On the Functions of Molecular Sponge in Heterophase Chain Reactions of Block Polymers (on the Example of Polystyrene Arylation by Dibenzoyl Peroxide)

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Features of interactions of amorphous polystyrene with dibenzoyl peroxide, which are not explained by the homogeneous mechanism, are described by the heterophase scheme possessing two conjugated reactionary paths, localized in separate structural zones of polymer matrix. The reaction scheme is based on the carcass-micellar model of supermolecular organization, according to which zones of two types exist in molecular-sponge cells. These zones, different by fluctuation dynamics of polymer chains and sizes of micropores (traps for reacting particles) provide inadequate condition for excitation of the acts of initiation, propagation and termination of the reaction sequences. The principle of the interzone conjugation of kinetic chains under the conditions of fluctuation dynamics of the molecular sponge chains, limited by the supermolecular carcass, is exhibited.

KEY WORDS Polystyrene, arylation, dibenzoyl peroxide, heterogeneous reaction mechanism.

1. INTRODUCTION: MORPHOLOGICAL MODEL OF AMORPHOUS POLYMER

The data known from literature and not yet published on the important features of kinetics and composition of the reaction products of amorphous polystyrene (PS) and dibenzoyl peroxide (BP) are analyzed in the paper. The yhe applied process theory accumulates all the key points of a new concept in chemism of block non-crystal polymers, which was developed during last ten years. The theory directly reflects the specificity of structural organisation of macromolecules in the matrix carcass.

The principle of this organisation is stated in the morphological model used. By this principle noncrystal polymer body represents an aggregate of tightly packed globules, formed by many macromolecules.[1-3] Let us remind in this case that electronic-microscopic investigations of specially prepared glassy polymers usually possess globules of 10–50 nm size.

According to the model, polymer chains are packed as felt (or sponge) inside the

globules. In addition, they do not reach the extremely dense packing of their units. So inside the globules the basic part of chain links exist assembled incompactly because a little part of other units of the polymer chains segregates to form thin covering of globule, which are composed into steady spatial carcass. The covering of every globule is composed as a mosaic consisted of paracrystalline domains — nanostructures, which include up to a ten of segments of macromolecules at their approximate parallel packing. Fixing the polymer body, this p-carcass serves as an open-work reinforcing construction. Fittings play the simultaneous role of mechanical clips, which do not allow the chains to be packed into dense statistic coils in the volume of globules (i.e. in p-carcass cells).

For the first time the existence of p-domains has been discovered during the analysis of the wide-angle X-ray scattering on samples of polystyrene, polycarbonate, polyethylene, polyethylene terephtalate and natural caoutchouc.[4] It was found that p-domains steadily keep crystallic regularity of the segments and their sizes independently on physical state of polymers (glass, high elasticity, melting). They were observed with the help of one of electron-microscopic methodics on thin films of polymethyl methacrylate (PMMA) in further experiments, and their sizes was found as of 1.5–3.0 nm.[5]

The fact of formation of rigid structural elements, which could be identified as p-domains, was pointed out also in the investigations of polymers solutions and melts by NMR and ESR methods. For example, occurrence of stable rigid aggregates of polymer chains in conditions of high dissolution was observed for solutions of specially labeled PS and PMMA (fragments of stable nitroxyl radicals served as lables), particularly 75% of dissolvent in PMMA mixture with chloroform and up to 40% of dissolvent in PS mixture with benzene.[6] During evaporation of dissolvents at 25°C, rigid elements of present systems compose a continuous carcass which fixes up to 20–30% of occluded solvent in gels formed. Thus each cell of this continuous carcass of gel-like polymers seals granules of the sponge, swollen in the solvent.

The formation of swollen chain-sponge granules, encapsulated by p-domains, at an intermediate stage of consolidation of the solution ensures that it is very often possible to introduce essential amounts (up to tens of percents) of compounds, which cannot dissolve the polymer and cause no swelling of it, into glassy polymers.[3] Many of substances such as crystal dibenzoyl peroxide, sterically hindered phenols and others are related to this class.

It is important that formed sponge granules of the carcass body, occluding admixtures, are isolated from each other by p-domain coverings of globules hermetically. This fact allows to perform a matrix "conservation" of substances cap, able for crystallysation, and volatile ones such as penthane, cyclohexane, heptane, etc. (which are applied for preparing foamy materials from PS and polycarbonate) without segregation of essential amount of them into a separate phase.[7–9]

As it was mentioned above, a polymer matrix reinforced by an open-work p-carcass excludes any possibility of complete collapse of polymer chains to the size of statistic coils and preserves a significant amount of elastic tension energy. In particular, this fact is displayed by an abrupt decrease of the internal pressure (and cohesion energy) in a narrow temperature range of polymer transition from highly elastic state to glass. Abrupt change of the internal pressure, which is experimentally

observed at glass transition of PS, PMMA and polyvinyl acetate, completes itself with the energy accumulation in chains up to 40 cal/cm^3.[10] Moreover, the method of neutron scattering testifies that the sizes of macromolecular coils in polymer glasses was always 20% higher than these of statistic coils in Θ-solvents.[11] This fact also points to structural porosity of the polymer chain packing fixed by p-carcass.

One can decrease the jump of internal pressure of glassified samples[10] treating PS melt by external pressure; thus it is possible to decrease the size of macromolecular coils, decreasing the volume of emptiness, stored in glass.[11] However the above mentioned changes do not cause equilibrium state of pressed patterns, because their annealing at temperatures even lower T_g restores "usual" sizes of macromolecular coils and balance of elastic forces, which initially existed between p-carcass and sponge granules.

Concerning this structure of granules, which fill p-carcass cells, we should mention that polymer chains under global extension form two structural zones which differ by the sizes of micropores (emptinesses, reaching 1–2 nm size) and by fluctuation dynamics of chains. Sponge functions, connected with its thin structure, will be considered in detail in the description of the polymer microreactor model. In this part we just outline the general idea, that structurally caused porosity of chain packing provides the appearance of colloid heterogeneity factor in an amorphous polymer. In essence, this factor is a new degree of latitude,[12] which cardinally differs polymer from homogeneous liquid and causes the appearance of new physical and chemical properties. In this sequence we can mention some physical properties, not formerly characterized, which were explained in papers[1–3,13] on the basis of properties of carcass stabilized molecular sponge.

Moreover, the important role of carcass-micellar structure was exhibited on the example of the model reaction of dibenzoyl peroxide with polymers, such as relatively rigid-chain polycarbonate and cellulose triacetate,[14–16] and flexible chain polypropylene,[17] polyethylene,[18] polyethylene oxide,[19] polyamide PA-548.[20] One must emphasize that BP possesses the property of active acceptor of free radicals as well as it is very effective initiator of radical transformations. The properties above gave the possibility to apply BP for kinetic sounding of structural features of the medium, which seriously change the kinetic law and the composition of the reaction products in polymer matrix, as displayed by the investigations.[14–20] Processes of all the above mentioned systems were quantitatively described in the ranges of general heterophase mechanism, which naturally correlates with simple formal kinetics and preserves its force for glassified, highly elastic and melt states of polymer samples.

The present investigation exhibits the principle of the heterophase mechanism on the example of BP reaction with PS. Bright features of this reaction are out of ranges of the homogeneous mechanism of BP interaction with liquid low-molecular analogs of polystyrene, well-known from literature. One of these analogs is hydrogenated monomer of polystyrene, in particular.

## 2. MECHANISM OF HOMOGENEOUS REACTION OF DIBENZOYL PEROXIDE WITH LIQUID HYDROCARBONS

Interactions of BP with liquid hydrocarbons proceed by free-radical mechanism, started by acts of dissociation on benzoyloxyl radicals:
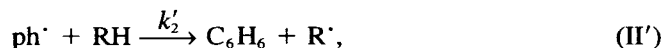
$$phCOO—OOCph \xrightarrow{k_0} 2phCOO^{\cdot}(r^{\cdot}).\qquad(0)$$

Further processes with benzoyloxyls are defined by ratio of rates of reactions of their decarboxylation:

$$r^{\cdot} \xrightarrow{k_1} ph^{\cdot} + CO_2 \qquad(I)$$

and hydrogen atoms detachment from alkyl fragments of solvent molecules:

$$r^{\cdot} + RH \xrightarrow{k_2} rH + R^{\cdot} \qquad(II)$$
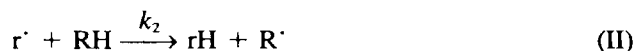
Alkyl radical $R^{\cdot}$ of solvent, formed at the participation of free phenyl

$$ph^{\cdot} + RH \xrightarrow{k_2'} C_6H_6 + R^{\cdot}, \qquad(II')$$

attacks benzene ring of dibenzoyl peroxide, inducing BP decomposition

$$R^{\cdot} + BP \xrightarrow{k_3} r^{\cdot} + products, \qquad(III)$$
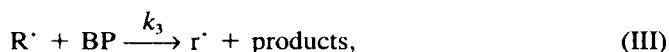
and participates in acts of death, if meets other radicals.

Total rate of BP decomposition summarizes the rates of spontaneous and chain reaction stages[21]

$$-\frac{dC}{dt} = k_0 C + k_i C^n,$$

where C is current concentration of BP, k_0 and k_i are the rate constants of BP decomposition in spontaneous and induced reactions, respectively; n is kinetic order of the chain reaction.

Particular structure of k_i and n coefficients of the chain item should be determined in accordance with acts of propagation (i.e. induced BP decomposition) and reaction chain termination, which are predominant in the particular liquid. The simplest formal kinetic schemes, exhibited in Reference 21, consider simultaneous participation of one type radicals, $r^{\cdot}$ or $R^{\cdot}$, in acts of propagation and quadratic termination. For the case when alkyl radical $R^{\cdot}$ is the main, i.e. reactions (III) and (IV) are combined,

$$R^{\cdot} + R^{\cdot} \xrightarrow{k_4} termination, \qquad(IV)$$
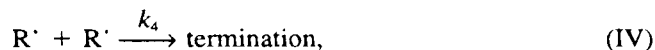
calculated rate of BP decomposition is described by the following equation:

$$-\frac{dC}{dt} = k_0 C + k_3 \left(\frac{k_0}{k_4}\right)^{0.5} C^{1.5}.$$

Expressions of other probable combinations of elementary reactions are considered in References 22 and 23. Particularly, if the reaction (III) is accompanied by acts of death of (r˙ + r˙) or (r˙ + R˙), peroxide order n is 0.5 and 1.0, respectively. If we consider BP decomposition induced by benzoyloxyls, the order can reach 1.5, 2.0 in relation to the acts of death of (r˙ + r˙), (r˙ + R˙) and (R˙ + R˙) radicals.

In fact, experimental value of n for the most of liquids equals 1.5. Very rare $n = 1$ and, apparently, there are not known the examples of $n = 0.5$ and 2.0 because of rather high rate of reactions (I), (II) and (II′). Actually, constant k_1 of decarboxylation shows high values of 1×10^8 s^{-1} (403 K) and 6×10^5 s^{-1} (313 K) for activation energy $E_1 = 58.6$ kJ/mol.[24] Reaction (II) with the participation of secondary CH-groups possesses activation energy $E_2 = 34.4$ kJ/mol and proceeds in conjugation with the reaction (I).[25] Taking into account high rate of reactions (I) and (II) one can suppose, that the attack of r˙ on benzene rings of BP, dissolved in hydrocarbons, is low-effective. This supposition is confirmed by the data of the composition of BP decomposition products in aliphatic hydrocarbons.[26-30]

It is known from the experiments with benzene solutions that free benzoyloxyl attaches itself to benzene ring, and that σ-complex, formed in the reaction, reversibly fast decomposes into initial benzene and r˙ radical.[31,32] At 353 K this reversible reaction is shifted to dissociation. One can heighten the role of other reactions with σ-complex of r-C$_6$H$_6$ by temperature decrease, its oxidation by dissolved oxygen that forms a noticeable amount of phenylbenzoate,[31,32] in particular. Besides, owing to reversibility of attachment of benzoyloxyl to benzene molecules, probability of formation of r-BP˙ complex also increases. Although this complex reversibly dissociates, but its small amounts transform into disalicylic ester, observed in the work.[33]

As for phenyl radical, it easily detaches hydrogen atom from aliphatic hydrocarbons. Corresponding rate constant $k_2' = (0.2 \div 6.2) \times 10^6$ M^{-1} s^{-1} is significantly higher than that of similar reaction of alkyl radicals,[34] which equals $10-10^3$ M^{-1} s^{-1}. The attack of free phenyls on BP present in solution forms small amounts of phenylbenzoic acids because of its faster interaction with the solvent. But in some cases their reaction with BP must be taken into account, for example, at explanation of isotope composition of reaction products of labeled substances.[36]

In line with all mentioned above we can suppose that induced decomposition of BP, as a rule, should be performed by solvent radicals. In nonaromatic liquids, alkyl radical occurring in acts (II) and (II′) generally attacks peroxide on phenyl nuclei

$$R˙ + BP \rightarrow R˙C_6H_5COOr(A˙).$$

After that σ-complex of A˙, formed in this reaction, interacts with another radical or undergoes the intramolecular transfer of hydrogen atom and peroxide bond termination[26,28-30]

$$A˙ \rightarrow RC_6H_4COOH(RC_6H_5 + CO_2) + r˙.$$

Decomposition of BP in benzene solution is accompanied by decarboxylation of all benzoyloxyls formed, and free radicals occurred in this process are preferably *attached to benzene* molecules and form σ-complexes

$$\text{ph}^{\cdot} \ + \ C_6H_6 \ \rightarrow \ \text{phphH}^{\cdot}.$$
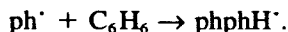
The latter attacks BP and is oxidized by hydrogen transfer

$$\text{phphH}^{\cdot} \ + \ BP \ \rightarrow \ \text{phph} \ + \ rH \ + \ r^{\cdot}.$$
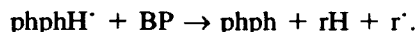
Moreover, it participates in acts of reaction chain terminations. The expression for peroxide decay rate becomes more complex than for nonaromatic hydrocarbons

$$-\frac{dC}{dt} = k_0 C \ + \ k_{i1} \ + \ k_i C^{1.5}.$$

It points out the proceeding of two chain stages, which possess first and one-and-half orders by BP. However the first of these stages differs by its significantly low activity, and the constant of it, $k_{i1} = 0.2 \times 10^{-5}$ s^{-1} (at 351 K), is lower than that of spontaneous decomposition,[35] $k_0 = 1.67 \times 10^{-5}$ s^{-1}.

Chain decomposition of BP in alkylbenzene solutions is induced by σ-complexes of phenyl and solvent ph$^{\cdot}$C$_6$H$_5$-Alk, and by alkyl radicals C$_6$H$_5$-Alk$^{\cdot}$. As this takes place, the reaction rate is composed of spontaneous and chain components, the latter of which possesses one-and-half order by peroxide.[37] Contrary to alkylbenzenes, a rare case of effective first order chain reaction is observed in chlorobenzene and bromobenzene. It is explained on the basis of the supposition that these media display the cross reaction chain termination as r$^{\cdot}$ radical meets σ-complex of haloidobenzene.[38]

The chain reaction rate of BP decomposition is the lowest in benzene, toluene, ethylbenzene and increases in nonaromatic solvents. Ratios of initial rates of chain and spontaneous components, set in the work[21] for different solvents,

$$\frac{W_i^0}{W_0^0} = \frac{k_i C_0^{0.5}}{k_0} \ (353 \text{ K}, \ C_0 = 0.2 \text{ M}),$$

dispose these solvents according to their efficiency into the sequence: benzene—0.58, toluene—0.58, carbon tetrachloride—0.79, cyclohexene—1.07, ethyl iodide—0.75, *tert*-butylbenzene—2.09, cyclohexane—2.29, ethyl acetate—1.82, acetic acid—2.81, acetic anhydride—1.82.

Low rate of the chain component in benzene and toluene is explained by high probability of quadratic termination of the reaction chains as the corresponding σ-complexes are met. Active participation of compositions containing phenyl groups in the acts of death of free radicals leads to deceleration of the chain process by products of BP decomposition, which are accumulated in nonaromatic liquids. For example, the efficiency of the chain stage in acetic anhydride decreases to 0.59 instead of initial 1.82 when attained the deep decomposition phase.[21]

The contribution of spontaneous reaction into BP expenditure increases with temperature of peroxide decomposition, because activation energy E_i of the chain component is smaller than E_0. As an example, $E_i = 105.5$ kJ/mol in benzene and 104.5

kJ/mol in acetic aldehyde.[21] At the same time the following values are applied for the constant of spontaneous decomposition, $k_0 = A \times \exp(-E_0/RT)$: $A = 1.18 \times 10^{14}$ s^{-1}, $E_0 = 125$ kJ/mol[23], $A = 3 \times 10^{13}$ s^{-1}, $E_0 = 124$ kJ/mol[40] (higher values of $E_0 = 138-139$ kJ/mol were observed also[21,41]). Thus, the efficiency of the chain component of the process in liquid depends on temperature according to calculated expression of the rate, in which E_i can include a half of E_0 only.

It can be said with respect to stoichiometric coefficient of free radical generation that in low viscous liquids it is close to maximum; in benzene, in particular, each act of spontaneous BP decomposition gives two free radicals. This fact is confirmed by independent investigations, performed for 351 K[35] and 318 K.[42]

To finish the review of liquid-phase process we should point out a significant sensitivity of the chain reaction to oxygen dissolved in liquids. Oxygen is strong inhibitor which acts by oxidation of active radicals into peroxyl ones to perform no reactions with dibenzoyl peroxide.[21,39]

3. PHENOMENOLOGY OF THE PROCESS IN POLYSTYRENE

Braitenbach and Frittum, who performed tests with chlorosubstituted derivatives of BP,[43] were among pioneers of investigation of the reaction we interested in. They met an anomalous behavior of benzoyloxyl radicals when realizing the experiments on deaerated PS films. It is a common knowledge that benzoyloxyl radicals decompose well in liquids to free phenyl radicals and carbon dioxide. But experiments[43] showed that they also attach to a polymer in significant amounts, which consist 40-50% of attached BP fragments. The rest of BP fragments was found in the composition of macromolecules as chlor-phenyl groups.

In experiments by Haas, performed on aerated PS films,[44-46] benzoyloxyls displayed much higher stability. Benzoic acid, phenyl benzoate and polymeric benzoates were obtained in these experiments among the main products of transformations. The latters, which are the only products of PS arylation, gave higher yield as compared with Reference 43. The data by Haas showed that benzoyloxyl, obtaining increased stability in the polymer medium, is attached by benzene rings and by secondary (but not tertiary) carbon atoms of the polymer chain.

Macroradicals, born in aerated PS films, decompose with termination of polymer chains and formation of low-molecular fragments with nonsaturated C=C-bonds. Strange as it may seem, these experiments displayed no reactions of alkyl macroradicals with the oxygen dissolved in the films. Despite free diffusion of air into the films, chemical analysis exhibited absolute absence of oxidation products. This property principally differs PS from its liquid chemical analog—diisopropylbenzene, which gives high yield of hydroperoxide at the initiated oxidation with BP.[47]

Detailed kinetic investigation, performed in References 44-46, exhibited that aerated PS films displayed nonchain reaction of BP and that Arrhenius law is not fulfilled for them. For example, if $E_0 = 126$ kJ/mol at 353 K temperature (which is near glass transition point $T_g = 373$ K) is as in liquids, then at temperature decreased to 329 K it increases up to 151 kJ/mol. This feature Haas assumed to rigid cage effect,
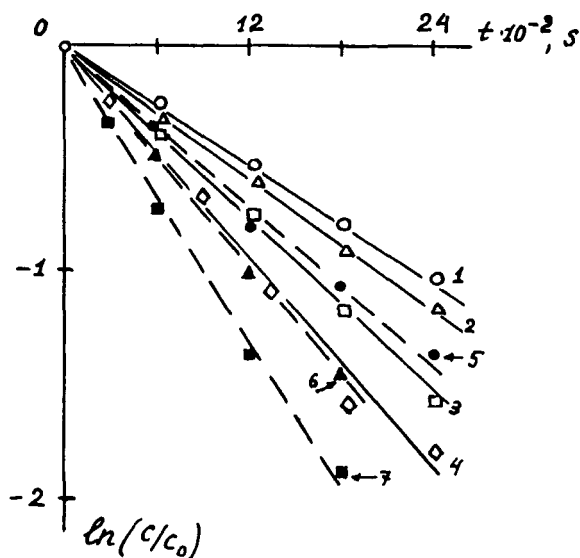
FIGURE 1   Plots of photochemical BP decay induced in the evacuated PS-films under the UV radiation (region 313 nm) at 299 (1–4) and 313 K (5–7), initial BP concentrations: 0.05 (1), 0.08 (2, 5), 0.28 (3, 6) and 0.68 mol/kg (4, 7).

but this supposition did not explain the independence of quantitative composition of reaction products on temperature, which was discovered by him, also.

Rado and Lazar, who have also studied this system,[48,49] discovered that oxygen removal from films caused the occurrence of BP chain reaction. Beside this fact detailed kinetic study of this reaction was not performed in References 48 and 49. Later on it was performed by Pustoshny together with one of the authors of the present review,[50] but unfortunately the mechanism of polystyrene arylation has not been efficiently discussed in Reference 50 because there existed not particular concept of heterophase reaction at that time. By now the necessary structural-kinetic model of the process has been already tested on the number of polymers (see the Introduction). It also forms the base for efficient analysis of features of radical transformations in the case of PS.

For this purpose let us refine the kinetic equation of anaerobic reaction. In accordance with the results, obtained in Reference 50 (in which polymer of $M_n = 150,000$ molecular mass and films 15–20 μm thick were applied), kinetics of BP expenditure in films under the conditions of thermal and photochemical born of radicals can be described by the following exponential equation:

$$-\frac{dC}{dt} = kC, \quad C = C_0 \times \exp(-kt), \tag{3.1}$$

where C_0 and C is initial and certain concentration of BP, respectively; k is effective rate constant, dependent on C_0. The data in Figure 1 testify this dependence. This figure shows as an example graphics of linear anamorphosises of curves of photochemical BP decomposition, taken from Reference 50, under the effect of UV-rays with wave-length in 313 nm range.
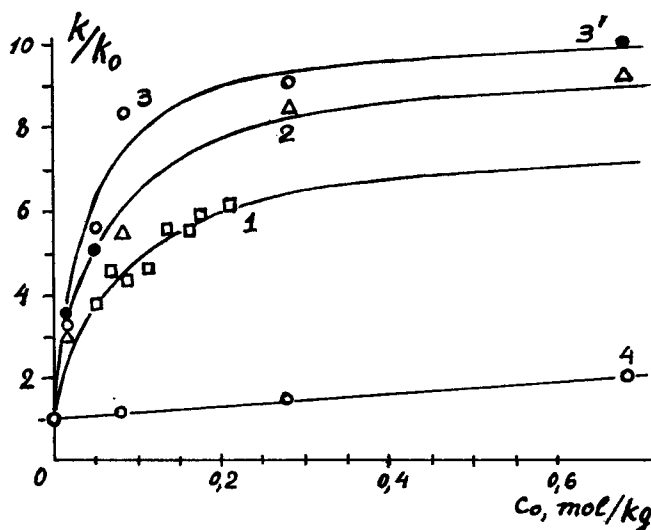
FIGURE 2 The relative rate constant of BP decomposition vs initial BP concentration at 353 (1), 363 (2), 372 (3, 3') and 313 K (4), the values are results of BP decay (1–4) and CO_2 evolution (3') from the evacuated PS-films, item (4) characterises the photochemical process.

Calculations, performed by us again, display that in the case of thermal reaction the dependence of constant k on concentration C_0 in 353–372 K temperature range can be described by the formula which is similar by its view to that set before for polyethylene and polyethylene oxide:

$$k = k_0 + \frac{k_0 a C_0}{(1 + bC_0)}. \tag{3.2}$$

Here both first and second terms are rate constants of nonchain and chain reaction, respectively; a and b are coefficients.

Curves 1–3, which characterize the dependence followed from the equation

$$\frac{k}{k_0} = 1 + \frac{aC_0}{(1 + bC_0)}, \tag{3.3}$$

are shown in Figure 2. As it can be seen, they correlate well with the experiment. The following values of coefficients were used in calculation of the curves: $k_0 \times 10^5$ = 1.11, 3.33, 10.0 s^{-1} (these constants were taken from works by Haas[44–46]); $a = 95$, 155, 280 kg/mol; $b = 14$, 18, 30 kg/mol for 353, 363 and 372 K, respectively. Points for curve 1 (353 K) were taken from Reference 48. They were calculated from BP conversions for fixed time and C_0. The rest of points were obtained from kinetic curves shown in Reference 50. Let us point out that a and b coefficients obtained can be characterized by approximately equal activation energies $E_a \approx E_b \approx 59$ kJ/mol.

Recall that the chain reaction of BP differs by lower rate in liquid aromatic hy-

drocarbons comparing with PS[50] and possesses the order of 1.5. The experiments on BP decomposition in deaerated toluene with sealed glass ampules, performed by Pustoshny for comparison, which displayed that the reaction rate at 372 K is described by usual equation of the liquid phase:

$$-\frac{dC}{dt} = k_{0l} + k_l C^{1.5}.$$

The values of the constants are: $k_{0l} = (3.0 \pm 0.2) \times 10^{-4}$ s^{-1} and $k_l = (2.4 \pm 0.5) \times 10^{-4}$ (l/mol)$^{0.5}$ s^{-1}.

We get that the initial efficiency of chain decomposition in liquid toluene at $C_0 = 0.25$ mol/kg is $k_l C_0^{0.5}/k_{0l} = 0.4$ in opposite to $(k - k_0)/k_0 = 8.0$ in the polymer, which possesses extremely high microscopic viscosity. From this results, it arises the conclusion that BP molecules are localised in polymer in such structural zones, where liquid-phase mobility is provided for moving particles.

BP molecules also display high mobility at lower temperatures of 299 and 313 K as demonstrated by a significant contribution of chain component into the rate of photochemical decomposition (Figure 1, Figure 2, line 4). In this case the dependence $k(C_0)$ is straight line as for other polymers: polycarbonate, cellulose triacetate and polyamide PA-548.[14,16,20] Taking into account that line 4 correlates with the expression (3.3) at $a = 1.3$ kg/mol ($b \approx 0$), values of a and b in 313–353 K temperature range can be connected with the activation energy $E_b \geq E_b \approx 96.5$ kJ/mol, which is sufficiently higher than 59 kJ/mol for 353–372 K range.

4. THE MODEL OF CHAIN-SPONGE MICROREACTOR

Considering structural features of local zones of polymer glass matrix, where admixed compounds obtain quaziliquid mobility enough for chemical transformations, we will base on the carcass-micellar model of supermolecular structure of amorphous polymer, described in the Introduction. In this case we take into account that only a small part of general amount of polymer chains is spent for the open-work paracrystalline mosaik construction.[4] At the same time, the general part of chains fills p-carcass cells, packed in sponge micelles.[1–3] Assembled to sponge granules polymer chains strive for reaching dense packing with the highest density of cohesion energy under the molecular forces. However chain units introduced into paracrystalline domains of globule coverings, composed into mosaic p-carcass, inhibit this process.

In this connection it can be supposed that polymer chains, constricted in the middle of p-carcass cell, form a more or less dense granule-core which split off itself from p-domain walls of the cell by forming the layer of chain segments, oriented in radial direction of the globule-micelle. These border segments play the role of mechanical bracings and form a rigid palisade, so they border spheric layer of stationary micropores. Micropores themselves must possess the sizes of thermodynamic segment order, which is in the range of 1.5–3.0 nm for such polymers as PS, PMMA, PVC, PE, PP.[51] They should be related to super-(s)-micropores according to their sizes.[52,53]

In this case we can say that stationary s-micropores form separate s-zones, which

are interlayers between paracrystal coverings of connected globules and intraglobular nucleus granules, filled by small v-micropores.

As it is known, glass flexible-chain polystyrene and polymethyl methacrylate are related to nonporous sorbents according to their sorptional properties.[54] We can suppose on this base that the size of micropores in nucleus granules of sponge micelles must not sufficiently exceed the thickness of polymer chains. Actually, direct experiments, performed in Reference 55 on glassy PMMA, displayed distinct distribution of micropores by sizes. It was found that the most of micropores in samples, frozen at 77 K, possessed radii below 2.5–3.3 Å, and only 1% of them possessed radii up to 12 Å.

The result, obtained in Reference 55, theoretically complies with the structural model of sponge micelle, which we roughly presented. Existence of physical surfaces and emptinesses, realized as stationary s-micropores and more fluctuationally dynamical v-micropores in micelles, introduces a new latitude into polymers—the factor of colloid dispersity. This factor should be taken into account under the consideration of physico-chemical processes connected with functions of sponge micelles. Let us show as an example a logic structure of the approach, in which the present model allows us to disclose physical nature of the phenomenon demonstrating unexpected and characteristic heat effects of polymer dissolution in its hydrogenated monomers, in particular.

It is known that mixing of low-molecular fractions of polystyrene, polymethyl methacrylate, triacetate cellulose with corresponding hydrogenated monomers proceeds with zero heat effect in contrast to glass high-molecular polymers dissolved with heat evolution.[56] The investigation of the heat phenomenon allowed to state[57] that heat amount, liberated from PS mixtures with toluene and ethylbenzene linearly decreases with the increase of mixture temperature from 6 and 7 cal/g (for toluene and ethylbenzene, respectively) at 303 K to ≈ 1 cal/g at 358 K. At higher temperatures of dissolution of the released heat is about 1 cal/g.

The analysis of the known data, performed in Reference 57, made it possible to exclude the supposition made in Reference 56 that the heat release recorded for the above mentioned processes is caused by relaxation of friably packed chains into dense state, accelerated by solvent effect. It was pointed out also that the effect is disconnected from the decrease of volume of mixed components, because the test performed in Reference 57 supported the fact, known from literature, that the amount of released heat was independent on external pressure under which samples were glassified.

At the same time, the discussion of the experimental material in Reference 57 lays in the ranges of the homogeneous model of amorphous polymer and that was not finished by construction of adequate physical picture of the process, while qualitatively obvious description can be made on the basis of the sponge micelle model.

It is evident that sponge dissolution in hydrogenated monomer causes annulment of free surfaces of narrow v-micropores as well as super micropores. In connection with the fact that narrow micropores possess higher sorption energy, compared with s-micropores,[52,53] solvent diffused into the polymer should occupy the system of narrow micropores first. In this case each sponge granule initially transforms to a homogeneous liquid drop of colloid size owing to cohesion equivalence of hydro-

genated monomer and monomeric chain units (similar parameters of dissolution). Transformations of nuclei to liquid drops is accompanied by annihilation of free surface of v-micropores and partial decrease of tensile strength of chains in drops. As a result, the corresponding amount of heat Θ_1 is released.

Let us point out that liquid-type drop is formed on the initial stage of micelle saturation by solvent only, when surface tension σ is preserved to impart a spheric form of drop and to detach it from p-domain walls of rigid carcass, when retaining the border-line layer of s-micropores. We should also mention that it is precisely this picture of the formation of drops (regularly packed in the polymer matrix, reached the size of tens of nanometers) that was shown by small-angle X-ray scattering method in experiments with PVC plasticizer mixtures.[55] Unlike plasticizers which cause swelling but do not dissolve the polymer, the solvent annihilates drops and their surfaces during mixing which are formed in p-carcass as intermediates. In this case potential energy of total surface S of drops is released as additional heat $\Theta_2 = \sigma S$.

Taking into account that surface tension of nonpolar liquids decreases linearly with temperature increase[55]

$$\sigma_T = \sigma_0 - \left(\frac{\partial \sigma}{\partial T}\right) \Delta T$$

(here σ_T and σ_0 is surface tension at current temperature and standard temperature, respectively; $(\partial \sigma / \partial T)$ is temperature coefficient of surface tension; ΔT is the difference between current and standard temperatures), we can express total heat amount as follows:

$$\Theta_1 + \Theta_2 = \Theta_1 + S\sigma_T = \Theta_1 + S\left[\sigma_0 - \left(\frac{\partial \sigma}{\partial T}\right) \Delta T\right].$$

It follows from this expression that total amount of heat, released as a result of initial formation and further destruction of drops, colloidly dispersed in the polymer, under the influence of hydrogenated monomer must decrease by linear law to some value Θ_1 as the mixing temperature increase. Qualitative correlation of this formula with the experiment[57] points out natural cause of the heat effect, which cannot be explained in supposition of homogeneous systems mixture.

As concerns compounds which do not dissolve amorphous polymers (such as crystal dibenzoyl peroxide, sterically hindered phenols and many of hydrocarbons and alcohols), it should be said that under conditions of direct contact without participation of general solvent they are able just to adsorb in polymer matrix in small amounts, if there is an access to surfaces of structural emptinesses. But the same compounds have very often to mix with polymer in sufficient amounts (tens of percents) through combined solutions.[1-3]

The fact is that during preparation of polymer samples the system reaches the stage of gel in the solvent evaporation process. Being formed swollen sponge granules with great amount of solvent are enveloped in carcass structure of the gel by thin hermetic coverings of paracrystal domains.[3] The solvent occluded in the gel

provides both high conformational variability and high dynamics of polymer chains in micelle sponge granules. Owing to this fact granules can accumulate big amounts of additives, which do not dissolve the polymer. They substitute the solvent in the swollen sponge simultaneously with its evaporation. Finally they are enveloped in p-carcass cells more or less hermetically, but preserve molecular dispersion degree. Owing to this fact the polymer is able to conservate micellar material with significant porosity degree (in accordance with that initially created by the solvent). It also fixes higher fluctuation dynamics of the chain units, as compare with pure glassy polymer.

Occupying the place of solvent molecule, molecule of nonsolvent must push apart polymer links (which would perform more dense packing in absence of additive) and regulate them in a certain way into large micropore. Formation of such a capsule from polymer links is combined with the preservation of particular excess of the surface energy and the decrease of chain entropy around additive molecule. These described phenomena require compensational increase of entropy of polymer chains about the capsule formed. Such increase is performed in certain ranges owing to the decrease of structural tension forces and the increase of the conformation amount of chains in the sponge.

Thus we obtain that nonsolvent molecule introduced into sponge affects its chains mechanically. In its turn, the sponge affected by an additive performs the opposite effect, producing negative pressure on additive through capsulating links. The end of this force balance, realized with the help of dispersion forces, is that additive molecule is localised in the volume of forming micropore and obtains relatively large space for rotation.

To support all said above let us mention the data of SPR method, which confirm the presence of high-frequent rotations of particles of paramagnetic probes in glassy polymers. These data say that probe particles dispose in micropores which provide such activation energies and rotation frequences as in ceolytes with channel diameter of 8–10 N.[59] We can also mention the data of investigations of plasticized polymers by NMR method, which confirms that there is a conformity between polymer-chain structure and that of microporous adsorbents.[59] For initial polymer glasses this conformity is not observed.

The study of mobility of additive particles in glassy PS with the help of paramagnetic probe—tetramethylpyperidinoxyl allowed us to determine local viscosity of the medium. It changes from 136 to 9 poises in 234–371 K temperature range.[61] Similar values of viscosity of liquid glycerin lies in the interval of 266–288 K.[61] These data are remarkable first by their essential difference from macroviscosity of PS (10^{12} poises in the point $T_g = 373$ K), and secondly, by their low value for PS instead of glycerin at low temperature of 266 K (by 2.5 times, approximately). This correlates well with stimulating effect of micellar chains on motion of additives.

Fluctuation dynamics in p-carcass cells also provides high rate for transit migration of particles with low molecular masses. This fact is undoubtedly confirmed, for example, by experiments on extinguishing of phosphorescence of aromatic admixtures in glassy PMMA by oxygen[62] and small amounts (up to 4%) of methylmethacrylate and methyl-isobutyrate, which do not affect macroscopic viscosity of the polymer.[63] The experiments on extinguishing of bisulfate quinine fluorescence by sodium chloride in glassy polyvinyl alcohol[64] are also very effective. Dynamic nature

of extinguishing acts, which shorten more so short lifetime of singlet-excited dye ($\approx 10^{-8}$ s), testifies very high frequency of contacts of additive molecules.

Turning back to the reaction of dibenzoyl peroxide decomposition, which we chose as the model reaction, let us remind that the rate of it in glassy PS is significantly higher than in medium of liquid hydrogenated monomers despite they differ from PS by the extremely low viscosity. In this case it can be considered that high mobility of BP molecules in polymer matrix is provided by active oscillation of polymer chain units and fluctuations of v-micropore sizes. Any way, all these motions are connected with pulsations of sponge granules stretched on coverings of p-carcass through border s-segments.

Existence of discrete microporous zones in sponge micelles is the cause of inhomogeneous distribution of BP molecules and acts of dissociation of this initiator. General amount of the additive is stored in nucleus granules of micelles, in narrow micropores, where steric conditions are unfavourable for dissociation to free radicals, as it is seen from the results of References 1, 2 and 14–20.

We paid attention before to the fact that fluctuation dynamics is high in nucleus granules, and it supports fast motion of additives. In this case it is impossible to exclude the fact that narrow v-micropores possess some probability for expansion to the sizes of super-micropores. However such s-micropores should differ by short life-time in comparison with characteristic time of dissociation of BP molecules.

Moving in micelle pores BP molecules obtain the possibility to dissociate to radicals in stationary super-micropores, which form border layers between nucleus granules and domain walls of p-carcass cells. Disposed in s-micropore, during general time BP molecule is adsorbed on rigidly fixed polymer segments which compose pore surface. Adsorption forces, acting in such a pore, help initial radicals to attack macromolecules, providing their reorientation and extraction from initial radical pair. Thus despite extremely high macroscopic viscosity of glassy polymer, additive initiator obtains the probability to dissociate in polymer-chain sponge according to heterogeneous mechanism.

The above mentioned features of the composition of sponge micelles also influence the fortune of macroradicals, able to decompose in liquids with polymer chain breaks. Rates of corresponding acts significantly decrease on the surface of narrow v-micropores. Such act requires enough room, but which can become empty under the condition only of synchronic pushing apart of a number of chains, which form cell walls. Considering the data from References 14–20, such situation in v-zones is very rare. At the same time acts of initiated degradation of macromolecules on the surface of stationary s-micropores proceed with a noticeable rate, probably, due to enough room and the presence of mechanical stretching of s-segments of polymer chains.

Thus complete scheme of the chain transformation, initiated in sponge micelle, should include the following stages: 1) scheme of initial reaction chain, which characterizes the sequence of elementary stages in s-zones; 2) scheme of secondary reaction chain of transformations in v-zones of sponge micelles; 3) scheme of interzone radical transfer.

The action of this particular mechanism was exhibited in papers[14–20] with the help of model reaction of BP in glassy, highly elastic and melt states of the above mentioned polymers.

5. MECHANISM OF POLYSTYRENE ARYLATION

In line with the model of microreactor considered initiated transformation of polymer is provided by the exchange of dibenzoyl peroxide molecules between v- and s-zones of sponge micelles:

$$BP_v \underset{k_{sv}}{\overset{k_{vs}}{\longleftrightarrow}} BP_s.$$
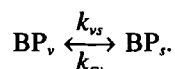
Here indexes v and s display molecules relation to the corresponding structural zone. Equilibrium condition for such exchange is

$$k_{vs}C_v = k_{sv}C_s, \text{ or } C_s = \left(\frac{k_{vs}}{k_{sv}}\right) C_v \approx \left(\frac{K''}{\alpha}\right) C \qquad (5.1)$$

(here C_s, C_v, C are BP concentrations in s- and v-zones and in the whole sample, respectively; α is mass part of intraglobular sponge filling; $K'' = (k_{vs}/k_{sv}) < 1$ is the constant of interzone equilibrium). It is rapidly set itself and is not disturbed by the reaction, the rate of which is significantly lower than that of BP molecules migration in micropores of the sponge zones of carcass micelles.
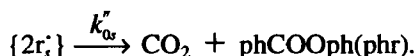
As it was mentioned, the acts of dissociation proceed in s-zones only and form initial radical pairs

$$BP_s \overset{k_{0s}}{\longrightarrow} \{2r_s^{\cdot}\}, \text{ where } r^{\cdot} \text{ is phCOO}^{\cdot},$$
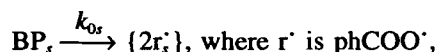
which partly decompose to free radicals

$$\{2r_s^{\cdot}\} \overset{k'_{0s}}{\longrightarrow} 2r_s^{\cdot},$$
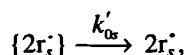
partly transform into phenyl benzoate

$$\{2r_s^{\cdot}\} \overset{k''_{0s}}{\longrightarrow} CO_2 + \text{phCOOph(phr)}.$$

Benzoyloxyls, when escaped the pair, react with PS, detaching hydrogen from tertiary atom of carbon polymer chain

$$r_s^{\cdot} \xrightarrow{k_{ls}(\text{CH}_{\text{tert},s})} rH + —\dot{C}(ph)CH_2 - (P_s^{\cdot}).$$
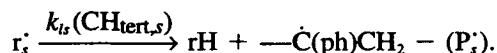
Backbone radicals $P_s^{\cdot}$, formed in this process, decompose with polymer chain breaking to fragments, which possess end unsaturated bonds and free valences

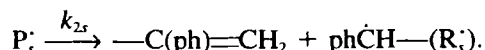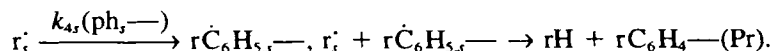$$P_s^\cdot \xrightarrow{k_{2s}} -C(ph){=}CH_2 + ph\dot{C}H-(R_s^\cdot).$$

These fragments recombine with benzoyloxyls

$$P_s^\cdot + r_s^\cdot \xrightarrow{k_{3s}} phCH(OCOph)-(Rr).$$

Moreover $r_s^\cdot$ radicals join phenyl cycles of PS

$$r_s^\cdot \xrightarrow{k_{4s}(ph_s-)} r\dot{C}_6H_{5,s}-, \quad r_s^\cdot + r\dot{C}_6H_{5,s}- \to rH + rC_6H_4-(Pr).$$

Change from plate to curved conformation, required on intermediate stage for phenyl ring, attached to s-segment, is performed owing to enough room of s-micropore.

Exhibited s-scheme reflects the ways of formation of all products of aerobic arylation, discovered by Haas, namely for benzoic acid rH, phenylbenzoate phr, broken macromolecules and benzoate polystyrene esters of two types, Pr and Rr. Acts of decarboxylation of $r_s^\cdot$ benzoyloxyls was not included into the scheme because they spend their lifetime adsorbed on segments of s-micropores (as every particle in supermicropores does).
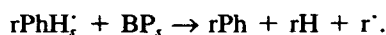
S-scheme also includes no acts of oxygen attachment to PS radicals. The absence of oxidative reactions of alkyl macroradicals, discovered in References 44–46, can be connected with structural factor. The fact is that as every low-molecular compound O_2 is preferably accumulated in narrow micropores of s-zones. There appears the inevitability to overcome obstacles, connected with the "sponge effect," which decreases frequency of O_2 penetration into s-micropores. Moreover, steric conditions in the pore impede interactions of $P_s^\cdot$ and $R_s^\cdot$ radicals, formed on rigid s-segments, with $O_{2,s}$ molecule which enters the pore. This molecule preferably exists on pore walls. Finally, the probability of non-oxidative transformations of $P_s^\cdot$ and $R_s^\cdot$ radicals increases significantly.

In condtions of quazi-solid dynamics of s-segments of carcass-sponge body, general amounts of s-radicals transforms without leaving their zones. Free valency transfer to v-zones of the sponge possesses low probability and requires help form movable particles.

In particular case such movable particle, which promote valency transfer, are BP itself and phenylbenzoate and benzoic acid formed in BP decomposition. Possessing phenyl nuclei (PhH), all of them can transform into σ-complexes through benzoyloxyl attachment.

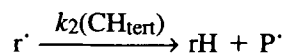$$r_S^\bullet + phCOO-X_s \text{ (PhH)} \xrightarrow{k_S} \text{(σ-complex)}-COO-X \quad (r\,PhH_S^\bullet).$$
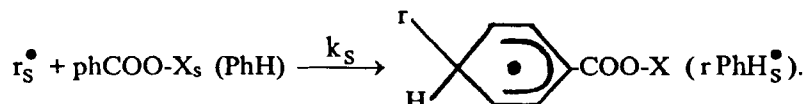
In its turn σ-conplex is able to induce BP decomposition
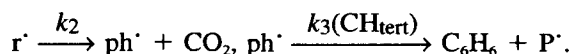
$$rPhH_s^\cdot + BP_s \to rPh + rH + r^\cdot.$$

If disposition of the attacked BP molecule is favourable in s-micropore, free valency possesses low probability for transer ot v-zone "on the back" of secondary (mobile) benzoyloxyl $r^{\cdot}$.

Migrating in micropores of v-zones benzoyloxyls detach hydrogen atoms from tertiary carbon atom of polymer chains

$$r^{\cdot} \xrightarrow{k_2(CH_{tert})} rH + P^{\cdot}$$

or is decarboxylated

$$r^{\cdot} \xrightarrow{k_2} ph^{\cdot} + CO_2, \ ph^{\cdot} \xrightarrow{k_3(CH_{tert})} C_6H_6 + P^{\cdot}.$$

The reactions of $r^{\cdot}$ radical mentioned require significantly lower activation energy, than the act of BP peroxide bond break, and, apparently, fluctuation activity of v-micropores is enough for them. We also an suppose that fluctuation pores create different probabilities for mentioned reactions, varying their sizes. In this case the poes of larger size should determine higher probability of $r^{\cdot}$ interaction with walls and higher yield of benzoic acid comparing with smaller fluctuation pores, in which excitation of decarboxylation acts prevails. It is significant that chain decomposition of BP in glassy polycarbonate and cellulose triacetate preferably gives benzoic acid[14] probably because significantly large and rigid segments of macromolecules of these polymers form the surface of v-micropores of the corresponding size. Opposite to this fact $r^{\cdot}$ radical in narrow v-micropore is preferably localised in its volume, the frequency of collisions with walls (and CH-bonds) decreases, and the probability of fluctuationally excited decarboxylation of it inceases, respectively.

Rigidity of the sponge carcass of v-zones and tightness of v-micropore room allows us to neglect the following processses in the v-scheme

1. Attachment of $r^{\cdot}$ and ph radicals to phenyl rings of PS (attachment requires bending of rings, rigidly mounted into rigid lattice);

2. Acts of polymer chains break through $P^{\cdot}$ radicals.

$P^{\cdot}$ radicals preserve probability of interaction with migrating molecules of BP, that induces chain arylation of PS:

$$P^{\cdot} + BP_v \xrightarrow{k_i} P—C_6H_4COOH + r^{\cdot}, \ P—ph + CO_2 + r^{\cdot}$$
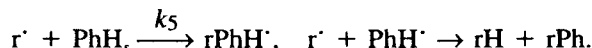
(we should emphasize that the present reaction is written down in analog with the reaction of liquid hydrocarbons arylation).

Termination of reactionary v-chains proceeds because of transfer of mobile radical to s-zone

$$r^{\cdot} \xrightarrow{k_4} r_s^{\cdot}$$
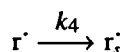
and its attachments to phenyl ring of additive phH-compound in v-micropore volume

$$r^\cdot + PhH_s \xrightarrow{k_5} rPhH^\cdot, \quad r^\cdot + PhH^\cdot \rightarrow rH + rPh.$$

The present scheme of transformation set key points of heterophase mechanism[14-20] and allows to display the reaction rate in elementary cell as the sum of local rates of BP decomposition in separate microphases. In this case specific rate of s-reaction, according to s-scheme, is

$$-\frac{dC_s}{dt} = k_{0s}C_s. \tag{5.2}$$

According to v-scheme specific rate of v-reaction is

$$-\frac{dC_v}{dt} = k_i[P^\cdot]C_v = (k_1 + k_2)[r^\cdot]. \tag{5.3}$$

Concentration of v-benzoyloxyls is determined from the equality of rates of initiation and termination of reaction v-chains:

$$[r^\cdot] = \frac{k_s[r_s^\cdot][PhH_s]}{(k_4 + 2k_5[PhH_v])},$$

and concentration of s-benzoyloxyls is obtained from balance of corresponding rates of s-reactions:

$$[r\cdot] = \frac{k'_{0s}k_{0s}C_s}{(k_{1s} + k_{4s})(k'_{0s} + k''_{0s})}. \tag{5.4}$$

Substituting concentrations of $r^\cdot$ and $r^\cdot_s$ into the Equation (5.3), we obtain specific rate of BP chain decomposition in v-zones

$$-\frac{dC_v}{dt} = \frac{(k_1 + k_2)k_s k'_{0s}[PhH_s]C_s}{(k_{1s} + k_{4s})(k'_{0s} + k''_{0s})(k_4 + 2k_5[PhH_v])}. \tag{5.5}$$

The interconnection exists between experimental and local rates, which we will disclose basing on the determination of concentrations

$$C_s = \frac{n_s}{m_s}, \quad C_v = \frac{n_v}{m_v}, \quad C = \frac{n}{m} = \frac{n_s}{m} + \frac{n_v}{m} = \frac{m_s C_s}{m} + \frac{m_v C_v}{m} \approx \frac{m_v C_v}{m} \approx \alpha C.$$

Here n_s, n_v, n is the number of moles of BP in s-, v-zones and in the whole sample, respectively; m_s, m_v, m is the mass of s-, v-zones and the whole sample, respectively; $\alpha = (m_s + m_v)/m \approx m_v/m_m$. Following this expression total rate of BP decomposition is

$$-\frac{dC}{dt} = -\frac{dC_s\left(\dfrac{m_s}{m}\right)}{dt} - \frac{dC_v\left(\dfrac{m_v}{m}\right)}{dt} = -\alpha\,\frac{dC_s\left(\dfrac{m_s}{m_v}\right)}{dt} - \alpha\,\frac{dC_v}{dt}.$$

Taking into account the expressions (5.2) and (5.5) we obtain that

$$-\frac{dC}{dt} = \alpha\left(\frac{m_s}{m_v}\right)k_{0s}C_s + \frac{\alpha(k_1 + k_2)k_s k'_{0s} k_{0s}[\mathrm{PhH}_s]C_s}{(k_{1s} + k_{4s})(k'_{0s} + k''_{0s})(k_4 + 2k_5[\mathrm{PhH}_v])}. \tag{5.6}$$

Let us express through concentration C of benzoyl peroxide the local concentrations C_s, $[\mathrm{PhH}_s]$, $[\mathrm{PhH}_v]$, which participate in (5.6) taking into account that a part of phenyl nuclei of BP is inoculated to the polymer during the reaction, and the equivalent amount of single-nuclear particles releases. Finally, the initial concentration of movable molecules is constant and all of them are preferable localized in v-zones:

$$C_v + [\mathrm{phr}_v] + [\mathrm{rH}_v] + [\mathrm{C}_6\mathrm{H}_{6,v}] = C_{0v} \approx \frac{C_0}{\alpha}. \tag{5.7}$$

Local concentrations of additive phenyl nuclei are connected with the concentration of molecules as follows:

$$[\mathrm{PhH}_s] = 2C_s + 2[\mathrm{phr}_s] + [\mathrm{rH}_s] + [\mathrm{C}_6\mathrm{H}_{6,s}], \tag{5.8}$$

$$[\mathrm{PhH}_v] = 2C_v + 2[\mathrm{phr}_v] + [\mathrm{rH}_v] + [\mathrm{C}_6\mathrm{H}_{6,v}]. \tag{5.9}$$

In this case it is natural to suppose that binuclear particles migrate in v-micropores twice slower than single-nuclear ones. Let us fix this fact in correlations of constants and equilibrium distributions of (5.1) type:

$$k'_{vs} = 2k''_{vs}, \quad k'_5 = 2k''_5, \quad K' = 2K'', \quad \frac{C_s}{C_v} = \frac{[\mathrm{phr}_s]}{[\mathrm{phr}_v]} = K'', \quad \frac{[\mathrm{rH}_s]}{[\mathrm{rH}_v]} = \frac{[\mathrm{C}_6\mathrm{H}_{6,s}]}{[\mathrm{C}_6\mathrm{H}_{6,v}]} = 2K'' \tag{5.10}$$

(here the number of strokes marks the number of phenyl nuclei in molecule). Owing to previous expressions, Equation (5.8) transforms to the following view:

$$[\mathrm{PhH}_s] = 2K''(C_v + [\mathrm{phr}_v] + [\mathrm{rH}_v] + [\mathrm{C}_6\mathrm{H}_{6,v}],$$

wherefrom we obtain, taking into account (5.7):

$$[\mathrm{PhH}_s] = \frac{2K''C_0}{\alpha}. \tag{5.11}$$

Despite the decrease of general content of nuclei because of their graft to PS, the

Equation (5.11) points out the preservation of unchangeable activity of phenyl nuclei in interzone translation of free valency.

Substitution of binuclear particles by more movable single-nuclear ones during the reaction provides also constant activity of PhH compounds in acts of reaction v-chain termination. It is the fact that the term $k_5[PhH_v]$ in denominator of (5.6) is displayed in the following view, taking into account expressions (5.9), (5.10) and (5.7):

$$k_5[PhH_v] = 2k_5''(C_v + [phr_v] + [rH_v] + [C_6H_{6,v}] = \frac{2k_5''C_0}{\alpha}. \qquad (5.12)$$

Finally, substituting (5.1), (5.8), (5.12) into (5.6), we obtain total rate of the reaction in the whole sample:

$$-\frac{dC}{dt} = k_0C + \frac{k_0aC_0C}{(1 + bC_0)}, \qquad (5.13)$$

where $k_0 = k_{0s}K''m_s/m_v$, $a = 2(k_1 + k_2)k_sk_{0s}'K''m_v/\alpha m_s(k_{1s} + k_{4s})(k_{0s}' + k_{0s}'')k_4$, $b = 4k_5''C_0/\alpha k_4$.

Expression (5.13) discloses the physical sense of empiric formulas (3.1)–(3.3) and their coefficients. In this case the incorrectness of Arrhenius Law, discovered by Haas in relation to effective constant k_0[44–46] (as similar incorrectness for coefficients a and b), probably reflects the influence of structural factor, translated through constants K'' and k_5''. It is temperature dependence of micropore sizes in the polymer-chain sponge.

The considered scheme takes off inconsistence between experimental results in papers[43] and References 44–46. The fact is that samples in Reference 43 possessed no dissolved oxygen, and the process of BP decomposition included both s- and v-reactions. Unlike Reference 43, the experiments in References 44–46 were performed at free access of oxygen, which inhibited chain reaction.[48,49] It should be mentioned that in liquid solutions oxygen does also inhibit chain decomposition of BP[21,39,47] because of alkyl radicals oxidation and absence of reaction ability for BP of peroxyls formed. However the inhibition mechanism in PS matrix is not in relation with the liquid one, because macroradicals were not oxidized in Haas experiments. apparently, interzone s, v-translation of free valency is excluded by oxidizing of σ-complexes, serving the translation in deaerated PS,

$$rPhH_s^{\cdot} + O_{2,s} \rightarrow rPh + HO_{2,s}^{\cdot}, \quad r_s^{\cdot} + HO_{2,s}^{\cdot} \rightarrow rH + O_2.$$

Owing to this fact chain processes of BP fragment losses for benzene and benzoic acid are moved, and the yield of PS benzoates increases.

Local rate of BP decomposition in Haas experiments should be characterised by the formula (5.2). At the recalculation for sample the rate is

$$-\frac{dC}{dt} = -\frac{\frac{m_s}{m} dC_s}{dt} = \left(\frac{m_s}{m_v}\right) k_{0s} K'' C = k_0 C,$$

and corresponding integral expression is

$$C = C_0 \times \exp(-k_0 t).$$

In this case according to s-scheme, acting in aerobic conditions, yields of the reaction products for dibenzoyl peroxide, decomposed during time t,

$$\Delta C_t = C_0[1 - \exp(-k_0 t)]$$

will be the following for PS benzoates, benzoic acid and phenylbenzoate, respectively:

$$\frac{([Pr] + [Rr])_t}{\Delta C_t} = \frac{mk'_{0s}}{(k'_{0s} + k''_{0s})m_s},$$

$$\frac{[rH]_t}{\Delta C_t} = \frac{mk'_{0s}k_{1s}}{(k'_{0s} + k''_{0s})(k_{1s} + k_{4s})m_s},$$

$$\frac{[phr]_t}{\Delta C_t} = \frac{mk''_{0s}}{(k'_{0s} + k''_{0s})m_s}.$$

Constants k_{0s} of BP dissociation and K'' of BP interzone exchange are absent in the present expressions, and numerators and denominators must similarly depend on temperature, if structure of polymer globules is constant during the experiment (i.e. at constant m_s and m). Then composition of the reaction products should not change in the temperature range of 329–363 K, where effective activation energy of decomposition (which, in fact, is the sum of dissociation E_{0s} and ΔH of interzone exchange) changes from 151 to 126 kJ/mol. This very constancy of the composition of aerobic reaction products of BP with PS was discovered by Haas.[44–46]

6. KINETIC FEATURES AND MECHANISM OF THE REACTION WITH PS IN PRESENCE OF STERICALLY HINDERED PHENOL

Sterically hindered phenols, 4-methyl-2,6-ditret-butylphenol (IH, ionol) in particular, inhibit BP decomposition induced by macroradicals of cellulose triacetate, polycarbonate, polyamide PA-548, but simultaneously catalyze a new chain reaction of BP decomposition in these polymers.[15,20,65]

We will consider appropriate features of transformations in polystyrene taking into account main reactions of sterically hindered phenols, disclosed in the works.[15,20,65] In this case we will compare theoretical conclusions with experimental results, ob-

tained fifteen years ago by V. P. Pustoshny together with one of the authors of the present work. These result were partly published in Reference 66 and were reported at the XV-th Collocvium of Danube countries on problems of natural and artificial aging of polymers.[67] We are reminded that in those experiments ionol and BP were introduced into PS from cooperative solution in methylene chloride. The samples were prepared as the films 15–20 μm thick. Unfortunately, the interesting facts discovered were not described theoretically, because the concept of heterophase mechanism was not formed yet.

It follows from the previous part that occurrence of conjugated reactions in the zones, inhomogeneous by micropore structure, requires translation of active radicals from s-zones into v-zones of sponge micelles. In absence of ionol this translation is performed with the participation of s-benzoyloxyls (which concentration is characterised by the Equation (5.4)) and movable particles PhH. In presence of ionol the reaction of promotion of s, v-translation occurs through the stage of formation of a new σ-complex:

$$r_s^{\cdot} + IH \xrightarrow{k_s'} (rIH_s^{\cdot}).$$
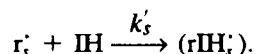
This complex is easily oxidized, transferring hydrogen atom of hydroxyl group to dibenzoyl peroxide

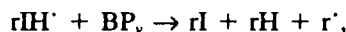$$rIH_s^{\cdot} + BP_s \rightarrow rI + rH + r^{\cdot}$$
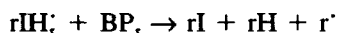
and increasing the probability of radicals $r^{\cdot}$ penetration into v-zones.

We should point out that new s, v-translation is performed simultaneously with the one, which is marked by constant k_s in the considered scheme, and that both ways of interzone chemical conjugation (with k_s and k_s') possess low probability and do not effect the expression (5.4).

Benzoyloxyls $r^{\cdot}$ preferably interact with ionol in micropores of v-zones, forming ionol σ-complexes

$$r^{\cdot} + IH \xrightarrow{k_6} rIH^{\cdot},$$
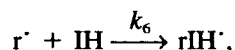
which induce chain decomposition of BP

$$rIH^{\cdot} + BP_v \rightarrow rI + rH + r^{\cdot},$$

or phenoxyls

$$r^{\cdot} + IH \xrightarrow{k_7} rH + I^{\cdot},$$
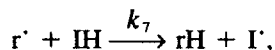
which participate in acts of reaction v-chains termination

$$r^{\cdot} + I^{\cdot} \rightarrow rI.$$

These acts proceed simultaneously with acts of termination, marked in the previous scheme by k_4 and k_5 constants.

Among these transformations of ionol we mention no reactions with alkyl macro-radicals $P_i^\cdot$, $R_i^\cdot$, $P^\cdot$, which we neglect because of their extremely low reactivity in relation to sterically hindered phenols.[68]

Combining all above-mentioned elementary acts with chemical acts of heterophase scheme of the previous part, we obtain broaden scheme of the process, which leads to the following expression of total rate of BP decomposition at application of the condition of steady state concentration of free radicals:

$$-\frac{dC}{dt} = \frac{\alpha k_{0s} C_s m_s}{m_v} + \alpha k_i [P^\cdot]C_v + \alpha k_6 [r^\cdot]C_{iv} = \frac{\alpha k_{0s} C_s m_s}{m_v} + \alpha(k_1 + k_2)[r^\cdot] + \alpha k_6 [r^\cdot]C_{iv},$$

(6.1)

where C_{iv} is ionol concentration in v-zones.

In the broaden scheme new balance of rates of initiation and termination of re-action v-chains determines new expression of v-benzoyloxyls concentration:

$$[r^\cdot] = \frac{(k_s [PhH_s] + k_s' C_{is} [r_s^\cdot]}{k_4 + 2k_5 [PhH_v] + 2k_7 C_{iv}},$$

(6.2)

here C_{is} is ionol concentration in s-zones.

Substituting (6.2) into (6.1) we obtain:

$$-\frac{dC}{dt} = \frac{\alpha k_{0s} C_s m_s}{m_v} + \frac{\alpha(k_1 + k_2)k_s [r_s^\cdot][PhH_s]}{k_4 + 2k_5 [PhH_v] + 2k_7 C_{iv}}$$

$$+ \frac{\alpha(k_6 C_{iv}[PhH_s]k_s + (k_1 + k_2)k_s' C_{is} + k_6 C_{iv}k_s' C_{is}[r_s^\cdot]}{k_4 + 2k_5 [PhH_v] + 2k_7 C_{iv}}.$$

(6.3)

It is easy to check that at substitution of zero concentration of ionol ($C_{iv} = C_{is} = 0$) in combination with the expression (5.4) into the Equation (6.3), it transits to (5.6) and, finally, to the formula (5.13), which describes the process in absence of IH. For sample possessing ionol in low concentration we already can apply inequality

$$(k_4 + 2k_5 [PhH_v]) < 2k_7 C_{iv},$$

which makes denominator of the third term in the Equation (6.3) more simple. Making necessary contractions and taking into account expressions (5.4), (5.7)–(5.12), (5.1) and condition of interzone equilibrium of IH, similar to (5.1),

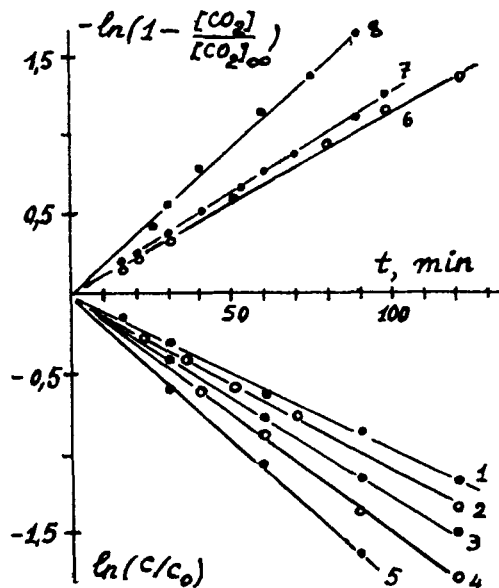$$C_{is} = \frac{K_i C_{iv}}{\alpha} \approx \frac{K_i C_i}{\alpha},$$

(6.4)

FIGURE 3   Semilogarithmic plots of BP decay (1–5) and CO_2 evolution (6–8) obtained at 372 K for the evacuated PS-films possessing with initial BP concentration of 0.016 (1, 4), 0.041 (2, 6), 0.33 (3, 7), 0.08 mol/kg (5, 8) and initial IH concentration of 0.09 (1–3, 6, 7), 0.35 mol/kg (4, 5, 8).

(here C_i is IH concentration, calculated for the whole sample), we finally obtain the following expression:

$$-\frac{dC}{dt} = k_0 C + \frac{k_0 a C_0 C}{(1 + bC_0 + gC_i)} + (M + NC_0 + PC)k_0 C = k_{IH}C, \quad (6.5)$$

here a, b, g, M, N, P are coefficients in the structure of effective rate constant k_{IH}.

Theoretical Equation (6.5) complies with the reaction of seeming first order by BP and qualitatively repeats the situation in ionol containing films of cellulose triacetate and polycarbonate.[14,66] Typical curves of BP decay in polystyrene in presence of IH are shown in Figure 3 in semilogarithmic coordinates, lines 1–5. According to the data of the Figure 3 the seeming first order of the reaction by BP is preserved at least, till 80% of decomposition. But in this case we obtain clear dependence of k_{IH} value on C_0 concentration of benzoyl peroxide and C_i concentration of ionol.

The dependence of relative constant k_{IH}/k_0 on initial concentrations of BP and IH, as a result of the expression (6.5), is characterised by the following formula:

$$\frac{k_{IH}}{k_0} = 1 + \frac{aC_0}{(1 + bC_0 + gC_i)} + M + NC_0 + PC_i. \quad (6.6)$$

This formula correlates well with experimental points, obtained at 372 K (Figure 4, curves 1–3). The following dimension coefficients were applied in calculations of curves 1–3 according to (6.6): $a = 280$; $b = 30$; $g = 2000$; $N = 7$; $P = 3.3$ kg/mol, and nondimensional coefficient $M = 0.2$. Here a and b preserve the same values as
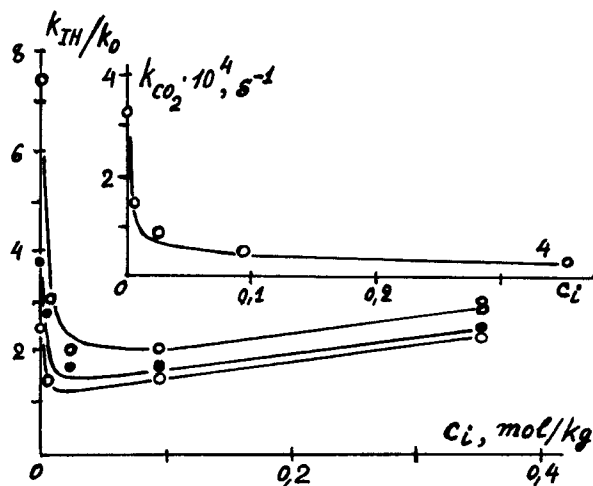
FIGURE 4 The relative rate constant of BP decomposition (1–3) and the CO_2 evolution constant (4) vs IH concentration, initial BP concentration are 0.004 (1), 0.016 (2) and 0.08 mol/kg (3, 4).

in absence of ionol in Equation (3.3), and M and N appear because of simplification of the formula (6.3) according to the condition

$$(k_4 + 2k_5[\text{PhH}_v]) < 2k_7 C_{iv},$$

which, however, loses its force at $C_i \to 0$.

Spread heterophase scheme explains the influence of IH on the rate of carbon dioxide formation in PS films, also. Reactions with CO_2 evolution, displayed in s- and v-schemes of the previous part, are characterised by the following local rates:

$$\omega^s_{\text{CO}_2} = k''_{0s}\{2r_s\} = \beta_s k_{0s} C_s \left(\text{here } \beta_s = \frac{k''_{0s}}{(k'_{0s} + k''_{0s})}\right),$$

$$\omega^v_{\text{CO}_2} = k_1[\text{r}^\cdot] = \beta_v(k_1 + k_2)[\text{r}^\cdot] \left(\text{here } \beta_v = \frac{k_2}{(k_1 + k_2)}\right).$$

Substituting Equation (6.2) into the expression of $\omega^v_{\text{CO}_2}$, we obtain

$$\omega^v_{\text{CO}_2} = \frac{\beta_v(k_1 + k_2)k_s[\text{PhH}_s][\text{r}_s^\cdot]}{k_4 + 2k_5[\text{PhH}_v] + 2k_7 C_{iv}} + \frac{\beta_v(k_1 + k_2)k'_s C_{is}[\text{r}_s^\cdot]}{k_4 + 2k_5[\text{PhH}_v] + 2k_7 C_{iv}}.$$

Here we simplify the second term using the inequality $(k_4 + 2k_5[\text{PhH}_v]) < 2k_7 C_{iv}$, and then substituting (5.4), we obtain

$$\omega^v_{\text{CO}_2} = \frac{\beta_v(k_1 + k_2)k_s[\text{PhH}_s]k'_{0s}k_{0s}C_s}{(k_4 + 2k_5[\text{PhH}_v] + 2k_7 C_{iv})(k_{1s} + k_{4s})(k'_{0s} + k''_{0s})}$$

$$+ \frac{\beta_v(k_1 + k_2)k_s' C_{is}k_{0s}' C_s}{2k_7 C_{iv}(k_{1s} + k_{4s})(k_{0s}' + k_{0s}'')}.$$

Total rate of CO_2 formation is obtained by summing up contributions of rates of s- and v-processes and taking into account expressions (5.1), (5.7)–(5.12), (6.4):

$$\frac{d[CO_2]}{dt} = \frac{\alpha m_s \omega_{CO_2}^s}{m_v} + \alpha \omega_{CO_2}^v = \beta_s k_0 C + \frac{\beta_v k_0 a C_0 C}{(1 + bC_0 + gC_i)} + \beta_\infty k_0 C$$

$$= k_{CO_2} = k_{CO_2} C_0 \exp(-k_{IH}t), \quad (6.7)$$

Here β_s, β_v, β_∞ are CO_2 yields in nonchain and both chain reactions induced by macroradicals and ionol, respectively. Integral kinetic equation, which follows from (6.7), is:

$$[CO_2] = \frac{k_{CO_2} C_0}{k_{IH}} [1 - \exp(-k_{IH}t)] = [CO_2]_\infty [1 - \exp(-k_{IH}t)] \quad (6.8)$$

It correlates well with experimental curves depicted in the Figure 3 (lines 6–8) in semilogarithmic scale, conformed to anamorphosis

$$\ln \left\{ \frac{[CO_2]_\infty + [CO_2]}{[CO_2]_\infty} \right\} = -k_{IH}t.$$

In this case it is significant that constant k_{IH}, calculated by tangent of curves 6–8 (Figure 3), possess the same value (in condition of equal values of C_i, C_0) as the ones, calculated according to anamorphosises of BP decay curves.

Effective parameter which participates in Equations (6.7) and (6.8):

$$k_{CO_2} = \beta_s k_0 + \frac{\beta_v k_0 a C_0}{(1 + bC_0 + gC_i)} + \beta_\infty k_0 \quad (6.9)$$

is experimentally determined by initial rates of CO_2 evolution from evacuated films:

$$k_{CO_2} = \frac{\omega_{CO_2}^0}{C_0}.$$

The results of corresponding measurements, performed by Pustoshny at 372 K, are shown in the Figure 4 (curve 4). As it is seen, curve 4, calculated with the application of previously found coefficients $\beta_s = 0.25$[44] and $\beta_v = 0.5$[50] as well as of newly obtained $\beta_\infty = 0.15$, correlates well with experiment. It can be said that accompanying calculated curves 1–3 (Figure 4), it connects together the results obtained in absence of IH[44,50] and in presence of IH in PS films.

The observed abrupt decrease on the initial parts of curves 1–4 (Figure 4) is stipulated by the decrease v-benzoyloxyls concentration as increase ionol content C_i

increase because of reaction chains termination on phenoxyls. In this case Equation (6.2) is transformed to the following view:

$$[r^\cdot] \rightarrow \frac{k_s' C_{is}[r_s^\cdot]}{2k_7 C_{iv}} \propto [r_s^\cdot],$$

when $[r^\cdot]$ concentration does not depend on C_i anymore because of equalizing of the rate of termination and catalysis of reaction chains with ionol, and chain decomposition of BP is generally performed by ionol σ-complexes $rIH^\cdot$.

Let us point out that benzoyloxyl σ-complexes of sterically hindered phenols in liquid solutions dissociate rapidly to initial $r^\cdot$ and IH compounds and do not promote further BP chain decomposition.[69,70] Test experiments, performed in this connection by Pustoshny with deaerated solution of BP and IH in tolyene (372 K, $C_0 = 0.023$, $C_i = 0.124$ mol/kg in sealed ampules), displayed nonchain reaction only with usual liquid rate constant $k_{0i} = 2.4 \times 10^{-4}$ s^{-1}, which does not depend on C_i.

Despite liquids, reverse dissociation of $rIH^\cdot$ to $r^\cdot$ and IH radicals in polymers is significantly suppressed by the force field form narrow micropores surface. It has been already mentioned during consideration of chain-sponge micelle properties that $rIH^\cdot$ particle, trapped by narrow pore, should be pushed into the pore volume, decreasing the number of collisions with walls simultaneously. As a result, $rIH^\cdot$ increases its stability to reverse dissociation, so competitive ability of oxidation acts of $rIH^\cdot$ by dibenzoyl peroxide increases, too.

It is necessary to point out one more feature of the reaction proceeding in polymer films. It is that concentration of ionol C_i participates in structure of effective constant k_{IH} (Equations (6.5), (6.7)) as constant value which does not change during BP decomposition. Real invariability of C_i was supported by spectra of IR-absorption of PS films, which contained 0.08 mol/kg of BP and 0.09 mol/kg of IH. These spectra displayed just insignificant decrease of light absorption by phenol OH-groups at 3620 cm^{-1}. (Such invariability is also characteristic for films of cellulose triacetate, polycarbonate and polyamide PA-548.) Apparently, polymers display ionol regeneration from the main products of their chain transformation rI, which possesses molecular structure as follows:
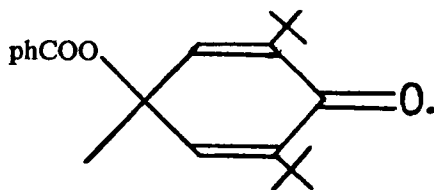
Compound rI, absolutely instable in liquid solutions,[70] probably dehydrogenates the polymer when v-micropores, occupied by rI, thermofluctuationally increase the sizes to wide super-micropores. Corresponding stage must be performed as hidden-radical ("cage") reaction, which proceeds subsequent to dissociation of rI compound during the lifetime of fluctuation short lifetime s-micropore. It can be presented as a sequence of acts of benzoyloxyl interaction with macromolecule and following phen-

oxyl disproportioning with macroradical. This results the formation of benzoic acid, IH and an unsaturated group on the polymer chain.

Finishing this paper we can conclude that heterophase mechanism of the chain process, formulated before, allowed us to connect features of chemical modification of PS in reaction with BP together with the features of the influence of sterically hindered phenol, ionol, on the rate of BP decomposition in the polymer matrix. Kinetic analysis, performed in the ranges of the present mechanism, of the known results in this field additionally interpreted hetrogeneous and heterophase chemical stages connected with specific structural organisation of "amorphous" polymer. As for the used model chain reaction of dibenzoyl peroxide, its application to block polymers was found very fruitful in relation to kinetic support of inhomogeneous structural zones in sponge micelles in the matrix of noncrystal polymer.

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