: 10.1063/1.1743032.
[167] H. W. Starkweather, R. H. Boyd, The Entropy of Melting of Some Linear Polymers, J. Phys. Chem., 64 (1960) 410–414 doi: 10.1021/j100833a008.
[168] G. L. Slonimskiy, A. A. Askadskii, A. I. Kitaygorodskiy, About packing of macromolecules in polymers, Vysokomol. Soedin. A, 12 (1970) 494–512.
[169] J. Bicerano, Prediction of polymer properties, 3rd ed. Marcel Dekker, New York, 2002.
[170] A. A. Askadskii, Yu. I. Matveev, Chemical structure and physical properties of polymers. Chemistry, Leningrad, 1983.
[171] M. Salame, Prediction of gas barrier properties of high polymers, Polym. Eng. Sci., 26 (1986) 1543–1546 doi: 10.1002/pen.760262203.
[172] M. Salame, S. Steingiser, Barrier Polymers, Polym.-Plast. Technol. Eng., 8 (1977) 155–175 doi: 10.1080/03602557708545034.
[173] M. Salame, Transport properties of nitrile polymers, J. Polym. Sci. Polym. Symp., 41 (1973) 1–15 doi: 10.1002/polc.5070410103.
[174] J. Y. Park, D. R. Paul, Correlation and prediction of gas permeability in glassy polymer membrane materials via a modified free volume-based group contribution method, J. Membr. Sci., 125 (1997) 23–39 doi: 10.1016/S0376-7388(96)00061-0.
[175] A. Yu. Alentiev, Gas transport properties of glassy polymers prediction: Role of the chemical structure and free volume, Ph.D. Thesis, A.V.Topchiev Institute of Petrochemical Synthesis, Moscow, 2003.
[176] Y. Yampolskii, S. Shishatskii, A. Alentiev, K. Loza, Correlations with and prediction of activation energies of gas permeation and diffusion in glassy polymers, J. Membr. Sci., 148 (1998) 59–69 doi: 10.1016/S0376-7388(98)00130-6.
[177] A. Yu. Alentiev, K. A. Loza, Yu. P. Yampolskii, Development of the methods for prediction of gas permeation parameters of glassy polymers: polyimides as alternating co-polymers, J. Membr. Sci., 167 (2000) 91–106 doi: 10.1016/S0376-7388(99)00271-9.
[178] S. Velioğlu, S. B. Tantekin-Ersolmaz, Prediction of gas permeability coefficients of copolyimides by group contribution methods, J. Membr. Sci., 480 (2015) 47–63 doi: 10.1016/j.memsci.2015.01.012.
[179] A. Yu. Alent'ev, Yu. P. Yampolskii, M. N. Vidyakin, Yu. N. Lazareva, Selection of membrane materials for separation of H_2-containing mixtures: Database analysis, Polym. Sci. Ser. A, 48 (2006) 1120–1127 doi: 10.1134/S0965545X06100154.
[180] Y. Hirayama, T. Yoshinaga, Y. Kusuki, K. Ninomiya, T. Sakakibara, T. Tamari, Relation of gas permeability with structure of aromatic polyimides I, J. Membr. Sci., 111 (1996) 169–182 doi: 10.1016/0376-7388(95)00172-7.
[181] A. Y. Alentiev, Y. P. Yampolskii, Free volume model and tradeoff relations of gas permeability and selectivity in glassy polymers, J. Membr. Sci., 165 (2000) 201–216 doi: 10.1016/s0376-7388(99)00229-x.
[182] L. M. Robeson, Z. P. Smith, B. D. Freeman, D. R. Paul, Contributions of diffusion and solubility selectivity to the upper bound analysis for glassy gas separation membranes, J. Membr. Sci., 453 (2014) 71–83 doi: 10.1016/j.memsci.2013.10.066.
[183] O. V. Malykh, A. Yu. Golub, V. V. Teplyakov, Polymeric membrane materials: New aspects of empirical approaches to prediction of gas permeability parameters in relation to permanent gases, linear lower

hydrocarbons and some toxic gases, Adv. Colloid Interface Sci., 164 (2011) 89–99 doi: 10.1016/j.cis.2010.10.004.
[184] A. Y. Alentiev, Yu. P. Yampolskii, Meares equation and the role of cohesion energy density in diffusion in polymers, J. Membr. Sci., 206 (2002) 291–306 doi: 10.1016/S0376-7388(01)00777-3.
[185] Y. Yampolskii, D. Wiley, C. Maher, Novel correlation for solubility of gases in polymers: effect of molecular surface area of gases, J. Appl. Polym. Sci., 76 (2000) 552–560 doi: https://doi.org/10.1002/(SICI)1097-4628(20000425)76:4<552::AID-APP13>3.0.CO;2-O.
[186] Y. Yampolskii, On Estimation of Concentration of Free Volume Elements in Polymers, Macromolecules, 43 (2010) 10185–10187 doi: 10.1021/ma102332u.
[187] A. Alentiev, Y. Yampolskii, Correlation of Gas Permeability and Diffusivity with Selectivity: Orientations of the Clouds of the Data Points and the Effects of Temperature, Ind. Eng. Chem. Res., 52 (2013) 8864–8874 doi: 10.1021/ie302680r.
[188] V. Ryzhikh, Development of Transport Parameters of Polymer Materials Prediction Using Database, Ph.D. Thesis, Topchiev Institute of Petrochemical Synthesis of Russian Academy of Sciences, Moscow, 2014.
[189] V. Ryzhikh, D. Tsarev, A. Alentiev, Yu. Yampolskii, A novel method for predictions of the gas permeation parameters of polymers on the basis of their chemical structure, J. Membr. Sci., 487 (2015) 189–198 doi: 10.1016/j.memsci.2015.03.055.
[190] A. Alentiev, Yu. Yampolskii, V. Ryzhikh, D. Tsarev, The database "Gas Separation Properties of Glassy Polymers" (Topchiev Institute): Capabilities and prospects, Pet. Chem., 53 (2013) 554–558 doi: 10.1134/S0965544113080033.
[191] National Institute for Materials Science (NIMS), Polymer Database "PoLyInfo." Available: https://polymer.nims.go.jp/en/
[192] Membrane Society of Australasia, Database "Polymer Gas Separation Membranes." Available: https://www.membrane-australasia.org/polymer-gas-separation-membranes/
[193] R. Paterson, Y. Yampol'skii, P. G. T. Fogg, A. Bokarev, V. Bondar, O. Ilinich, S. Shishatskii, IUPAC-NIST Solubility Data Series 70. Solubility of Gases in Glassy Polymers, J. Phys. Chem. Ref. Data, 28 (1999) 1255–1450 doi: 10.1063/1.556050.
[194] M. Goubko, O. Miloserdov, Y. Yampolskii, A. Alentiev, V. Ryzhikh, A novel model to predict infinite dilution solubility coefficients in glassy polymers, J. Polym. Sci. Part B Polym. Phys., 55 (2017) 228–244 doi: 10.1002/polb.24263.
[195] M. V. Goubko, O. A. Miloserdov, Yu. P. Yampolskii, V. Ye. Ryzhikh, Prediction of Solubility Parameters of Light Gases in Glassy Polymers on the Basis of Simulation of a Short Segment of a Polymer Chain, Polym. Sci. Ser. A, 61 (2019) 718–732 doi: 10.1134/S0965545X19050067.
[196] O. Miloserdov, Classifying Amorphous Polymers for Membrane Technology Basing on Accessible Surface Area of Their Conformations, Adv. Syst. Sci. Appl., 20 (2020) 91–104 doi: 10.25728/ASSA.2020.20.3.897.
[197] A. Alentiev, S. Chirkov, R. Nikiforov, M. Buzin, O. Miloserdov, V. Ryzhikh, N. Belov, V. Shaposhnikova, S. Salazkin, Structure-Property Relationship on the Example of Gas Separation Characteristics of Poly(Arylene Ether Ketone)s and Poly(Diphenylene Phtalide), Membranes, 11 (2021) 677 doi: 10.3390/membranes11090677.
[198] M. Heuchel, D. Fritsch, P. M. Budd, N. B. McKeown, D. Hofmann, Atomistic packing model and free volume distribution of a polymer with intrinsic microporosity (PIM-1), J. Membr. Sci., 318 (2008) 84–99 doi: 10.1016/j.memsci.2008.02.038.
[199] J. Kruse, J. Kanzow, K. Rätzke, F. Faupel, M. Heuchel, J. Frahn, D. Hofmann, Free Volume in Polyimides: Positron Annihilation Experiments and Molecular Modeling, Macromolecules, 38 (2005) 9638–9643 doi: 10.1021/ma0473521.
[200] M. Heuchel, D. Hofmann, P. Pullumbi, Molecular Modeling of Small-Molecule Permeation in Polyimides and Its Correlation to Free-Volume Distributions, Macromolecules, 37 (2004) 201–214 doi: 10.1021/ma035360w.
[201] A. Alentiev, I. G. Economou, E. Finkelshtein, J. Petrou, V. E. Raptis, M. Sanopoulou, S. Soloviev, N. Ushakov, Y. Yampolskii, Transport properties of silmethylene homo-polymers and random copolymers: experimental measurements and molecular simulation, Polymer, 45 (2004) 6933–6944 doi: 10.1016/j.polymer.2004.08.005.
[202] M. Mazo, N. Balabaev, A. Alentiev, Y. Yampolskii, Molecular Dynamics Simulation of Nanostructure of High Free Volume Polymers with $SiMe_3$ Side Groups, Macromolecules, 51 (2018) 1398–1408 doi: 10.1021/acs.macromol.7b02470.
[203] M. Mazo, N. Balabaev, A. Alentiev, I. Strelnikov, Y. Yampolskii, Structure and Properties of High and Low Free Volume Polymers Studied by Molecular Dynamics Simulation, Computation, 7 (2019) 27 doi: 10.3390/computation7020027.