Russian Chemical Reviews **66** (11) 963 – 974 (1997) © 1997 Russian Academy of Sciences and Turpion Ltd

UDC 541.6

The role of topological disorder in the physical chemistry of polymers

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Abstract. The topological disorder, which consists of a set of diverse knots, folds, and entanglements of polymer chains, determines many properties of a polymeric substance. It is manifested in processes involving the sorption of low-molecular substances by the polymer and in the chemical reactions of the substances dissolved in the polymer. The bibliography includes 59 references.

I. Introduction

Zones with a relative degree of order in the disposition of monomer uits (short-range order), which alternate with zones where this order is violated, are known to exist in real polymers. The zones with disturbed order arise around topological structures such as loops, folds, various entanglements of the polymer chains (see, for example, Yeh [1]), and also at the ends of macromolecules. The majority of zones of short-range order violation [units of disorder (UOD)] are formed in the synthesis of the polymer or during its precipitation from solution and are retained throughout the existence of the given polymer sample, not disappearing even on melting. The set of diverse UOD is referred to as the stable topological disorder, which determines many properties of the polymer.[2, 3] According to the present author, the degree of topological disorder is the missing parameter without considering which it is impossible to describe quantitatively the properties of a polymeric substance.[4] Examples of the simplest UOD are illustrated in Fig. 1.

There have been numerous studies devoted to the role of entanglements of the macromolecules in the dynamics of melts and concentrated polymer solutions.[5–8] The level of disorder must influence the mechanical properties of the polymeric substance, which depend on the nature of the entanglements of the macromolecules.[9] However, consideration of these questions is outside the scope of the present review, in which attention is concentrated on the relation between the topological disorder and the physicochemical properties of the polymer – low-molecular substance system.

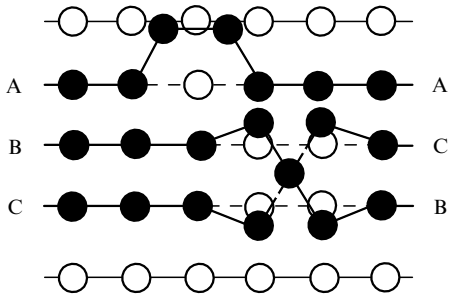


Figure 1. Schematic illustration of the simplest unit of disorder: A – A — fold; B – B and C – C — entanglement.

II. The homopolymer as a two-component system

There exists an extensive class of crystallising polymers, such as polyethylene, polypropylene, poly(vinyl chloride), aliphatic polyamides, *etc*. A characteristic feature of these polymers is incomplete crystallisation. The physical cause preventing the complete crystallisation of the polymeric substance is the presence of a stable disorder in the arrangement of the polymer chains. The 'crystallinity', *i.e*. the content of the crystalline substance in such polymers, varies as a rule within wide limits (from 20% to 80%) [10] and may change reversibly with temperature [11] and apparently with pressure. It is noteworthy that the absolute value of the 'crystallinity' of the same polymer measured in different ways can differ appreciably, so that in speaking of the 'crystallinity' of the

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Received 29 January 1997
Uspekhi Khimii **66** (11) 1064 – 1076 (1997); translated by A K Grzybowski

polymer it is always necessary to indicate the method used for its measurement.[12]

Incomplete crystallisation implies that two phases coexist in the individual homopolymer over a certain range of temperatures and pressures: crystalline and amorphous. According to Gibbs' phase rule

$$F + P \leqslant C + 2, \tag{1}$$

where $F = 2$ is the number of degrees of freedom (temperature and pressure), $P = 2$ is the number of phases (crystalline and amorphous), and C is the number of components which should be at least two. If the disorder units (or the units of disorder) are adopted as the quasi-molecules of a second component, then the degree of disorder can be expressed in concentration units. Taking into account the wide variety of the disorder elements ζ_i, one can write

$$[\zeta] = \sum [\zeta_i] = \frac{1}{VN_A} \sum N_i \,, \tag{2}$$

where V is the volume of the sample, N_A is the Avogadro number, and N_i is the number of UOD of the ith type in the sample.

Like the species of a low-molecular substance, the quasi-molecules can migrate, although to a limited extent, in the polymer melt; the folds (A – A in Fig. 1) migrate *via* a wavelike motion ('reptation'[7]), whilst the simplest knots (B – B and C – C) migrate *via* a mechanism in which the monomer units adjoining the knot change places ('sliding' along parallel chains).

Assuming that the complete crystallisation of the polymer is prevented by the osmotic pressure of the solution of the UOD in the noncrystallised part of the polymer, which is $P_{os} = RT[\zeta](1-x)^{-1}$ (x is the degree of crystallinity), the author of the present review[2] proposed an equation describing the dependence of the degree of crystallinity of the polymer on the concentration of extraneous units ω_i

$$(1 - x) = \frac{RT[\zeta]}{-\Delta F_{cr} - \sum_i \varkappa_i [\omega_i]} \,, \tag{3}$$

where $-\Delta F_{cr}$ is the decrease in free energy on crystallysation of the polymer calculated per unit mass of the latter and $\varkappa_i$ are coefficients taking into account the decrease in $-\Delta F_{cr}$ when foreign units of the ith type are incorporated in the crystallite. As can be seen from Eqn (3), for $[\zeta] = 0$ the polymer crystallises fully (*i.e.* $x = 1$) and conversely, above a certain value of $[\zeta]$, the polymer is fully amorphous.

III. Methods for the investigation of the degree of disorder

Any violation of short-range order is associated with a certain excess volume: the density of the polymeric substance in the region of the entanglement of the polymer chains should be reduced. Thus the UOD, or more precisely the structural formations Z_j arising from them, may be regarded as elements of the free volume. Just as one can measure the volume of a vessel by filling it with water or another liquid, the free volume corresponding to the structural formation Z_j is measured by filling it with a low-molecular substance. However, owing to the smallness of the volume of the element Z_j, only those substances the molecular volume of which V_A is not greater than the free volume V_j contained in this element can fill it (or, more precisely, be placed in it):

$$V_A \leqslant \beta V_j \,, \tag{4}$$

where β is the coefficient taking into account the lack of correspondence between the shapes of the molecule of substance A and the volume element ζ_j. Thus, by investigating the dissolution (sorption) of various low-molecular substances in the polymer, it is possible to obtain information about the concentration of the UOD and their size distribution for the dissolved (sorbed) molecules.

The density of the polymer or, more precisely, the difference between the theoretical calculated volume of unit mass of the ideally crystallised polymer and the real volume of unit mass of the sample studied (the so-called free volume) might serve as a natural measure of the free volume, but in such an approach we cannot estimate the size distribution of the elements of the free volume. Furthermore, the most sensitive method for the determination of density — hydrostatic weighing — requires the immersion of the sample in a low-molecular liquid the molecules of which partly fill these elements.

Assuming that the sorption of substance A includes a stage involving the formation of a true solution of A in the amorphous part of the polymer with its subsequent permeation into the sorption centres in accordance with the scheme

$$A + Z_j \underset{}{\overset{K_j}{\rightleftharpoons}} AZ_j \,, \tag{5}$$

and that the first stage obeys Henry's law

$$[A] = \gamma_A [A]_m \,, \tag{6}$$

where [A] is the concentration of truly dissolved molecules of A, $[A]_m$ is the concentration of A in the surrounding medium, and γ_A is Henry's coefficient, it is easy to find the isotherm for the sorption of substance A by the polymer from the formula

$$[A]_p = \gamma_A [A]_m + \sum_j [AZ_j] = \gamma_A [A]_m + \sum_j \frac{\gamma_A K_j [Z_j][A]_m}{1 + \gamma_A K_j [A]_m} \tag{7}$$

or, neglecting the true solubility of A outside the sorption centres, from the formula

$$[A]_p = \sum_j \frac{\gamma_A K_j [Z_j][A]_m}{1 + \gamma_A K_j [A]_m} \,. \tag{8}$$

With increase in the concentration of the molecules of A in the surrounding medium, each term in Eqn (8) tends to $[Z_j]$ and $[A]_p$ tends to $\Sigma[Z_j] = [Z_A]$ (the overall concentration of the centres sorbing the given substance).

It will be shown below that, even for considerable differences between the sorption constants K_j, the isotherm for sorption on inhomogeneous centres is experimentally indistinguishable from the Langmuir isotherm

$$[A]_p = \frac{a[A]_m}{1 + b[A]_m} \,. \tag{9}$$

However, for high values of $[A]_m$, this relation may break down. Remaining in the region where the Langmuir Law holds, it is possible to determine the 'Langmuir sorption capacity',[13,14] *i.e.* the value $[Z_A]$. The type (9) Langmuir relation can be transformed into a straight line in terms of the variables $1/[A]_m$ and $1/[A]_p$, whereupon the intercept made by the straight line on the ordinate axis corresponds to the reciprocal of the concentration of the sorption centres: $b/a = 1/[Z_A]$.

On the simplest assumption that within a certain range $K_1 \leqslant K_i \leqslant K_2$ the value of

$$\rho = \frac{\Delta[Z_i]}{\Delta K_i} = \frac{[Z_A]}{K_2 - K_1} \tag{10}$$

is constant and that outside this range it is zero, we arrive at the following expression after substituting the sum (8) by the integral:

$$[A]_p = \rho \int_{K_1}^{K_2} \frac{K\gamma_A [A]_m \mathrm{d}K}{1 + K\gamma_A [A]_m} = \tag{11}$$

$$= [Z_A] \left\{ 1 + \frac{1}{(K_2 - K_1)\gamma_A [A]_m} \ln \frac{1 + K_1 \gamma_A [A]_m}{1 + K_2 \gamma_A [A]_m} \right\} .$$

When $[A]_m \to \infty$, the value $[A]_p$ tends to the limit $\lim[A]_p = [Z_A]$.

Figure 2 presents the curve for the dependence of $[A]_p$, or, more precisely, of the ratio $[A]_p/[Z_A]$, on $[A]_m$, calculated by

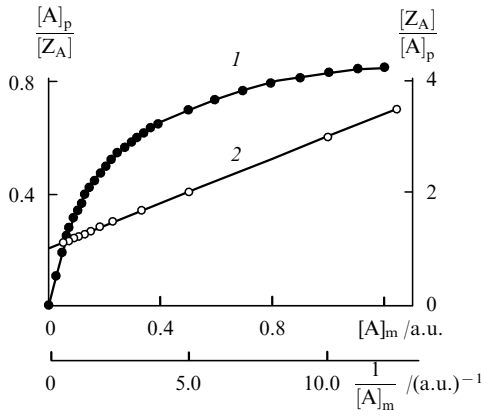


Figure 2. The sorption isotherm of a low-molecular substance by a polymer in direct (*1*) and inverse (*2*) coordinates: calculation by Eqn (11) with $K_2/K_1 = 10$.

Eqn (11) with $\gamma_A = 1$, $K = 1$, and $K_2 = 10$ in terms of the direct variables and their reciprocals. It is seen from the figure that the curve described by Eqn (11) in inverse coordinates $1/[A]_p$ *vs.* $1/[A]_m$ is transformed into a straight line, which means that Eqn (11) may be replaced by the simpler expression

$$[A]_p = \frac{[Z]_A K\gamma_A [A]_m}{1 + K\gamma_A [A]_m}.$$

Apparently the majority of the phenomena associated with the role of disorder may be satisfactorily explained by assuming that the UOD can be divided, for any influence, into those participating or not participating in the process and those which respond in different ways to the given influence (in all cases, the quantitative differences within each group are neglected).

In certain cases, it is possible to employ the equilibrium solubility of substance A in the polymer (S_A) as a measure of the concentration of the centres $[Z_A]$. Evidently the value S_A is always smaller than $[Z_A]$, but in some instances, when S_A is close to its theoretical limit $[Z_A]$, one can assume that $S_A \approx [Z_A]$. The closeness of S_A to $[Z_A]$ may be indicated, for example, by a weak temperature dependence of the solubility.

If the substance dissolved in the polymer is an antioxidant, it is possible to estimate the change in the concentration of its mobile part by the method of critical concentrations. This method has been described in detail [15, 16] and here we shall consider only its simplified version.

In order to inhibit a radical chain oxidation reaction occurring in a polymer consisting of RH units, *i.e.*

$$R^{\bullet} + O_2 \xrightarrow{k_1} RO_2^{\bullet},$$

$$RO_2^{\bullet} + RH \xrightarrow{k_2} \cdots \longrightarrow \alpha ROOH + R^{\bullet},$$

$$ROOH + RH \xrightarrow{k_{hp}} \cdots \longrightarrow \sigma R^{\bullet} + \text{products},$$

where $R^{\bullet}$ is a free radical (usually a hydrocarbon), ROOH is the branching product reacting with the initial substance to form new free radicals, α is the yield of hydroperoxy-groups, and σ is the probability of degenerate chain branching, it is necessary to introduce into the reacting substance an inhibitor IH.[17]

$$RO_2^{\bullet} + IH \xrightarrow{k_t} \cdots \longrightarrow \text{products}, \qquad (12)$$

or a substance Y which reacts with the branching product, *i.e.*

$$ROOH + Y \longrightarrow \text{products}.$$

In the former case, the balance of the $RO_2^{\bullet}$ and ROOH concentrations is described by the system of equations

$$\frac{d[RO_2^{\bullet}]}{dt} = W_0 + \sigma k_{hp}[ROOH][RH] - k_t[RO_2^{\bullet}][IH], \qquad (13)$$

$$\frac{d[ROOH]}{dt} = \alpha k_2[RO_2^{\bullet}][RH] - k_{hp}[ROOH][RH]. \qquad (14)$$

Here W_0 is the rate of chain initiation.

Assuming that the $RO_2^{\bullet}$ concentration is stationary, *i.e.* that the rates of formation and consumption of $RO_2^{\bullet}$ are equal, $d[RO_2^{\bullet}]/dt = 0$, one can write

$$[RO_2^{\bullet}] = \frac{W_0 + \sigma k_{hp}[ROOH][RH]}{k_t[IH]}.$$

Neglecting the rate of chain initiation W_0 compared with the rate of branching $\sigma k_{hp}[ROOH]$, we find

$$\frac{d[ROOH]}{dt} = \frac{k_{hp}[ROOH][RH]}{k_t[IH]}(\alpha\sigma k_2[RH] - k_t[IH]). \qquad (15)$$

As can be seen from the last expression, the value of $d[ROOH]/dt$ is positive, *i.e.* the process is self-accelerated, provided that the expression in brackets is positive, *i.e.*

$$(\alpha\sigma k_2[RH] - k_t[IH]) > 0 \qquad (16)$$

or

$$[IH] < [IH]_{cr} = \frac{\alpha\sigma k_2[RH]}{k_t} \qquad (17)$$

and, conversely, the rate of the process decreases, tending to a limit, if this expression is less than zero.

The quantity $[IH]_{cr}$, *i.e.* the concentration of the inhibitor (antioxidant) corresponding to the boundary between the two reaction regimes, is called the critical concentration. Compounds which decompose the branching product may displace the critical concentration of the inhibitor but they themselves do not have a critical concentration in the absence of an inhibitor.[16, 17]

The critical concentration of the antioxidant can be determined experimentally comparatively easily as the boundary between the region of the relatively slow stationary process and the fast self-accelerated process.[18] In particular, the induction period, *i.e.* the period during which the fast reaction is suppressed by the antioxidant, does not increase or increases slowly for $[IH] < [IH]_{cr}$ and rapidly for $[IH] > [IH]_{cr}$, which is manifested as a break in the curve for the dependence of the induction period on the initial antioxidant concentration for $[IH]_0 = [IH]_{cr}$.[16, 18]

The antioxidant molecules are divided into those bound into the complexes Z_iIH with the sorption centres and the mobile molecules IH. Mainly the mobile molecules IH participate in the chain termination in the solution in the polymer with participation of the macroradicals $M^{\bullet}$ and $MO_2^{\bullet}$, the translational mobility of which is close to zero. The concentration of mobile molecules is related to the overall IH concentration in the polymer by the expression

$$[IH] = \frac{[IH]_p}{K_{IH}[Z_{IH}]} \qquad (18)$$

where $[Z_{IH}]$ is the concentration of the IH-sorbing centres and K_{IH} is the sorption equilibrium constant; the equation is valid only at low antioxidant concentrations $[IH] \ll [Z_{IH}]$, such as the critical concentrations. Thus the difference between the experimental critical concentrations of the same antioxidant in different samples of a polymer of the same chemical nature is determined by the difference between the concentrations and properties of the sorption centres, *i.e.* the difference in the character of the disorder in the arrangement of the polymer chains. The method of critical concentrations can be used in those cases where the method for the investigation of the sorption isotherm is for one or another reason inapplicable, in particular in the study of polymer melts.

IV. Sorption of low-molecular substances by the polymer

We shall examine the equilibrium sorption of a low-molecular substance — phenyl benzoate (A) — by polyethylene as the simplest example. The curves for the dependence of the concentration of this substance in polyethylene $[A]_p$ on its concentration in the gas phase $[A]_m$ surrounding the polymer are transformed into straight lines when $1/[A]_p$ is plotted against $1/[A]_m$ (Fig. 3)[19] and all the straight lines corresponding to temperatures ranging from 80 to 180 °C, *i.e.* from the solid polymer to its melt, intersect the ordinate axis at the same point corresponding to $[Z_A] = 0.55$ mol kg^{-1}. The experimentally observed linear relations of the type

$$\frac{1}{[A]_p} = \frac{1}{[Z_A]} + \frac{K_A \gamma_A [Z_A]}{[A]_m} \tag{19}$$

may be transformed into relations of the 'Langmuir' type

$$[A]_p = \frac{K_A \gamma_A [Z_A][A]_m}{1 + K_A \gamma_A [A]_m} \tag{20}$$

with $[Z_A] = \text{const}$.

The temperature independence of $[Z_A]$ and the fact that it does not change even on passing through the melting region ($\sim$ 130 °C for polyethylene) agree well with the topological nature of the sorption centres: the folds, knots, and entanglements of the long polymer chains do not disappear on melting the polymer. Many other substances behave similarly to phenyl benzoate on sorption from both the gas phase and from solutions in low-molecular liquids (Fig. 4).[20] The limit of the sorption from solutions, *i.e.* the value $[Z_A]$, is as a rule lower than in sorption from the gas phase and depends on the nature of the solvent.[21] In more complex cases at simultaneous sorption of two different substances from the same solvent, one substance is displaced from solution in the polymer by the other.

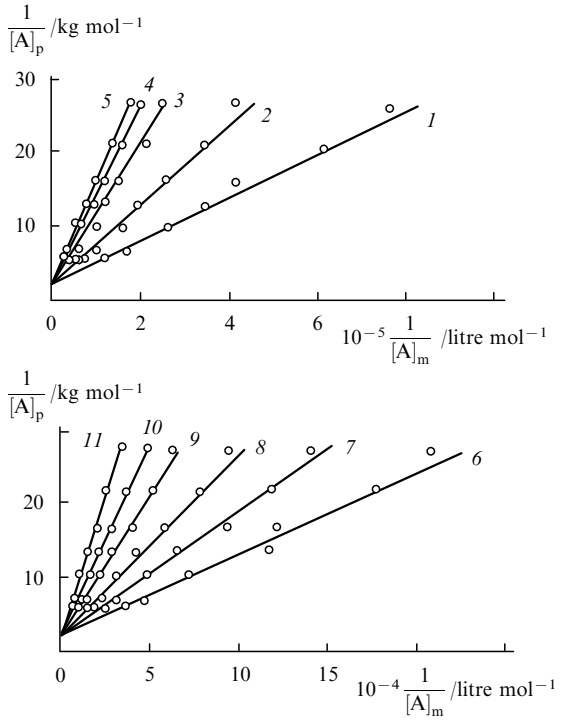


Figure 3. The sorption isotherm of phenyl benzoate by high-density polyethylene from the gas phase.[19] Temperature (°C): (*1*) 80; (*2*) 90; (*3*) 100; (*4*) 110; (*5*) 120; (*6*) 130; (*7*) 140; (*8*) 150; (*9*) 160; (*10*) 170; (*11*) 180.

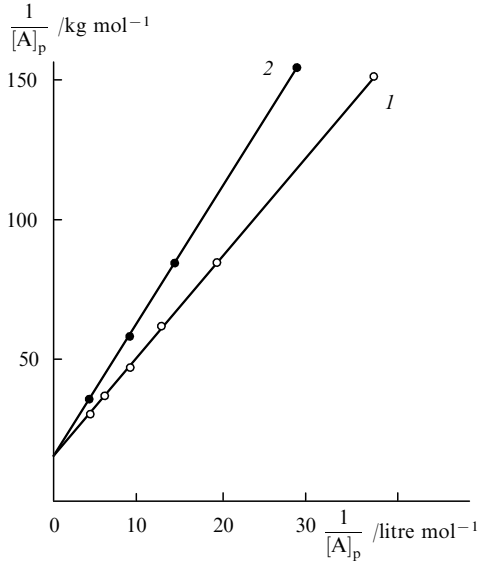


Figure 4. The sorption isotherm of phenyl benzoate (*1*) and diphenylamine (*2*) by high-density polyethylene from n-hexane at 50 °C in the coordinates $1/[A]_p - 1/[A]_m$.[20]

Suppose that two substances, A and B, are sorbed by the same centres Z_i. One may then expect that these substances will compete for the sorption centres, *i.e.* the process

$$AZ_i + B \longrightarrow A + BZ_i \tag{21}$$

will take place. As a result, the solubility of substance A in the polymer will decrease with increase in the concentration of substance B in the surrounding medium. Such a relation has been frequently observed in practice (Fig. 5).[20, 22]

However, in certain cases a more complex relation holds: maxima appear on the descending curve for the dependence of the solubility of one substance on the concentration of the other (Fig. 6).[20] These maxima can be explained by the formation of more complicated complexes ABZ_j on certain sorption centres Z_j.

$$AZ_j + B \longrightarrow ABZ_j . \tag{22}$$

The solvent can also function as the second substance, which results in a change of the nature of the sorption isotherm. This explains the dependence of the solubility of low-molecular substances on the nature of the solvent from which the given substance is sorbed, which has been observed in a number of experiments.[21]

The sorption centres may be various microcavities the formation of which is not connected directly to the disorder in the

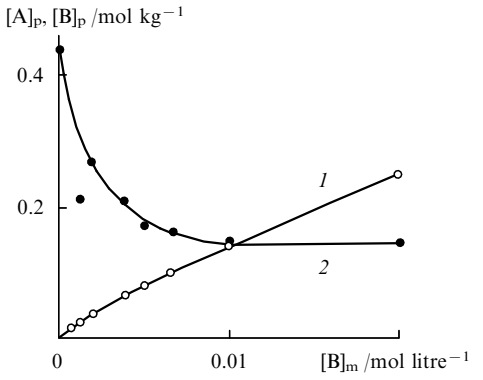


Figure 5. Dependence of the concentrations of α-naphthol (A) (*1*) and α-naphthylamine (B) (*2*) in high-density polyethylene on the α-naphthylamine concentration in hexane at 50 °C.[20]

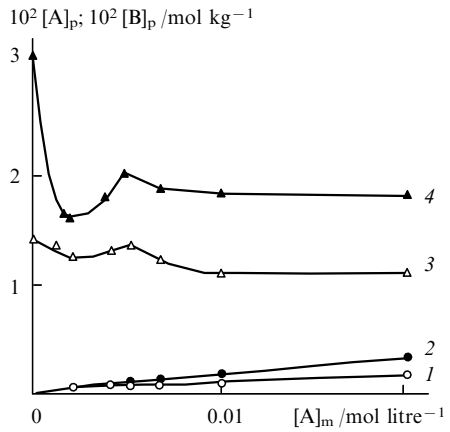


Figure 6. Dependence of the equilibrium concentrations of α-naphthol $[A]_p$ (*1*, *2*) and diphenylmethane $[B]_p$ (*3*, *4*) in high-density polyethylene (*1*, *3*) and low-density polyethylene (*2*, *4*) on the α-naphthol concentration in isopropyl alcohol at 50 °C {diphenylmethane concentration in solution $[B]_m = 0.2$ M}.[20]

arrangement of the polymer chains and which vanish when the samples are pressed under high pressure.[23]

The sorption is related directly to the diffusion of the dissolved substance. Assuming that only the mobile molecules of A outside these centres participate in the diffusion, it is possible to find the theoretical dependence of the (observed) diffusion coefficient on the overall concentration of substance A in the polymer. According to Fick's first law, the flow of molecules of A through a unit cross-section of the polymer sample, perpendicular to the x axis, is

$$\Phi = -D_r \frac{d[A]}{dx} = -D_r \frac{d[A]}{d[A]_p}\frac{d[A]_p}{dx} = -D_{eff}\frac{d[A]_p}{dx}, \qquad (23)$$

where D_r and D_{eff} are the true and observed diffusion coefficients.

The observed diffusion coefficient of substance A in the polymer is given by $D_{eff} = D_r\{d[A]/d[A]_p\}$. For low values of $[A]_p$ $\{[A]_p < [Z_A]\}$, we have $[A] = [A]_p/K_A\{[Z_A] - [A]_p\}$. On differentiating this value with respect to $[A]_p$, we obtain [24]

$$D_{eff} = \frac{D_r[Z_A]}{K_A([Z_A] - [A]_p)^2}. \qquad (24)$$

A similar formula has been derived by Fujita.[25] In a study [26] of the diffusion of 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol), labelled with ^{14}C, into polyethylene containing the same but not radioactive substance at different concentrations, not only was Eqn (24) confirmed but a value of $[Z_A]$ virtually identical with the solubility (0.034 mol kg^{-1} at 80 °C) was calculated.

It was later shown with the aid of the NMR method [27] that the molecules of ammonia dissolved in polystyrene can be divided into highly and weakly mobile, their mobilities differing by a factor of 20.

V. Formation of sorption centres in the sedimentation of polymers from solution

We shall consider the case where the polymer is formed in sedimentation from solution in a low-molecular liquid.[28] Evidently, the sedimentation must be preceded by the sticking together of sections of the polymer chains and the elements of future disturbed-order knots ζ_i^* are then laid down in the polymer.

Suppose that the element ζ_i^* contains a certain volume of the solvent v_i^*. Assuming that the energy of formation of this volume is proportional to the latter and to the difference between the energies of the interaction of the monomer unit of the polymer with another such unit and with the solvent $(q_p - q_s)$, *i.e.* $\varepsilon_i = v_i^*(q_p - q_s)$, we find that the probability of the formation of the volume element $v_i^* \geqslant v_A^*$ is

$$p_A = C\exp\left(\frac{-\varepsilon_A}{kT}\right) = C\exp\left[\frac{-v_A^*(q_p - q_s)}{kT}\right]. \qquad (25)$$

On sedimentation of the polymer, the structures ζ_i^* are deformed. It is natural to postulate that the greater the volume v_i^* of the element ζ_i^* present in the solution the greater the volume v_i^* of the element ζ_i^* produced from it in the polymeric substance formed. After introducing the proportionality coefficient β, we find an expression for the concentration of the centres $[Z_A]$ in the deposited polymer:

$$[Z_A] = [Z]_0\exp\left[\frac{-v_A^*\beta(q_p - q_s)}{kT}\right]. \qquad (26)$$

The value $[Z_A]$ in Eqn (26) is equal to the concentration of the UOD around which the elements of the free volume may be formed. If it is assumed that such centres are produced around the point of contact between two sections of the same or different polymer chains, then the concentration of these elements is higher, the higher the concentration of the polymer in solution at the instant of sedimentation.

Eqn (26) describes the law of the distribution of the sorption centres with respect to the volume of the molecules sorbed by them. In the sorption of organic substances consisting of C, H, O, and N atoms, the densities of which in the pure state differ little ($\rho_A = 1.1 \pm 0.1$ g cm^{-3}), one can assume that $v_A = M_A(\rho_A N_A)^{-1}$, where $N_A = 6.02 \times 10^{23}$ is the Avogadro number. In this case, Eqn (26) transforms into

$$[Z_A] = [Z]_0\exp(-\varkappa M), \qquad (27)$$

where

$$\varkappa = \frac{\beta(q_p - q_s)}{\rho N_A k T_s}. \qquad (28)$$

Here T_s denotes the temperature of the formation of the centre, *i.e.* the temperature of the sedimentation of the polymer from solution.

As can be seen from Fig. 7,[28,29] Eqn (28) agrees well with experimental data and the value $q_p - q_s$ found from the slope of the straight line proved to be 51 J cm^{-3}. For comparison, we may note that the heat of melting of polyethylene crystals is 293 J g^{-1}.

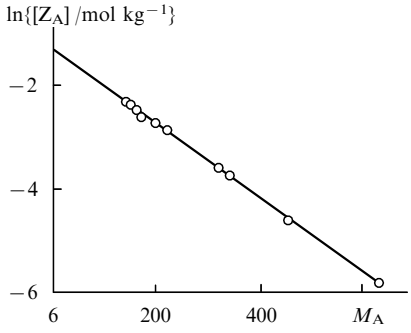


Figure 7. Dependence of the logarithm of the concentration of the sorption centres for low-molecular substances $\ln[Z_A]$ in high-density polyethylene on the molecular mass of the sorbed substance (M_A) at 50 °C (solvent — n-hexane).[29]

VI. Rearrangement of the sorption centres under the influence of the dissolved substance

As shown above (Fig. 3), the Langmuir sorption limit, *i.e.* the value $[Z_A]$, in most cases remains constant over a wide range of temperatures (from the temperature of the existence of the solid polymer to the melting point). However, when an additive is

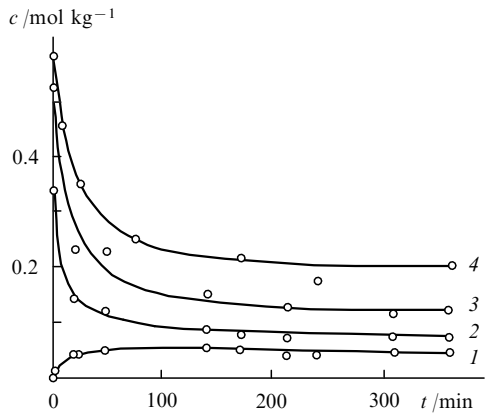


Figure 8. Variation of the concentration of phenyl benzoate in isotactic polypropylene in the saturated vapour of this compound at 40 °C. Initial phenyl benzoate concentration in the melt (240 °C) (mol kg^{-1}) (*1*) 0; (*2*) 0.34; (*3*) 0.53; (*4*) 0.58.[33]

introduced directly into the melt, the sorption law may be infringed.[30–33] The sorption limit may then increase significantly.

Figure 8 illustrates the variation of the concentration of phenyl benzoate, introduced into a melt of isotactic polypropylene at different initial concentrations, when cooled polymer samples are kept in sealed tubes containing an excess of phenyl benzoate. In the course of such experiments, a large proportion of the dissolved substance escapes from the polymer, but its residual concentration exceeds appreciably the solubility in the untreated polymer. If a low-molecular substance A is introduced into the polymer melt at a concentration exceeding the solubility $\{[A]_p > [Z_A]\}$ and the substance is then extracted from the melt with alcohol at a low temperature (40 °C), then its solubility in the treated polymer is found to be appreciably higher than in the untreated polymer.[30] When such samples are heated to 80–100 °C, the solubility gradually falls to the initial value. These processes may be represented schematically as follows:

$$\zeta_k + A \longrightarrow AZ_k,$$

where ζ_k are the elements of disorder, which do not give rise to sorption centres under normal conditions, while Z_k are sorption centres formed around these elements at high concentrations of substance A.

The rearrangement of the elements ζ_k to sorption centres is accompanied by an increase in the free volume contained in them, which requires the consumption of the energy $\Delta\varepsilon_k = (q_p - q_A)\Delta v_k$ where q_A is the energy of the interaction of the element of the polymer chain with the additive A referred to unit volume. The dimensions of the values q_p, q_s, and q_A (energy/volume) are identical with the dimension of pressure and in terms of its physical significance q is equal to the osmotic pressure of substance A in the polymer required for the rearrangement of the centres (*i.e.* for the 'fracture' of the polymer structure):

$$RT[A] \approx \frac{RT[A_p]}{[Z_A]K_A},$$

where [A] is the concentration of mobile molecules, while $[A]_p$ is the overall concentration of substance A in the polymer. Since the parameters of the initial elements ζ_k do not enter into the expression for $\Delta\varepsilon_k$, this pressure must be identical for all the elements and the rearrangement of all the centres must begin at the same concentration of the given additive. As can be seen from Fig. 9, the solubilities (L) of phenyl-β-naphthylamine and phenyl benzoate in polypropylene begin to increase at the following concentrations of these additives in the melt; ~0.15 and 0.25 mol kg^{-1} respectively.

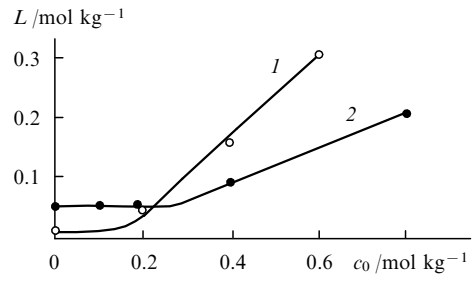


Figure 9. The solubilities (L) of phenyl-β-naphthylamine (*1*) and phenyl benzoate (*2*) in isotactic polypropylene at 40 °C as a function of the initial concentration of the same substance in the melt (240 °C).[34]

VII. The possibility of varying the degree of disorder on reprecipitation of the polymer

According to Eqns (26) and (27),[28] the level of topological disorder, *i.e.* the overall concentration of the elements ζ_i and their size distribution, depend on the conditions governing the formation of the polymeric substance during its sedimentation from solution — on the nature of the solvent, the concentration, and temperature, *i.e.* on the value q_A. All these methods for the variation of the level of disorder have been used in our studies.

It is natural to postulate that the smallest values of q_A will be observed on precipitation of nonpolar polyalkenes from their low-molecular analogues — saturated hydrocarbons, and the highest will be observed on sedimentation from polar aromatic compounds. Indeed, the samples obtained by the reprecipitation of isotactic polypropylene from solutions in n-decane and chlorobenzene (5 g per 150 ml) differed appreciably in their properties. The crystallinities of polypropylene reprecipitated from n-decane and chlorobenzene, determined by differential scanning calorimetry, were 61.2% and 69.2%, and their densities were 0.9115 and 0.9179 g cm^{-3} respectively. The equilibrium solubilities of antioxidants in the samples of isotactic polypropylene precipitated from solutions in n-decane and chlorobenzene at 60 °C were 0.02 and 0.01 mol kg^{-1} for phenyl-β-naphthylamine and 0.17 and 0.13 mol kg^{-1} for phenyl benzoate which has the lower molecular weight. The sorption isotherms of phenyl-β-naphthylamine from alcohol by these samples (Fig. 10) differed even more [34] while the values of $[Z]_A$ calculated from them differed by a factor of 7.7 (0.30 and 0.039 mol kg^{-1}). It must be emphasised that the powders obtained on reprecipitation of polypropylene were pressed into films at temperatures in the range 200–220 °C, *i.e.* above the melting points of both samples (158.5 and 160.1 °C respectively).

The inhibited oxidation of the polymer samples was investigated at 180 °C, *i.e.* above the melting point. The experiments showed that the critical concentrations of the antioxidant (phenyl-

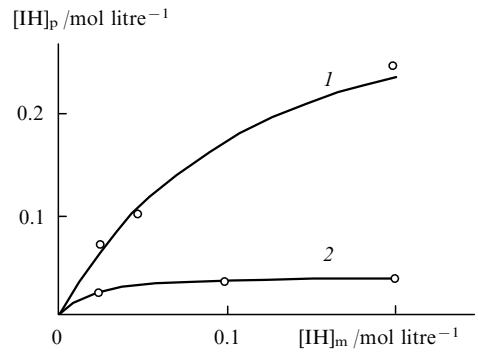


Figure 10. The sorption isotherms of phenyl-β-naphthylamine by samples of polypropylene reprecipitated from n-decane (*1*) and chlorobenzene (*2*) (solvent — alcohol, temperature — 40 °C).[34]

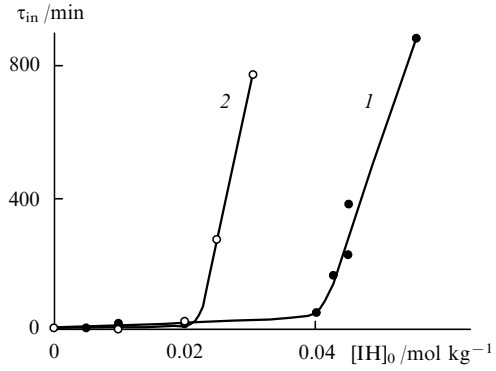


Figure 11. Dependence of the induction period in the oxidation of polypropylene samples on the initial concentration of phenyl-β-naphthylamine (180 °C, oxygen, 300 mmHg): (*1*) polymer reprecipitated from n-decane; (*2*) polymer reprecipitated from chlorobenzene.[30]

β-naphthylamine) in these samples differed by a factor of 1.9 (Fig. 11), the higher value corresponding to samples reprecipitated from n-decane.[34] Thus the difference between the concentrations of the sorption centres arising on reprecipitation of the polymer is preserved also in the melt.

Eqn (28) contains the temperature of the polymer sedimentation T_s. In the study of Kolesnikova and Shlyapnikov,[35] a solution of polypropylene in *m*-xylene at a temperature of 130 °C was either mixed with cold alcohol (rapid cooling) or was slowly cooled to room temperature. In the former case, the centres existing at 130 °C (isothermal conditions) were rapidly frozen, while in the latter the sedimentation occurred under nonisothermal conditions (~ 80 °C). The polypropylene samples obtained differed both in the sorption isotherms of phenyl-β-naphthylamine from ethyl alcohol and in the critical concentrations of the phenyl-β-naphthylamine used as the antioxidant in the oxidation of their melts; the latter are 0.055 mol kg^{-1} (in the samples prepared by rapid cooling) and 0.040 mol kg^{-1} (in the samples prepared by the slow cooling of the solution).

In the study of Mar'in *et al.*,[36] samples of isotactic polypropylene were subjected to a treatment involving repeated 'melting–crystallisation' cycles in accordance with the following scheme: heating to 250 °C, maintenance at this temperature for 90 min, cooling to 150 °C for 120 min, maintenance at this temperature for 120 min, and then cooling to room temperature. It was postulated that, by displacing segments of the macromolecules, the growing crystal facets can 'disentangle' some of their knots. The solubilities of diphenylamine, phenyl benzoate, and phenyl-β-naphthylamine but not the sorption isotherms were used as a measure of disorder. It can be seen from Table 1 [36] that, as a result of seven cycles, the solubility of diphenylamine (molecular mass $M = 169$) decreased 3.7 fold, that of phenyl benzoate ($M = 199$) fell by a factor of 1.6, while that of phenyl-β-naphthylamine ($M = 219$) decreased by only 15%. Thus the larger the molecule, the greater the volume of its sorption centre and hence the more complex the UOD constituting its basis and the greater its resistance to disentanglement.

Table 1. Variation of the solubilities of low-molecular probe substances as a function of the number of melting–crystallisation cycles of isotactic polypropylene (according to the data of Shlyapnikov and coworkers [19, 36]).

Substance	Molecular mass	Number of cycles			
		1	3	5	7
Diphenylamine	169	0.234	0.208	0.068	0.063
Phenyl benzoate	199	0.162	0.142	0.130	0.102
Phenyl-β-naphthylamine	219	0.0148	0.0138	0.0135	0.0128

VIII. The anomalies in certain equilibria

It follows from Eqn (27) that the value of $[Z]_0$ depends on the concentration of the polymer solution from which the sample has been prepared by precipitation.

The formation of a complex between tetracyanoethylene (TCE) and hexamethylbenzene (HMB) in polyethylene and polypropylene has been investigated.[37]

$$\mathrm{TCE} + \mathrm{HMB} \underset{}{\overset{K_C}{\rightleftharpoons}} \mathrm{TCE \cdot HMB}. \qquad (29)$$

In our study of complex formation in the polymer, we were forced to compare the overall concentrations of the individual substances and complexes, *i.e.* to assume that $[TCE]_p \approx [TCE \cdot Z_{TCE}]$, *etc.*, whereas in fact a series of equilibria of type (21) occur in the polymer. According to Eqn (26), the concentrations of sorption centres decrease rapidly with increase in the molecular mass of the sorbed substance. Since the concentration of the complex under the comparatively mild conditions used in the study of the reaction (20–60 °C) cannot be higher than the concentration of the centres sorbing these complexes, a dependence of the concentration of the complexes, and of the complex formation constant K_c calculated from it, on the concentration of the solution of polyethylene in n-decane at the instant of its sedimentation was observed in the experiments (Fig. 12).

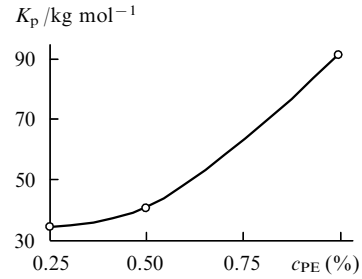


Figure 12. Dependence of the apparent equilibrium constant (measured at 22 °C) for the formation of a complex between hexamethylbenzene and tetracyanoethene in polyethylene on the concentration of polyethylene at the instant of its sedimentation in n-decane at 120 °C.[38]

IX. Characteristic features of the kinetics of chemical reactions in polymers

Three types of relatively simple nonchain reactions occurring in polymers have been studied in detail.

$$\mathrm{A} \longrightarrow \text{products}, \qquad (30)$$

$$\mathrm{A} + \mathrm{B} \longrightarrow \text{products}, \qquad (31)$$

$$2\mathrm{A} + \text{polymer} \longrightarrow \text{products}. \qquad (32)$$

Deviations from the regular features of the analogous reactions in the liquid phase were discovered.

A reaction of the first type may take place *via* two mechanisms: within and outside the centres Z_A and the centres can in their turn differ in their sorption energy. In order to simplify the calculations, we shall assume that all the centres are identical and that the reaction can proceed either within the centres or outside them. Denoting the rate constant for the reaction within the centres by k_{AZ} and that outside the centres by k_A, we find the expression for the overall rate of reaction;

$$-\frac{\mathrm{d}[\mathrm{A}]_p}{\mathrm{d}t} = k_A[\mathrm{A}] + k_{AZ}([\mathrm{A}]_p - [\mathrm{A}]). \qquad (33)$$

Since a large proportion of the dissolved substance is usually contained within the sorption centres, *i.e.* $[A] \ll [A]_p$, appreciable deviations of the reactions from first order are observed only in the case where $k_A \gg k_{AZ}$. If compound A decomposes *via* the intermediate reversible formation of a radical pair,

$$A \rightleftharpoons 2X^{\bullet} \longrightarrow \cdots \longrightarrow \text{products},$$

then the volume required for the formation of the pair will be always greater than the volume of the initial molecule and the formation of a 'cage', coinciding with the sorption centre, will require an additional energy. For this reason, the rate of reaction within the centre should be appreciably lower than outside it. In the centres the shape of which corresponds most closely to that of the molecules contained in them, any reactions proceeding with a change in the shape of the reacting molecule will be hindered.

On the basis of general considerations, one may expect that the condition $k_A \gg k_{AZ}$ is obeyed and that the apparent rate constant (the ratio of the rate to the product of the concentrations of the reactants) increases with increase in the initial concentration of the reactant. Indeed, such a relation has been observed in the thermal decomposition of benzoyl peroxide $C_6H_5C(O)-O-O-C(O)C_6H_5$ in isotactic polypropylene (Fig. 13).[38] The reaction was catalysed by adding phenyl benzoate, which could substitute the peroxide molecules in the sorption centres. Similarly, the rate of isomerisation of dimethylbenzylsilyl peroxide in the same polymer increased with increase in its concentration.[39] It has been shown[40] that the total yield of the free radicals formed on decomposition of azobisisobutyronitrile in isotactic polypropylene at 80 °C increases nonlinearly with increase in the concentration of this substance: from 0.12 (at an initial concentration of 0.075 mol kg^{-1}) to 0.40 (at a concentration of 0.025 mol kg^{-1}).

Reactions of the second type have been investigated in detail in the interaction of benzoyl peroxide and diphenylethyl hydroperoxide with dibenzyl sulfide[41–43] and of benzoyl peroxide with

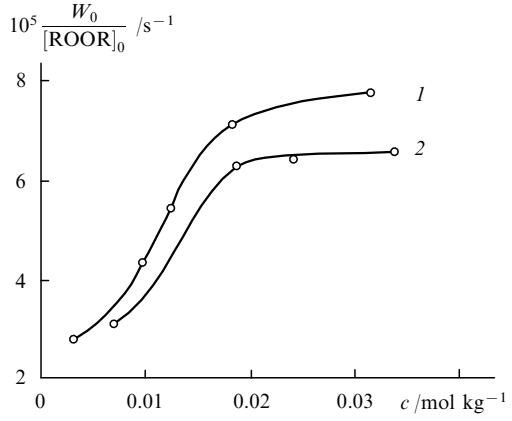


Figure 13. Dependence of the effective rate constant of the thermal decomposition of benzoyl peroxide (80 °C) in isotactic polypropylene on the initial peroxide concentration: (*1*) usual polymer; (*2*) polymer with an increased concentration of sorption centres.[38]

diphenylamine.[44] These reactions can proceed *via* several paths:

$$A + B \longrightarrow \text{products}, \quad (34)$$

$$A + BZ_B \longrightarrow \text{products}, \quad (35)$$

$$AZ_A + B \longrightarrow \text{products}, \quad (36)$$

$$ABZ_{AB} \longrightarrow \text{products}. \quad (37)$$

If the concentrations of the free molecules of A and B are low compared with those of the bound molecules, the first path appears improbable and we shall therefore consider only the three remaining ones.

It was shown above that, despite the diversity of the sorption centres, the sorption isotherms of the individual substances are described satisfactorily by Langmuir isotherms in which K_A and K_B are average values and $[Z_A]$ and $[Z_B]$ are the total concentrations of the centres sorbing the given substance.

On solving the equation $[AZ_A] = K_A[Z_A][A]\{1 + K_A[A]\}^{-1}$ for [A] and substituting $[AZ_A] + [A] = [A]_p$, we obtain a fairly cumbersome expression:[44]

$$[A] = \frac{K_A[A]_p - K_A[Z_A] - 1}{2K_A} + \frac{\sqrt{(1 + K_A[Z_A] - K_A[A]_p)^2 + 4K_A[A]_p}}{2K_A}. \quad (38)$$

The dependence of $[A]/[A]_p$ (the fraction of mobile molecules) on $[A]_p/[Z_A]$ calculated by this formula is presented in Fig. 14 for different values of K_A. As can be seen from the figure, the fraction of mobile molecules increases with increase in the overall concentration of the reactant $[A]_p$, the increase being especially rapid starting from $[A]_p/[Z_A] = 1$.

The concentration of the complexes ABZ_{AB} varies with increase in the concentrations of the reactants in accordance with the equation[41,42]

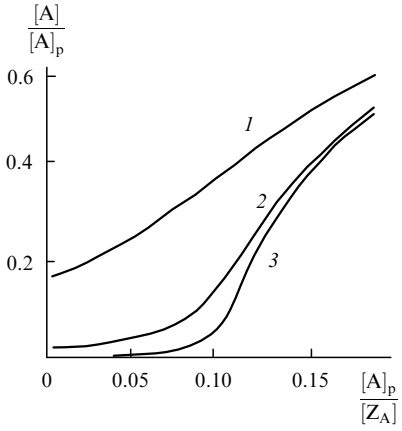


Figure 14. Dependence of the fraction of mobile molecules {of the ratio $[A]/[A]_p$} on the overall concentration of substance A in the polymer {in units of $[A]_p/[Z_A]$} [calculation by Eqn (38)].[41,43]

$$[ABZ_{AB}] = \frac{K_{AB}[Z_{AB}][A][B]}{1 + K_{AB}[A][B]}. \quad (39)$$

At low concentrations of A and B $\{[A]_p \ll [Z_A]; [B]_p \gg [Z_B]\}$, one may put $[A] = [A]_p/K_A[Z_A]$ and $[B] = [B]_p/K_B[Z_B]$. In this case, Eqn (39) transforms into

$$[ABZ_{AB}] = \frac{K_{AB}[Z_{AB}][A]_p[B]_p}{K_AK_B[Z_A][Z_B] + K_{AB}[A]_p[B]_p}. \quad (40)$$

The rate of reaction (37) is $W_{AB} = k_{AB}[ABZ_{AB}]$, whence the apparent rate constant at low concentrations is

$$k_{AB} = \frac{W_{AB}}{[A]_p[B]_p} = \frac{k_{ZAB}K_{AB}[Z_{AB}]}{K_AK_B[Z_A][Z_B] + K_{AB}[A]_p[B]_p}. \quad (41)$$

According to this equation, the constant k_{AB} decreases with increase in both $[A]_p$ and $[B]_p$.

It is known that the second-order reactions require rapid mixing of the reactants in solution in polymers and they were

therefore investigated in amorphous polymers — atactic polypropylene and polyisobutylene — samples of which, each containing one of the two reactants, were mixed by repeated pressing. The experiments showed that the apparent rate constant for the reaction of benzoyl peroxide with dibenzyl sulfide varies with the concentration of each reactant and passes through a minimum (Fig. 15). This relation can be regarded as the sum of the curves described by Eqns (38) and (41).[42,43] In polyisobutylene, in which the solubilities of the reactants {and apparently the values of $[Z_A]$ and $[Z_B]$} were 1.6 times lower than in polypropylene (the solubilities of benzoyl peroxide in these polymers at 50 °C were $S_A = 0.15$ and 0.23, whilst those of dibenzyl sulfide were $S_B = 0.32$ and 0.54 mol kg^{-1} respectively), the minimum rate constant was observed at lower concentrations of the reactants.

The existence of two reaction paths [reactions (35), (36), and (37)] has also been confirmed by qualitative experiments: the 'inert' phenyl benzoate, which does not participate in the reaction, substitutes a molecule of benzoyl peroxide in the sorption centres

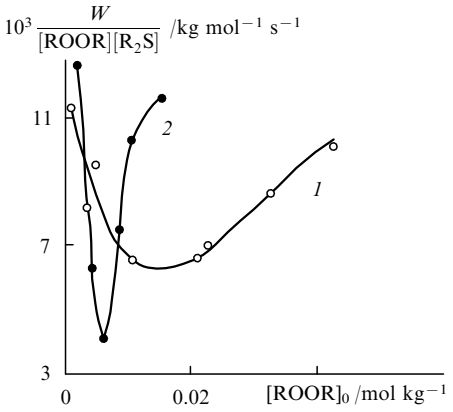


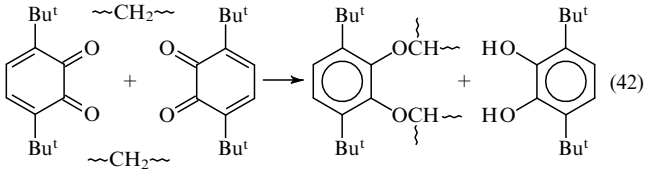
Figure 15. Dependence of the effective rate constant of the reaction of benzoyl peroxide with dibenzyl sulfide in atactic polypropylene (*1*) and polyisobutylene (*2*) on the initial peroxide concentration $[ROOR]_0$ (temperature is 50 °C).[43]

of both types — $[Z_A]$ and $[Z_{AB}]$ — and lowers the rate of reaction in the region of low concentrations, when the mechanism of the pseudounimolecular conversion of the complexes ABZ_{AB} [reaction (37)] predominates, and accelerates the reaction at high concentrations, displacing the peroxide (and possibly also the sulfide) from complexes of the type AZ_A and BZ_B and increasing thereby the concentrations of the mobile molecules participating in reactions (35) and (36).

It is of interest that the rate of interaction of benzoyl peroxide with dibenzyl sulfide in polypropylene may be higher than the rate of the same reaction in its low-molecular analogue — isooctane, where the rate constant is independent of the initial concentration and is $(13.2 \pm 0.3) \times 10^{-3}$ litre mol^{-1} s^{-1} under the same conditions (50 °C).

The slight increase of the rate constant for the bimolecular interaction of a phenolic antioxidant — 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) — with stearic acid as its concentration in polypropylene increases has been noted.[45]

As an example of reactions of the type 2A + polymer the interaction of substituted *o*-benzoquinones with polyethylene and polypropylene have been studied.[46,47]



According to the Scheme (42), the reaction is accompanied by cross-linking of the polymer, the yield of substituted catechol amounting to 50% – 60%. Assuming that a reaction of this kind may proceed only in large centres, each accommodating two reactant molecules, and replacing all B by A in Eqn (41), we obtain

$$W = \frac{k_{ZAA} K_{AA} [Z_{AA}] [A]_A^2}{K_A^2 [Z_A]^2 + K_{AB} [A_p]^2} . \qquad (43)$$

According to Eqn (43), the rate of reaction tends rapidly to the limit $k_{ZAA}[Z_{AA}]$ *i.e.* becomes independent of the concentration of the quinone. On the other hand, as the concentration of the quinone increases, the initial rate of reaction tends to a limit in accordance with Eqn (43) (Fig. 16).[46]

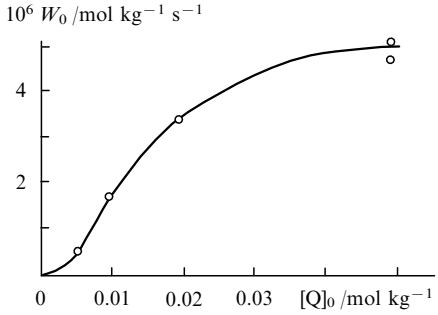


Figure 16. Dependence of the initial rate of reaction between 3,6-di-*tert*-butyl-1,2-benzoquinone (Q) and atactic polypropylene on the initial quinone concentration in the polymer (temperature is 180 °C).[46]

In isotactic polypropylene, the initial rate of reaction is directly proportional to the initial quinone concentration, but a zero reaction order with respect to the quinone is observed in the course of the reaction over a long period of the latter.[47] Apparently the reaction in this 'rigid' polymer proceeds mainly in the centres formed as a result of the rearrangement of the polymer structure, similarly to the rearrangement described above (see Section V).[30–32] Apparently the reactions in polyethylene and ethylene – propylene copolymers proceed in accordance with the same law.[48]

X. Displacement catalysis and nonchemical synergism

It has been shown[38] that the rate of thermal decomposition of benzoyl peroxide in isotactic polypropylene increases when phenyl benzoate, 'inert' in relation to this reaction in low-molecular media, is introduced into the polymer. Similarly, the rate of isomerisation of dimethylbenzylsilyl peroxide increases in the presence of the isomerisation product.[39] This phenomenon, associated with the displacement of the reactant molecules from centres more 'convenient' for them, the filling of which prevents a change in the shape or size of the reactant molecules necessary for the occurrence of the reaction, has been called[38] 'displacement catalysis'.

The main reaction on which the inhibition of oxidation is based — chain termination processes by the antioxidant (IH) — proceeds in accordance with the scheme

$$RO_2^{\bullet} + IH \longrightarrow ROOH + I^{\bullet}.$$

In polymers, the radicals (more correctly the macroradicals) $RO_2^{\bullet}$ cannot move freely and, for the occurrence of reaction (12), it is essential that the molecules of IH should possess translational mobility. Evidently the complexes between the antioxidant and the sorption centres $IH \cdot Z_{IH}$ are also immobile and the chain termination reaction must be preceded by the liberation of the IH molecule from the sorption centre.

Conversely, mobile oxygen molecules participate in the main side reaction — direct oxidation of IH — which leads to accelerated consumption of the antioxidant. Evidently the rate of oxidation of IH molecules in the centres 'convenient' for IH, *i.e.*

$$Z_{IH} \cdot IH + O_2 \longrightarrow Z_{IH} \cdot I^{\bullet} + HO_2^{\bullet}, \quad (44)$$

is lower than the rate of oxidation of the same molecules outside the sorption centres, *i.e.*

$$IH + O_2 \longrightarrow I^{\bullet} + HO_2^{\bullet}, \quad (45)$$

but in all cases the fraction of mobile molecules is small. Subsequently the $I^{\bullet}$ and $HO_2^{\bullet}$ radicals participate in a wide variety of reactions, most of which reduce the effectiveness of the inhibition of the process, for example $HO_2^{\bullet} + IH \rightarrow H_2O_2 + I^{\bullet}$. By increasing the fraction of mobile molecules, it is possible to increase selectively the rate of chain termination, altering slightly the rate of the undesirable stages of the process.

According to Eqn (21), substance B, which is relatively resistant to oxidation and reactions with peroxy-radicals but is capable of displacing IH from the centres Z_{AH}, may increase the fraction of mobile IH molecules at the same or even smaller overall concentration of the antioxidant. Assuming for simplicity that all the molecules of B are present in the polymer as complexes with Z_{AH} we find

$$[IH] = \frac{[IH]_{hp}}{K_{AH}\{[Z_{AH}] - [B]_p\}}. \quad (46)$$

The apparent chain termination rate constant is related to the true constant k_r for the $IH + RO_2^{\bullet}$ reaction by the expression

$$k_t = \frac{k_r}{K_{AH}\{[Z_{AH}] - [B_p]\}}. \quad (47)$$

Experiments have shown that comparatively 'inert' substances such as phenyl benzoate, octamethylcyclotetrasiloxane, and heptadecane (a low-molecular hydrocarbon) increase appreciably the effectiveness of phenolic antioxidants, distinct maxima appearing on the composition–induction period (*i.e.* the period of the effective retardation of the oxidation reaction) curve obtained at a constant overall concentration of the additives (Fig. 17). In contrast to the similar effect induced by chemically reactive additives, we called this phenomenon 'nonchemical synergism'.[49–51] At high concentrations, the 'inert' additive disrupts the structure of the polymer and, in contrast to the usual 'chemical' synergism, the effect involving an increase in effectiveness vanishes.[52]

It is seen from Fig. 18 [52] that, when an 'inert' additive such as octamethylcyclotetrasiloxane (at a variable concentration) is introduced into polypropylene containing phenyl-β-naphthylamine (PNA) as the antioxidant (at a constant concentration), the concentration of substance A in the gas phase initially increases owing to its displacement [Eqn (21)] and then decreases as a result of the rearrangement of the sorption centres {the increase in $[Z_k]$} and then again increases owing to the displacement of A but this time from the new centres. This phenomenon is satisfactorily reproduced for various pairs of dissolved substances (see, for example Shlyapnikov *et al.*[50]).

Thus the elements of topological disorder, *i.e.* the various entanglements of monomer chains, behave in polymers as quasi-

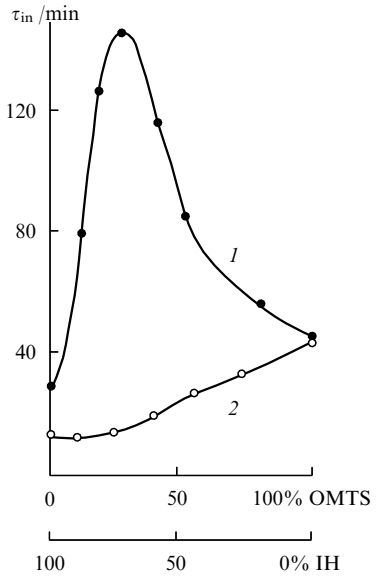


Figure 17. Dependence of the induction period in the oxidation of polyamide 12 on the composition of a mixture of 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (IH) and octamethylcyclotetrasiloxane (OMTS) at 170 °C (*1*) and 190 °C (*2*). Overall concentration of additives 0.02 mol kg^{-1} oxidant — oxygen, pressure — 300 mmHg.[51]

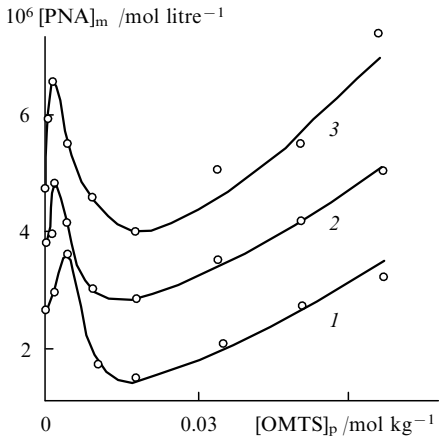


Figure 18. The concentration of phenyl-β-naphthylamine in the gas phase $\{[PNA]_m\}$ over polyethylene as a function of the concentration of octamethylcyclotetrasiloxane at different temperatures (°C): (*1*) 180; (*2*) 190; (*3*) 200 $\{[PNA]_p = 0.08$ mol $kg^{-1}\}$.[52]

molecules differing in their properties and reactivity from the polymeric substance surrounding them.

XI. The zone model of the oxidation of polymers

The presence in the sorption centres Z_i of a free volume sufficient, on the one hand, to accommodate the molecules of low-molecular substances, including oxygen, and,on the other hand, sufficient for the formation of an activated complex in the $RO_2^{\bullet} + RH$ and $R^{\bullet} + O_2$ reactions may lead to a significant difference between the reactivities of the polymeric substance present in the centres Z_i and the surrounding polymeric substance in which short-range order is maintained. It may be postulated that oxidation reactions proceed only in such centres and that a free valence is transferred from centre to centre either as a result of migration along the polymer chain [53] or as a result of the diffusion of light radicals.[54] We shall consider the consequences of this model.[3, 55]

Suppose that a single free valence, responsible for the formation of the radical $RO_2^{\bullet}$, enters a zone having a volume v_z with the concentration of monomer units $[RH]_Z$ and a sufficient con-

centration of oxygen, which converts the radicals R$^{\bullet}$ into $RO_2^{\bullet}$. The concentration of the radical $RO_2^{\bullet}$ in the zone is $[RO_2^{\bullet}]_Z = 1/\upsilon_Z$. The consumption of the reactive groups $[RH_Z]$ in the zone is described by the equation

$$-\frac{d[RH]_Z}{dt} = \frac{k_2[RH]_Z}{\upsilon_Z}, \tag{48}$$

where

$$[RH]_Z = ([RH]_Z)_0 \exp\left(\frac{-k_2 t}{\upsilon_Z}\right). \tag{49}$$

According to Eqn (49), the reactive substance is almost fully consumed during the time $\tau \approx 5\upsilon_Z/k_2$.

Next there is a possibility of two versions of the development of the process. If the residence time of the free valence in a single zone is $\vartheta \leqslant \tau$, then the free valence migrates from zone to zone faster than the substance of the zone is consumed. In this case, the rate of reaction is determined by the elementary constants k_1, k_2, *etc*. and the only difference between the kinetics of the reaction and the kinetics of the oxidation of low-molecular liquids is the incomplete consumption of the substance being oxidised: after the consumption of the substance, present in disturbed-order zones, the process is strongly retarded or comes to a complete stop. On the other hand, if $\vartheta \gg \tau$, then the free valence remains in the zone also after the consumption of the reactive substance contained in it and the rate of reaction is given by

$$W = \frac{\upsilon_Z[RH]_Z[RO_2^{\bullet}]}{\vartheta}. \tag{50}$$

The observed chain transfer rate constant $(k_2)_{eff}$ is described by the expression

$$(k_2)_{eff} = W[RO_2^{\bullet}][RH] = \frac{\upsilon_Z[RH]_Z}{[RH]\vartheta}, \tag{51}$$

i.e., subject to the assumptions made above, the experimentally observed constant $(k_2)_{eff}$ does not depend explicitly on the true elementary constants (including the chain propagation constant k_2).

The observed (effective) chain termination rate constant can be determined similarly. The rate of chain termination is equal to the frequency with which two free valences enter a single zone minus the rate of liberation of the unreacted valences from the zone, *i.e*.

$$W_t = 2\frac{(1-\chi)[RO_2^{\bullet}]^2}{[Z]\vartheta} = 2(k_t)_{eff}[RO_2^{\bullet}]^2, \tag{52}$$

where [Z] is the concentration of the zones and χ is the probability that a pair of free valences which have entered a single zone will leave it without recombination. If the value χ is sufficiently small, then the effective chain termination rate constant is given by

$$(k_t)_{eff} = \frac{2}{[Z]\vartheta}. \tag{53}$$

According to the proposed model, the local concentrations of low-molecular substances in the zones (sorption centres) may exceed by a large factor the average concentrations of these compounds in the polymer, which explains the strong influence of antioxidants [56] and oxygen [57, 58] on the yield of radicals from the 'cage' formed on decomposition of the hydroperoxy-group.

The zone model is illustrated by the scheme shown in Fig. 19.

The characteristic features of the extensive oxidation of a number of polymers may serve as confirmation of the model. Thus the rate of the high-temperature oxidation of polymers is second order with respect to the RH groups being oxidised:[58]

$$W_{O_2} = \frac{k_1 k_2 k_3[RH]^2[O_2]}{2k_{3a}k_t} = k_e[RH]^2, \tag{54}$$

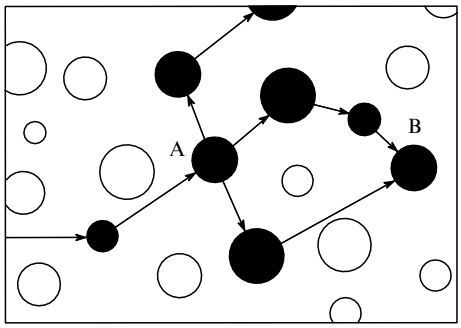


Figure 19. Schematic illustration of the propagation of the reaction in the polymer; open circles — zones of order violation before reaction; filled circles — ditto after reaction; A — chain branching site; B — chain termination site.

where k_3 is the rate constant for the decomposition of the radical $RO_2^{\bullet}$:

$$RO_2^{\bullet} \xrightarrow{k_3} \begin{cases} \xrightarrow{k_{3a}} {}^{\bullet}OH + \text{products}, \\ \xrightarrow{k_{3b}} R^{\bullet} + \text{products}. \end{cases} \tag{55}$$

Assuming that not the entire polymer but only a proportion of its monomer units $[RH^*] = \upsilon_Z[Z][RH]_Z$ participate in the oxidation reaction and that q oxygen molecules are consumed per mole of the groups RH, one can formulate the following equation:

$$-\frac{d[RH^*]}{dt} = k_e[RH^*]^2 = k_e\left([RH^*]_0 - \frac{N_{O_2}}{q}\right)^2, \tag{56}$$

the solution of which gives

$$\frac{1}{[RH^*]_0 - N_{O_2}/q} - \frac{1}{[RH^*]_0} = k_e t.$$

Calculations have shown that, for the transformation of experimental oxygen absorption curves into straight lines in terms of the variables of Eqn (56), it is necessary to assume that $[RH^*]_0 \ll [RH]_0$, *i.e*. that only a small proportion of the volume of the polymer is oxidised. Under these conditions, q was assumed to be unity, since no other real values of q permit the assumption that $[RH^*]_0 = [RH]_0$. In particular, in the oxidation of polyamide 12 (the concentration of the monomer units is 5.076 mol kg^{-1} and that of CH_2 groups is 55.8 g-equiv. kg^{-1}) the transformation of kinetic curves requires the assumption that $[RH^*]_0 =$ 0.6 mol kg^{-1} (Fig. 20).[59] As can be seen from the figure, the

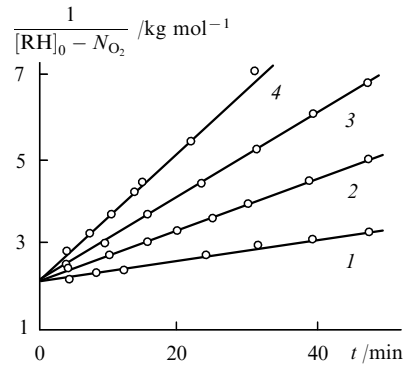


Figure 20. Variation of the concentration of the reactive part of the polymer during the oxidation of polyamide 12 (200 °C, oxygen) in coordinates for a second-order reaction (according to data of Monakhova *et al*.[59]) at differentt pressures (mmHg); (*1*) 50; (*2*) 150; (*3*) 310; (*4*) 510. In the calculations, it was assumed that $[RH^*] = 0.6$ mol kg^{-1}.

straight lines referring to different oxygen pressures intersect at a single point, *i.e.* the fraction of the substance being oxidised $[RH^*]_0$ is independent of the O_2 pressure.

XII. Conclusion

It follows from the data described that there exists a series of processes in which the elements of topological disorder present in the polymeric substance may be regarded as species which differ to some extent in their properties and reactivity from the relatively ordered substance surrounding them and that the distribution of the elements of disorder in the polymeric substance can be regarded as a negative image of its morphological (supermolecular) structure.[3] Therefore, if the disorder is not taken into account as a separate component, the properties of the polymer will not be an unambiguous function of its composition and molecular mass distribution.

We believe that purpose-directed formation of topological structures in a polymeric material would be the next natural step in the physical chemistry of polymers and in the technology of polymeric materials.

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