Diffusion of C1-C3 Alkanes in Semicrystalline Poly(4-Methyl-1-Pentene) as a Two-Phase Polymeric System

S.Y. Markova¹, I.N. Beckman¹,² and V.V. Teplyakov¹,*

¹A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Leninsky prospect, 29 Russia
²M.V. Lomonosov Moscow State University, Chemical Faculty, Russia

Abstract: Poly(4-methyl-1-pentene) (PMP) is using up to now as the hollow fiber air separation membranes. This polymer with good resistance to organics attack can be prospective for separation of lower hydrocarbons. An attempt for the theoretical consideration and experimental study of the C₁-C₃ alkanes diffusion in poly(4-methyl-1-pentene) (PMP) as a binary system in the temperature range from 253,K to 353, K covering the glass transition region of PMP (~ 303, K) is carried out in this work. The permeability of CH₄, C₂H₆, C₃H₈ has been measured by the permeability differential method under the partial pressure drop across the membrane 1 bar with the gas chromatography analysis of the permeate flux. The diffusion coefficients have been calculated from the experimental differential permeability curves by using linearization method developed earlier. Novelty of results is that at temperatures below Tg, PMP can be considered as a single-phase system from the gas transfer point of view. At the temperatures above Tg, PMP can be considered as a two-phase medium with diffusion coefficients of C₁-C₃ alkanes in amorphous (Dₐ) and crystalline phases (Dc) which differ by not more than an one order of magnitude. For the first time it is shown that the diffusivity of C1-C3 alkanes in amorphous and crystalline PMP phases is decreasing in accordance with sequence Dₐ(H₈) > Dₐ(CH₄) > Dₐ(C₂H₆) > Dₐ(C₃H₈). A certain scatter of the PMP data published in the literature was noted. Obtained data can be relatively compared with published ones only for methane: for virgin PMP films we obtained P(CH₄) = 16.7 Barrer; it is known for the extrusion PMP films that P(CH₄) = 14.6 – 19.8 Barrer, for casted PMP films P(CH₄) = 0.4 – 1.2 Barrer. The values for ethane and propane in crystalline phase of PMP are obtained for the first time. Evaluation of permeability through crystalline phase at temperature 313,K shows that P(CH₄) = 15 Barrer; P(C₂H₆) = 5 Barrer. For real estimation of the separation efficiency PMP it is needed an additional research with taking into account the crystallinity and temperature dependences for diffusivity based on results of this study.

Keywords: C₁-C₃ alkanes diffusion, Semicrystalline poly(4-methyl-1-pentene).

INTRODUCTION

Modern synthetic capabilities allow for designing and manufacturing of statistical, graft, and block-copolymers with a wide variety of physical and chemical properties including mechanical, thermal, diffusion, etc. [1-5]. As a rule, chemical heterogeneity results in physical non-uniformity. Thus, phase dispersion with regular or statistical distribution of various particle shapes, layered, interpenetrating and other structures are obtained. Examples of such structures are reported for set of block-copolymers (BCs) [6-9]. Semicrystalline polymers can be considered as two phase polymers with selective gas transfer depending on the crystallinity degree as well. At the same time a little attention has been paid to the gas selective properties of two-phase membrane materials. The gas transport theory in two-phase systems outlined in [10] has mostly been developed in the 90s [11-13]. One of the more recent publications is [14].

A number of mathematic models describing non-uniform (heterogeneous, including two-phase) materials targeting such properties as electric and heat conductance [15-26]. Some models have also been used to describe the gas permeability in BCs and, rarely, for semicrystalline polymers, e.g. poly-4-methyl-1-pentene (PMP) [12]. In the latter case we consider the polymeric medium as a binary system with permeable crystalline phase. It should be noted that in spite of the set of papers describing the gas transport in PMP the published data are fragmented: they demonstrate the permanent gas permeability coefficients under definite (e.g., room) temperature. The published data for C₁-C₃ alkanes are not numerous and they have a wide range [12, 27, 28]. All of this complicates the comparison of PMP samples with the different crystalline degree. This work is focused on the gas selective transport through PMP as well known membrane polymer. In spite of a long history of PMP investigation the scientific interest to this membrane material and the gas separating hollow fibers based on it are in the frames of active research now [29, 30] and of the applications [31, 32]. PMP is using up to now as the hollow fiber air separation membranes. PMP as an attractive polymeric membrane material has a good...
resistance towards organic attack including lower hydrocarbons transfer data of which are limited (most published data are focused on permanent gases [33, 34]). Set of modern studies describe the preparation of PMP membranes as porous ones by extrusion processing [35, 36] for filtration or gas separation of mixtures containing organic components. On the other hand there are set of publications describing the modification of PMP membranes via preparation of blends [37]. In whole, PMP membranes with good resistance to organics attack can be prospective for separation of lower hydrocarbons.

The aim of the paper is to describe the contribution of the gas diffusion as the key parameter into selective gas permeability through PMP with the different degree of crystallinity for better understanding of the selective transport of lower alkanes. The experimental part of work includes the measurements of the diffusion (D) and permeability (P) coefficients and their temperature dependences for C$_1$-C$_3$ alkanes. The theoretical approach which is focused on a mathematical description of the gas diffusion in two-phase polymeric system as the most sensitive to structure of polymeric medium has been used for determination of D values in crystalline and amorphous phases. The values for ethane and propane in crystalline phase of PMP are obtained for the first time. The new results demonstrate the successive attempt to describe the gas diffusion in two phase systems for determination of the C$_1$-C$_3$ alkanes permeability parameters in amorphous and crystalline phases.

THEORETICAL APPROACH

The molecular transport through a uniform polymeric membrane consists of the following steps: gas sorption on a surface of a film, migration through the volume of the membrane towards the other surface, and desorption from that surface. The membrane technology is based on the permeability method where the flux through a film is measured in a stationary regime. In this traditional scheme the gas flux exiting a flat membrane is defined by the 1$^{st}$ Fick’s Law [38]. Stationary flux of a gas through the membrane is given by:

$$J_{ss} = ADS \frac{\Delta P}{H} = AP \frac{\Delta P}{H} \tag{1}$$

where $J_{ss}$ is a steady-state flux of a gas through a membrane, $A$ is the membrane area, $D$ is a diffusion coefficient, $S$ is a gas solubility coefficient, $P = DS$ is the permeability coefficient, $H$ is a membrane thickness, $\Delta P$ is the pressure drop across the membrane.

The common units of the transport parameters are $P$ [Barrer = 10$^{-10}$ cm$^3$.cm/cm$^2$.sec.cmHg], $D$ [cm$^2$/sec], $S$ [cm$^3$(STP, gas)/cm$^3$ (polymer).cmHg]. Separation of a two gas mixture within this ideal selectivity model is given by:

$$a_{ss} = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B} = a_p a_s \tag{2}$$

where $P_A$ and $P_B$ are permeability coefficients of gases $A$ and $B$, respectively; $D_A$ and $D_B$ are diffusion coefficients of gases $A$ and $B$, respectively; $S_A$ and $S_B$ are solubility coefficients for gases $A$ and $B$, respectively. Here, $a_{ss} = P_A / P_B$ is ideal selectivity (components $A$ and $B$) mixture separation, $a_p = D_A / D_B$ is the kinetic component of selectivity (separation because of the difference in diffusion coefficients), and $a_s = S_A / S_B$ is the thermodynamic component of selectivity (separation because of the difference in gas solubility).

In the case of PMP as two-phase system where the transport process occurs in both phases which can also exchange the diffusant, the gas transport can be described by a system of equations of dissociative diffusion [13, 14]:

$$\begin{align*}
\frac{\partial C_1}{\partial t} &= D_1 \frac{\partial^2 C_1}{\partial x^2} - k_1 \phi_2 C_1 + k_2 \phi_2 C_2 \\
\frac{\partial C_2}{\partial t} &= D_2 \frac{\partial^2 C_2}{\partial x^2} + k_1 \phi_2 C_1 - k_2 \phi_2 C_2
\end{align*} \tag{3}$$

where $D_1$ and $D_2$ are diffusion coefficients in phases 1 and 2, $C_1$ and $C_2$ are concentrations of the diffusant in phases 1 and 2; $k_1$ is a local rate constant for the exchange of the diffusant between phase 1 and phase 2; $k_2$ is a local rate constant for the exchange of the diffusant between phase 2 and phase 1; $\phi_1$ and $\phi_2$ are volume fractions of phase 1 (dispersing media) and 2 (dispersing inclusions), respectively, ($\phi_1 + \phi_2 = 1$).

For the case when the thickness of a membrane is substantially larger than the particle dimensions of the dispersion phase, or more strictly speaking, when the rate of migration of molecule through the interface boundary substantially higher than the overall rate of diffusion, the flux of the penetrant through the two-phase system can be described by a classical equation [14]:
\[ J(t) = J_{ss} \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left( -\frac{n^2 \pi^2 D_{eff} t}{L^2} \right) \right] \]  

(4)

where \( J_{ss} \) is steady state flux.

\[ D_{eff} = \frac{D_a \varphi_a k_1 + D_c \varphi_c k_1}{\varphi_a k_1 + \varphi_c k_2} \]  

(5)

It should be noted that the values of \( D_{eff} \) are between \( D_a \) and \( D_c \).

For thin membranes, if the particle dimensions of the dispersed inclusions are comparable with the membrane thickness, two fluxes are observed experimentally and the kinetics is described by two diffusion coefficients \( D_a \) and \( D_c \) [14]. If the particle dimensions of the dispersed phase are much smaller than the membrane thickness, the kinetics is described by equation (4) with a single effective diffusion coefficient that can be considered as an integral (effective) parameter of the entire two-phase system. It should be noted that, e.g., in the experimental studies with silane-siloxane BCs [39], all of the differential curves of permeability were described by equation (4) with correlation factors of at least 0.999. In other words, the applicability of equation (3) is confirmed. However, the values of \( D_a \) and \( D_c \) in two-phase systems depend not only on the actual diffusion coefficients but also on the tortuosity of the diffusion pathways. At the same time, parameters \( k_i \) and \( k_j \) depend on the shapes and sizes of the inclusions and on the area of the phase boundary.

After stationary flux is achieved through a non-uniform (two-phase) polymeric film (membrane) at \( t \to \infty \), the solution of the system of equations (2) leads to a standard expression with a single permeability value for two-phase systems:

\[ J_{ss} = AD_{eff} \frac{\Delta C}{H} \]  

(6)

where \( \Delta C / H \) is the stationary concentration gradient. Of course, in this system, all the relations between permeability parameters and their temperature coefficients should remain the same:

\[ P_{eff} = D_{eff} S_{eff} \]  

(7)

Assuming that equation (7) is correct and \( S_{eff} \) is \( S_a \) (gas solubility in amorphous phase as the dispersion media forming the surface of a polymeric film), it is possible to estimate \( D_{eff} \) of PMP as dispersion [14]:

\[ D_{eff} = \frac{D_i + k \varphi_i D_2}{1 + k \varphi_2 \varphi_i} \]  

(8)

where \( K = \frac{1}{3} \sum_{i=1}^{3} \frac{1}{1 + \frac{A_i}{2} \left( \frac{D_i}{D_{eff}} - 1 - \frac{W}{D_i} \right)} \]  

(9)

\( A_i \) is the shape parameter varying from 0 to 1 (for spherical particles \( A_i = 0.66 \)); \( W \) is the coefficient introduced for concentrated dispersions which is defined as the correction of diffusion fluxes for account of the neighboring particles influence (for spherical particles) according to the formula [10]:

\[ W = 0.78 \frac{(D_a - D_c)^2}{2D_a + D_c} \]  

(10)

where \( D_i = D_a \) is the diffusion coefficient in amorphous phase; \( D_c = D_2 \) is the diffusion coefficient in crystalline phase.

Thus, the values of \( D_{eff} \) for PMP films include the components for the amorphous (\( D_a \)) and crystalline (\( D_c \)) phases. In the present study, the values of \( D_{eff} \) and \( P_{eff} \) for PMP films were experimentally determined in the temperature range from 253 to 353, K covering \( T_g \) of the polymer (\( T_g \approx 303, K \)). The decomposition of the experimental values obtained at various temperatures into components (\( D_a \) values for amorphous and \( D_c \) for the crystalline phase) was carried out taking into account the mathematical approach described above (equations (8-10)).

**MATERIALS AND METHODS OF MEASUREMENT**

Poly(4-methyl-1-pentene) from two different sources was used in this work. The first one obtained by suspension polymerization of 4-methyl-1-pentene [40] was available from the laboratory of the organometallic catalysis (TIPS RAS). PMP films were obtained by heating of PMP pellets to a temperature of 523,K followed by pressing of the melt to obtain a flat work-piece which is then rolled between the rollers with a fixed gap in order to produce a sample with a desired thickness. The second one was kindly supplied by Mitsui Chemicals (Japan) as a PMP films. The sample thicknesses for both kinds were 50±2 \( \mu \)m. Structural formula of poly(4-methyl-1-pentene is shown in Figure 1
Figure 1: Structural formula of poly(4-methyl-1-pentene).

PMP is a semicrystalline polymer with the density of the crystalline phase (0.827 g/cm³) being lower than that of the amorphous phase (0.835 g/cm³) at room temperature [41]. This unusual property raises the question about the possibility of selective transport of gases through the crystalline phase of PMP. The crystal structure of PMP due to the regular packing of macromolecules segments forms cavities having a size of about 4Å according to X-ray diffraction data [42].

The degree of crystallinity was evaluated from the heat of fusion as,

$$X_c = \frac{\Delta H_f}{\Delta H_f^0}$$  \hspace{1cm} (11)

where $X_c$, $\Delta H_f$, $\Delta H_f^0$ are the degree of crystallinity, the observed heat of fusion of PMP and the heat of fusion for the 100% crystalline polymer. Heats of fusion $\Delta H_f$ were measured by DSC analysis and $\Delta H_f^0$ = 14.8 cal g⁻¹ [41] (Table 1). DSC analysis was carried out on DSC823e (Mettler Toledo) at heating rate 10 °C/min under argon atmosphere.

Table 1: The Degree of PMP Crystallinity Evaluated from the Heat of Fusion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Xc</th>
<th>Tg, K</th>
<th>Tm, K</th>
<th>$\Delta H_f$, cal g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>commercial sample</td>
<td>0.37</td>
<td>303</td>
<td>502</td>
<td>5.5</td>
</tr>
<tr>
<td>laboratory sample</td>
<td>0.7</td>
<td>303</td>
<td>508</td>
<td>10.3</td>
</tr>
</tbody>
</table>

The permeability of CH₄, C₂H₆, C₃H₈ has been measured by the permeability differential method under the partial pressure drop across the membrane 1 bar with the gas chromatography analysis of the permeate flux. The diffusion coefficients have been calculated from the experimental differential permeability curves by using linearization method [43]. The gas transfer parameters were studied at temperatures in the range from 253,K to 353, K covering the glassy and rubbery states of the PMP amorphous phase. The variations of the PMP density for amorphous (ρₐ) and crystalline (ρₖ) phases calculated by using data of [44] are shown in

Figure 2. As it can be seen the values of ρₐ and ρₖ are enough similar: ρₐ < ρₖ at T < Tg and ρₐ > ρₖ at T > Tg. It means that crystalline phase should be permeable as it has been noted in [12].

Figure 2: The temperature dependence of the amorphous and crystalline phase density of the PMP (based on data of [44]).

RESULTS AND DISCUSSION

The experimental temperature dependences of $P_{eff}$ and $D_{eff}$ in Arrhenius plots are shown in Figures 3 and 4.
As shown in Figures 3 and 4 there is a general tendency in the series of CH$_4$, C$_2$H$_6$, C$_3$H$_8$ permeability: PMP can be considered as a single-phase system at T<T$_g$. In this region the physical densities of the amorphous and crystalline phases are close (see Figure 2). At T>T$_g$ PMP demonstrates the properties of a binary system when the gas permeability and diffusion coefficients increase with decreasing the crystallinity degree (Figures 3 and 4). This effect is less sensitive to CH$_4$ permeability and it is more noticeable for C$_2$-C$_3$ alkanes. Figure 4 also shows that at T>T$_g$ the gas diffusion is more sensitive to the PMP structure: the $D_{eff}$ values of gases become higher for a sample with a lower degree of crystallinity. The obtained dependences are difficult to interpret as a linear with a flex-point in the T$_g$ region. These temperature diffusion data are in contrary with permeability data for CO$_2$ in PMP [45]. In whole, PMP can be considered as a two phase polymer with $\rho_a \sim \rho_c$ at T~T$_g$. The sizes of the crystallites are in the range of 15-35 nm [46], which are definitely smaller than thickness of the films studied. In the region at T>T$_g$ the obtained $D_{eff}$ values have been decomposed into contributions due to diffusion in the crystalline ($D_c$) and amorphous ($D_a$) phases of the PMP using equations (8-10) assuming that the shape of the crystallite particles is close to spherical ones. Previously, only the gas permeability estimation was carried out by using Higuchi’s equation [12]. For estimation of diffusion coefficients this approach has been applied for PMP for the first time in the present study. It turned out that the values of $D_a > D_c$ differ by not more than an order of magnitude, while the shape of dispersed particles (crystallites) practically does not affect the diffusion of C$_1$-C$_3$ alkanes in a two-phase medium as we considered specially by using equations (8-10). Table 2 shows the diffusion of $D_a$ and $D_c$ for C$_1$-C$_3$ alkanes at temperatures of 283-353, K. Thus, we have obtained confirmation that the crystalline phase of the PMP is diffusively permeable.

Unfortunately, obtained data can be relatively compared with published one only for methane: for virgin PMP films we have $P_{CH4} = 16.7$ Barrer; it is known for the extrusion PMP films $P_{CH4} = 14.6 – 19.8$ [12], for casted PMP films $P_{CH4} = 0.4 – 1.2$ [28]. In latter case the authors [28] consider the more dense packing of macromolecules. The values for ethane and propane are obtained for the first time.

To estimate the gas permeability coefficients as the first approximation we used equation (7) assuming that at T<T$_g$ we have deal with single phase system; at T>T$_g$ the system is considered as two phases one. As...


Table 2: Gas Diffusion Coefficients in Amorphous (Da) and the Crystalline (Dc) Phases of PMP at Different Temperatures

<table>
<thead>
<tr>
<th></th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>D, cm²/1/s, 10⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Da</td>
<td>7.8</td>
<td>7.5</td>
<td>5.4</td>
</tr>
<tr>
<td>T = 353, K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dc</td>
<td>1.4</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>T = 333, K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Da</td>
<td>7.2</td>
<td>5.2</td>
<td>2.5</td>
</tr>
<tr>
<td>T = 313, K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dc</td>
<td>1.4</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>T = 283, K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Da</td>
<td>5.5</td>
<td>1.8</td>
<td>0.52</td>
</tr>
<tr>
<td>Dc</td>
<td>1.4</td>
<td>0.8</td>
<td>0.12</td>
</tr>
<tr>
<td>Da</td>
<td>1.9</td>
<td>0.28</td>
<td>-</td>
</tr>
<tr>
<td>Dc</td>
<td>1.3</td>
<td>0.26</td>
<td>-</td>
</tr>
</tbody>
</table>

an example we estimated permeability of C₁-C₃ alkanes through crystalline phase at temperature 313, K: P(CH₄) = 14 Barrer; P(C₂H₆) = 15 Barrer; P(C₃H₈) = 5 Barrer. These values are lower at 273, K: P(CH₄) = 5.7 Barrer; P(C₂H₆) = 5.3 Barrer (P(C₃H₈) is not determined). In whole, diffusivity of C₁-C₃ alkanes in amorphous and crystalline phases is decreasing in accordance with sequence D(CH₄) > D(C₂H₆) > D(C₃H₈) for more than 10 times. So, PMP membranes can be used for C₁-C₃ alkanes separation. For real estimation of the separation efficiency PMP it is needed additional study with taking into account the crystallinity and temperature dependences for diffusivity based on obtained data. If to have in mind that there are attempts to prepare PMP membrane consisting mainly from crystallites [46] one can expect the appearance of the molecular sieving effect for C₄-C₆ hydrocarbons when the dimensions of the diffusing molecules will be close to the pore size in the PMP crystallites.

The proposed approach to the mathematical description of diffusion in PMP made it possible to obtain for the first time not only the temperature dependences of the C₁-C₃ alkanes diffusivity in crystalline and amorphous phase, but also to conclude that diffusion plays a key role in the selective transport of gases in PMP.

CONCLUSION

Poly(4-methyl-1-pentene) (PMP) is using up to now as the hollow fiber air separation membranes. This polymer with good resistance to organics attack can be prospective for separation of lower hydrocarbons.

An attempt for the theoretical consideration and experimental study of the C₁-C₃ alkanes diffusion in poly(4-methyl-1-pentene) (PMP) as a binary system in the temperature range from 253,K to 353, K covering the glass transition region of PMP (~ 303, K) is carried out in this work. Novelty of results is that at temperatures below T₉ PMP can be considered as a single-phase system from the gas transfer point of view. At the temperatures above T₉ PMP can be considered as a two-phase medium with diffusion coefficients of C₁-C₃ alkanes in amorphous (Dₐ) and crystalline phases (D₈) (D₈ > Dₐ) which differ by not more than an one order of magnitude. For the first time it is shown that the diffusivity of C₁-C₃ alkanes in amorphous and crystalline PMP phases is decreasing in accordance with sequence D(CH₄) > D(C₂H₆) > D(C₃H₈). A certain scatter of the PMP data published in the literature was noted. Obtained data can be relatively compared with published ones only for methane: for virgin PMP films we obtained P(CH₄) = 16.7 Barrer; it is known for the extrusion PMP films that P(CH₄) = 14.6 ~ 19.8 Barrer, for casted PMP films P(CH₄) = 0.4 ~ 1.2 Barrer. The values for ethane and propane in crystalline phase of PMP are obtained for the first time. Evaluation of permeability through crystalline phase at temperature 313,K shows that P(C₂H₆) = 15 Barrer; P(C₃H₈) = 5 Barrer. For real estimation of the separation efficiency PMP it is needed an additional research with taking into account the crystallinity and temperature dependences for diffusivity based on results of this study. If the attempts to prepare PMP membrane consisting mainly from crystallites [46] will be successful one can expect the appearance of the molecular sieving effect for C₄-C₆ hydrocarbons when the dimensions of the diffusing molecules will be close to the pore size in the PMP crystallites. In any case the proposed approach to the mathematical description of diffusion in PMP made it possible to obtain for the first time not only the temperature dependences of the C₁-C₃ alkanes diffusivity in crystalline and amorphous phase, but also to conclude that diffusion plays a key role in the selective transport of gases in semi crystalline PMP.

ACKNOWLEDGEMENT

The authors thank V.I. Kleiner for providing PMP polymer, N.M Smirnova for the films preparation and G.A. Shandryuk for carrying out the DSC analysis. Equipment for the gas permeability measurement from
the Center of collective use of TIPS RAS was applied. Results presented in this paper were obtained with financial support of RFBR Grant 15-03-03033.

LIST OF SYMBOLS

- PMP is poly(4-methyl-1-penten)
- BC is block-copolymer
- $X_C$ is degree of crystallinity
- $\Delta H_f$ is heat of fusion of PMP, cal g$^{-1}$
- $\Delta H_f^0$ is the heat of fusion for the 100% crystalline polymer, cal g$^{-1}$
- DSC is differential scanning calorimeter
- $T_g$ is the glassy temperature, K
- $T_m$ is the melting temperature, K
- $J$ is gas flux through membrane [cm$^3$/s];
- $J_{ss}$ is steady-state gas flux [cm$^3$/s];
- $A$ is the membrane area [cm$^2$];
- $H$ is a membrane thickness [cm];
- $C(x,t)$ is gas concentration in a sample [cm$^3$ (STP)/cm$^3$];
- $t$ is diffusion time [s];
- $x$ is coordinate [cm];
- $\Delta p$ is the gas pressure drop across the membrane [cm Hg];
- $P$ is the gas permeability coefficient [Barrer = 10$^{-10}$ cm$^2$ cm$^2$.sec.cm Hg], (the common units);
- $D$ is the gas diffusion coefficient [cm$^2$/sec], (the common units);
- $S$ is the gas solubility coefficient [cm$^3$(STP, gas)/cm$^3$ (polymer) cm Hg], (the common units);
- $\alpha_{SS}$ is an ideal selectivity of binary (components A and B) mixture separation;
- $\alpha_D$ is the kinetic component of ideal selectivity (separation because of the difference in diffusion coefficients);
- $\alpha_S$ is the thermodynamic component of ideal selectivity (separation because of the difference in gas solubility);
- $D_1$ is the diffusion coefficient in phase 1, [cm$^2$/sec];
- $D_2$ is the diffusion coefficient in phase 2, [cm$^2$/sec];
- $C_1$ is concentration of the diffusant in phase 1 [cm$^3$ (STP)/cm$^3$];
- $C_2$ is concentration of the diffusant in phase 2 [cm$^3$ (STP)/cm$^3$];
- $k_1$ is a local rate constant for the exchange of the diffusant between phase 1 and phase 2;
- $k_2$ is a local rate constant for the exchange of the diffusant between phase 2 and phase 1;
- $\varphi_1$ is volume fraction of phase 1 (dispersing media);
- $\varphi_2$ is volume fraction of phase 2 (dispersive inclusions), respectively ($\varphi_1+\varphi_2=1$);
- $D_{eff}$ is effective gas diffusion coefficient in binary heterogeneous polymeric systems;
- $S_{eff}$ is effective gas solubility coefficient in binary heterogeneous polymeric systems;
- $P_{eff}$ is effective gas permeability coefficient in binary heterogeneous polymeric systems;
- $K$ is constant considering an influence of the shape and concentration of inclusions on gas diffusivity;
- $W$ is factor taking into account of interacting particles for concentrated dispersion of sphericin inclusions.

REFERENCES

Diffusion of C2-C, Alkanes in Semicrystalline Poly

10: 2210-2216.


https://doi.org/10.1016/0033-3811(89)80060-8


https://doi.org/10.1016/j.cis.2014.10.004


https://doi.org/10.1016/S0376-7388(00)80160-X


https://doi.org/10.1103/PhysRev.24.575


https://doi.org/10.1016/S0376-7388(00)80161-1


https://doi.org/10.1002/andp.19354160706


https://doi.org/10.1002/app.1959.070010312


https://doi.org/10.2120/jps.3030490910


https://doi.org/10.1002/app.1968.070121207


https://doi.org/10.1002/pen.760203010


https://doi.org/10.1063/1.1731066


https://doi.org/10.1021/ie030789x


https://doi.org/10.1016/j.polymer.2013.05.074


https://doi.org/10.1016/j.jmbbm.2016.01.032


https://doi.org/10.1016/j.apsusc.2015.11.236


https://doi.org/10.1016/j.polymer.2013.05.075


https://doi.org/10.1155/2017/4250927


https://doi.org/10.1002/app.10164


https://doi.org/10.1002/app.10395


https://doi.org/10.1557/jmr.2016.471


https://doi.org/10.1007/978-94-009-1766-8


https://doi.org/10.1002/polb.1986.090240705


https://doi.org/10.1002/pol.1978.180160112


https://doi.org/10.1134/S0965544116100054

[44] Griffin JH, Ranby BG. Dilatometric Measurements on poly(4- methyl-1-pentene) glass and melt transition temperatures,
https://doi.org/10.1002/pol.1960.1204414408


https://doi.org/10.1002/polb.24150

Received on 24-04-2017 Accepted on 24-05-2017 Published on 31-05-2017

http://dx.doi.org/10.15379/2410-1869.2017.04.01.04

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0/), which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.