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A novel method for predictions of the gas permeation parameters of polymers on the basis of their chemical structure

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ABSTRACT

This work presents the results of further development of incremental (group contribution) methods for prediction of the gas transport parameters (permeability (*P*) and diffusion (*D*) coefficients) of amorphous glassy polymers. The source of information was a big Database that comprises the *P* and *D* values for about 900 polymers. The method of the modified atomic contributions was revisited using much enlarged set of polymeric structures. In addition, a novel one, the bond contribution method, was employed for the first time for predictions of the *P* and *D* values of a standard set of gases (He, H_2, O_2, N_2, CO_2 and CH_4). It was shown that both approaches allow the accurate (improved) predictions of the gas permeation parameters but the latter is more precise (correlation factors $R^2 > 0.9$). It was also demonstrated that found group contributions permit predictions of the permeability coefficients of random copolymers of different classes.

1. Introduction

A search for relationship between chemical structure and properties of organic compounds is a traditional problem of physical chemistry. When such quantitative relationship is found, it forms a basis for prediction of properties of unknown compounds. Among the properties successfully predicted one can mention enthalpy of formation of hydrocarbons [1], critical temperature and pressure of hydrocarbons [2] and other thermodynamic properties of low molecular weight organic compounds [3]. An important contribution in the chemical kinetics was a development of the predictions of the rate and equilibrium constants made by S.W. Benson and his school [4,5].

Predictions of the properties of polymers were started somewhat later. Here, the most important contribution was made in the book by Van Krevelen [6]. Another approach for predictions of the various properties of polymers was proposed by Askadskii [7]. A relevant parameter of polymers related to their applications in gas separation membranes is their permeability coefficients P_i. The first attempts to predict the P_i values on the basis of chemical structure of polymers using the group contribution method were made by Salame [8,9]. However, the disadvantage of these early works was an absence of detailed information on gas permeability of polymers with different chemical structure.

Various observations prompted that there exists relationship between the chemical structure of polymers and their gas permeation parameters. Thus, introduction of $Si(CH_3)_3$ groups into various main chains resulted in increases in permeability and diffusion coefficients of polymers [10]. Similar effects though not so strong are exerted by appearance of CH_3 or CF_3 groups in aromatic backbones of polymers [11].

Extensive accumulation of the information of this kind started in the middle of 1980s [12], so a possibility appeared for predictions of the gas permeation parameters of polymers with much more widely varying structure. Jia and Xu [13] using regression analysis treated the permeability data of about 60 polymers for 6 gases. An interesting approach was proposed by Park and Paul [14]. In the works by Robeson et al. [15,16] the group contribution method was applied for the determination of the increments for relatively large structure elements of 65 amorphous glassy polymers with aromatic backbones studied in a single laboratory. A larger set of glassy polymers was used by Yampolskii et al. [17] who considered about 300 of amorphous glassy polymers that belonged to different chemical classes. In this work atomic contributions were sought for and the different contributions were ascribed for the same atoms in the main chain and side groups. Polyimides formed a significant part of the analyzed polymer structures, so it was possible to consider this chemical class of membrane materials separately. Since polyimides can be formally

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considered as alternative copolymers of diamine and dianhydride units, Alentiev et al. [18] found and used the contributions for these structural elements with the accuracy of predictions better than that given by the method of modified atomic contributions. Other attempts were made to predict gas permeability of gases in polymers [19].

During the subsequent years much more information on gas permeation parameters (permeability and diffusion coefficients) was accumulated. In order to take this information into account, a Database [20,21] was created in A.V. Topchiev Institute of Petrochemical Synthesis. The Database contains now the information on almost 900 amorphous glassy polymers. The following parameters are tabulated: permeability coefficients (P), diffusion coefficients (D), solubility coefficients (S), activation energies of permeability (E_P), and activation energies of diffusion (E_D), some other physicochemical properties of polymers where available. The tabulated values of P and D are cited for the temperature at which the measurement was performed according to the original publication; however, they are reduced to a standard temperature of 308 K using the values of E_P and E_D (original or obtained with the aid of specially developed correlations [22]). This is necessary for a comparison of different polymers and used for the predictions of transport parameters. Several correlations of E_P and E_D were considered in this work: the correlations with the fractional free volume, with activation energies found via the group contribution method, and the correlations of activation energies with the permeability coefficients at certain reference temperature (a consequence of kinetic compensation effect). The latter procedure was found to be the most accurate and subsequently was used for investigation of the temperature dependence of P and D in polymers.

The most complete information is given for permeability coefficients: about 5500 records are available for P.

In the present work attempts are made to address the two problems:

(i) to examine to what extent an expansion of the size of basic set of polymer structures affects the accuracy of the prediction of the gas permeation parameters;
(ii) to investigate a novel approach for predictions of the permeability and diffusion coefficients, the one based not on atomic group contributions but on the increments characteristic for certain bonds within polymeric repeat units.

2. Principles of calculations

For all the group contribution method, it is characteristic to represent the structure formulas of repeat units as a molecular graph. All the atoms of the repeat units except hydrogen are considered as vertices while bonds connecting those atoms are considered as edges. In relation to polymers, structural formula of the repeat unit is presented as a sum of fragments (in the simplest case it might be atoms or bonds), and a group contribution or increment is assigned to every such fragment. Summing up of these contributions with account for a number of corresponding fragments in the repeat unit can allow making a number estimation of necessary physicochemical parameter. A way of splitting of polymer structure into such fragments is a key point that determines the accuracy of the predictions.

In the *method of the modified atomic contributions*, the same one that has been used previously [17], the polymer structure is split into the main chain and side groups. Different increments were assigned to the same atom when it appears either in the main chain or in side groups. It is assumed that the increments are constant for the whole set of complex structures, i.e. do not depend on a mutual arrangement of the groups or their possible interactions. It is considered that the vertex of the molecular graph belongs to the main chain if there is at least one way from "head to tail" that includes this vertex by such traveling along the molecular graph when it is allowed to "visit" each vertex only once. In the opposite cases it is considered that this vertex belongs to side groups. Thus, while proceeding from polymer's structural formula one can obtain a unique set of fragments.

The Database [20] was used in the calculations. It contains information for about 900 different amorphous glassy polymers that belong to different classes: Polyimides (315 structures), Polyacetylenes (107), Polyesters (86), Polyetheres (67), Polynorbornenes (53), Polysulfons (51) and other polymer classes. The values of P and D are tabulated in the Database for 26 various gases but the most extensive information is available for He, H_2, O_2, N_2, CO_2 and CH_4. The whole set of the included polymers can be described using 16 fragments that belong to the main chain and 19 fragments of the side groups. These fragments and corresponding increments are given in Table 1S (see Supporting Information). In this way, a overdetermined system of equation was prepared. The prerequisite for such system is the inequality

$$k \gg n \tag{1}$$

where n is the number of different groups that are used to draw the structure of the repeat units of all k polymers. Such system is presented below:

$$\begin{cases} \lg X_1 = \sum \frac{m_i * n_{i1}}{M_1} * I_i \\ \lg X_2 = \sum \frac{m_i * n_{i2}}{M_2} * I_i \\ \lg X_k = \sum \frac{m_i * n_{ik}}{M_k} * I_i \end{cases} \tag{2}$$

where X is the physicochemical parameter, m_i is atomic mass of the i-th atom, n_i is the number of atoms of i-th type, M is the molecular mass of the repeat unit, I_i is the increment (contribution) that corresponds to i-th type of atom. The solution of this overestimated system was performed using SVD method (Singular Value Decomposition) [23] and it gave optimal values of the increments for every fragment. These parameters can be used eventually for predictions of the properties of polymers comprised of the same fragments. An example of the splitting of a model polymer structure using this approach is given in Fig. 1 and Table 1.

In the *bond contribution method* each edge of the molecular graph is classified as follows: single, double triple bonds and aromatic bonds. The bonds are considered separately if they connect different atoms. Thus, a certain property (type of the bond) is ascribed to each edge. The vertices of the molecular graph that are located at the ends of edges are considered in the same way as in the method of modified atomic contributions. Hence, the fragments of the structure are differed by the type of bond and end atoms. Because of this, the number of corresponding increments is significantly greater than in the method of modified atomic contributions. The corresponding increments are given in Table 2S (see Supporting Information). Accordingly, the following system of

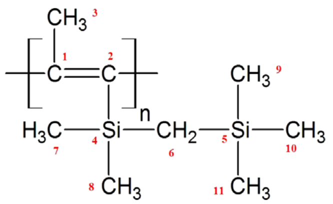

Fig. 1. Example of splitting of a model polymeric structure in the method of modified atomic contributions.