THEORY OF EMANATION THERMAL ANALYSIS IX. Inert gas release during thermal decomposition of solids

I. N. Beckman[1] *and V. Balek*[2]

[1]Department of Chemistry, Moscow State University, 199234 Moscow, Russia
[2]Nuclear Research Institute, CZ-25068 Řež, Czech Republic

The paper dedicated to K. B. Zaborenko, Emeritus Professor of the Moscow State University, at the occasion of her 80th birthday

Abstract

In the Emanation Thermal Analysis the release of inert gas atoms previously incorporated in the sample is measured. Results of the statistical modelling of the inert gas release during thermal decomposition of solids are presented. The updated model supposing three components in the solid-state reaction system including the formation of an intermediate metastable component on the surface of the newly formed component was proposed for the modelling of the ETA curves. The release of inert gas atoms previously incorporated into the sample is used as a probe of microstructure changes. The random nucleation mechanism was considered in the modelling. The model can be used in modelling ETA curves of solid-solid, solid-gas and solid-liquid interactions where the existence of metastable intermediate component is supposed.

Keywords: EGA, emanation thermal analysis, ETA, evolved gas analysis, inert gas release, micro-structure changes, modelling, thermal decomposition

Introduction

In numerous papers, review articles [1-6] and a monograph [7] the ETA has been described as a microstructure probe giving valuable information about solid-state processes. The microstructure and surface area changes are monitored by means of the ETA continuously at 'in situ' conditions of the sample heating. In addition to traditional methods of thermal analysis the ETA is able to reflect the topological aspects of thermal decomposition reactions. Comparison of the ETA results with the results of thermogravimetry or Evolved Gas Analysis (EGA) makes it possible to obtain an information about the topology and kinetics of the formation of the new phases. Differences in the EGA and ETA curves were used in the assessment or the mechanism of solid state processes, taking into account the morphology changes of the sample during these processes.

In the previous paper [8] we have demonstrated the EGA curves reflecting the release of gaseous products of thermal decomposition which may not correlate with the ETA curves, based on the measurements of inert gas release from samples previously labelled. Moreover, it was shown [8] that the TG and EGA curves may not correspond to the true picture of thermal decomposition of solids, which can lead to false conclusions on the mechanism of solid-state processes.

The theoretical approach proposed in [8] enabled us to explain (interpret) the ETA results. Nevertheless, peak-like effects on the experimentally obtained ETA curves observed, e.g. at temperatures corresponding to the maximal rate of thermal decomposition of solid, were not possible to be interpreted and mathematically treated in the frame of the model, designed in [8].

In this paper we describe an upgraded model of thermal decomposition of solid and the behaviour of inert gases release from the sample during thermal decomposition.

Used concept of the mathematical modelling

From the results of the modelling curves presented in work [8] we have seen that the time dependences of the radon release rate (from samples labelled by inert gas ancestor nuclides) are characterized by monotonously increasing or decreasing curves. However, the experimental ETA curves are often characterized by maxima at singular points, which cannot be simulated by means of the 'two-component model' used in [8]. In order to simulate ETA curves with maxima we have developed the model of thermal decomposition of solids supposing the presence of three components differing in their diffusion properties.

For the description of thermal decomposition reactions from the viewpoint of their time dependences and the development in volume the statistical modelling methods were used. The same method was used for the description of the release of gaseous reaction products and the release of inert gas previously introduced into the sample to serve as the morphology probe. The upgraded model supposes the random nucleation of the newly formed components and the formation of an intermediate (metastable) component on the interface between old and final component of the thermal decomposition of the sample.

The flux of gaseous products of thermal decomposition (EGA curve) and of the inert gas atoms (ETA curve) released during sample heating at a constant rate were simulated during modelling. The results of computer modelling were compared with the experimentally obtained curves.

Topological aspects of the solid state processes were discussed on the bases on comparison of EGA and ETA curves measured under conditions of sample heating at a constant rate.

Statistical modelling based on the 'three-component' model of the thermal decomposition of solids

In the proposed model we suppose the presence of three components of the mixture differing in the gas diffusion coefficients: the first, initial component, the intermediate metastable component, and the final stable new component. The new components possess different types of crystal lattice and different package density of the structure than the old one. Consequently, high strengths are imposed at the grain boundaries of the components resulting in the formation of mi-crodefects and possibly in the formation of an amorphous layer at the grain boundaries. The intermediate component is considered as a highly disordered material, characterized by a high diffusion coefficient of gaseous reaction products as well as inert gases (Rn) to be used as a probe of the sample microstructure.
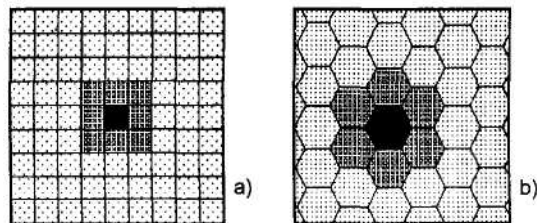

Fig. 1 Schemes demonstrating the effect of the shape of the lattice unit of the newly formed component on the intermediate component during thermal decomposition reaction; case a) cubic structure unit; case b) hexagonal structure unit

In order to demonstrate the order - disorder transition we have introduced the parameter A called as 'microstractural co-ordinating number'. The parameter Λ reflects the number of elementary units of the new component formed as the results of the transformation of one elementary unit of the initial component.

Two schematic drawings in Fig. 1 demonstrate the effect of the elementary lattice unit of the morphology of newly formed component formed on the interface of the initial and the new components. As it follows from Fig. 1 the size and shape of the elementary lattice unit can differ, causing mechanical stress in the interface and changes in whole lattice including the surface relief of the solid grains. Changes in the grain's surface may considerably affect fluxes of the fluids to released form the sample (i.e. gaseous reaction products, and inert gases, etc.)

The proposed model makes it possible to assess the influence of the intermediate component on the migration of gases. In this paper we have considered several cases of the thermal decomposition of solids differing in the Rn diffusion properties in the components.

Percolation theory

For the description of topological characteristics of gas migration in the heterogeneous medium of the sample during thermal decomposition the percolation theory [9, 10] was used. The percolation theory makes it possible to understand the role of irregular morphology in non-steady state solid state reactions and diffusion processes taking place in disordered structures. The percolation theory allows one to establish the relationship between the volume content of a new component and its fraction connected with the surface of a sample, since the gaseous products of reaction may migrate to the sample surface using diffusion pathways available at this component.

The main advantage of the percolation theory use in the modelling of thermal analysis results consists in the possibility to establish interrelations between the conversion degree and experimentally measured parameters, e.g. the mass of sample, the flux of gaseous reaction products released, etc.

Different mechanisms of the solid-state reactions can be considered in the interpretation of the thermal analysis results.

The differerce of the upgraded statistical model in comparison with the traditional percolation theory can be outlined as follows:

(i) Three distribution functions, namely for the components present in the sample and two values of the percolation threshold are considered in the upgraded 'three-component model'.

(ii) In the traditional percolation theory it is supposed that the amount of the new component increases monotonously. In the upgraded model, which considers the heating of the sample at the controlled temperature program, the kinetic parameters of the formation of the new components are depending on temperature, and are changing on heating.

(iii) In the traditional percolation theory approach one component is considered as totally impermeable for gases, the second component is considered as totally permeable for the gases. In the upgraded three-component model different values of gas permeability are considered for various microstructure of the components present in the sample.

Release of gaseous products of thermal decomposition and of inert gas used as the microstructure probe

In this paper the migration of gaseous reaction products measured at temperature controlled heating is controlled by diffusion, described by Arrhenius equations. For the description of the migration of inert gases three additional Arrhenius equations are used. The constants in the Arrhenius equations can be considered as parameters characterizing the effects of morphologies of the individual phases on the migration of gases.

During modelling the migration of gaseous products of solid-state reactions we have supposed that the gaseous products of the thermal decomposition reaction have been formed uniformly in the sample and migrate in the sample. The Fick's second law applied to the 'three-component' heterogeneous system was used in the description of the gas migration. The flux $J(t)$ of the gaseous products released from the

sample was determined using Fick's first law as depending on the shape and size of the sample, on the value of effective diffusion coefficient of the gas and on the concentration gradient of the gaseous products in the sample.

The inert gas is usually introduced into the solid sample by diffusion at elevated temperatures and pressure or by ion bombardment. In most cases the distribution of the inert gas in the sample is not uniform. The concentration profile depends on the conditions used for the inert gas introduction and the subsequent thermal treatment of the sample. The concentration profile must be taken into account in the modelling inert gas release curves (ETA curves).

For cases when the inert gas (Rn-220) is introduced into the sample by the recoil of its parent radionuclides (Th-228 and Ra-224, the recoil energy being 85 keV/atom) the concentration profile of the radon atoms is determined by the concentration profile of the parent radionuclides in the sample.

For a finely dispersed sample consisting of grains comparable to the path of the recoiled atoms of Ra and Rn a uniform labelling of the sample grains can be achieved, when the grains are comparable to the recoil depth (e.g. the silica the recoil depth is 65.4 nm for Rn-220 and 61.0 nm for Ra-224) [7]. Th-228 is considered as a quasi-permanent source of the inert gas atoms of Rn-220. In modelling the release curves of radon from a sample labelled by this way both diffusion and recoil mechanisms [7] of the inert gas release must be considered.

Analytical model of the gas release during thermal decomposition of solid samples

There is a disadvantage of the 'three-component' mathematical model developed for the release of gases during thermal decomposition of solids, as the diffusion equations used have no analytical solution. The modelling is based on Monte-Carlo method. Therefore this approach is not suitable for computer processing of EGA or ETA experimental data. The algorithms suitable for computer processing of EGA and ETA results were designed in the frame of a simplified model in which the diffusion equations have analytical solutions.

In the frame of the parallel diffusion mechanisms we have supposed that the total value of the total emanation power of the sample is composed by the sum of the emanation power values of individual components

$$E(t) = E_1\alpha_1(t)+E_2\alpha_2(t)+E_3\alpha_3(t) \qquad (1)$$

where α_1 α_2 and α_3 ($\alpha_1+\alpha_2+\alpha_3=1$) are volume fractions of the solid components present in the sample, namely α_1 is the old (initial) component, α_2 is the intermediate metastable component, α_3 is the new (final) component. The values of radon diffusion coefficient of the solid components of the sample D_1, D_2 and D_3 resp. are defined as $D_2>>D_1$ and $D_2>>D_3$. The random nucleation of the newly formed phases (described by the first-order reaction kinetic) is supposed.

The relationship (1) is valid for the isothermal conditions.

The emanation power of the slab-like sample of the thickness L can be expressed as follows

$$E_i=(1/L)(D_i/\lambda)^{1/2}\mathrm{th}L(\lambda/D_i)^{1/2} \qquad (2)$$

where λ is the radioactive decay constant of radon, D_i is the radon diffusion coefficient in individual component of the solid.

In the case that the solid state reaction takes place at the non-isothermal conditions, e.g. during the constant heating rate conditions, the temperature dependence of the radon diffusion coefficient can be written as follows, considering Arrhenius law

$$D=D_0\exp(-Q/RT(T_0+\beta t)) \qquad (3)$$

where Q is the activation energy of radon diffusion in the respective phase, D_0 is the pre-exponential factor characterizing the crystal lattice of the sample, T_0 is the temperature of the peak onset, β is the

heating rate, t is time.

During the random nucleation, the time dependence of the decrease of the amount of the initial component is determined by the integral Gauss distribution curve

$$\alpha_1(t) = \text{erf}\, z = \left(2/\pi^{1/2}\right)\int_0^z \exp\left(-t^2\right)\mathrm{d}t \qquad (4)$$

whereas the increase in the amount of the component new (final) can be written as

$$\alpha_3(t) = 1 - \alpha_1(t) = \text{erfc}\, z = 1 - \text{erf}\, z \qquad (5)$$

The time dependence of the amount changes of the content of the intermediate (metastable) component is expressed by the differential Gauss distribution curve

$$\alpha_2 = A\frac{\mathrm{d}}{\mathrm{d}t}\left[\alpha_3\left(Kt - T_m\right)\right] \qquad (6)$$

where A is the number of elementary lattice units of the metastable (intermediate) component which have been formed as the result of the transition of the elementary lattice unit of the initial component (The parameter A was introduced as a 'morphological co-ordination number'). The value of the parameter A reflects the height of the peak α_2 described by Eq. (6). K is the equilibrium constant of the solid state reaction yielding the intermediate (metastable) component, determined as the ratio $K = k_1/k_2$ where k_1 and k_2 are rate constants of the formation of the metastable intermediate component and the rate constant of the formation of the final component by the transformation of the metastable component, resp. The parameter K reflects the intensity of the solid state process, i.e. the width if the peak $\alpha_2(t)$ the parameter T_m reflects the position of the peak on the curve expressed by $\alpha_2(t)$ in the curve 2, Fig. 3.

On the bases of the simplified model a software package for the computer treatment of the EGA and ETA results was designed.

Results of thermal analysis curves simulation

Use of the THERMOKIN (simulated solid-state reaction) software package [11, 12] combined with the set of DIGS package (diffusion of inert gases in solids) [13] gave us the possibility to simulate inert gas probes diffusion in disordered solids and evolution of gaseous products of thermal decomposition at various experimental conditions.

In this paper the space distributions of the reaction components (both solid and gaseous) in the surface and whole volume of the sample calculated in the modelling process are presented. Following characteristics of the thermal decomposition kinetics and the gas evolution were calculated:

- time dependence of the volume fraction of initial component, $\alpha_1(t)$;
- time dependence of the volume of the newly formed component, $\alpha_3(t)$;
- time dependence of the volume metastable newly formed component, $\alpha_2(t)$;
- time dependence of the sample mass, $M(t)$;
- time dependence of the flux, $J(t)$, of the reaction products released from the sample;
- time dependences of the release of inert gases previously introduced into the sample, $J_{ig}(t)$;
- time dependences of the release of inert gases from samples labelled by the parent nuclides (emanation release rate, ETA-curve), $E(t)$.

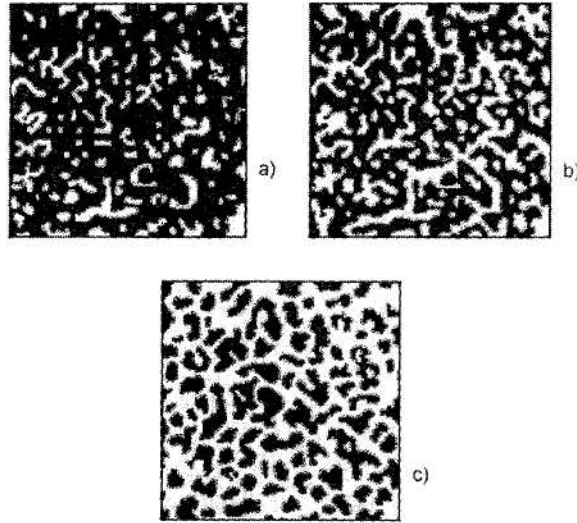The computer experiments were performed in two steps, using the statistical model described above.

Fig. 2 Statistical modelling of thermal decomposition of solids using a 'three component' model where the existence of a metastable intermediate component is considered, a) The initial period of the reaction (isolated clusters of the new phase are totally surrounded by the initial component); b) The stage of the reaction corresponding to the interconnection of the intermediate components; c) The final stage of the reaction. Following symbols denoted the individual components: black - initial (old) component; hatched - intermediate metastable component; white - stable final (new) component of the thermal decomposition

First step consisted of the calculations of volume distribution of each of the three components present in the sample for several temperatures. In Fig. 2 we demonstrate three examples of the statistical modelling experiment describing three stages of the thermal decomposition of material. The mechanism of a random nucleation of the new phase throughout the whole volume of the initial phase, accompanied by the gaseous products production was considered. The decomposition of the initial phase is described by the first-order kinetics. The kinetic parameter of the nucleation of the new components were considered as constant, the intermediate (metastable) components is situated on the interphase boundaries between the initial and new components.

At the very beginning of the thermal decomposition clusters of the newly formed component are totally surrounded by the initial phase (Fig. 2a). In the course of thermal decomposition reaction the intensity of the nucleation of the new component increases, the clusters of the new metastable component become interconnected, enabling the gaseous products to migrate to the surface of the grain (Fig. 2b). As long as the amount of the initial component diminishes and the amount of the new component increases, the structure of the sample is broken which enhances the release of the gaseous reaction products from the sample.

It is to point out that the intermediate component is a highly disordered material characterised by a high inert gas diffusivity. The increasing amount of the new component is reflected by the EGA and ETA curves as a sharp increase of the inert gas release. From the metastable component the stable component of the final product is formed. The amount of the intermediate metastable component first increases and after reaching its maximal value decreases. The amount of the stable final component increases, starting from a certain moment. At the final stage of the thermal decomposition reaction isolated clusters of the old component surrounded by the new components of the sample exist. This stage is schematically demonstrated in Fig. 2c. At the very end of the reaction a homogeneous material consist only of the new final component.

Second step of the statistical modelling consisted in the calculation of the flux $J(t)$ of gaseous products. The ETA curves were modelled for samples labelled by inert gases as such as well as for samples labelled by the inert gas parent nu-clides, Th-228 and Ra-224. The results obtained by numerical

methods were compared with the ETA curves obtained by analytical methods. The resulting curves are identical. Therefore, we shall present here the results obtained by means of the simplified model described above.

Following parameters characterizing thermal decomposition reaction and transport properties of the individual component were considered in the modelling: $A=0.25$, $K=T_m=2.2$. The values of parameters E_1 E_2, E_3 correspond to the state, when the intermediate phase possesses a much higher disorder degree than the initial and final phases, resp. i.e. $E_1=0.04$; $E_2=1.0$; $E3=0.4$. The isothermal conditions of the thermal decomposition were considered.

The calculations made by using the Eqs (4), (5) and (6) enabled us to obtain time dependence of the concentrations of the initial, final and intermediate phases, resp.

As it follows from Fig. 3, curves 1-3, the amount of the initial phase monotonously decreases from 1 to 0 (curve 1) whereas the amount of the final phase increases from 0 to 1 (curve 2). The time dependence of the amount of the intermediate metastable phase is described by a peak-like curve (curve 3). The model ETA curves were obtained using Eq. (1), and taking into account Eqs (2) (3) and (6). In Fig. 3, curve 4, we demonstrated the model ETA curves reflecting the subsequent processes order-disorder-order taking place in the sample due to changes of the morphology during thermal decomposition.
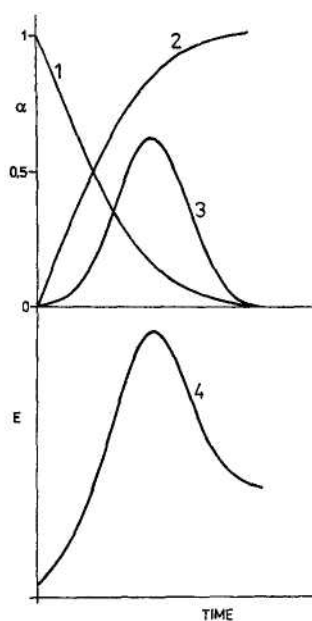

Fig. 3 Isothermal kinetic curves of thermal decomposition reaction of a solid sample based on the 'three-component model'. Curves 1, 2 and 3 describe changes of the amount of the respective components 1, 2 and 3 in the sample; curve 4 describe changes of the emanation power E of the sample labelled uniformly by the radon parent nuclide. Following parameters were used in the modelling : $A=0.25$, $K=2.2$, $T_m=2.2$, $E_1=0.04$, $E_2=1.0$, $E_3=0.4$
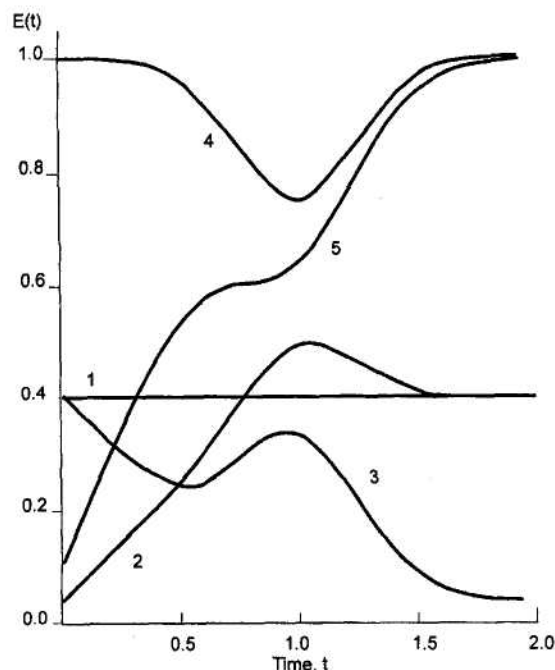
Fig. 4 Time dependences of the emanating power E characterizing morphology changes during thermal decomposition of a solid sample at isothermal conditions. The curves were obtained by mathematical modelling using the 'three-component model' and supposing a uniform labelling of the sample by the inert gas parent nuclides. Various values of E_1 E_2 and E_3 were considered in the model curves 1-5. Following parameters of the solid-state reactions were considered in the modelling: $A=0.08$, $K=T_m=2.7$

Table 1 Values of E_1, E_2, and E_3 considered in the simulated ETA curves

Curve	E_1	E_2	E_3
1	0.4	0.4	0.4
2	0.04	1.0	0.4
3	0.4	1.0	0.04
4	1.0	0.005	1.0
5	0.1	0.1	1.0

In Fig. 4 we demonstrate ETA model curves as obtained by the mathematical modelling supposing isothermal heating. Curves 1-5 in Fig. 4 correspond to cases where different values of E_1, E_2 and E_3 of the components present in the sample are supposed. Table 1 lists the respective values of E_1, E_2 and E_3.

From Fig. 4 it is obvious that the shapes of ETA curves are strongly dependent on the values of the emanating power of the phases present in the sample, E_1, E_2 and E_3. The values of E_1, E_2 and E_3 depend on the values of the radon diffusion coefficient corresponding to the respective phases.

The simulated ETA curves depend also on the rate constant of the thermal decomposition reaction, and on the parameter A called the microstructural coordinating number, reflecting the number of lattice unit of the new component formed due to the transformation of one lattice unit of the initial phase, and on other parameters describing the solid state process.

From Fig. 4 it follows that the time dependence of the total emanating power E (the ETA curves) may considerably change in the course of the solid state reaction. From the above discussion of the ETA curves it became obvious, that the ETA is a sensitive method making possible to reveal the presence of intermediate metastable component during solid-state reaction, as well as the dynamics of its formation

from the initial component and its subsequent transformation to the final component. By this way the emanation thermal analysis is sensitive enough to the changes in the microstructure of the sample taking place as a result of the various solid state processes.

The presented model approach enabled us to consider different properties (radon diffusion coefficient values) for the reaction intermediate products with regard to the initial solid and final reaction products.

Conclusions

The presented 'three-component' model enabled us to consider different transport properties (expressed by the values of radon diffusion coefficient) for the reaction intermediate products with regard to the initial solid and final reaction products. Five different cases of the ETA model curves describing varying morphology changes during solid-state reaction are presented using this model. This theoretical work represents the bases for the upgraded interpretation of the ETA experimental results and demonstrates the wide potential of the ETA use in the characterization of solid-state processes.

References

1　K. B. Zaborenko, R. Thatner and L. L. Melikhov, Soviet Radiochem., 5 (1963) 360.
2　V. Balek, S. D. Baikov and K. B. Zaborenko, Soviet Radiochem., 12 (1979) 137.
3　K. B. Zaborenko, L. L. Melikhov and V. A. Portyanoi, Soviet Radiochem., 7 (1965) 319.
4　 K. B. Zaborenko and I. N. Beckman, Soviet Radiochem., 10 (1968) 268.
5　K. B. Zaborenko and V. Balek, Russ. J. Inorg. Chem., 11 (1969) 457.
6　V. Balek, Thermochim. Acta, 192 (1991) 1.
7　V. Balek and J.Tölgyesy, Emanation thermal analysis and other radiometric emanation methods in: Wilson and Wilson's Comprehensive Analytical Chemistry, part XII C, Elsevier Science Publishers, 1984, p. 304.
8　V. Balek and I. N. Beckman, 'Modelling thermal decomposition of solids as reflected by gas evolution curves', Thermochim. Acta, (1998) (in print).
9　S. Kirkpatrick, Reviews of modern physics, 45 (1973) 574.
10 Fractal in physics.-Ed. by L. Pietronero and E. Tosatti, Proc. of the Sixth Trieste Int. Symp. on Fractal in Physics, ICTP, Trieste, Italy, 1985, p. 625.
11 I. N. Beckman, A. V. Zheleznov and V. Balek, J. Thermal Anal., 37 (1991) 1479.
12 V. Balek, I. N. Beckman and A.V. Zheleznov, J. Thermal Anal., 39 (1993) 1019.
13 I. N. Beckman, A. A. Shviryaev and V. Balek, Synthetic polymeric membranes (Eds. B. Sedláček and J. Kahovec) 1987, Walter de Gruyter & Co.Berlin-New York, p. 363.