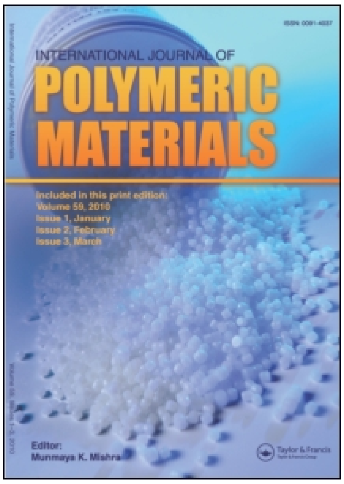

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A New Structural Model of the Amorphous Polymer for the Description of Initiated Chain Reactions

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The structural–physical bases of a kinetic description of chain reactions in amorphous polymers are presented. A model of the supermolecular "carcass-cellular" structure is formulated and discussed. The ways in which microheterogeneous elements of the polymeric body must act in the chain reaction are outlined. In the model, a special role is attached to the carcass cell which localizes within itself the molecules of admixed initiators. The carcass cell has the structure of a micelle. Its shell is composed of a mosaic of paracrystalline domains which are oriented with their planes along the micellar surface. In bulk polymer, the shell domains of adjacent micelles are coalesced to form the unified three-dimensional paracrystalline carcass. The portions of the polymer chain links, which are not included in the carcass, form the microporous spongy core within the cells.

There are peculiarities connected with the structure of the intracellular sponge, which cause certain free radical processes initiated in the cell to be separated into coupled nonidentical reaction chains which are distributed among the intracellular microphases being formed. In addition, the reactional nonsteady state must appear if structural changes occur simultaneously in the spongy core.

KEY WORDS Structure, amorphous polymers, initiation

INTRODUCTION

Amorphous polymers possess nonuniform packing of the macromolecules, which is observed as aggregates of microheterogeneous dispersity.[1–3] The simplest of them—the paracrystalline domains—include not more than ten segments packed approximately parallel to each other with a periodicity of 4–6 Å.[3] The larger aggregates (the globules or nodules) are of many tens or even hundreds of Å in size.

The idea that structural microheterogeneity has an effect on the chemical conversion of the polymer has long been accepted. Thus, it was established,[4] that the physical structure of polyacrylic and polymethacrylic acid films changed during photolysis: transparent specimens became milk-white in color due to the formation of zones which differed in their refractive indices. This phenomenon, induced by chain scission and cross-linking, was attributed to the functioning of the supermolecular structure of the original polymers.

The physical structure of amorphous polymers affects the chemical process in the direction of evident heterogeneity. The action of the structural factor in the chemical process distinguishes polymers from structureless materials and requires a knowledge of the ways in which the supermolecular zones function in the reactions.

The studies, which followed the work above[4] and which were devoted to elementary radical reaction, revealed a number of important peculiarities which distinguish polymers from homogeneous liquids: kinetic nonequivalence of the chemical acts, decrease in the rate constant, change in the activation energy and in the pre-exponential factor in the rate constant.[5-9]

These peculiarities are usually attributed to the structural heterogeneity of the medium and to the specificity of the motion of the molecular-chain units which include the reaction centers.

It was also shown that change in the physical structure of the polymer influences the rate of chemical conversion. For example, the introduction of the particles of solid fillers TiO_2, NB, $TiH_{1,6}$ (1.65 mass.%) into the melts of polypropylene (PP) and polyethylene (PE), to modify mechanical characteristics, increases the stability of the materials in the process of thermal and photochemical aging.[10] The rate of degradation of PMMA decreases during γ-irradiation as a result of the filling of the polymer with dispersed glass powder.[11]

Films of the copolymer of butylmethacrylate and methacrylic acid, prepared from solutions in good and poor solvents, being significantly different as regards the sizes of the supermolecular globules and the mechanical characteristics, have different rates of the photooxidative splitting of the ester groups, the rate being slower in specimens with small compact globules.[12]

It was shown for cellulose acetate that another method of structural rearrangement, by the orientational drawing, also decreases the rate of photochemical and photooxidative splitting of the acetylic and carboxylic groups and retards the loss of the mechanical properties of the polymer.[13]

On the contrary, oriented poly(ethylene terephtalate) has a higher rate of photooxidative degradation than the isotropic polymer.[14] Yet, at an advanced stage of polymer chain scission, the degree of chain orientation maintains its original value and at the same time the mechanical properties are retained at a higher value than in aged isotropic polymer. It can be assumed that orientating drawing does increase the resistance of the supermolecular carcass to the destructive affect.

The drawing increases the induction period in the autooxidation of PP films considerably as a result of the change in the physical structure of the oxidizable amorphous phase of the polymer. According to the authors in Reference 8, the amorphous phase of the drawn PP can be described in the form of two parts: one part possesses mainly the coiled conformers of the macromolecules and is liable for chain oxidation with the production of hydroperoxide, while the other rigid part with the strained conformers does not produce hydroperoxide and is responsible for the preservation of the mechanical properties of PP during the autooxidation.

The examples above demonstrate the existence of an interrelationship between a chemical process and the character of the structure of the noncrystalline polymer.

However, the ways in which the structural zones function has not been examined so far by applying structural-kinetic models to complex radical reactions. Theoretical considerations (such as in photochemical and thermal aging of the polymers) do not usually go beyond consideration of the homogeneous reaction model.

It should be noted that the whole range of supermolecular effects in the chemistry and physics of amorphous polymers cannot be put into the frame of the homogeneous model, nor the "fringed micelle" model.[3] The latter presents a two-phase system that is too simplified in which the paracrystalline domains form a dispersed phase, while the unordered macromolecules form a continuous medium without definite structure. At the same time the physical structure of the amorphous polymer phase, which is not associated with the domains, is of great interest in chemistry.

It is evident that the simple idea of "microheterogeneity" is not sufficient to explain the broad complex of physical and chemical properties of amorphous polymers. To achieve this, a model is required which adequately reproduces the main principles of assembly of the structural elements.

The present article considers the microheterogeneity problem from the point of view of the supermolecular "carcass-cellular" model. A paracrystalline carcass and its cell, enveloped with domains and occupied by a microporous core ball of coiled polymer chains, served as the basic component of this model.

The structural role of the paracrystalline domain

At the present time the picture of the physical structure of the amorphous polymer is not well defined.[15] In the initial stage of the search for an adequate model, the idea of the spatial superdomain carcass was proposed. A fibrilla, consisting of a folded package of segment of polymer chains, was considered as the main morphological element.[2,16] According to the model, the superdomains are formed from such fibrillas to give the spatial carcass of the macroscopic polymeric body.

Recently, the superglobular carcass model has been considered, in which the main morphological unit is formed from many globule-macromolecules.[17]

The superglobule is proposed to possess a dense nucleus with a fringe of segments of polymer chains. The process of superglobule coupling is assumed to proceed by mutual overlapping of the fringes of adjacent globules.

It should be noted that the second model does not consider the question of the structural role of the paracrystalline domains.

At the same time, it is known that the domains possess stable structures in all physical states: glassy, highly elastic and molten.[3] Instability, which is characteristic of colloidal suspension, is not realized either by disintegration of domains or by their growth of distinct crystallites.

This structural stability suggests that the domains exist not as a free colloidal suspension in the structureless medium, but as incorporated elements of the supermolecular carcass. One can assume that the incorporation of the domains into the carcass, which appears as a specific coagulational structure, is the probable cause of their structural stability.

The idea above allows us to assume that following the assemblage of macromolecules into large globules, they are enclosed by the thin sheets of domains rather than by the fringe. Such domains encapsulate the globular contents by arranging the globule surface into a mosaic capsule. In such a case the polymeric body is formed by the coupling of the globules through their superficial domains.

The globule agglomeration finally results in a delicate carcass of a paracrystalline mosaic. One part of such a mosaic may be assembled due to adhesion (by accidental mutual orientation of the domains of the adjoining globules), the other part may be assembled due to cohesion (by "cocrystallizing" of the adjoining domains or with a large number of binding polymeric chains from adjoining domains).

The carcass-cellular model differs from the fringed micelle model both in respect to the domains, which are organized in a continuous paracrystalline phase, and the disordered segments of polymer chains, which form a disperse intracellular phase. That is to say, we obtain a phasically inverted version of the fringed micelle model, whose main morphological element is a globule which is enveloped with the domain mosaic capsule.

In order to confirm the carcass-cellular model, we present the following known facts. Consider, for example, specimens of dilated polystyrene (PS) aerogel, obtained from frozen benzene solution by freeze drying in a vacuum.[18] Fixation of the spatial carcass in the course of drying is observed at an initial polymer concentration of 1%, and contraction in this case is only 50% of the initial solution volume. At a PS concentration of over 1%, the contraction significantly decreases.

The dry dilated specimens contain a large excess of free volume. This is shown by the increase in the number of micropores (cavities having sizes of 6–15 Å), capable of absorbing molecules of inert gases.

However, the excess of free volume causes neither enchancement of molecular mobility nor polymer contraction in a dry state. Contraction occurs only during heating.[19] In other words, the excessive free volume of the dilated polymer is excluded from the process of polymer softening by the paracrystalline carcass.

The "amorphous" carcass affects the alternative way of structuring, that is, the crystallization process.

It is well known that the velocity of melt cooling and the presence of foreign crystallization centers influences the completeness of the crystallization process, the dimensions and the shape of crystallites.[20] These peculiarities are probably associated with the operation of the paracrystalline domain. Being both the original nucleator of a crystallization and at the same time as an attribute of the micelle, the domain can become "cocrystallized" with the growing crystallite and with the domain of the other micelle. As a result, it is possible that by coupling with each other around the growing crystallite, the micelles isolate the crystallite with an enclosing paracrystalline lattice which interrupts the growth of the crystallite.

For this reason, fast cooling of the polymer melt completely inhibits crystallization.

Thus, for example, by pouring of melted sulfur into cool water one can obtain its plastic modification. By fast quenching the PP melt, specimens are obtained with globules of 200–500 Å size only,[20] and only upon heating are a broad range of crystalline spherulitic forms created in them.

It is known that crystallization can be controlled by introducing heterogeneity into the polymer melt.[20,21]

This phenomenon can probably be attributed to the fact that the boundary surface forces fix the paracrystalline domains thus increasing the area covered by arranged segments of polymer chains. In the polymer melt, the coupling strength of micelles is considerably decreased, and in such conditions the expanded domain planes assume the role of crystallization nuclei.

Many polymer characteristics can be associated with the coupling properties of domains in the paracrystalline lattice. It is known, for example, that the solubility of hydrogen in PE monocrystals is very high, i.e., 10 times higher, than in ordinary partially crystalline PE. The latter dissolves hydrogen predominantly in its noncrystalline part, while assessibility of the crystals is considerably limited.[7] Probably, the paracrystalline lattice of ordinary PE rather efficiently isolates the crystals, and the chain segments in the domains are packed as perfectly as in the paraffin crystals $C_{10}H_{12}$ which practically do not dissolve hydrogen.

All this is confirmed by demonstrating the readily orientable paracrystalline zone in the amorphous part of PE by using X-ray scattering analysis.[22]

Envelopes of the domains, i.e., the mosaic capsules of the carcass cell-micelles, can be directly related to production of foamed polymers. A volatile nondissolvent is usually introduced into polymer to achieve foaming.

For example, by mixing polycarbonate (PC) with 15–25 mass % of cyclohexane at 230–240°C and under a pressure of 20 kg/cm^2, a transparent glassy material can be obtained on cooling. This material can be stored for a long time at room temperature, and can be converted into small-poriferous intumesced foam by heating in an open mold to 150°C.[23]

Foamable PS can also be obtained in the form of transparent glass by occluding pentane at the polymerization stage.[24] The optical transparency of the polymer glasses containing a large amount of nonsolvent (hydrocarbon) means that the latter has not escaped into interglobular cavities to form the own microdrops. This is prevented by the closed structure of the mosaic capsule of cell-micelles, and hydrocarbon is in the state of molecular dispersity in the intra-micellar microporous sponges.

It has been established,[25,26] that the drawing of the films of poly(ethylene terephtalate), polycaproamide, poly(vinyl chloride) and polyvinyl alcohol in liquid alcohols (methanol, propanol, hexanol, decanol) results in firm occlusion of the liquid in the carcass cells. Even prolonged drying in vacuum leaves large amounts of alcohol in the polymer, as the cells are not connected to each other and with environment via sufficiently wide channels.

The carcass cells are capable of immobilizing within themselves a considerable amount of free volume. The above-dilated PS can serve as an example. The excess free volume can also be introduced into the polymer by the replacement of solvent with precipitator[27] or by splitting off molecular fragments from macromolecules. Thus, uv irradiation of poly(methyl methacrylate) (PMMA) induces breakage of the side ester groups with the formation of volatile products, readily removable from thin films.[28,29] Providing itself in this way with additional free volume, PMMA achieves the capability of absorbing cyclohexane[28] and becomes brittle instead of plastic.

The irradiated film preserves its initial optical transparency, but under the influence of cold ethanol or hot water it turns white due to aggregation of micropores into large pores which cause light scattering.

Thus, the large amount of "pure" free volume stored in the carcass cells is not efficient in softening glassy polymer. It can unite into large pores only by forced activation of the mobility of the carcass domains.

It cannot be excluded that the paracrystalline carcass and the intracellular microporous sponges determine the value of the thermal dilation coefficient which for polymeric glasses has a value close to the coefficient for crystals, and for melts is lower than for low-molecular weight liquids.[30]

Structure and properties of the microporous carcass cells

A condensed body, packed with microporous globules possessing firm capsules, inevitably includes microcavities of two types: interglobular mesopores (with sizes as for domains or globules, i.e., 30–300Å) and intraglobular micropores having sizes from 6 to 20 Å.

Both types of pores, being responsible for sorption characteristics of polymers,[31,32] differ in sorption energy and sorption mechanism.[31-34]

Micropores have a size comparable with that of monomer molecules. Absorption in micropores is accompanied by a change in chemical potential of both the absorbent and the captured particle. The absorption energy is higher than the adsorption energy on the surface of mesopores, and therefore spongy core balls of the globules create a sponge effect when specimens are formed from the melt or solution.

The effect consists of the withdrawing of the admixed material from interglobular cavities into the micelles being capsulated, and in the transition of the additive to the molecularly dispersed state.

In order for the sponge effect to take place, the admixture-containing fluid must effectively moisten the internal surface of the pore system, which is formed at the stage of cooling of the melt or drying of the gel. Otherwise the system breaks down by the escape of nonmoistening fluid into the interglobular mesopores.

Structural peculiarities of the paracrystalline carcass and microporous cells are the cause of the known discrepancy between the macroscopic and local characteristics of amorphous polymers.

For example, the thermomechanical viscosity of polymers at T_g is close to 10^{12} poise, and the microviscosity in controlling the local mobility of small molecules amounts only to about tens of poise, even in the glassy state. In particular, in PMMA glasses at 22°C the experimentally determined oxygen diffusion coefficient[35,36] of $3 \cdot 10^{-9}$ cm^2 s^{-1} corresponds to a viscosity of 40 poise, and differs considerably from the calculated macroviscometric value of 10^{-20} cm^2 s^{-1}.

This coefficient is determined for PMMA glass rods by the shift velocity of the boundary of the phosphorescent zone generated by the photoexcited additives of phenanthrene and triphenylene by observing the cross section of the rod. The activation energy of oxygen diffusion proves to be very low: 0.74 and 0.25 kcal/mol. It can be assumed, that this process is controlled by the transfer of oxygen molecules through the carcass defects into the microporous cells which accumulate the aromatic phosphors.

The fact of the intracellular accumulation of aromatic phosphors is confirmed by experiments (conducted by us together with L. N. Guseva) using naphthalene, diphenyl and α-naphtol. PMMA films, with these materials added, were prepared using two methods: (1) by phosphor absorption from the gas phase at 75°C up to contents of 1 mass %; (2) from joint solution with polymer in methylene chloride at the same phosphor contents.

Specimens (1) and (2), in an environment of inert CO_2, respond in a rather different way to the effect of uv irradiation ($300 < \lambda < 400$ nm). While film (2) shows distinct phosphorescence (green with naphthalene and α-naphtol, and blue with diphenyl) which decays in 2–3 sec, film (1) shows no phosphorescence.

There is a similar difference in the desorption velocities of these volatile compounds: heating for 1 h at 98.5°C results in an almost complete loss of naphthalene from film (1), but practically does not affect film (2).

The experiments above demonstrate the existence of carcass boundaries between microcavities of two types as well as the selectivity of filling these cavities with additives. Triplet excited aromatic molecules, localized in the mesopores of films (1) are rapidly deactivated by collisions with the surface of mesopores and by participating in chemical acts.

To the contrary, in films (2) the additives are captured by microporous cells. In this case each phosphor molecule is fixed in the micropore volume by adsorption surface forces, the frequency of its collisions with the micropore walls decreases, and the lifetime of the triplet molecule increases to such a degree that light emission becomes the main path for triplet deactivation.

Taking this into account, one can assume that the viscosity of PMMA microporous zones is even less than the experimental value of 40 poise.[35,36] It is of interest, that the other oxygen diffusion method—the method of "bleaching" of the polymeric colored centers produced by γ-radiation—results in an underestimate of the diffusion coefficient of $6.2 \cdot 10^{-10}$ cm^2 s^{-1} and in the overestimation of the activation energy of 13 kcal/mol for oxygen diffusion. Probably, in this case the oxygen-sensitive particles are localized in the special zones, for example, on the paracrystalline domains (see the next section).

The well-developed system of communicating micropores within the carcass cell is capable of providing significant translational mobility for the low molecular weight admixed compounds. Thus, the triplet excited naphthalene and phenanthrene are deactivated in the PMMA films also by additives of methyl methacrylate and that of methyl isobutyrate.[37] The quenching effect is very significant even with small amounts of these additives (<4%) which does not change the macroscopic viscosity of PMMA. NMR spectra of these films confirm a considerable local mobility of aromatic molecules.[37]

A high frequency of mutual collisions of the additive molecules in the polymer matrix is also demonstrated for glassy polyvinyl alcohol by an increase in the velocity of the decay of fluorescence of quinine bisulphate in the presence of the quencher-sodium chloride.[38] Despite the very short lifetime ($\approx 10^{-8}$ s) of the fluorescent singlet excited dye molecules they undergo dynamic quenching with the particles of NaCl.

It should be also noted, that for isotactic PP, the known values of diffusion

It should be also noted, that for isotactic PP, the known values of diffusion constants from recombination rates of phenoxy radicals with polymer peroxyls ($10^6 \div 10^7$ kg M^{-1} s^{-1} at 80°C[7]) correspond, according to the Debye equation $k = 8\, RT/3000\eta$, to a viscosity of $\eta = 8 \div 80$ poise. This value is significantly less than the macroviscosity of the amorphous regions of PP, and again testified to the microporosity of the carcass cells.

This feature has also been confirmed using the paramagnetic probe method. Rotation of the probe radicals in polymeric glasses has a low activation energy (less than 40 kJ/mol) and a high rate ($10^7 \div 10^9$ s^{-1}), exceeding by several orders that of the motion of the polymer chain segments.[7]

Such a discrepancy is caused by autonomic rotation of the probe particles in the volumes of the micropores. Above the glass-transition point T_g, the rotation of the probe particles loses its autonomy, and it gets into correlation with the motion of small chain segments and with the dynamics of the fluctuation of the elements of free volume.[7]

Probably, softening of the polymer is accompanied by considerable loss of carcass hardness and by the enhancement of the mobility of both domains and micropores. However, in the range above T_g, the micropores preserve their structural specificity and determine the law of gas sorption despite their loss of quasi-static state and attaining the fluctuational dynamism.[32]

It is known from colloid chemistry that microporous bodies, being influenced by their surface tension, undergo permanent compression by Laplacian pressure.[33,39,40]

However, self-liquidation of micropores in the amorphous polymer is prevented by the paracrystalline carcass. The carcass domains must resist disrupting effects exerted by the micro-porous core balls of the adjacent cells. The degree of hardness of the carcass directly affects the state of the micropores.

The above is confirmed by an abrupt change in the internal pressure in the polymer at T_g within the range of a few degrees. This pressure, below T_g, is approximately half[41] that predicted from the characteristics of a highly elastic state, it corresponds to the accumulation in glasses of a considerable amount of free energy which practically does not escape in the form of heat. For example, in PS such accumulation reaches 40 cal/cm^3.

In other words, the hard supermolecular carcass of polymeric glass must strain the intracellular chains of the macromolecules. Due to that, the discrepancy is demonstrative in the results of paramagnetic probing of "amorphous" PS and actually amorphous glycerol[42]: an equal interval of microviscosity, from 136 to 9 poise, did correspond to the unequal temperature intervals, a short one in glycerol ($-7 - +15$°C) and a wide one in PS ($-39 - +98$°C).

It is seen that the local viscosity of PS has a lower tempo of change as compared with a homogeneous liquid. That is, the process of cooling, respectively the thermal contraction of material, in the true amorphous phase decreases free volume and inhibits the rotation of the probe particles more efficiently than in the microporous phase of polymer.

Thus, the supermolecular carcass maintains a steady excess of free volume as compared with a liquid, and mechanically fixes the microporosity of the core balls within the globule-micelles.

The paracrystalline domains of adjacent globules must undergo a mechanical tension to opposite sides. Mechanical stability of the carcass requires a balance between the split-trending forces and the couple-trending forces applied to the adjacent globules being coupled. In some polymers, the adhesion of globules prevails and the balance of internal forces is easily disturbed by moistening with nonsolvents.

This seeming mild affect is capable of resulting in a catastrophic structural transition when crumbling the polymer.[41] For example, there is destruction of PC films in acetone,[43] that of atactic PP in chloroform and PMMA films in hot ethanol on cooling.

The process of carcass disintegration in moistening can be incomplete and stops upon formation of large pores and a turbid film which is originally transparent. For example, PS and polyepoxide films become opalescent upon their cooling after boiling in water, changing their permeability to water.[44]

The intracellular microporous sponges, being a source of internal mechanical forces, can induce some anomalies in crystalline polymers. In particular, the process of crystallization, thus affected, is capable of distributing the crystallites as regards their defects. This results in a broad interval of melting temperatures,[20] in addition in the multiplet of T_m values. The latter has been observed in PC,[45] polypropylenoxide,[46] poly(1,4-phenylene) ethers,[47] PE[48] and it has no relation to crystalline modifications.

The elastic forces and free volumes, which appear in the microporous carcass cells, predetermine a variety of thermomechanical relaxational processes. Consider, for example, the annealing of PC specimens at T below T_g. It increases the sizes of globules and the hardness of the environment for the particles of the absorbed paramagnetic probe,[49] and changes the character of mechanical failure of PC films from ductile to brittle.[23,49-51]

The annealing of glassy poly(ethylene terephthalate) modifies the X-ray scattering in large angles.[3] First, the change reflects a growth of the structural perfection of domains; second, it indicates the local crystallization of the polymer chain segments, which differs from the ordinary crystallization by folding of the polymer chain.[3]

The effect of annealing of a polymer specimen can be attributed to a certain rearrangement of the core ball in the carcass cells, namely, to the "local crystallization" in forming the fringed bunches of a few chain segments. The bunches must, in fact, play the role of mechanical distance-piece within the carcass cell.

Thus, the core "bunch-framework," resulting from the core balls in the carcass cells on annealing or aging, decreases the ability of damping of the mechanical affects. Therefore, the polymer becomes more brittle.

The ordering above is structurally reversible. In order to restore the initial properties of the polymer, the aged specimens should be heated close to T_g, then quenched. Probably, the restoration of the initial properties is caused by disordering of the intracellular bunch-framework.

This process, by analogy with mechanical thixotropy, can be called "thermal thixotropy" because the results of excitations of the both types are similar, and both affects disperse the framework that occurred in the carcass cell to a more homogeneous microporous core ball.

It should be noted that the structural state of the microporous intracellular ball can be directly related to the known phenomenon of antiplasticization, which has not been clearly explained so far.[52] From the point of view of the model, the antiplasticization is provided because the microporous balls, being filled with a certain amount of compatible additives, decrease their energy and elastic forces which tense the carcass domains of adjacent globule-micelles. Because of that a firmer coupling of the carcass domains can be provided and the hardness of the polymeric body must increase simultaneously.

The orientational drawing of polymers should be also mentioned. For this structural transition, the formation of a fibrillar structure is the most important feature.

The fibrillation is characteristic of both crystalline and amorphous polymers.[53] The carcass-cellular model allows us to compose a sketch of the drawn polymer as a packet of the micellar capsules drawn in tubules. Each tubule contains the core of polymer chains arranged into chain bundles. The core bundles are fixed along the drawing axis by a suitably organized paracrystalline carcass.

In the tubule, the core chain bundle coexists with the microporous underskin layer which appears in escaping of the micropores from the core ball on its reorganizing in the core bundle. Accordingly, the drawn carcass body is described as a honeycomb construction consisting of tightly packed sealed tubules.

Both the mechanical forces and the free volume, which are frozen in the supermolecular lattice, must be redistributed on chemical aging of a polymer which is induced by scissions and cross-linkings of the polymer chains.

A structural transition, induced by the chemical acts, is capable of changing in the appearance of the polymer specimen (as in films of polyacrylic and polymethacrylic acids[4]). As a general rule, the chemotriggered carcass damage is accompanied by the appearance of the overloaded polymer chains,[54,55] by formation of crazes and as a result by a complete loss of the durability of a polymeric body.

Microporous cell as a chemical reactor

The data above show that noncrystalline polymers are real colloidal bodies having a set of microheterogeneous structural elements, including micropores. The carcass-cellular model of the amorphous polymer allows the participation as an ordinary chemical microreactor of any component of the spatial carcass, as the domains, mesopores and microporous cells.

We consider the latter, as they absorb the low molecular additives and so must determine the fate of molecules of initiators in the chemical processes.

It is known from the science of surface phenomena that the reactional abilities of particles, as well as the position of chemical equilibrium, depend on the degree of dispersity of the reacting objects. Thus, for the spherical colloidal particles, the increment of Gibbs energy (induced by a dispersity) is expressed by the following formula[33]:

$$\Delta G_d = \pm 2\sigma V/R \tag{1}$$

where V is the molar volume of the substance being dispersed, R is the curvature radius and σ is the surface tension compressing the microsphere.

The chemical equilibrium is also determined by a dispersity

$$-\Delta G_d^0 = RT\ln(K_d/K),$$

where ΔG_d^0 is the increment of chemical affinity, K_d and K are the equilibrium constants for the dispersed and nondispersed compounds, respectively.

It is seen from equation (1) that the increment of reactivity of the particles, which is induced by adsorption forces of a curved surface, is proportional to the curvature ($1/R$) and depends on its sign. The micropores have the negative curvature of the surface, so, their equation (1) has a minus sign, i.e., the particles attributed to the micropores (the units of macromolecules or the absorbed molecules) decrease their reactivity. This is, in particular, evidenced by the earlier mentioned increase of lifetime of phosphorescent aromatic molecules. A considerable decrease in the aggressiveness of oxygen to macroradicals,[56] that for singlet O_2 to C=C groups of rubbers,[57] for the methyl radical[7] and atomic chlorine[58] to C—H bonds of macromolecules can also be attributed to the effect of micropores.

The intracellular micropores appear in two kinds of structures (one covers the inner surface (S), another belongs to the core volume (V) of the cell) that differ by their resistances in a thermomechanical rearrangement.

The S-kind is mechanically stabilized by the strained chain links outgoing from the carcass to the core ball, while the V-kind is weaker. Occurring in one or another way, a rearrangement of intracellular framework changes the size of S-, V-micropores unequally, because inside the core ball (V-zone) the micropore system has more possibilities of its rearrangement. The reactivity of reactional centers, belonging to S-, V-zones, must change simultaneously.

The relaxational nature of any thermomechanical process predetermines the importance of the prehistory of the polymer in chemical reactions. This coexists with a dispersion of elementary rate constants of the reactional centers which occupy the micropores with unequal sizes. As a result, it appears as a "polychromatic kinetics" kind of reaction in its static or dynamic regimes. The occurrence of one or another reactional regimes depends on the structural steady or unsteady state of the intracellular microporous reactors.

If a stationary system of the freely communicating micropores is formed in the carcass cell then the low-molecular weight additives receive a high translational mobility, and the cell can be liken to a drop of more or less associated viscous liquid containing the hard lattice of core sponge.

A peculiarity of the intracellular sponge is that its V-zone acts as a compressor while the S-zone must be strained, i.e., the latter is more favorable for polymer chain scissions. In the S-zone appear the adsorption forces generated by the paracrystalline carcass. This makes the S-zone serve as a structural trap for the charged and radical particles occurring in the cell.

The following experiments testify to the action of the S-zone as a trap for the active particles. The powder and milk-white films of PMMA, which possess a developed internal surface, do accumulate a large amount of ion-radicals and macroradicals $—CH_2\dot{C}(CH_3)COOCH_3$ when exposed to γ-radiation[59] at 77 K.

A very weak ESR signal with indistinguishable line structure is observed in the ordinary transparent films under similar conditions.

It is characteristic that the ESR-spectrum of the nontransparent specimen was a four-line one instead of the ordinary nine-line one. This is explained by a hard fixation of the terminal group of the macroradical when excluding the rotation around the $CH_2—\dot{C}$ bond. In that radical conformation, the unpaired electron interacts with protons of the easily rotating methyl group and does not interact with methylene protons.[59] The ordinary nine-line ESR spectrum is reproduced by heating the specimen to room temperature only.

The noted fact can reflect the structural immobilization of the tail-end of the polymer chain with carcass domains after the scission of the polymer *S*-chain link. It should be noted that the immobilization of small-scale units of macromolecules is also manifested with the infrared spectra of PMMA specimens obtained by precipitation with ethanol or heptane from solutions in benzene. In such specimens, the band of infrared absorption of CO groups 1710 cm^{-1} splits into the bands 1680, 1710, 1740 cm^{-1} due to the development of the structural zones in which CO groups interact with each other as in the crystalline lattice.[60]

It also cannot be excluded, that the mosaic paracrystalline capsules of the carcass cells are responsible for the peculiar type of stabilization of radicals (in groups) in the polymer matrix under the γ-radiolysis of PMMA.[61]

The model of dissociation of the admixed initiator

Taking into account the microporous structure of carcass cells it is possible to propose the way in which the free radicals in a polymer appear from the admixed initiator.

It is known that in homogeneous liquids, the rate of dissociation of an initiator, as well as the yield of radicals, decreases with the increase in viscosity of the medium.[62,63] For example, on thickening of chlorobenzene solutions with polyethylsiloxane from 0.5 to 4 santipoises at 403 K, the rate constants of dissociation of the dissolved α-oxyalkyl-*tert*-butylperoxides decrease by 3–6 times, while the rate constants of initiation decrease by 20–40 times.[64] A similar case is observed in the reactions of diperoxides,[65] dicyclohexylperoxydicarbonate[66] and other initiators.[67]

However, for a more viscous medium, the rate of dissociation of an initiator stops to decrease.[66,68] Moreover, the quantitative analysis of experimental data shows that the theory of "cage effect," in the form suggested by Rabinovitch and Neues, disagrees with the experiment as regards polymers by many orders, both the diffusional and radical-acceptor mechanism of radical escape do not describe the real process.

The classic theory of cage effect fails for both polymers and rather viscous liquids, which, as we assume, could be explained by the appearance of a cellular system with operating microporous zones. The process of dissociation in that system differs from the homogeneous one by its direct correlation with the microporosity of the matter. The adsorption forces of micropore having a high negative curvature of surface, first, decrease the thermodynamical reactivity of weak bond in the initiator, and second, prevent the radical escape from the occurred radical pair by compressing the latter within the volume of the micropore.

If the affect of micropores is powerful then the dissociation must be practically inhibited, as is required by the classic theory of cage effect for a highly viscous medium. This will correspond to the highest degree of "kinetical polychromatism" with a real kinetical stop that could be applied to the relatively compact micropores of the *V*-zone inside the carcass cells.

The expanded micropores of the *S*-zone of the carcass cell are more favorable for the dissociation. In the *S*-zone, the adsorption forces of the paracrystalline carcass facilitate the reorientation of primary radicals in its pair and provide their escape by adsorbing on the carcass domains (so, the surface activity of radicals associated with their unpaired electrons is realized).

Thus, despite a high macroviscosity of the polymer matter, the admixed initiator may have the possibility of dissociating by a heterogeneous mechanism.

The escape of radicals from the primary pair results in subsequent chemical conversions, and, unlike that for the homogeneous liquids, separate occupancy is possible of the *S*- and *V*-zones with the reactional acts. One can say that the layer of expanded *S*-micropores, severing the cellular mosaic shell from the intracellular spongy ball, acts as a structural hindrance for the interzonal transfer of free valency. If the concrete structural conditions provide the *S*, *V*-transfer, so the heterophasic coupled reactional chains appear in the both zones. As a rule, they should differ by their stages of initiation, propagation and termination.

Thus, the discussed structural model predicts that the initiated conversion of an amorphous polymer can proceed both with "polychromatical kinetics" (in its static or dynamic state) and with the heterophasic distribution of reactional stages among the structural zones. The author has the intent of demonstrating the characteristic feature of heterophasic process in further publications.[69]

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