Translated from *Uspekhi Khimii*, **57**, 903-928 (1988) U.D.C. 532.72 + 533.15 : 539.216.2

Modern Ideas About Diffusion in Polymer Systems

A.E.Chalykh and V.B.Zlobin

The experimental data and theoretical approaches concerning processes involving the diffusion of low-molecular-weight substances in polymer systems are examined. Information is presented about the influence on diffusion of the degree of crystallinity and filling, of the physical state of the diffusion media and the size of spherulites, of the composition and structure of the copolymer macromolecular chains, and of the size of the diffusing molecules. The possibility of using diffusion measurements to investigate the phase and supermolecular structures of polymers, the construction of phase diagrams, and to determine the thermodynamic parameters of the interaction of the components of polymer solutions is demonstrated. The bibliography includes 101 references.

CONTENTS

I. Introduction 504
II. The influence of the nature of low-molecular-weight substances on their diffusion in polymers 505
III. The influence of the nature of the high-molecular-weight component 507
IV. Diffusion in heterogeneous systems 511
V. Diffusion methods for the study of polymer systems 515

I. INTRODUCTION

Considerable interest has been shown in recent years in the study of diffusion phenomena in polymers. In our country alone, a whole series of monographs[1-10] devoted to the consideration of various aspects of this problem were published between 1980 and 1987. There are several causes of such interest. Firstly, the vigorous development of membrane technology, the need to create effective anticorrosion polymer coatings, and the description of the kinetics of phase decompositions, structure formation, as well as polymerisation at high conversions require detailed information about the mutual diffusion and self-diffusion coefficients and their dependence on concentration, temperature, pressure, and phase and supermolecular structures of polymeric media. Secondly, the development of theoretical concepts, mainly reptation ideas concerning the translational mobility of macromolecules in solutions and melts,[10,11] has stimulated experimental studies on the molecular dynamics of chains[1,10] and the development of new methods for the investigation of the local mobility of end groups, monomeric units, and macromolecules as a whole.[8,9] The development of the theory of free volume and activation zones[7,10] plays an analogous role in the study of the diffusion of low-molecular-weight substances. Thirdly, the creation of effective methods for the investigation of mutual diffusion and self-diffusion, on the one hand, and the development of phenomenological and thermodynamic approaches,[12] on the other, promoted in their turn not only the solution of a whole series of practical problems but also the development of a new trend—the use of diffusion measurements for the study of molecular, phase, thermodynamic, and defect characteristics of polymer materials.[3,6,7,10,13]

Evidently, in a single review it is impossible to consider even in a concise form the present state of research into various aspects of the problem of diffusion phenomena in polymers. We shall therefore confine ourselves to a small group of questions which are fundamentally important both for the prediction of the separating properties of membranes and for the analysis of the characteristics of their formation and the determination of their structural-morphological and phase inhomogeneities.

The review does not discuss the question of the mechanism of the diffusion of low-molecular substances in polymeric media. However, one should bear in mind that, in considering research results, we were guided by the following postulates. The translational thermal movement of small molecules in polymers takes place, regardless of their physical state, as a result of consecutive elementary jumps over distances of the order of the molecular diameter of the diffusing species. The occurrence of an elementary jump requires the presence near the molecule of a microcavity—vacancy, whose volume v^* is greater than the volume of the diffusing molecule V or is comparable to it. A vacancy is formed via a thermofluctuation mechanism as a result of a set of small-scale segmental movements manifested in a β-relaxation process.[1,8,14] The rotation of low-molecular-weight species in polymer media is a faster process than translation and during the period of its "settled life" the molecule has sufficient time to undergo repeated changes in its orientation.[1]

Within the framework of a qualitative picture of the mechanism of diffusion in polymers, two virtually equivalent expressions are used for the diffusion coefficient:

$$D = D_0 \cdot \exp(-E/RT) \quad (1)$$

(the so called activated diffusion model) and

$$D = A_1 \cdot \exp\left(-\gamma \frac{v^*}{v}\right) \text{ or } D = A_2 \cdot \exp\left(-\frac{B}{f}\right) \quad (2)$$

(the free volume model). Here D_0, A_1, and A_2 are the pre-exponential factors, E is the apparent activation energy for diffusion, R is the gas constant, γ and B are constants, and v and f are the free volume and the fraction of the free volume in the diffusion medium. Different expressions for D_0, E, and f can be found in a number of publications.[1,7,10]

II. THE INFLUENCE OF THE NATURE OF LOW-MOLECULAR-WEIGHT SUBSTANCES ON THEIR DIFFUSION IN POLYMERS

It has been shown[1-10] that the rate of mutual diffusion and self-diffusion in polymer systems is determined not only by external factors (temperature, composition, and pressure) but by a whole series of internal parameters, which depend both on the individual characteristics of the system components and on the properties of the system as a whole. We shall enumerate some of them: molecular weight (M_1) and molecular weight distribution (MWD) of the polymer, the monomeric coefficient of friction, the microviscosity, and the thermodynamic non-ideality of the solution. The influence of molecular-chemical parameters of the low-molecular-weight component (diffusant, penetrant, sorbate, and solvent) and, in particular, its M_1 and the dimensions, shape, and structure of its molecules on its diffusion in polymeric media is considered in this Section. We may note that the determination of a quantitative relationship between the molecular characteristics of the diffusant and its diffusion parameters in polymers is one of the main problems of diffusion kinetics, because it opens up extensive possibilities for predicting the selective and protective properties of membranes, coatings, and shells.

1. The Influence of the Molecular Weight of the Diffusant

In considering the influence of the molecular weight of the molecules diffusing in polymers on D, one usually employs the empirical Auerbach equation

$$D = KM_1^{-b} \quad , \tag{3}$$

where K nd b are constants. This type of relation is common to all cases of translational migration of molecules in viscous media and, from a formal point of view, it follows from hydrodynamic ideas concerning diffusion.[15] Eqn.(3) holds both in low-molecular-weight media, for example in the diffusion of saturated hydrocarbons, alcohols, diols, and triols in benzene, methanol, and water,[2,16] and in the diffusion of macromolecules in infinitely dilute solutions; in the former case, $b = 1$, while in the latter b varies from 1/2 to 1.[15,17]

The diffusion of low-molecular-weight substances in polymeric media of different nature is in most cases described satisfactorily by Eqn.(3). Comparative analysis of the numerical values of the constants of Eqn.(3) for different homologous series, carried out by a number of investigators,[2,7,9] permits the following conclusions. Firstly, Eqn.(3) holds as a rule within the limits of a single homologous series of diffusants, for example, $Y-(CH_2)_n-CH_3$, i.e. when the functional group P is constant and only the number of repeating units n changes. When Y is altered, i.e. on passing from one homologous series to another, the $\lg D - \lg M_1$ plot shifts along the ordinate axis, but b remains almost unchanged. This effect is observed, for example, for polybutadiene, polyethylene, polyisoprene, and polyvinyltrimethylsilane on passing from saturated hydrocarbons to their isomers, alkylbenzenes, and dibasic saturated and aromatic acid esters.[7,9]

Secondly, for polymeric media, we have $b > 0.5$ and its value increases on passing from one polymer to another in proportion to the increase in their molar cohesion energy δ_2 (δ_2 is the solubility parameter[18,19]). The quantity K varies in inverse proportion to the monomeric coefficient of friction of the macromolecules ξ and the molar volume of the diffusing molecule or functional group V_x. The following expressions have been proposed:[7]

$$b = 1.4(\delta_2 - \delta_0) \text{ and } K = kT/V_x\xi,$$

where k is an empirical constant and δ_0 the minimum value of δ_2 for polymers.[18] This makes is possible to estimate the diffusional component of the separation coefficient for the polymer membrane:

$$\alpha = \frac{D_i}{D_j} = \frac{V_{xj}}{V_{xi}}\left(\frac{M_i}{M_j}\right)^{-1.4(\delta_i-\delta_0)} , \tag{4}$$

where the indices i and j denote diffusants of different nature.

Thirdly, cyclic, halogen-containing, and aromatic compounds with condensed benzene rings constitute a special group among hydrocarbons. For these classes of diffusants, as for azo-dyes and antioxidants,[20,22] the slope of the $\lg D - \lg M_1$ straight line is fairly large ($b \geqslant 4$). Two factors should be noted: (1) the $\lg D - \lg M_1$ straight lines for the above systems intersect on extrapolation with the corresponding straight line for saturated hydrocarbons at the point which corresponds to the molecular weight of methane; (2) when a new repeating group, for example CH_2, is introduced into the molecules of these compounds, they initiate new $\lg D - \lg M_1$ straight lines. The unusual behaviour of diffusants of these classes compared with open-chain hydrocarbons is due to the fact that the introduction of a certain repeating group alters not only M_1 each time but also the cross-section of the diffusing species.

Finally, the displacement of the functional group along the skeleton of the diffusant molecule and the change in its nature for V_x = const. as a rule do not affect D even if one is dealing with the translational diffusion of polar substances in polar polymers.[23,24]

Together with the molecular weight, in the analysis of diffusion processes involving low-molecular-weight substances in polymeric media the geometrical parameters of the diffusing molecules are widely used: the molar volume V, the length l, and the cross-section σ. The above data permit the claim, in our view, that the molecular weight as well as other indirect characteristics (the critical volume V_{cr}, the constant b_W in the van der Waals' equation, and the viscosities of liquids) play the role of independent arguments in the equation for the rate of transport only because they characterise the geometry and structure of the diffusing molecules. For example, the relation between D and M_1 for the homologous series of alkanes is determined by the fact that M_1 is directly related to the length of the molecules; in the case of cyclic hydrocarbons, the variation of M_1 characterises to a first approximation the variation of the cross-section of the diffusing molecules. The role of the geometrical constants of molecules diffusing in polymeric media has been examined in a number of studies.[24-30]

The free volume model is the most convenient for the analysis of the influence of molecular volume on the diffusion of molecules in polymers. It is natural to suppose that the critical volume of the vacancies is proportional to the molar volume of the diffusing molecule: $v^* \cong aV$, where a is a constant. Evidently a similar relation can be formulated also for V_{cr} and b_W. On substituting these relations in Eqn.(2), we obtain the expression[7]

$$\ln D = \ln A - \gamma \frac{a}{v} V \tag{5}$$

The activated diffusion model, where it is assumed that $E = E_0 + bV$, leads to an analogous result.[6,10,31]

Analysis of the experimental data within the framework of this approach showed[3,7,9,20,31] that, for the majority of systems where the shape of the diffusant molecules is close to spherical, a satisfactory agreement with theoretical predictions is observed. The experimental points corresponding to different representatives of homologous,

genetic, and, what is especially important, isolytic series are disposed in the vicinity of $\ln D - V$ straight lines whose slope is determined by the average free volume of the polymeric diffusion medium.

However, in the case of significantly asymmetric diffusant molecules, even for members of a single homologous series, Eqn.(5) is valid only to a first approximation. This is associated with the fact that, in the derivation of Eqn.(5), no account was taken of the specific features of the structure of both the diffusant molecules and the vacancies in the polymeric medium: they were all represented approximately by effective spheres, in conformity with the solid sphere model. On the other hand, it has been noted[7] that a is a function of the ratio σ/l; the smaller a is, the smaller is the ratio σ/l. Analysis of these data permitted[7] a number of conclusions concerning the character of the orientation of molecules in polymeric media relative to the direction of the diffusion flux. It was established that the transverse dimensions of the vacancies for linear and bulky molecules are significantly smaller than their length and effective cross-section (solid sphere) and are identical—for members of the given homologous series—with the dimensions of the largest functional group. For all the members of a single homologous series, the cross-sections of the vacancies remain unchanged. Under these conditions, they depend only slightly on the nature of the polymeric medium in which the diffusion process takes place.

From this it follows that molecules with a complex structure are oriented in the diffusion flux relative to the concentration gradient in such a way that they suffer the least resistance from the polymer matrix.

2. Activation Energy for Diffusion and Molecular Size

Depending on the structure and shape of the diffusant molecules, they can be divided into four groups: spherical, non-spherical, bulky, and linear.

Spherical molecules. This group includes, for example, the inert gas molecules. Analysis of experimental data has shown that the number of studies of diffusion in the same polymers of four and more types of spherical molecules is small.[31,32] For these diffusants, E increases with increase in the diameter d of the molecules (Fig.1). On passing from one polymer to another, the character of the dependence of E and d remains the same and only its steepness changes. Thus the dependence of E and d for polydimethylsiloxane can be fitted by the power equation $E \propto d^n$, where $n = 1$; for *cis*-polyisoprene and polyethylene $n = 2$ and for poly(vinyl acetate), poly(vinyl chloride), and poly(ethyl methacrylate) $n = 3$. Thus the power exponent increases with increase in the molar energy of cohesion of the polymeric medium. The unusual behaviour of E for diffusion in polar and non-polar polymers at temperatures above the glass point is striking. For the diffusion of He and Me in polyisoprene and polyethylene, E was found to be greater than for the diffusion in poly(vinyl acetate) and poly(ethyl methacrylate), while the opposite effect was observed for Ar, Kr, and Xe.

The experimental relations between E and d for the simplest diffusants cannot be fully accounted for within the framework of the Meers, Brandt, Pola – Di Binedetto, and Pace – Datyner models,[10,33,34] although they all correctly predict the qualitative picture of the changes in the activation energy for diffusion as a function of the molecular diameter, the size of the macromolecular segment, and the molar energy of cohesion of the polymeric medium. It has been shown[7,35] that a balanced approach requires not only the introduction of two different expressions for the energy formation of vacancies in the diffusion medium ($E_g \propto X^2$ and $E_g \propto X^3$, where X is the diameter of the vacancies) but also the allowance for the character of the distribution of vacancies with respect to size. Only then is it possible to explain also the anomalies in the variation of E for $d \leqslant 2.8$ Å and the dependence of E on the previous thermal history of polymer membranes.[36]

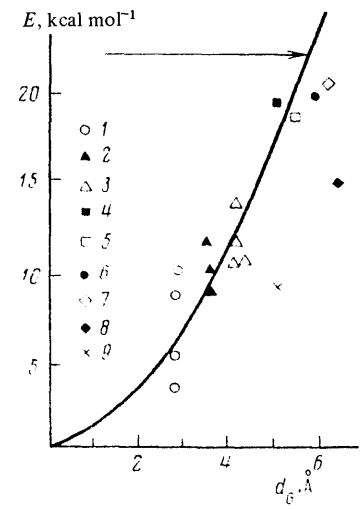


Figure 1. Dependence of the activation energy for the diffusion of gases in polyethylene on their gas-kinetic diameter:[7] 1) He; 2) Ne; 3) Ar; 4) Kr; 5) Rn; 6) CCl_4; 7) $C(CH_3)_4$; 8) SF_6; 9) CH_4. The continuous curve was calculated by the equation $E \propto d^n$, where $n = 2$; the arrow denotes the activation energy for the viscous flow of the polyethylene melt.

Non-spherical molecules. The molecules of simple gases can be included in this classes of diffusants: H_2, N_2, O_2, CO, CO_2 etc. By analogy with the inert gases, the gas-kinetic diameter d_G is usually employed as the main parameter characterising their dimensions. However, the behaviour of these molecules in diffusion processes in gaseous and condensed media is fundamentally different. Non-spherical molecules in the gas phase exist most of the time in a state of "free motion" and they interact with one another during a relatively short fraction of the time. During their movement, the molecules rotate freely, which leads to the absence of a correlation and the mutual orientation of the molecules during subsequent collisions.

In a polymeric phase the position is different. The dissolved gas molecule vibrates most of the time in a cell[1] until a vacancy of specific size appears next to it. For a spherical molecule, it is immaterial on which side a vacancy appears provided only that the relation $X > d$ holds. The situation is different for non-spherical molecules. Their shape can be represented approximately by an ellipsoid of rotation[37] with longitudinal ($d_{\parallel}$) and transverse ($d_{\perp}$) dimensions. Evidently, since $d_{\parallel} > d_{\perp}$, the probability of the appearance of

a vacancy with $X \geqslant d_{\perp}$ is greater than that of the appearance of a vacancy with $X \geqslant d_{||}$. Therefore the gas-kinetic diameters of these molecules are always greater than the diameters of the vacancies.[35,37]

The following mechanism has been proposed[32,37] for the determination of the effective sizes of non-spherical molecules diffusing in polymers. It is based on the experimental graphical dependence of E on d for the diffusion of inert gases in the given polymer. The effective diameter d_{eff} of any molecule, including a non-spherical molecule, can be determined from this relation and the activation energy for the diffusion of the diffusant investigated, which is also found experimentally. It has been shown[7] that d_{eff} for diffusing molecules changes somewhat (up to 8%) both on passing from one polymer to another and when the conditions in the preparation of the same polymer are altered. Thus, for this group of diffusants one can use in the calculation of E the power relations $E \propto d^n$, which have been obtained for spherical test molecules, but for d one must use not the gas-kinetic but an effective molecular diameter.

Bulky molecules. The CH_4, CCl_4, $C(CH_3)_4$, C_6Cl_6, SF_6, etc. molecules belong to this class of diffusants. If their size is estimated from d_6 or from the structural diameter, than the values of E for such substances should not fit on the relation between E and d obtained for the inert gases (Fig.1). The values of d_{eff} found by the above method for these molecules are always smaller than d_G and for bulky molecules the discrepancies are greater than in the case of non-spherical molecules. Graphical analysis[37] has shown that the minimum dimensions of the molecules which determine their motion in the polymer matrix are similar for all the substances enumerated.

A characteristic feature of bulky molecules is their variable diameter along the threefold symmetry axis in the tetrahedron [CH_4, CCl_4, $C(CH_3)_4$] and along the fourfold axis in the octahedron (SF_6). Thus in methane the apical atom has a diameter of 2.34 Å, while the diameter of the plane of the base of the pyramid is 4.4 Å. For sulphur hexafluoride, these values are 1.86 and 6.4 Å. Comparison of these quantities shows that the diameters of the apical atoms are always smaller than the values of d_G, which are in their turn smaller than the molecular sizes in other cross-sections. It follows from the foregoing that vacancies whose critical diameters are smaller than d_G are responsible for the migration of bulky molecules in polymeric media.

Linear and chain molecules. For diffusants of this class, the parameter characterising the molecular size used traditionally has been either their molecular weight, or the number of repeating groups, or the number of carbon atoms in the chains n_C. For these systems, the dependence of E on M_1 can be fitted by the semi-empirical expression

$$E = A + B \lg M_1 , \qquad (6)$$

where A and B are empirical constants. The method described above has been used[7,37] to estimate the sizes of vacancies through which the elementary step in the translational movement of oligomeric and polymeric molecules takes place. Comparison of the relations between E and n_C for different members of the homologous series of olefins, including polyethylene melts,[2,10] with the corresponding relation between E and d for the molecules of ideal gases shows that the size of the vacancy changes from 3.4 to 5.6 Å on passing from methane to a polyethylene macromolecule with $M \cong 10^5$. Assuming that the movement of linear molecules takes place via the reptation mechanism, it is easy to demonstrate that 4–5 monomeric units participate in the formation of the reptation loop of the polyolefin.

Theoretical studies on the activated model of diffusion in polymers have been directed mainly towards the development of the ideas of Brandt and Meers. At the present time the most effective molecular theory of diffusion is the Pace–Datyner theory,[33,34] which made it possible to obtain analytical expressions for D_0 and E in the Arrhenius equation on the basis of information about the macromolecular structure, crystallographic data, intermolecular interaction parameters, and the molecular diameter. One should also note a theoretical study[35,37] in which an attempt was made to take into account the contribution to E by the size distribution of the free volume vacancies of the polymeric medium. In these investigations, expressions were obtained for the average size of the free volume vacancy and the average size of the vacancy participating in the elementary diffusion step; the form of the relation between E and d was discovered and a formula was proposed for the determination of the volume of activation. Presumably these investigations permit the solution also of the converse problem—the determination of the size distribution of the free volume vacancies in the polymer membrane from data for the diffusion of the inert gases.

III. THE INFLUENCE OF THE NATURE OF THE HIGH-MOLECULAR-WEIGHT COMPONENT

1. The Influence of the Molecular Weight, the Molecular Weight Distribution, and the Three-dimensional Cross-linking

The influence of the molecular weight (MW) of the polymers on their permeability to gases and vapour has been most fully studied.[20] It has been found that a change in the MW of the macromolecules in the diffusion medium from 1×10^4 to 1×10^6 does not affect the rate of transport of gases and vapours. A small change in the permeability of polyisobutylene to moisture (from 10.7×10^{-13} to 3.3×10^{-13} mol cm^{-2} cm^{-1} h^{-1}) has been noted after an increase in its MW from 4.5×10^3 to 25×10^3.[38] The influence of the MW of polymers on the diffusion of monomers, solvents, and oligomers has been studied in less detail.

Most of the experimental data obtained for such systems refer to infinitely dilute solutions of polymers.[10,15] For this range of concentrations in binary systems, the mutual diffusion coefficient D_{21}, characterising the translational mobility of macromolecules in solvents, varies with the MW of the polymer (M_2) in accordance with the equation

$$D_{21} = K M_2^{-b} , \qquad (7)$$

where K and b are constants. Individual investigations have been carried out in the field of concentrated solutions.[2,7] With increase in the MW of the polymer, the diffusion coefficients in these solutions either remain unchanged, as, for example, in the benzene–polycarbonate, benzene–polystyrene, and octadecane–*cis*-polyisoprene systems or decrease, tending asymptotically to their limiting values for a certain M_2', as has been observed, for example, in the dioctyl phthalate–poly(vinyl chloride) ($M_2' = 4 \times 10^4$), cyclohexanone–polyhydroxyesters ($M_2' = 1.5 \times 10^4$), and hexadecane–polyethylene ($M_2' = 5 \times 10^3$) systems. The polystyrene–cyclohexanol, polybutadiene–diheptyl phthalate, and polyhydroxyesters–dibutyl

phthalate systems, for which the mutual diffusion coefficient in the middle range of solution compositions increases with increase in the MW of the polymer, are exceptions.

In the middle 1970s, the interest in this problem grew again in connection with the creation of telomers and oligomers with a narrow MWD and the development of methods permitting the measurement of the partial mobilities of solution components.[10,11] Interesting results were obtained for the influence of the MW of the polymeric component on the self-diffusion (D_1^*) and mutual diffusion (D_V) of the solvents and empirical relations linking D_V and D_1^* to the MW of the polymers were proposed;

$$\lg D_V = \lg D_{V,\infty} + A/M_2 \text{ and } \lg D_1^* = \lg D_{1,\infty}^* + B/M_2 , \quad (8)$$

where A and B are empirical constants and $D_{i,\infty}$ are the diffusion coefficients at $M_2 \to \infty$. It was shown that the anomalies described above in the variation of the diffusion coefficients are associated with the thermodynamic non-ideality of the systems and the remoteness of their state from the critical state.[2-10]

It has been shown[2,7] that the problem of the influence of the MW of the macromolecules on the diffusion properties of polymer matrices and membranes can be approached from the standpoints of the free volume theory, because the fraction of the free volume of the diffusion medium f depends on M_2 as a consequence of the variation in the number of end groups per unit volume. It follows from the statistical theory of polymers and the results of numerical modelling that the Brownian movement of the end groups of linear macromolecules is more intense than the thermal movement of the units of the main chain. This effect has been called the "hot ends" effect.[11,39] Semiquantitative estimates have shown that the end groups of macromolecules possess kinetic energy which is greater by 20–25% than that of the internal groups.[40] Frenkel' suggested that the mobility of the end groups be characterised by the diffusion coefficient of the monomer.[41] Direct estimates of the rotational and translational mobilities of the chain units and end groups of macromolecules in the condensed phase and in solution have been made.[1,42]

All these factors make it possible to attribute to the end groups of the macromolecules a local free volume different from the local free volume of the main chain units and the monomer. The average free volume of the diffusion medium made up of such molecules can then be represented by the sum of the local free volumes. In accordance with this hypothesis, the following relations have been obtained for polymer melts:

$$\ln \frac{D}{D_\infty} = \frac{B}{f_\infty} \cdot \frac{aM_2^{-1}}{f_\infty + aM_2^{-1}} , \quad (9)$$

$$\lg D \simeq \lg D_\infty + A/M_2 . \quad (10)$$

The last equation holds for $M_2 > 10^3$. Here a and A are constants and f_∞ is the fraction of the free volume of the polymer membrane at $M_2 \to \infty$. It can be seen that Eqn.(10) agrees fully with the empirical expressions (8). These equations have been used in calculations from experimental data of the numerical values of the free volumes corresponding to the end groups (f_e) and the monomeric units (f_{un}). It has been shown that $f_{un} < f_e < f_1$, where f_1 is the free volume per unit of monomer. Under these conditions, f_e is greater by 15–30% than f_{un}. The quantity f_e can be regulated by varying the chemical nature of the functional end group.[43]

In conclusion of this Section we may note that, firstly, the diffusion coefficients of low-molecular-weight substances in polymer glasses also decrease with increase in the MW of the macromolecules. However, this dependence is less pronounced, is observed in the region of low molecular weights, and is manifested against the background of a considerable scatter of experimental points.[44] Subsequently, direct experiment demonstrated[10,44] that the rates of diffusion of gases and solvents in polymers are determined by their number-average MW in conformity with the conclusions which follow from the free volume theory.

The question of the influence of the MW of macromolecules on the diffusion properties of polymeric media is in its theoretical aspect part of the more general problem of the contribution of the end units of macromolecules to the kinetic properties of polymeric bodies. One must distinguish two extreme cases: in the first, the free or "hot" ends of the chains are of decisive importance, while in the second fixed or "cold" ends are important. The first case obtains in systems with linear macromolecules and the second in systems incorporating three-dimensionally cross-linked structures. Whereas the free ends of the chains exert a perturbing influence on the conformational state of the segments of macromolecules, increasing their mobility and free volume, the fixed chain ends have the opposite effect.

Experimental studies on the molecular movements and the rates of diffusion of low-molecular-weight substances in cross-linked polymers have demonstrated unambiguously the retarding effect of the modes of the three-dimensional network on the mobility of the structural elements of polymer chains.[8,11,31,45] Evidently, for a quantitative description of the effect of cross-links on the parameters of polymer matrices and membranes, one can use the ideas concerning the local free volumes of the units and modes. Within the framework of this approach, the following expressions have been obtained:

$$\ln D = \ln D_\infty - \frac{B}{f_\infty} \cdot \frac{a' M_n^{-1}}{f_\infty - a' M_n^{-1}} , \quad (11)$$

$$\ln D = \ln D_\infty - \frac{B a'}{f_\infty^2} \cdot M_n^{-1} . \quad (12)$$

Eqn.(12) holds for $M_n \geqslant 8 \times 10^2$. Here B and a' are constants and M_n is the molecular weight between the nodes of the three-dimensional network. Eqn.(12) agrees with the empirical relation between D and M_n.[20,31] One should bear in mind that Eqn.(12) is valid only for sufficiently high M_n, typical for vulcanised elastomers, whereas Eqn.(11) is valid over the entire range of densities of three-dimensional networks, up to the values of M_n characteristic of resites, epoxides, and polyesters. Eqn.(11) can be extended also to the vitreous and crystalline states of three-dimensionally cross-linked polymers. The rate of diffusion can be related with the aid of Eqn.(11) also to the number of nodes in the three-dimensional network, the molecular parameters of the cross-linking agent, the content of the hardening agent, the radiation dose, and the kinetics of the process leading to the formation of networks.[7,20,46,47]

2. Diffusion in Static Copolymers and Polymer–Solvent 1–Solvent 2 Systems

The introduction into the polymer chain of units differing from the elements of the main chain in chemical composition, structure, and stereochemical parameters imposes a definite imprint on the molecular movement within the polymer systems, altering the rate of diffusion in them. In terms of the character of their behaviour, any polymer chains whose monomeric units differ in some way from one another can be included in the class of copolymers. However, the diffusion properties of copolymers cannot be described in a unique

fashion. This is because the properties of copolymers are determined not only by the concentration of units of different types but also by the character of their distribution along the chain, the stereochemical interaction, the phase structure of the system, and the nature of the solvent. It is therefore always essential to take into account the specific features of the real system investigated.

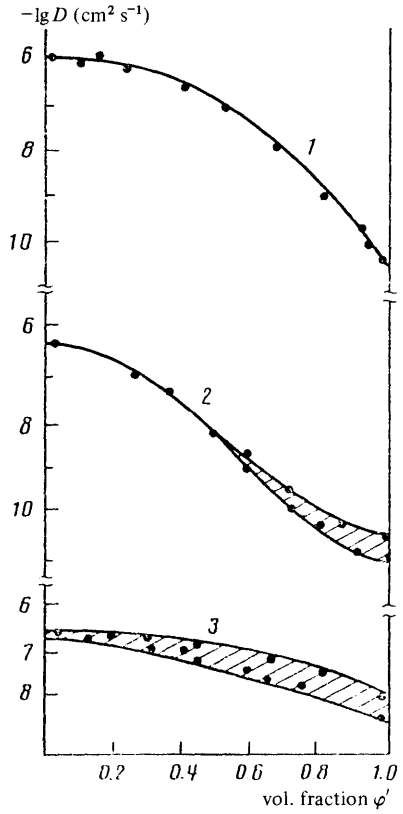


Figure 2. Dependence of the diffusion coefficients of low-molecular-weight substances on the composition of statistical copolymers: 1) styrene–butadiene copolymer in dibutyl sebacate (70 °C); 2) styrene–butadiene copolymer in benzene (25 °C); 3) vinyl chloride–vinyl acetate copolymer in water (20 °C).[9,31,92]

In this Section we shall consider the diffusion properties of single-phase amorphous statistical copolymers. Fig.2 presents typical dependences of the diffusion coefficients of low-molecular-weight substances on the composition of the copolymers. It can be seen that, for different states of the statistical copolymer, three types of dependence of D on φ' obtain (φ' is the volume fraction of the homopolymer units in the chain). If $T_{exp} > T_g$ (T_{exp} is the experimental temperature) for any composition of the copolymer, including homopolymers, then the decrease of D with increased presence in the chain of units which increase its kinetic rigidity is as a rule described by a smooth convex curve (curve *1* in Fig.2). The diffusion coefficients are in this case extrapolated from the average range of compositions of the copolymers to values corresponding to D in the homopolymers. If the diffusion medium is in the vitreous state ($T_{exp} < T_g$) for any composition of the copolymer, including homopolymers, then the overall tendency in the variation of D, mentioned above, persists but the dependence becomes less pronounced (curve *3* in Fig.2). This is caused by the insignificant change in D on passing from one homopolymer to another combined with the significant dependence of the absolute values of D on the previous thermal history of the specimens.[20,31]

The third type of dependence (curve *2* in Fig.2) is characteristic of systems in which the transition from the highly elastic to the vitreous state occurs for a definite composition of the copolymer ($T_g' < T_{exp} < T_g''$, where T_g' and T_g'' are the glass points of the homopolymers). In these systems, the dependence of D on φ' acquires an S-shaped character and the diffusion coefficients obtained by extrapolation from the range of compositions corresponding to the highly elastic state to the region of the vitreous state (D_{exp}) do not as a rule agree with the experimental values of D for the homopolymers. It has been suggested[46–48] that the ratio D_{exp}/D_{ext} be used as the coefficient of the structural non-equilibrium of the given copolymer or homopolymer.

According to Reitlinger's classification,[20] the polymer–solvent 1–solvent 2 systems belong to the class of polymer–liquid–gas systems. The inclusion of these systems in the group of statistical polymers may give rise to surprise. There are two reasons for such inclusion: firstly, the identity of the phase states of diffusion media of this type; secondly, the qualitatively identical effects of the copolymer units and the molecules of the dissolved liquids on the segmental mobility of the macromolecules and hence on the diffusion properties of the membranes.

The polymer–solvent 1–solvent 2 systems include two groups of three-component systems differing solely in the character of the distribution of one of the components in the polymer matrix. The first (and main) group comprises systems in which the polymer membrane is in contact with a mixture of two or more solvents which penetrate it simultaneously. In systems of the second group (plasticised and modified polymers, moistened polymers, and polymers saturated with the vapours of monomers, solvents, etc.[31,49]), one of the components was distributed in the membrane beforehand while the other participates in the transport process. Here it is significant that the concentration of the first component is kept constant throughout the process. Despite the different form of treatment of the mass transfer process kinetics in these systems, the self-diffusion coefficients of the low-molecular-weight substances in these media can be analysed within the framework of a single approach.[7,53]

Although there have been numerous experimental or, more precisely, technological studies of the permeability of polymer membranes to various mixtures of low-molecular-weight substances,[49,50] few investigations have been devoted to the kinetics of the transport and diffusion of individual components. Nevertheless, one can already claim unambiguously that the variation of the ratio of the components in the media in contact with the polymer membrane has little effect in the course of the process: the same sequence of partial fluxes is retained as for the individual components, but their absolute magnitudes and the diffusion coefficients found from the delay time for each partial flux (D_θ) change somewhat.[51] Under these conditions, a feature common to all mixtures is observed: the greater the content in the solution of the solvent diffusing at the lowest rate, the smaller the difference between the partial fluxes D_θ of the mixture components; the overall flux of the mixture as a whole has as a rule a value intermediate between the partial fluxes

of the individual components; the overall flux usually attains a stationary value when stationary transport of the component diffusion at the lowest rate is established.

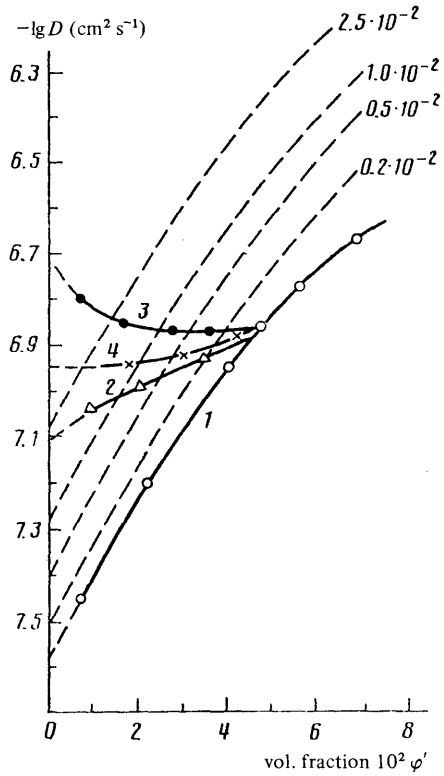


Figure 3. Dependence of the individual (curve *1*) and partial (curves *2*–*4*) diffusion coefficients of hexane in polyethylene on its content in various systems: 1) polyethylene–hexane; 2) polyethylene–hexane–pentachloroethane; 3) polyethylene–hexane–ethyl acetate; 4) polyethylene–hexane–cyclohexane. Dashed curves—theoretical relations calculated by Eqn.(14) for different contents of pentachloroethane in polyethylene (the numerals opposite the curves denote the concentrations φ'' in volume fractions).

The sequence of the permeation of the solvents through membranes affects the diffusion coefficients found along different sections of the non-stationary stage of the process. The variation of D_θ with the time of observation, described by Ferry,[51] is related to the mutual influence of the solvents in the course of their joint permeation. Special attention should be paid to the values of D_θ calculated in the initial stages of the permeation of the diffusants. Comparison of the partial flux D_θ of the solvent which diffuses first with its coefficient D_s calculated from the results of sorption measurements demonstrates their satisfactory agreement, while D_θ for the solvent diffusing after the first is higher, i.e. the effect involving the mutual plasticisation of the polymer membrane in the transport process takes place. Such effects are naturally not observed in the study of the kinetics of permeation and sorption (swelling) in systems of the second group.[48]

In the study of the characteristics of the diffusion and permeability of polymer membranes with respect to mixtures of low-molecular-weight substances, the composition of the solutions of the low-molecular-weight substances is usually employed as an independent argument. In our view, the use of the solubilities of the components in the polymeric medium as the independent variables is more promising for the analysis of the transport processes of multicomponent systems through polymer membranes. In this case, the experimental diffusion coefficients can be related to the concentration dependence of D in the polymer–diffusant binary system. Indeed, the partial diffusion coefficients of hexane diffusing from mixtures with different solvents have as a rule larger absolute values than in the polyethylene–hexane binary system (curve *1* in Fig.3). With increase in the concentration of hexane in the polymer (this corresponds to the increase in its content in the solution in contact), its partial diffusion coefficient can both gradually increase (curve *2* in Fig.3) and decrease (curve *3*) or can remain unchanged (curve *4* in Fig.3. However, and this is the most important factor, in all cases the partial concentration variations of D for this solvent approach the corresponding variations for the same component in the binary system. Extrapolation of the variation of the partial values of D to $\varphi_1 = 0$ makes it possible to find the diffusion coefficients of the given component in the matrix containing the maximum possible amount of the sorbed solvent 2. These values of D are specific to each polymer–solvent 2 system. As a rule, $D'' > D'$, where D' is the diffusion coefficient of solvent 1 in the polymer for $\varphi_1 = 0$ and D'' is the partial diffusion coefficient of the same solvent in the polymer saturated with solvent 2. The ratio of these diffusion coefficients can be used to estimate the plasticising effect undergone by the polymer matrix under the conditions of the simultaneous diffusion in the latter of the two solvents.

For three-component systems of the second group, analogous relations have been found experimentally. In this case, when a plasticising component is introduced into the polymer, the value of D for low-molecular-weight substances increases with increasing plasticiser concentration, as happens when copolymer units are introduced into the macromolecular chain. Only in isolated instances where the plasticiser reduces the segmental mobility, i.e. behaves as an antiplasticiser, do the diffusion coefficients of gases, water, and solvents diminish somewhat under these conditions.[52]

In order to interpret the results and to predict the diffusion properties of copolymers plasticised in three-component systems, one may use the expression

$$\ln\frac{D}{D'} = \frac{B}{f'}\left(\frac{\beta\varphi''}{f' + \beta\varphi''}\right) , \qquad (13)$$

$$\ln\frac{D}{D'} = \frac{B}{f'}\left(\frac{\beta_1\varphi_1'' + \beta_2\varphi_2''}{f' + \beta_1\varphi_1'' + \beta_2\varphi_2''}\right) , \qquad (14)$$

which follow from the classical free volume theory.[7] In Eqn.(13), D' is the diffusion coefficient of the test component in the homopolymer, f' its free volume fraction, φ'' the volume fraction of either the copolymer units or the plasticiser, $\beta = f' - f''$, and f'' is the free volume fraction either in the second homopolymer or in the plasticiser. In Eqn.(14), D' is the partial diffusion coefficient of the test component in the polymer, f' its free volume fraction, $\beta_1 = f_1'' - f'$, and $\beta_2 = f_2'' - f'$, where f_i'' is the free volume fraction in each solvent, φ_i'' the volume fraction of the corresponding solvent, and B are constants. The results of the calculation by Eqn.(14) for the polyethylene–hexane–pentachloroethane system are presented in Fig.3 in the form of dashed lines (each dashed line corresponds to a specific value of D for pentachloroethane). It can be seen that the

experimental curve for the partial diffusion coefficients (curve *2*) intersects the theoretical relation at certain points corresponding to the average values of D for the given composition of the polymer – solvent 1 – solvent 2 system. In recent years, this method has been developed further.[53]

3. Diffusion in Polymeric Glasses

It has been shown in a whole series of experimental studies[3,5,6,9] that, when $T < T_g$, the mass transfer of low-molecular-weight substances in polymeric diffusion media cannot be described using solely the molecular characteristics of the macromolecules. The activation energy for the diffusion of low-molecular-weight substances in polymeric glasses is as a rule lower than in the highly elastic state of the same medium. Admittedly, for certain diffusants, usually helium and hydrogen, these differences do not exist. For the same diffusant, the quantity E in the polymeric glass is a function of the excess free volume: the greater the latter, the smaller the value of E. A linear realation is observed between the diffusion coefficients of the low-molecular-weight substances and the densities of the glasses ρ and the latter vary comparatively little; for example, $\lg D = 8.2 - 14.5\rho$ ($1.19 \leqslant \rho \leqslant 1.23$ g cm^{-3}) for the diffusion coefficients of water in hardened epoxide resins.[46]

All these facts led many investigators[55-58] to turn to a more detailed consideration of the structure of the polymeric glass and to the study of the characteristics of mass transfer at $T < T_g$.

In our view, there are no fundamental differences between the mechanisms of the diffusion of fairly large molecules of low-molecular-weight substances in polymeric media at temperatures below and above T_g: in both cases the vibration of the diffusing molecule takes place as a result of the appearance near it of a microcavity vacancy of the appropriate size. The number of vacancies per unit volume depends in the general case on temperature, the packing density of the macromolecules, pressure, the content of modifying agents, etc. Thus one can assume that the principal relation (2) of the free volume theory is valid also for polymeric glasses.

According to this approach, the difference between the states of the polymer matrix above and below T_g is associated with the fact that the thermal movement of the structural elements of the macromolecule, responsible for the diffusional migration of the low-molecular-weight substances, takes place under these conditions for different supermolecular organisations of the medium. At $T > T_g$, the diffusion process takes place in a medium with an equilibrium or nearly equilibrium packing of the chains ($f = f_t$, where f_t is the free volume fraction associated with the thermal expansion of the matrix), whereas at $T < T_g$ the process takes place under the conditions of a non-equilibrium albeit quasi-stationary structural organisation of the matrix, for which $f > f_t$. It is natural to assume that in the latter case $f = f_t + f_v$, where f_v is the free volume fraction association with the non-equilibrium nature of the matrix, the so called excess free volume. Evidently, f_v is the "frozen" free volume determined by the non-equilibrium nature of the structure and the relaxation nature of the vitrification process. It is determined by the previous history of the specimen, whereas f_t is determined by its chemical nature, composition, and external conditions. One may say that f_t is the level of defectiveness of the structure against the background of which the effect of f_v is manifested. The fact that f_t plays a definite role also at $T < T_g$ is indicated by relaxation spectrometric data.[54,60,61] Since the diffusion coefficients of low-molecular-weight substances in polymers are an integral characteristic of the mobility of the macromolecular fragments, the nature of these elements and their concentration must inevitably influence the mass transfer process also at $T < T_g$. At any rate, a whole series of properties of polymeric glasses exhibit a dependence on the molecular characteristics of the system, which although weak is nevertheless explicit.[61]

Unfortunately, neither the vacancy solution model, nor the Simha – Boyer model, nor the results of experiments on the annihilation of positrons[62,63] permit an unambiguous differentiation of the contributions to f by f_t and f_v. Attention is therefore concentrated nowadays on the search for direct correlations between the diffusion permeability constants, on the one hand, and the results of structural studies on the other. The equation

$$\ln \frac{D}{D_s} = \frac{B}{f_s}\left[\frac{(1-f_s)(1-\rho/\rho_s)}{(1-f_s)\rho/\rho_s - 1}\right] \qquad (15)$$

has been obtained[7,46] within the framework of the free volume theory. For a narrow range of variation of the density of the polymer matrix, it can be put into the simple form

$$\ln D = \alpha - \gamma\rho \qquad (16)$$

It relates the diffusion parameters to an integral structural characteristic of the polymer ρ, namely its density, and agrees well with experimental data. In Eqns.(15) and (16), α and γ are constants and ρ_s, f_s, and D_s are respectively the density, the free volume, and the diffusion coefficient of the polymer in a selected standard state (for example, at T_g).

The experimental data accumulated to date on the diffusion absorption of gases and solvents in polymeric glasses and the permeability to these substances are consistent with the qualitative structure of the model. The vacancies constituting the free volume are combined into vacancy capillaries with a variable radius and a thermally fluctuating wall, i.e. one which constantly alters the "frozen" average size of the vacancy capillary. The size of the vacancy capillary (its average radius and the radii at the narrowest and widest points) is determined by the parameters of the vacancies at $T > T_g$.[33,34] The thermal mobility of the macromolecular fragments at $T < T_g$ (i.e. f_t) is localised in the outer layers of the capillary and is independent of its size. Hence it follows, for example, that E and the character of the mass transfer process depend on the ratio of the average vacancy diameter $\bar{X}$ and the diffusant diameter d. Evidently, the greater the value of $\bar{X}$, the smaller that of E. For certain values of $\bar{X}$, the quantity E, measured at a temperature above T_g, is equal to the activation energy for diffusion in the vitreous state. For $\bar{X} \gg d$, there is a possibility of a non-activated mechanism of gas permeability.[20,31] If this model is adopted, then, in order to create highly productive and selective membranes, one must use polymers whose macromolecules are separated from one another by a fairly large distance and which have large groups characterised by a high effective modulus of the bending of the chain and which also contain mobile fragments. An indirect confirmation of this model is probably provided by data for gas separation on polytrimethylsilyl-propyne.[64]

IV. DIFFUSION IN HETEROGENEOUS SYSTEMS

A fairly large group of polymer systems belongs to the class of heterogeneous diffusion media: crystalline homopolymers and copolymers, polymer blends and block copolymers, filled and gas-filled polymers, multilayer and combined film materials, protective

coatings, and membranes, i.e. one-component or multicomponent systems which exist under the experimental conditions in two-phase or multiphase states. The study of diffusion processes in these systems is prosecuted nowadays in three directions. In the first place, a detailed study is made of translational diffusion processes involving the components or macromolecular fragments responsible for the formation of the phase structure of these media. This aspect of the problem has been analysed in detail in relation to a whole series of binary polymer systems: reactive oligomer–elastomer systems,[65,66] gas-filled elastomers and plastics,[7,67] the formation of a porous structure,[68] and the growth of the particles of the disperse phase in the metastable and labile regions of the phase diagram.[69,70] The second direction is associated with the study of the role of diffusion processes in the formation of transitional zones in multilayer systems.[71] The third direction combines studies on the diffusion properties of heterogeneous polymeric media, mainly in relation to gases, water, organic solvents, electrolytes, monomers, etc.

Despite the fact that the first two directions are closely related to mass-exchange processes between individual phases in heterogeneous systems, this relation is mainly terminological. To a large extent, they are associated with mutual diffusion and self-diffusion processes in various zones of the phase diagram, on the one hand, and with the phase decomposition kinetics, on the other. We shall therefore deal here only with the studies of the diffusion of low-molecular-weight substances in heterogeneous polymeric materials.

Following Chalykh,[7] we shall divide all heterogeneous polymer systems into two large groups. In the first group, we shall place systems whose disperse phase does not participate in the sorption and diffusion processes involving low-molecular-weight substances and influences them only indirectly by acting on the density and segmental mobility of the chains in the dispersion medium. This group includes crystalline polymers, melts comprising crystalline polmers with elastomers and thermoplastics, and polymers filled with mineral powders or fibres. The second group is made up of systems whose disperse phase and dispersion medium participate simultaneously in the sorption, diffusion, and permeation processes. Mixtures of amorphous polymers, block copolymers, and gas-filled systems belong to this group.

1. Diffusion in Systems with Impermeable Particles of the Disperse Phase

It has been demonstrated convincingly by X-ray diffraction that the crystalline phase of the majority of synthetic and natural polymers is impermeable to the molecules of various diffusants. Systems in which the diffusants form solvates with the macromolecules, clathrate complexes, or molecular complexes should probably be exceptions.[72] However, there is so far no information about the translational diffusion coefficients in such phase formations.

The diffusion low-molecular-weight substances in partly crystalline polymers has now been studied in greatest detail.[1,6,7,20,31] Nevertheless, the following main problem still remains open: what is the relation between the supermolecular and phase organisations of these polymers, on the one hand, and the translational mobility of the low-molecular weight substances dissolved in it, on the other. The crystallite is usually employed as the structural element constituting the diffusion medium and the diffusion and permeability coefficients are related to the degree of crystallinity φ_c, using for this purpose empirical or semiempirical relations:

$$D = D_a(1-\varphi_i)^n; \quad P = P_a(1-\rho)^m \quad , \tag{17}$$

$$D = D_a \exp\left(-\frac{B}{f_a}\cdot\frac{\varphi_c}{1-\varphi_c}\right) \quad , \tag{18}$$

$$D = D_a(\tau\beta)^{-1} \quad . \tag{19}$$

where D_a is the diffusion coefficient of low-molecular-weight substances in the amorphous phase or in the amorphous analogue of the crystalline polymer, P_a the permeability coefficient of the same media, τ the tortuosity factor of the pathway, β the immobilisation factor of the crossing chains, f_a the fraction of free volume in the amorphous phase of the polymer, and n, m, and B are empirical constants. It has been shown in a number of studies that n varies in the range from 1.3 to 2.[7,20,31] According to self-diffusion data, $n = 8$.[73]

Another view has been expressed in a number of studies[74–76] whose authors suggest that the diffusion properties of crystalline polymers are determined by their spherulitic level and that the variation of D and P should be attributed not to the variation of φ_c but to the variation of the "degree of spherulitic character". This approach is based on two groups of experimental results; firstly, there are autoradiographic data, according to which the transport of the diffusant in coarsely spherulitic specimens takes place along the boundaries of the spherulites and, secondly, the results of numerical calculations of the permeability coefficients, according to which the peripheral regions of the spherulites are more permeable than their middle section. However, it has been shown for the majority of crystalline polymers that the variation of the size of the spherulites Φ from 2 to 40 μm for film thicknesses in the range 150–300 μm does not affect D and P. An increase in D and P has been observed only for values of Φ comparable to the thickness of the membranes, whereupon breaks in continuity within the spherulites and along their periphery go right through these formations. Therefore one should probably not use the spherulitic level as the cornerstone it being more useful to treat the problem in terms of the spectrum of translation pathways localised both in the intercrystallite and interspherulite spaces, differing from one another in tortuosity, in the packing density of the crossing chains, and in the number of defects.

This problem has been solved[77] within the framework of the permeation theory. It was assumed that the problem of mass transfer in partly crystalline polymers can be formalised as the problem of nodes whose size is much smaller than the thickness of the membrane. A node is permeable when it contains the amorphous phase and is impermeable when it contains a crystallite. Diffusion in such a system occurs only when the fragments of the permeable phase form an infinite cluster, i.e. when the content of the amorphous phase exceeds the permeation threshold φ_a^c, which is 0.16 for the model considered. Using the relation between the tortuosity of the infinite cluster and the fraction of the permeable nodes[78] $\tau \propto (\varphi_a - \varphi_a^c)^t$, where t is the critical index which varies from 1.6 to 2 (the space is three-dimensional) and Eqn.(15), one can obtain the expression

$$D = D_a(\varphi_a - \varphi_a^c)^t \quad , \tag{20}$$

which describes satisfactorily the experimental data over a fairly wide range of variation of the degree of crystallinity of the polymers. It is noteworthy that the critical index is extremely sensitive to the molecular weight, the MWD, the composition of the macromolecules, and the degree of branching of the latter.

However, there exists a fairly large group of experimental data which indicates an anomalous variation of the diffusion properties of crystalline polymers: an increase in D and φ_a with increase in φ_c, the variation of the critical index for φ_c = const., and the decrease in the activation energy for diffusion with increase in φ_c. These results (Fig.4) have been obtained as a rule for high degrees of crystallinity in the vicinity of φ_a^c. The rate of increase in D with increase in φ_c can vary. For some specimens, an almost abrupt increase in D is observed, for others, a more common case, there is a gradual increase, and for the third group, D = const. This character of the variation of D with φ_c has been attributed[58,79,80] to the decrease in the immobilisation factor of the crossing chains. This effect has been explained[7] by the variation of the chain packing density ρ_a in the amorphous phase.

The anomalous variation of D can be explained analogously also within the framework of the percolation approach. Indeed, we shall begin with the hypothesis that the tortuosity of the transport channel increases with increase in φ_c in accordance with Eqn.(20). Then all the structural changes occurring within the channel must be reflected in D_a. Fig.4 shows that most of the experimental data for this range of values of φ_c occupy an intermediate position between two curves calculated by Eqn.(20) for $D_a = 10^{-7}$ cm^2 s^{-1} and for $D_a = 10^{-3}$ cm^2 s^{-1}. The first value corresponds to the diffusion coefficient of the low-molecular-weight substance in the amorphous analogue of the polymer, for example, polyethylene, while the second corresponds to the diffusion coefficient of the same diffusant but in the gas phase, where the transport channel is identified with a crossing pore having Knudsen dimensions.[81]

Evidently, there may be several versions of structural organisation for the transport channel in real materials: the appearance within the channel of local breaks in continuity—closed pore and microcracks; an inhomogeneous distribution of density along the channel cross-section; a general decrease in the density of the amorphous phase. Calculations have shown that, when the first version of the channel structure obtains, a deviation from the theoretical relation (20) is observed only for $\varphi_c \geqslant 0.7$ (curve *9* in Fig.4), i.e. virtually near the permeation threshold. The appearance in the channel of defects of the second type leads to an abrupt alteration of D and its subsequent decrease with increase in φ_c (curve *7* in Fig.4). Finally in the third case D = const., or a weak increase in D, or sharp increase with increase in φ_c can be attained depending on the character of the variation of φ_c (curve *8* in Fig.4). Comparison of these results with experimental data shows that the formation of the transport channel with the first and third versions of the defective structure is more realistic under normal crystallisation conditions.

In the case of crystallisable copolymers and comb polymers, their diffusion properties in each specific case are determined by the coefficient D of the low-molecular-weight substances in the homopolymers, the composition of the crossing chain, the kinetic mobility of the segments, and the degree of crystallinity. An attempt to predict the diffusion properties of crystalline variable-composition copolymers has been undertaken[7,84] within the framework of the free volume theory and the statistical theory of the crystallisation of copolymers.[85] It has been shown that account must be taken of at least three variable parameters for the description and prediction of their properties: φ_c, the composition of the crossing chains, and the

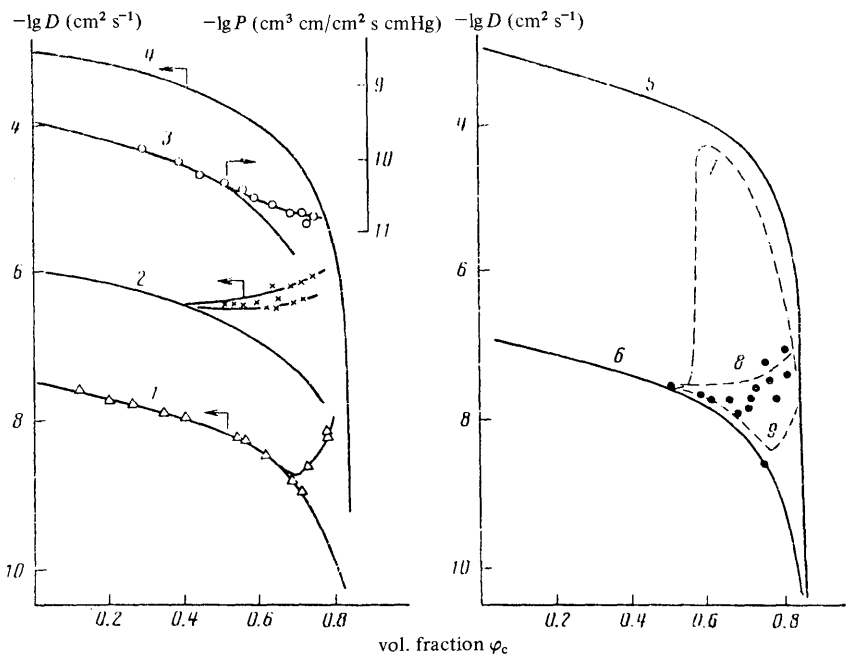


Figure 4. Dependence of the diffusion and permeability coefficients of low-molecular-weight substances on the degree of crystallinity of the polymers: 1) polypropylene–hexane; 2) polyethylene–methane; 3) polyethylene–nitrogen; 4) and 5) calculation by Eqn.(20) for $D_a = 10^{-3}$ cm^2 s^{-1}; 6) calculation by Eqn.(20) for $D_a = 10^{-7}$ cm^2 s^{-1}; 7)–9) calculation by Eqn.(20) for different models of the structure of the amorphous phase (for explanation, see text).

distance of the system from the permeation threshold. Analogous calculations can probably be performed also with the aid of Eqn.(20).

For amorphous polymers filled with the impermeable particles of a disperse phase with a different chemical nature, it is also possible to differentiate three regions of the degree of filling (φ_f) in which the diffusion parameters depend on φ_f in different ways: the region $\varphi_f \leqslant 0.10$ where the introduction of the filler decreases D and P; the region $\varphi_f > 0.20$ where as a rule D and P increase with increase in φ_f; the region of middle compositions of disperse systems where both the constancy of D and P and their extreme changes can be observed as a function of the nature of the polymer and the filler. Thus the general tendency in the variation of the diffusion properties of filled polymers is analogous to that described above for crystalline polymers. The specific features of filled systems are manifested by the fact that all the phenomena described occur in a comparatively narrow range of the bulk phase content of the disperse phase particles. The few structural-morphological studies on these systems have shown that the deviations from Eqn.(20) are associated, on the one hand, with the flocculation of the particles of the disperse phase to give chain cluster formations, and, on the other hand, with the formation of defects—local breaks in continuity concentrated either at the interface or within the cluster structures. Direct evidence for the formation of such structures has been obtained in a study of the gas permeability of porous membranes formed by filling elastomers with powdered salts and their subsequent elution.[86] The formation of crossing porosity has been noted[87] already at $\varphi_f \cong 0.05$.

In conclusion of this Section, we may note that, despite the large amount of experimental data on diffusion in filled polymers and on their permeability, they still remain the least investigated. This is due to the virtual lack of combined studies in which diffusion data would have been supplemented by structural-morphological information, the determination of local diffusion coefficients, and the estimation of the degree of defectivness of the medium. The study[88] in which the percolation approach was used to analyse mass exchange processes in multicomponent polymer coatings is not an exception in this sense.

2. Diffusion in Block Copolymers, Polymer Blends, and Gas-filled Polymers

Assessment of the set of experimental data obtained for the diffusion behaviour of media containing a permeable disperse phase permits the conclusion that the behaviour of these systems shows no fundamental qualitative and quantitative differences despite the significant difference in the chemical and phase states of the particles of the disperse phase, their disperse characteristics, structural organisation, and local diffusion coefficients. When the disperse phase is impermeable to low-molecular-weight components for thermodynamic reasons, the diffusion properties of all these media are characterised by a single transport or macroscopic diffusion coefficient, while the sorption and permeation kinetics are of the normal, Fick type. On the other hand, if both the disperse phase and the dispersion medium are involved simultaneously in the diffusional transport of low-molecular-weight substances, then distinct pseudo-normal sorption and permeation kinetics are observed,[7] while the diffusion properties of the system are characterised by local and effective diffusion coefficients. The reproducible anomaly in the kinetics of the attainment of sorption equilibrium observed in these polymers after repeated sorption–desorption cycles yields direct information about the disperse structural organisation of the medium. The diffusion properties of such media are influenced by the differences between the diffusion coefficients of low-molecular-weight substances in the disperse phase and the dispersion medium. Since D for organic solvents is a function of concentration,[91] it is frequently found that in one region of sorption isotherms the medium is "heterogeneous" according to diffusion data while in another it is "diffusionally homogeneous".

The dual character of the behaviour of polymer media containing permeable particles of the disperse phase is also manifested when diffusion coefficients measured by different methods are compared. Thus the rotational and translational diffusion coefficients of iminoxy-radicals, found by microwave spectroscopic methods (D_R), exceed the corresponding coefficients of translational mobility obtained by sorption–permeability methods (D_S).[42] Whereas D_S diminishes with increasing content of the disperse phase, D_R = const.

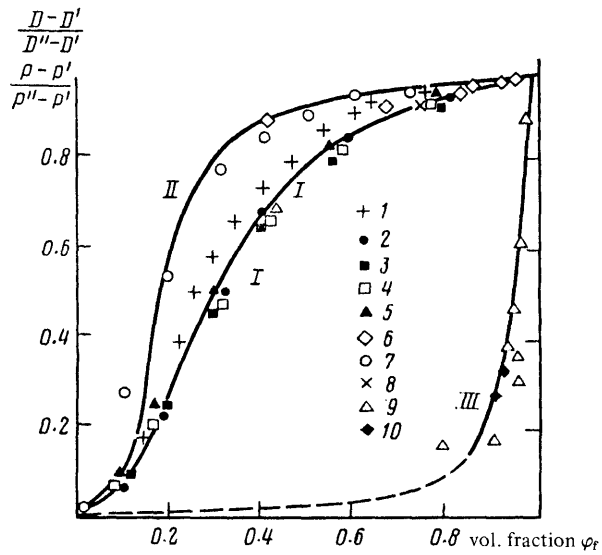


Figure 5. Dependence of the reduced diffusion coefficients of low-molecular-weight substances (I) and of the reduced permeability coefficients of heterogeneous polmeric materials (II) as well as gas-filled polymeric systems obtained by sintering (II) and foam formation (III) on the porosity and content of the permeable phase: 1) "Silar" poly(block copolymer); 2) polystyrene–polybutadiene blend; 3) styrene–butadiene block copolymer; 4) sulphone–butadiene block copolymer; 5) blend of poly(vinyl chloride) and nitrile rubber; gas-filled polymers; 6) SKN-30 nitrile rubber (elution of KCl); 7) polyurethane (sintering of particles); 8) polyamide fibres (unwoven material); 9) polyester-urethane foam; 10) polystyrene foam; D, D', and D'' are the diffusion coefficients and P, P, and P'' are the permeability coefficients of the mixture and of each pure components respectively; φ_f is the content of the permeable phase (in the case of gas-filled polymers, it is their porosity).

Fig.5 presents experimental reduced diffusion and permeability coefficients for many polymeric media with a permeable disperse phase. Curves illustrating the variation of the permeability of gas-filled polymer systems obtained by sintering powders and by foam formation are presented for comparison.[89,90] For all the systems, the

character of the variation of the effective coefficients D and P is the same. In the region of phase reversal (which occurs in the vicinity of the permeation threshold when the problem of nodes in a lattice-free model is considered), D and P undergo the greatest changes. The critical index t is close to 1.7 even for gas-filled systems. The dependence of the permeability coefficients on the porosity—the volume fraction of the permeable phase for polymeric foam materials—is of special interest. Despite the fact that the content of gas inclusions reaches up to 93 vol.%, the permeation threshold in this system has not been attained. These results can be explained within the framework of the problem of connections.[90] The accumulation in the specimen of pore walls disrupted by influences of one kind or another leads to the formation of passable connections between the lattice nodes and to the appearance of an infinite cluster, which is manifested by a sharp and abrupt increase in gas permeability.

Several approaches have been proposed for the theoretical study of the diffusion of low-molecular-weight substances in heterogeneous polymer systems with a permeable disperse phase: the Maxwell, Nielson, and Robinson equations, the Zolotarev–Dubinin bidisperse model, and the percolation model. It is necessary to compare the proposed equations, to determine their scope in predicting the behaviour of heterogeneous diffusion systems, and to estimate the structural-morphological features of the test objects. First attempts of this kind have already been undertaken.[7,88,91–93]

V. DIFFUSION METHODS FOR THE STUDY OF POLYMER SYSTEMS

1. Construction of Phase Diagrams

The diffusion methods for the study of polymer systems are based on the investigation of the concentration distribution of the components in the mutual diffusion zone, i.e. in the zone corresponding to the spontaneous mixing of the components. At the present time, it has been demonstrated for various systems that the characters of the concentration profile and of the phase diagram for the system are closely interrelated (Fig.6). Thus, if the polymer system is characterised by amorphous layer formation and exists during the experiment above the upper consolute temperature (UCT) or below the lower consolute temperature (LCT), then the distribution curves indicate a continuous variation of concentration on passing from one component to another. At $T <$ UCT (or $T >$ LCT), a concentration jump is observed on the diffusion profiles, whose position corresponds to the two-phase region on the concentration scale of the phase diagram. The composition of the solutions on either side of the phase boundary then coincides with the composition of the

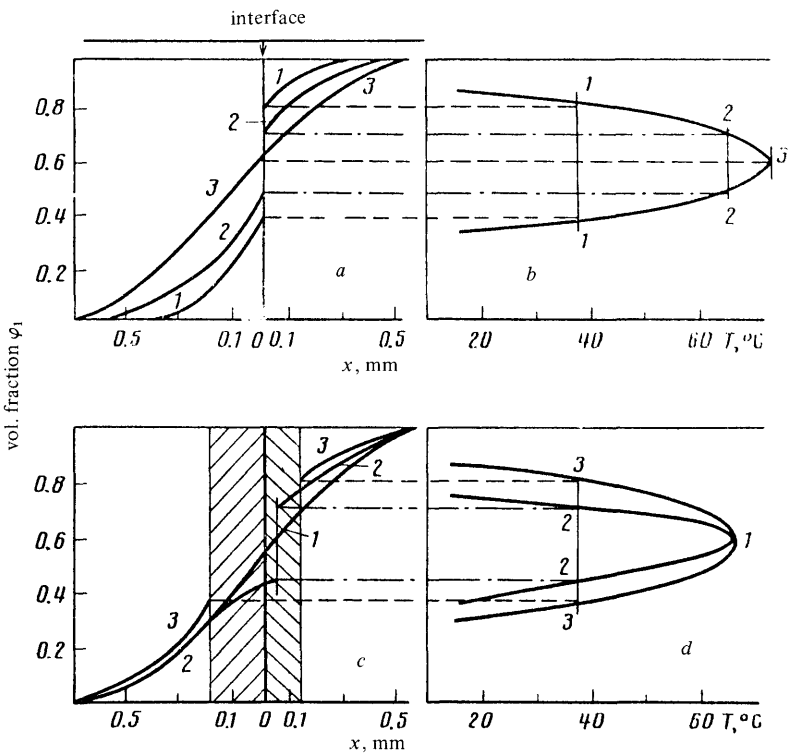


Figure 6. Concentration distribution curves in the mutual diffusion zone (*a*, *c*) and the phase diagrams (*b*, *d*) constructed on their basis. Curves *1*–*3* corresponding to increasing (*a*) and decreasing (*c*) temperatures; the boundary concentrations on curves *2* and *3* (*c*) correspond to the spinodal and binodal curves. The phase decomposition regions are shown cross-hatched; x is the diffusion coordinate.

coexisting phases. Thus, by determining the variation of the boundary concentrations at different temperatures and the instant of disappearance of the interface, one can plot, as shown in Fig.6, the binodal curve of the phase diagram.

If the binary system is characterised by a crystalline equilibrium (in the general case by a combination of crystalline and amorphous equilibria), then the distribution of concentration in the mutual diffusion zone includes additional regions corresponding to the dissolution of the diffusant in the crystalline polymer and its fusion if the dissolution takes place at $T < T_m$ [T_m is the melting point]. In order to characterise this region, it is necessary to identify experimentally the amorphous and crystalline states of the solutions. For example, when measurements are performed by the interference or polarisation-interference methods, the concentration profiles must be recorded in both ordinary and polarised light.[94]

An inherent feature of the diffusion method for the construction of phase diagrams is the possibility of determining the spinodal curve and also of the kinetics of phase decomposition in the region of metastable and labile solutions.[95] For this purpose, the diffusion process is carried out initially under conditions such that a concentration field arises in the miscibility zone and the range of variation of the composition of the solutions must be fairly broad. By driving the system as a result of a sharp change in temperature to the region of phase separation, it is possible to observe and record different stages in the decomposition of labile and metastable solutions. By determining under these conditions the boundary concentrations, established at different times near the phase boundary, one can plot (Fig.6) the spinodal curve, test the position of the binodal curve, and determine the concentration-temperature range corresponding to phase reversal. These methods are of great practical interest, because it is precisely under these conditions (i.e. in the presence of the concentration or diffusion coefficient gradient) that the stuctures of coatings, membranes, and adhesion junctions are established.

2. Phase and Structural Analysis of Polymer Blends and Block Copolymers

The phase and structural analysis of heterogeneous polymer systems presupposes the determination of quantitative information about the phase composition of the specimen, the size and shape of the particles of the disperse phases, the compositions of the coexisting phases, and the size and structure of the interfaces. Detailed investigations of various aspects of mass transfer process involving low-molecular-weight substances in such systems have shown that the characteristic features of their phase state and supermolecular organisation are most strikingly manifested in the kinetics of the attainment of sorption equilibrium.[13,91,98]

The kinetics of the sorption (desorption) of solvents by block copolymers and polymer blends are characterised by a series of specific features, which make it possible to differentiate them as a special class of heterogeneous sorbents. In the first place, the type of kinetic curve depends on the nature of the sorbate and its thermodynamic affinity for the blocks forming the disperse phase and the dispersion medium. Thus, when a selective solvent (SS) which is not sorbed by the disperse phase is used as the sorbate and the dispersion medium is in the highly elastic state, then the sorption kinetics are as a rule of the normal, Fick type. The situation is different if the sorbate is a common solvent (CS) for both phases. In this case, the type of the kinetic curve depends on how much the diffusion coefficients of the sorbate in the disperse phase (D') and in the dispersion medium (D'') differ.

The diffusion in such systems can be naturally characterised with the aid of models taking into account the phase structure of the sorbent, for example, with the aid of the bidisperse Zolotarev–Dubinin model. Two diffusional relaxation times have been introduced in this model: $T = \Gamma L^2/D''$ for the dispersion medium and $\tau = R^2/D$ for the disperse phase. Here L and R are the sizes of the specimen and the phase inclusion respectively and Γ is the Henry coefficient. Depending on the ratio of T and τ, the following cases can obtain: for $T \gg \tau$, the rate of sorption and the type of kinetics are determined by the transport in the dispersion medium; for $T \ll \tau$, the sorption kinetics are determined by the diffusion initially into the dispersion medium and then into the disperse phase and there is a possibility of both two-stage and pseudo-normal kinetics; for $T \cong \tau$, an intermediate case arises; when $\tau \to \infty$, normal sorption, involving the transport of the test substance in the dispersion medium, takes place. Thus, having determined from the experimental data for the sorption kinetics the values of T and τ and having assumed that the diffusion phase coefficients in the disperse phase and in the dispersion medium are close to the diffusion coefficients of the corresponding homopolymers, it is possible to estimate the average sizes of the particles of the disperse phases.

Several methods have been proposed for carrying out calculations of this kind.[13] The most rational procedure for the treatment of kinetic sorption curves has been described in a study[99] whose authors derived simple relations between the principal process characteristics by the numerical calculation of various linear and concave sorption isotherms for sorbents with a bidisperse structure:

$$\gamma(t) = 1 - \exp\left\{A(\varepsilon)\left(\frac{t}{\tau+T}\right)^{B(\varepsilon)}\right\} \qquad (21)$$

where γ is the relative degree of filling of the sorbent by the sorbate, t the time, $\varepsilon = \tau/(\tau + T)$, and $A(\varepsilon)$ and $B(\varepsilon)$ are empirical coefficients which depend on the form of the disperse phase. Their numerical values have been published.[99] These analytical formulae can be used to find from the experimental curves both D' and D'' and the corresponding diffusion relaxation times and hence also certain structural parameters of the medium. It is significant that this method does not require the knowledge of the entire sorption curve.

3. Determination of the Thermodynamic Parameters of the Mixing of the Components

New possibilities for the determination of the chemical potentials of the components in solutions of polymers (μ_i) are provided by the method of non-equilibrium thermodynamics, which makes it possible to relate in a fairly general and clear form the mutual diffusion and partial self-diffusion ($D^*_{i,\varphi}$) coefficients of the components to the thermodynamic characteristics of the solutions:

$$D_V = D^*_{i\varphi}\frac{\partial \ln a_i}{\partial \ln \varphi_i} = D^*_{i,\varphi}\frac{\varphi_i}{RT}\frac{\partial \Delta\mu_i}{\partial \varphi_i} \quad , \qquad (22)$$

where a_i is the activity of the ith component and φ_i its volume fraction. It follows from Eqn.(23) that

$$\Delta\mu_i = RT\int_1^{\varphi_i}\left(\frac{D_V}{D_{i,\varphi}}\right)\varphi_i^{-1}\,d\varphi_i \qquad (23)$$

Eqn.(23) makes it possible to determine the change in the chemical

potential of any component of the diffusion system.[7,100] The calculations can be performed in accordance with the following scheme: initially, one determines experimentally the concentration dependence of D_V and then also experimentally or by calculation, using the Fujita equation, one finds the concentration variation of the partial self-diffusion coefficient of the ith component. Next $D_V/D^*_{i,\varphi}$ is plotted against $\ln \varphi_i$, graphical integration is carried out, and finally $\Delta\mu_i$ is determined by Eqn.(23). The subsequent treatment of the $\Delta\mu_i - \varphi_i$ relation in order to obtain the Gibbs free energy is traditional.[101]

It has been suggested[7] that the concentration variations of D_V and D^*_i be used to determine the interaction parameters χ characterising the thermodynamic affinity of the components in the Flory–Huggins theory. For this purpose, one can use the equation

$$D_V = D^*_{i,\varphi}\left[1 - \left(1 - \frac{V_1}{V_2}\right)\varphi_1 - \chi 2\varphi_1\varphi_2\right] , \qquad (24)$$

where V_1 and V_2 are the molar volumes of the components and φ_1 and φ_2 are their volume fractions. For polymer–low-molecular-weight substance systems with $V_1 \ll V_2$, this relation assumes the form

$$D_V = D^*_{i,\varphi}(1 - \varphi_1 - 2\chi\varphi_1\varphi_2) . \qquad (25)$$

If one uses the relative diffusion coefficient D_1, then, instead of Eqn.(25), one can obtain the simplest expression for the calculation of χ in a binary polymer system:

$$D_1 = D^*_1(1 - 2\chi\varphi_1) . \qquad (26)$$

Thus, both in the determination of $\Delta\mu_1$ and $\Delta\mu_2$ and in calculations of χ, it is essential to have information about the concentration variations of D_v and D^*_i. The integral values of χ can be estimated by means of extrapolated values of $D_{11}(\varphi_1 \to 1)$ and D^*_{11}, because $D_{11}/D^*_{11} = 1 - 2\chi$. The errors in the determination of $\Delta\mu_i$ and χ are related mainly to the error in the measurement of the mutual diffusion and self-diffusion coefficients and amount to ~15%.

4. Structural Studies on Crystalline and Filled Polymers

It is possible to differentiate several structural-morphological levels in these systems. The first is associated with the organisation of the crossing chains in the amorphous phase and determines its density, the distribution of density on passing from one crystallite to another, and the positions of the end groups and folds. The second has a bearing on the relative positions of the crystallites in space, their size, character, aggregation, internal structure, and degree of defectiveness. The third, superspherulitic level determines the character of the packing of the spherulites and their interrelation and internal structure. This structural hierarchy can be extended also to filled polymers after the introduction of the corresponding terminological refinements. Thus the amorphous phase of crystalline polymers is identical with the polymeric dispersion medium, the second level determines the distribution of the particles of the disperse phase, and the third determines the distribution of aggregates of the filler particles.

Analysis of experimental data has shown that the results of diffusion measurements make it possible to characterise to some extent each of the above structural-morphological levels. However, we believe that it is most useful to employ diffusion measurements for the study of the structure of the amorphous phase of crystalline polymers.

It has been suggested[58,80] that diffusion methods be used for the structural analysis of crystalline polymers. However, the authors confine themselves to the establishment of qualitative relations between the diffusion coefficients and the structural parameters of the media determined by other methods. This approach cannot be regarded as a method of structural analysis, because it reduces essentially to the solution of the converse problem—the use of information about the structure of the specimens for the interpretation of the results of diffusion measurements.

As already mentioned above, the application of diffusion methods in structural analysis presupposes something different: the determination of quantitative analytical relations between the diffusion constants and the structural characteristics of crystalline and filled polymer matrices. If Eqn.(18) is used for this purpose, then, when information is available about D and D_a, it is possible to estimate φ_c, and, when D and φ_c data are used, one can calculate the density of the amorphous phase in real polymeric materials. These estimates can be performed with the aid of the equation

$$\frac{\rho}{\rho_a} = \frac{\rho_c}{\rho_a}\left(1 - A + \frac{\rho_a}{\rho_c}A\right) , \qquad (27)$$

where ρ_c, ρ_a, and ρ are respectively the densities of the crystallites, the amorphous analogue, and the amorphous phase of the real polymer, $A = \ln(D/D_a)/\ln(D_{calc}/D_a)$, D_a and D are respectively the diffusion coefficients of the low-molecular-weight substances in the amorphous analogue and in the real polymer, and D_{calc} is the diffusion coefficient calculated by Eqn.(18) from D_a, f_a, and φ_c. On passing to filled polymers, the approach remains the same and only the physical significance of the symbols in Eqn.(27) changes.[7]

In this Section, we have considered certain possibilities in the application of diffusion methods to the physicochemical analysis of polymer systems. It is to be expected, that, as the methodological, molecular-kinetic, and phenomenological approaches are perfected, these possibilities will expand and will find an honourable place among other integral methods for the analysis of real polymeric materials.

REFERENCES

1. N.M.Emanuel' and A.L.Buchachenko, "Khimicheskaya Fizika Stareniya i Stabil'nosti Polimerov" (Chemical Physics of the Ageing and Stability of Polymers), Izd.Nauka, Moscow, 1982, 359 pp.
2. V.P.Budtov and V.V.Konsetov, "Teplomassoperenos v Polimerizatsionnykh Protsessakh" (Heat and Mass Transfer in Polymerisation Processes), Izd.Khimiya, Leningrad, 1983, 280 pp.
3. G.E.Zaikov, A.L.Iordanskii, and V.S.Markin, "Diffuziya Elektrolitov v Polimerakh" (Diffusion of Electrolytes in Polymers), Izd.Khimiya, Moscow, 1984, 237 pp.
4. G.E.Krichevskii, "Diffuziya i Sorbtsiya v Protsessakh Krasheniya i Pechataniya" (Diffusion and Sorption in Dyeing and Printing Processes), Izd.Legkaya Industriya, Moscow, 1981, 207 pp.
5. S.F.Timashev, A.A.Ovchinnikov, and A.A.Belyi, "Kinetika Diffuzionnokontroliruemykh Khimicheskikh Protsessov" (Kinetics of Diffusion-controlled Chemical Processes), Izd. Khimiya, Moscow, 1986, 287 pp.

6. V.N.Manin, A.N.Gromov, and V.P.Grigor'ev, "Defektnost' i Ekspluatatsionnye Svoistva Polimernykh Materialov" (The Degree of Defectiveness and Operating Properties of Polymeric Materials), Izd.Khimiya, Moscow, 1986, 180 pp.
7. A.E.Chalykh, "Diffuziya i Polymernykh Sistemakh" (Diffusion in Polymer Systems), Izd.Khimiya, Moscow, 1987, 312 pp.
8. A.M.Vasserman and A.L.Kovarskii, "Spinovye Metki i Zondy v Fizikokhimii Poliermov" (Spin Labels and Probes in the Physical Chemistry of Polymers), Izd.Nauka, Moscow, 1986, 243 pp.
9. N.I.Nikolaev, "Diffuziya v Membranakh" (Diffusion in Membranes), Izd.Khimiya, Moscow, 1980, 231 pp.
10. A.I.Maklakov, V.D.Skirda, and N.F.Fatkulin, "Samodiffuziya v Rastvorakh i Rasplavakh Makromolekul" (Self-diffusion in Solutions and Melts of Macromolecules), Izd.Kiev.Gos.Univ., Kiev, 1987, 224 pp.
11. Yu.Ya.Gotlib, A.A.Darinskii, and Yu.E.Svetlov, "Fizicheskaya Kinetika Makromolekul" (Physical Kinetics of Macromolecules), Izd.Khimiya, Moscow, 1986, 272 pp.
12. A.I.Raichenko, "Matematicheskaya Teoriya Diffuzii v Prilozheniyakh" (Applications of the Mathematical Theory of Diffusion), Izd.Naukova Dumka, Kiev, 1981, 391 pp.
13. A.Ya.Malkin and A.E.Chalykh "Diffuziya i Vyazkost' Polimerov. Metody Issledovaniya" (Diffusion and Viscosity of Polymers. Research Methods), Izd.Khimiya, Moscow, 1979, 301 pp.
14. V.A.Birshtein and V.M.Egorov, Vysokomol.Soed., 1985, **27A**, 2440.
15. V.N.Tsvetkov, V.E.Eskin, and S.Ya.Frenkel', "Struktura Makromolekul v Rastvorakh" (The Structure of Macromolecules in Solutions), Izd.Nauka, Moscow, 1964, 719 pp.
16. R.C.Reid and T.K.Sherwood, "The Properties of Gases and Liquids: Their Estimation and Correlation" (Translated into Russian), Gostoptekhizdat, Moscow, 1964, 334 pp.
17. V.N.Tsvetkov, "Zhestkotsepnye Polimernye Molekuly" (Rigid Chain Polymer Molecules), Izd.Nauka, Moscow, 1986, 379 pp.
18. D.W.Van Krevelen, "Properties of Polymers: Correlations with Chemical Structure" (Translated into Russian), Izd.Khimiya, Moscow, 1976, 414 pp.
19. A.A.Askadskii and Yu.I.Matveev, "Khimicheskoe Stroenie i Fizicheskie Svoistva Polimerov" (The Chemical Structure and Physical Properties of Polymers), Izd.Khimiya, Moscow, 1983, 248 pp.
20. S.A.Reitlinger, "Pronitsaemost' Polimernykh Materialov" (Permeability of Polymeric Materials), Izd.Khimiya, Moscow, 1974, 272 pp.
21. J.I.Moisan, Europ.Polym.J., 1980, **16**, 986.
22. I.A.Tutorskii, B.S.Grishin, and I.S.Yurovskaya, "Diffuzionnye Yavleniya v Polimerakh" (Diffusion Phenomena in Polymers), Chernogolovka, 1985, p.18.
23. I.V.Chernova and R.M.Vasenin, Vysokomol.Soed., 1964, **6**, 1704.
24. S.N.Zhurkov and G.Ya.Ryskin, Zhur.Tekh.Fiz., 1954, **24**, 797.
25. R.M.Vasenin, Vysokomol.Soed., 1961, **3**, 1220.
26. R.M.Vasenin, Vysokomol.Soed., 1960, **2**, 857.
27. S.P.Orlova, A.E.Chalykh, and R.M.Vasenin, Vysokomol.Soed., 1968, **10A**, 1778.
28. V.K.Gromov, A.E.Chalykh, R.M.Vasenin, and S.S.Voyutskii, Vysokomol.Soed., 1965, **7**, 2117.
29. M.I.Artsis, A.E.Chalykh, Yu.V.Moiseev, and G.E.Zaikov, Vysokomol.Soed., 1973, **15A**, 63.
30. V.V.Arkhangel'skii, A.E.Chalykh, V.M.Rudoi, and V.A.Ogarev, Vysokomol.Soed., 1977, **19B**, 891.
31. C.E.Rogers, "Problems of the Physics and Chemistry of the Solid State of Organic Compounds" (Translated into Russian), Izd.Mir, Moscow, 1968, p.229.
32. V.B.Teplyakov and S.G.Durgar'yan, Vysokomol.Soed., 1986, **28A**, 564.
33. R.J.Pace and A.Datyner, J.Polym.Sci., Polym.Phys.Ed., 1979, **17**, 437.
34. R.J.Pace and A.Datyner, J.Polym.Sci., Polym.Phys.Ed., 1979, **17**, 1675.
35. B.I.Golikov and A.E.Chalykh, Dokl.Akad.Nauk SSSR, 1979, **248**, 902.
36. K.K.Evstrop'ev, "Diffuzionnye Protsessy v Stekle" (Diffusion Processes in Glass), Stroiizdat, Moscow, 1970, 167 pp.
37. B.I.Golikov, Candidate's Thesis in Chemical Sciences, Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow, 1980, 136 pp.
38. R.M.Barer, J.A.Barrie, and J.Slater, J.Polym.Sci., 1958, **28**, 117.
39. E.E.Shnol', N.K.Balabaev, and A.G.Grivtsov, "Chislennye Eksperimenty po Modelirovaniyu Dvizheniya Molekul" (Numerical Experiments on the Modelling of the Motion of the Molecules), Inst.Prikl.Mat.Akad.Nauk SSSR, Moscow, 1972, Preprint 4, p.31.
40. E.E.Shnol', "O Dvizhenii Kontsevykh Atomov Dlinnykh Molekul" (The Movement of the End Atoms of Long Molecules), Inst.Prikl.Mat.Akad.Nauk SSSR, Moscow, 1974, Preprint 74, p.35.
41. Ya.I.Frenkel', "Kineticheskaya Teoriya Zhidkostei" (Kinetic Theory of Liquids), Izd.Nauka, Moscow, 1975, 592 pp.
42. A.L.Buchachenko, A.L.Kovarskii, and A.M.Vasserman, Uspekhi Khimii i Fiziki Polimerov" (Advances in the Chemistry and Physics of Polymers) (Edited by Z.A.Rogovin), Izd. Khimiya, Moscow, 1973, p.31.
43. S.G.Entelis, V.V.Evreinov, and A.I.Kuzaev, "Reaktsionnosposobnye Oligomery" (Reactive Oligomers), Izd.Khimiya, Moscow, 1985, 304 pp.
44. A.E.Chalykh, V.V.Arkhangel'skii, and S.A.Nenakhov, Vysokomol.Soed., 1977, **19B**, 521.
45. D.S.Sanditov and G.M.Bartenev, "Fizicheskie Svoistva Neuporyadochennykh Struktur" (Physical Properties of Nonordered Structures), Izd.Nauka, Moscow, 1982, 256 pp.
46. S.A.Nenakov, Candidate's Thesis in Chemical Sciences, Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow, 1977, 232 pp.
47. S.A.Nenakhov and A.E.Chalykh, Vysokomol.Soed., 1979, **21B**, 513.
48. V.V.Volkov, S.G.Durgar'yan, and E.G.Novitskii, "Diffuzionnye Yavleniya v Polimerakh" (Diffusion Phenomena in Polymers), Izd.Rizhsk.Politekh.Inst., Riga, 1977, Vol.2, p.242.
49. Yu.I.Dyternskii, "Membrannye Protsessy Razdeleniya Zhidkikh Smesei" (Membrane Liquid Mixture Separation Processes), Izd.Khimiya, Moscow, 1975, 229 pp.
50. S.-T.Hwang and K.Kammermeyer, "Membrane Separation Processes" (Translated into Russian), Izd.Khimiya, Moscow, 1981, 464 pp.
51. A.E.Chalykh and V.N.Krivoshei, Vysokomol.Soed., 1982, **24A**, 1640.
52. A.A.Polyanskii and V.G.Khozin, "Diffuzionnye Yavleniya v Polimerakh" (Diffusion Phenomena in Polymers), Chernogolovka, 1985, p.19.

53. J.S.Duda and J.L.Vrentas, J.Polym.Sci., Polym.Phys.Ed., 1977, **15**, 403.
54. J.D.Ferry, "Viscoelastic Properties of Polymers" (Translated into Russian), Izd.Mir, Moscow, 1963, 534 pp.
55. D.R.Paul and W.J.Koros, J.Polym.Sci., Polym.Phys.Ed., 1976, **14**, 675.
56. J.U.Petropoulos and P.P.Roussis, J.Membr.Sci., 1978, **3**, 343.
57. Yu.P.Yampol'skii and O.G.Durgar'yan, Neftekhimiya, 1983, **23**, 435.
58. H.L.Frisch and S.A.Stern, CRC Critical Reviews, 1982, **11**(2), 123.
59. B.P.Shtarkman, "Plastifikatsiya Polivinilkhlorida" (Plastification of Polyvinyl Chloride), Izd.Khimiya, Moscow, 1975, 248 pp.
60. A.V.Sidorovich and E.V.Kushinskii, "Relaksatsionnye Yavleniya v Polimerkah" (Relaxation Phenomena in Polymers) (Edited by G.M.Bartenev and Yu.V.Zelenev), Izd.Khimiya, Moscow, 1972, p.63.
61. V.I.Gol'danskii, "Fizicheskaya Khimiya Pozitrona i Pozitroniya" (The Physical Chemistry of the Positron and Positronium), Izd.Nauka, Moscow, 1968, 242 pp.
62. V.V.Volkov, A.V.Gol'danskii, S.G.Durgar'yan, et al., Vysokomol.Soed., 1987, **29A**, 192.
63. G.M.Bartenev and D.S.Sanditov, "Relaksatsionnye Protsessy v Stekloorbraznykh Sistemakh" (Relaxation Processes in Vitreous Systems), Izd.Nauka, Moscow, 1986, 236 pp.
64. K.Takada, H.Matsuya, T.Matsuda, and Higashimura, J.Appl.Polym.Sci., 1985, **30**, 1605.
65. B.A.Rozenberg, G.F.Roginskaya, A.E.Chalykh, and V.P.Volkov, Uspekhi Khim., 1982, **51**, 1733 [Russ.Chem.Rev., 1982(10)].
66. P.G.Babaevski, "Diffuzionnye Yavleniya v Polimerakh" (Diffusion Phenoman in Polmers), Chernogolovka, 1985, p.74.
67. A.A.Berlin and F.A.Shutov, "Khimiya i Tekhnologiya Gazonapolnennykh Vysokopolimerov" (The Chemistry and Technolgoxy of Gas-filled High Polymers), Izd.Nauka, Moscow, 1980, 504 pp.
68. A.E.Chalykh, K.I.Fredgeim, and V.I.Alekseenko, Vysokomol. Soed., 1972, **14B**, 93.
69. S.P.Papkov, "Ravnovesie Faz v Sistemakh Polimer–Rastvoritel'" (Phase Equilibrium in Polymer–Solvent Systems), Izd. Khimiya, Moscow, 1981, 272 pp.
70. T.K.Kwei and T.T.Wang, "Polymer Blends" (Edited by D.R.Paul and S.Newman) (Translated into Russian), Izd.Mir, Moscow, 1981, 220 pp.
71. V.L.Vakula and L.M.Pritykin, "Fizicheskaya Khimiya Adgezii Polimerov" (Physical Chemistry of the Adhesion of Polymers), Izd.Khimiya, Moscow, 1984, 224 pp.
72. A.Sh.Goikman and V.P.Solomko, "Vysokomolekulyarnye Soedineniya Vklyucheniya" (High-molecular-weight Clathrate Compounds), Izd.Naukova Dumka, Kiev, 1982, 192 pp.
73. G.Fleischer, Polym.Bull., 1982, **7**, 423.
74. I.N.Bekman, I.M.Buntseva, V.I.Korobkov, and E.E.Finkel', Radiokhimiya, 1986, **28**, 222.
75. I.N.Bekman, A.A.Shvyryaev, and I.M.Buntseva, "Diffuzionnye Yavleniya v Polimerakh" (Diffusion Phenomena in Polymers), Chernogolovka, 1985, p.45.
76. V.P.Vorob'ev, Candidate's Thesis in Physical-mathematical Sciences, Institute of Macromolecular Compounds, Leningrad, 1981, 127 pp.
77. A.E.Chalykh, V.B.Zlobin, and V.K.Gerasimov, Vysokomol. Soed. (in the Press).
78. B.P.Shkovskii and A.L.Efros, "Elektronnye Svoistva Legirovannykh Poluprovodnikov" (Electronic Properties of Doped Semiconductors), Izd.Nauka, Moscow, 1979, 416 pp.
79. C.E.Rogers, "Engineering Design for Plastics" (Edited by E.Baer), Izd.Khimiya, Moscow, 1967, p.463.
80. M.Sefton and K.T.Chiang, "Latest Instrumental Methods for the Study of the Structure of Polymers" (Edited by J.King) (Translated into Russian), Izd.Mir, Moscow, 1982, p.264.
81. S.P.Rudobashta, "Massoperenos v Sistemakh s Tverdoi Fazoi" (Mass Transfer in Systems with a Solid Phase), Izd.Khimiya, Moscow, 1980, 245 pp.
82. A.Kreitus, A.E.Chalykh, and E.Viatere, "Modifikatsiya Polimernykh Materialov" (Modification of Polymeric Materials), Izd.Rizhsk.Politekh.Inst., Riga, 1978, p.49.
83. V.P.Vorob'ev, M.A.Martynov, B.A.Sazhin, and G.A.Vinogradova, Vysokomol.Soed., 1980, **22A**, 2472.
84. A.E.Chalykh, Doctoral Thesis in Chemical Sciences, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow, 1975, 415 pp.
85. L.Mandelcorn, "Crystallisation of Polymers" (Translated into Russian), Izd.Khimiya, Moscow, 1966, 331 pp.
86. L.Benguigui, J.Yacubowicz, and M.Narkis, J.Polym.Sci., Polym.Phys.Ed., 1987, **25**, 127.
87. I.A.Shtern, I.V.Plotnikov, and S.A.Pavlov, "Problemy Fizikokhimicheskoi Mekhaniki Voloknistykh i Poristykh Dispersnykh Strutkur" (Problems of the Physical Chemistry of the Mechanics of Fibrous and Porous Disperse Structures), Izd.Zinatne, Riga, 1967, p.343.
88. S.L.Kurochkin, L.I.Klushin, A.M.El'yashevich, et al., Lakokrasochnye Materialy i Ikh Primenenie, 1986(5), 41.
89. V.K.Gerasimov, V.B.Zlobin, and A.E.Chalykh, Vysokomol. Soed., 1986, **28A**, 1977.
90. V.B.Zlobin, A.E.Chalykh, E.A.Terman, et al., Kozh.-obuvn. Prom., 1985(5), 45.
91. A.E.Chalykh, "Sintez i Svoistva Blok-Sopolimerov" (The Synthesis and Properties of Block Copolymers), Izd.Naukova Dumka, Kiev, 1983, p.123.
92. A.E.Chalykh and A.Avgonov, Dokl.Akad.Nauk Tadzh.SSR, 1983, 26, 427.
93. V.V.Teplyakov, A.L.Ievlev, and S.G.Durgar'yan, Vysokomol. Soed., 1985, **27A**, 818.
94. S.G.Kulichikhin, N.N.Avdeev, A.E.Chalykh, and A.Ya.Malkin, Vysokomol.Soed., 1978, **20B**, 842.
95. A.E.Chalykh and V.G.Chertkov, Vysokomol.Soed., 1984, **26A**, 2231.
96. A.E.Chalykh, I.N.Sapozhnikova, and A.D.Aliev, Dokl.Akad. Nauk SSSR, 1978, **238**, 144.
97. A.E.Chalykh, E.D.Popova, and N.N.Avdeev, Vysokomol. Soed., 1984, **26A**, 1420.
98. T.I.Chalykh, "Diffuzionnye Yavleniya v Polimerakh" (Diffusion Phenomena in Polymers), Izd.Rizhsk.Politekh.Inst., Riga, 1977, Vol.1, p.199.
99. P.P.Zolotarev, V.I.Ulin, and S.N.Efremov, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 906.
100. A.E.Chalykh, N.I.Druz', and A.E.Kreitus, Vysokomol.Soed., 1982, **24B**, 747.
101. A.A.Tager, "Fizikokhimiya Polimerov" (Physical Chemistry of Polymers), Izd.Khimiya, Moscow, 1978, 544 pp.

Institute of Physical Chemistry,
USSR Academy of Sciences,
Moscow