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Application of radical cage reactions in studies of microstructures of polymers and composites †

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Abstract. The potentialities of radical cage reactions as a tool for investigating the chemical structures of polymers are considered. The kinetic regularities of triplet carbene reactions in the matrix-isolated state and in clusters are analysed to reveal structural features of the cage surroundings. The possibility of determination of structural characteristics of filled polymers from kinetic data is discussed. The bibliography includes 103 references.

I. Introduction

The first ideas about the relationship between chemical kinetics and molecular organisation of media were formulated by academician N M Emanuel back in the 1960s. In particular, he initiated studies on the influence of the physical structure of polymeric systems on the kinetics and mechanisms of reactions which occur in them. These studies were aimed, on the one hand, at creating a theory of processes of polymer ageing [1] and, on the other hand, at the development of scientifically substantiated methods for their stabilisation and prediction of their lifetime under different operation conditions.[2] Numerous studies carried out in this direction have shown that kinetic regularities of the reactions occurring in solid polymers are functions of their physical-structural properties. In particular, the kinetics of such reactions is associated with the kinetics of molecular motions of macromolecules. Simple kinetic laws were found to be as a rule inapplicable for the description of chemical processes occurring in solid polymers at temperatures below ‡ the glass transition.[3–5]

The formal kinetic regularities of a chemical process in a condensed medium depend on the rapidity of changes in local medium properties, which influence the reactivity of the species involved, *i.e.*, on the relationship of three temporal parameters, *viz.*, the characteristic time of a chemical transformation (τ_{ch}), the lifetime (τ_l) of the process-controlling active centre and the correlation time (τ_c), which is sufficient for all the reactive species present in a given medium to pass through all possible states where they have different reactivities.[6] If the condensed medium is represented by solid polymers, the correlation time is much longer than the reaction time ($\tau_c \gg \tau_{ch}$), *i.e.*, dispersion of species as regards their reactivities is observed (such species are kinetically non-equivalent).[6] The observed process rate depends on the distribution pattern of the reacting species and its variation with time. In this context, the kinetics of even an elementary reaction in solid polymers is determined by a set of rate constants which characterise the reactivity of a species in a particular surrounding. The effect of local structural-physical properties of solid polymers on the kinetics of reactions occurring in them is the reason for the structural 'memory' of the reacting species on their initial distribution as a function of reactivity. Therefore, the kinetics of chemical reactions in polymers depend on the sample prehistory.[7]

Despite the complexity of the analysis of experimental results, kinetic studies of the reactions occurring in solid polymers are of a tremendous theoretical and applied interest. These offer a unique opportunity for elucidating peculiarities of the microstructures of these subjects, since the reaction kinetics is dependent on the initial polymer state and on changes in the distribution of reacting species over local structural parameters. The present review considers the validity of the approach to the estimation of structural-physical and molecular-dynamic characteristics of solid polymers based on the kinetic analysis of a series of pseudoelementary radical cage reactions, in particular, low-temperature decay of triplet carbenes, thermal dissociation of dimers of stable radicals as well as dissociation of macroradicals induced by nitrogen dioxide and salts of transition metals.

II. The choice of model reactions for the investigation of structural-physical properties of polymers

Certain difficulties are related to the choice of versatile model cage reactions, the kinetics of which may be purposefully used for structural studies of polymers. Apparently, this objective can be hardly achieved using complex free-radical processes, such as thermo- and photooxidation including migration of free valence, decay of macroradicals and reactions of oxidation products. The point is that it is difficult to isolate the stages sensitive to definite structural-physical properties of the matrix in these multistage

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† Dedicated to the blessed memory of academician N M Emanuel (1915 – 1984).

‡ As the temperature increases (above T_g) the intensity of molecular motions is enhanced and the 'solid-phase' formal kinetics approaches the conventional liquid-phase kinetics.

processes on the basis of measured kinetic parameters. Even the simpler reaction of thermal decay of radicals cannot always be used as a model. Thus, the death of macroradicals generated by low-temperature photolysis, radiolysis or mechanical impacts on polymers cannot be regarded as the versatile model suitable for the estimation of structural-physical properties, because in this case the mechanism of macroradical decay is rather complicated and may be accompanied by migration of the free valence over considerable distances as the result of diffusion and chemical relay-race. Numerous studies established a characteristic feature of this reaction in solid polymers, *viz*., its kinetic arrest at constant temperature or its 'stepwise' character.[6,8] The nature of this phenomenon was rationalised from different stands taking into account the structural-physical heterogeneity of the matrix,[9,10] differences in the interradical distances,[11] increased concentration of radicals in structural defects,[12] *etc*. However, the kinetic regularities observed in this process can be regarded only as an indirect indication to the dependence of the reactivity-based distribution of radicals on the structural-physical properties of polymers.

Direct analysis of the relationship between kinetic parameters and structural features of the nearest cage environments is confined to those reactions which are not complicated by migration of active centres over considerable distances. These types of processes include, for example, thermal decay of radical pairs (RP) in a cage. In most cases, RP are formed in low-temperature photolysis and γ-radiolysis of frozen solutions or polymers.[13] The radical pairs arising in radiolysis are sufficiently stable at the temperature of their generation, and processes of their recombination, disproportionation and their exit from the cage can be investigated in the thermal annealing of samples.

Kinetic studies of the RP formation during photodisintegration of a number of low-molecular-weight additives can be used, *e.g*., for the establishment of the mechanism of radical initiation in the solid phase. The radical pairs offer a unique opportunity for studying structural-physical properties of the medium. The interradical distances in such pairs can be measured directly by EPR spectroscopy. Thus it was established from the EPR spectra [14] that the mean distance between radicals in the RP generated in the photolysis of a solution of 3,6-di-*tert*-butyl-*o*-benzoquinone and diphenylamine in chlorobenzene changes from 0.62 to 0.64 nm (the accuracy of measurements was 0.005 nm) in the course of RP accumulation, which may be indicative of different geometry of molecular complexes from which these RP were formed.[15] The radical pairs formed under the action of light in monocrystalline matrices in the course of redox reactions involving molecular complexes of quinonediazides with catechols [16,17] also proved to be kinetically non-equivalent, as followed from the scatter of the rates of their decay during annealing. The solid-phase transfer of hydrogen atoms accompanied by the formation of RP stable at room temperature has been detected in quinone–catechol polycrystalline mixtures under the action of elastic wave pulses.[18–21] It was shown that in these systems the polymeric matrix decreases the threshold of the elastic wave strength required for the formation of paramagnetic products and enhances the RP stability. It was established [22] that the dispersion with respect to the interradical distances in RP is proportional to the difference between the maximum and minimum activation energies of their decay.

The kinetic non-equivalence of RP may be determined not only by the differences in the interradical distances, but also by the structural distinctions of the nearest surroundings.[23,24] Thus the kinetics of thermal dissociation of RP in oriented polyethylene is described by several rate constants, though the mean distance between the radicals ($r_m = 0.53$ nm) remains constant throughout the process. The formation of four types of RP was established in the low-temperature photolysis of single crystals of tetraphenylhydrazine.[25] Their formation results from disintegration of molecules differently oriented in a magnetic field. All the four types are characterised by identical magnetic properties but different rate constants of their decay.

The kinetics of transformation of the RP generated upon γ-irradiation of dimethylglyoxime and dimethylglyoxime-d_2 had been used for the determination of the constants of their decay, the kinetic isotope effect (KIE), the direction of the free valence migration and the distance of the hydrogen atom transfer.[26–28] Characteristic features of the free valence migration are its stereospecificity, anisotropy of the valence migration directions and sensitivity to weak molecular interactions.

The process of RP recombination does not require relocations of radicals to considerable distances but is rather sensitive to local molecular motions.[29] This allows the use of RP reactions for studies of structural transitions and characteristic frequencies of small-scale molecular mobility in a polymeric matrix. Thus in the temperature range from 160 to 260 K, the curves of RP defrosting in polyethylene revealed two structural transitions in the crystalline regions of the matrix. Structural and phase transitions can also be registered from the mean distance between radicals in RP over a wide temperature range.[13] Kinetic measurements of the exit of radicals from the cage allow determination of the frequency of translational motions.[23,30]

In principle, the abstraction of a hydrogen atom from the molecules of the medium by active radicals with the formation of a radical matrix can be used as a model of cage reactions.[25,30] Taking into account that the distance of hydrogen atom transfer is ~ 0.3 nm, one can presume that the kinetic features of this reaction should reflect directly the structural effect of the nearest cage surroundings. However, examples of kinetic studies of the RP reactions and hydrogen abstraction by radicals are mainly confined to the investigations of frozen solutions of low-molecular-weight compounds as well as of mono- and polycrystalline substances (see, *e.g*., Refs 31–33).

The effect of structural peculiarities of a polymeric matrix at the level of reaction cages on the kinetics of the reactions occurring in the matrix can be studied using the approach proposed by Denisov *et al*.[34–37] where the reaction of spatially hindered phenoxyl radicals with the hydroperoxide groups of macromolecules has been used for the development of a model of cage reactions

$$PhO^{\cdot} + ROOH \longrightarrow PhOH + RO_2^{\cdot}, \quad (1)$$

$$PhO^{\cdot} + RO_2^{\cdot} \longrightarrow \text{products}. \quad (2)$$

Reaction (1) is the rate-limiting one. This reaction is slow and is not limited by the diffusion of reagents in the case of regular distribution of radicals in the matrix.The phenoxyl radical and the hydroperoxide group enter the reaction cage and react only when they possess sufficient energy E and have a favourable mutual configurations. However, the walls of the cage prevent the achievement of such configuration, and the more 'rigid' the walls the higher the activation energy of the elementary reaction (1). To study the kinetics of this reaction, a stable nitroxyl radical as a spin probe was added along with a phenoxyl radical to the polymer. In this case, the rate constant of the reaction (1) correlated linearly with the frequency of the spin probe rotation (ν_r). Thus the activation energies of the nitroxyl radical rotation in polyethylene, polypropylene and chlorobenzene measured using the EPR spectra at 290–370 K were 28, 32 and 12 kJ mol^{-1}, respectively. The difference in the activation energies of the nitroxyl radical rotation in polymers and chlorobenzene virtually coincided with those for the reaction (1) in the polymer and chlorobenzene.

The results obtained permitted expression of the rate constant of the cage bimolecular reaction (1) in the form

$$k = \frac{6\nu}{n} K_{AB} P_r P \exp\left(-\frac{E_r + E}{RT}\right), \quad (3)$$

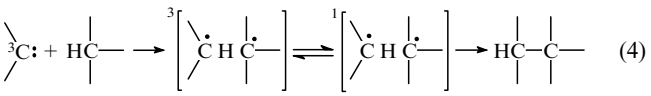
where ν and n are the frequency of collisions and the number of 'neighbours' in the cage, K_{AB} is the equilibrium constant of the

A + B pair formation in the cage, $P_r \exp(-E_r/RT)$ is the probability of rotation of the reagents in the cage resulting in the activated complex configuration and P is the steric factor of the reaction in the liquid phase.[36] Thus, the rotation frequency of the reagents in the cage and the frequency-related reaction rate constant characterise the cage surrounding of reagents in polymers.

Of special interest for studies of the microstructures of polymeric objects are versatile cage reactions which can be initiated in various matrices over a wide temperature range. In this connection, many possibilities are provided, *e.g.*, by radical processes such as low-temperature decay of triplet carbenes, macroradical dissociation reactions induced by nitrogen dioxide and photoreduction of transition metal salts and thermal dissociation of dimers of stable radicals.

III. Assessment of the structural-physical heterogeneity of polymers from the kinetics of thermal decay of carbenes

Carbenes are most often generated in thermal, thermocatalytic and photochemical degradation of diazo compounds.[38] The reactivities of the carbenes formed depend on their spin states.[39,40] Insertion into ordinary chemical bonds in a one-step mechanism and also stereospecific addition to double bonds with formation of cyclopropanes are typical reactions of carbenes in a singlet state. The triplet carbenes are also characterised by insertion reactions but these are multistep reactions. Let us consider the reaction of low-temperature decay of triplet carbenes in solid polymeric matrices.



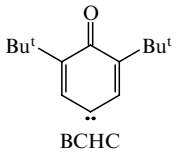
(4)

In the first step, the transfer of hydrogen atom§ from the surrounding macromolecules to a matrix-isolated triplet carbene results in the formation of a short-lived RP in the triplet state which then undergoes triplet–singlet conversion. The RP in the singlet state resulting from this conversion can recombine with formation of the final product of carbene insertion into the C–H bond of the macromolecule. The dynamics of H atom transfer and RP recombination in polymers depends on the polymer structure.

The frequency of the triplet–singlet transition in RP is $\sim 10^8$ s^{-1} (Ref. 41). It is known that the frequency of small-scale molecular motions associated with rotational oscillations of the side groups of macromolecules is of the same order.[42] Thus, the spin evolution of RP generated in reaction (4) is within the same time scale as the molecular dynamics, which determines dislocations and rotations of the side groups of macromolecules in the cage.

Numerous studies have shown that if the ground state of carbenes is triplet, then the efficiency of carbene transformations by the 'abstraction–recombination' mechanism (4) in the transition from the liquid to the solid phase with a decrease in temperature is drastically increased.[38,43,44] The effective constants of the decay rate of triplet carbenes determined experimentally at cryogenic temperatures are very small. For example, they amount to 10^{-3}–10^{-4} s^{-1} for different frozen organic matrices (Ref. 45).

One should note the principal distinction of the short-lived RP, appearing as active intermediates in the process of triplet carbene decay from the RP which can be registered owing to the characteristic EPR spectra in frozen solutions of low-molecular-weight compounds and polymers.[13] The former type includes the short-lived species whose lifetime in the cage is comparable with the time of their spin conversion ($\sim 10^{-8}$ s^{-1}). They cannot be recorded by the usual EPR method. However, the existence of such species is confirmed by the influence of the magnetic field on the decay rate of the triplet di-*tert*-butylcyclohexadienone carbene (BCHC) (at 77 K) in hexaethyldisiloxane, ethyl acetate, poly(methyl methacrylate) (PMMA) and cellulose triacetate (CTA).[46,47]



BCHC

The high decay rate of the intermediate RP formed in this process is determined by a small interradical distance (~ 0.3 nm) and retardation of rehybridisation of chemical bonds[48] in the radicals of the ion pair due to difficulties in structural relaxation. As a result of relaxation processes, such pairs can be transformed into RP of the second type ($r > 0.3$ nm) which are comparable with free radicals in their thermal stabilities.

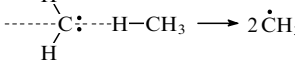
1. The effect of spatial orientation factors on the decay kinetics of carbenes in polymers

A characteristic feature of cage reaction (4) of low-temperature decay of carbenes in solid polymers is the kinetic non-equivalence of species.[49] The time dependence of carbene concentration (N) is described by the following expression:

$$N(t) = N_0 \int_{k_{min}}^{k_{max}} \rho(k) \exp(-kt) \mathrm{d}k, \qquad (5)$$

where $\rho(k)$ is the distribution function of carbenes over decay rate constants. It is natural to presume that the reactivities of carbenes depend on local orientations of the carbene centre and the C–H bonds of the macromolecular matrix in the cage, with a definite decay rate constant corresponding to each orientation. In the system of reaction cages, the distribution $\rho(k)$ changes with the gradual disappearance of carbenes which are best suited for the H atom transfer onto them. Because there is strong restraint of molecular motions in the solid matrix at low temperatures, the favourable orientations of carbenes are not recovered. This structural effect was illustrated by the dependence of the initial decay rate of diphenylcarbenes (DPC) in propanol at 77 K on the duration of their photoregeneration from diphenyldiazomethane (DDM).[50,51]

The results reported by Bauschlicher *et al.*[52] can be used for the theoretical substantiation of the decisive effect of carbene distribution over spatially oriented parameters on their kinetic non-equivalence in the insertion into the C–H bonds of the solid matrix. These authors calculated the ideal geometric configuration of the classical transition state, which corresponds to the minimum height of the potential barrier of the reaction of triplet methylene with a hydrogen molecule and methane. It was shown that hydrogen atom transfer over the trajectory lying in the methylene plane and passing along the bisecting line of the H–C–H angle corresponds to this configuration:



In this case the calculated height of the potential barrier was 103 kJ mol^{-1}. Upon changes in the geometric configuration of the transition state, *i.e.*, the deviation of the trajectory of the migrating hydrogen atom from the ideal one by 20–40°, the height of the potential barrier increased to 110 kJ mol^{-1}.

The decay kinetics of cyclohexadienone carbenes (CHC) in PMMA at 77–160 K is well described by the equation[53]

§ The transfer of an H atom requires the approaching of carbene and C–H bond of the macromolecule to a distance of 0.3–0.4 nm and it is these distances that are realised in the cage.

$$N(t) = N_0 \exp(-at^{1/2}), \quad (6)$$

where a is the temperature-dependent parameter. This equation also describes the decay of other carbenes in the glassy and polycrystalline matrices of low-molecular-weight compounds.[51, 54, 55] Kinetic equation (6) is derived from Eqn (5) where the distribution function $\rho(k)$ is expressed as:[56, 57]

$$\rho(k) = \frac{a}{k^{3/2}} \exp\left(-\frac{a^2}{4k}\right). \quad (7)$$

The distribution function (7) has a maximum at $k = a^2/6 = k'$. The latter value is the most probable magnitude of the rate constant. Thus, the observed kinetic regularities of the CHC decay in PMMA are explained by the distribution of decay rate constants over the species.

A different kinetic law was established for the decay of BCHC in PMMA.[58] In this case, the kinetic curves are linearised in the coordinates N/N_0 *vs.* $\ln t$. It is this kinetic description that is characteristic of the processes with a kinetic arrest, for which the function of distribution over rate constants has usually the form [59]

$$\rho(k) = \frac{1}{k \ln(k_{max}/k_{min})}, \quad (8)$$

where k_{max} and k_{min} are the boundary values of rate constants. Function (8) corresponds to a rather wide distribution of carbenes with respect to their reactivities, while the kinetic dependence satisfying this distribution is expressed as

$$N(t) = N_0 \left[-\frac{\ln(k_{min}t)}{\ln(k_{max}/k_{min})}\right]. \quad (9)$$

Yakimchenko and Degtyarev [57] noted that the distribution function (7) is approximated by function (8) for the values of $k > k'$, *i.e.*, where the distribution of species over rate constants is rather narrow: $\ln(k_{max}/k_{min}) < 10$. In this case, the k' value correlates with k_{min}, whereas the k_{max} value may be determined from the initial decay rate of carbenes.

The effect of the spatial orientation factor on the kinetic non-equivalence of carbenes results directly from comparison of the reactivities of CHC and BCHC. Thus at 77 K, the width of distribution regarding the rate constants of CHC decay $\ln(k_{max}/k_{min})$ is equal to 5, whereas the same parameter for BCHC is 13. Apparently, introduction of bulky *tert*-butyl substituents into the carbene structure increases the set of the carbene centre orientations relative to the C–H bonds of the surrounding macromolecules and largely expands the distribution of carbenes regarding their reactivities.

The temperature dependences of the rate constants of the H atom transfer to carbenes in polymers (*e.g.*, upon decay of DPC in PMMA) confirm the decisive effect of spatial orientations in the cages on the kinetic non-equivalence of carbene species, which is evidenced by an obvious deviation of these dependences (Fig. 1, lines *1* and *2*) from the Arrhenius law (dashed lines in Fig. 1). The effective activation energies decrease with a decrease in temperature from 12–16 kJ mol^{-1} to an abnormally low value of $\sim$ 5 kJ mol^{-1} (see Refs 49, 53, 58, 60–62).

The qualitatively similar temperature dependences were also observed for the cage reaction of hydrogen atom abstraction from the solid matrix molecules by free radicals following the tunnelling mechanism.[31, 63] This mechanism takes into account the intermolecular oscillations resulting in changes in the height and width of the potential barrier of the process.[31, 64, 65] The temperature dependences of rate constants in both processes can be expressed by the exponential law

$$k(T) = \alpha \exp(\beta T), \quad (10)$$

where α and β are the parameters characterising the properties of the species and the matrix.

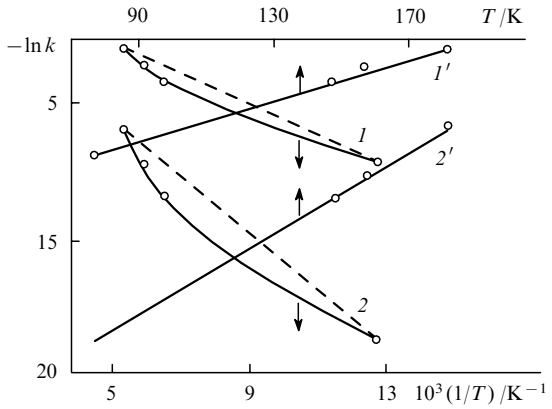
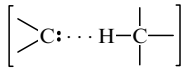


Figure 1. Temperature dependences of the rate constants of DPC decay in PMMA k_{max} (*1*, *1′*) and k_{min} (*2*, *2′*);[60] (*1*) and (*2*) dependences of the form $-\ln k \sim T$; (*1′*) and (*2′*) dependences of the form $-\ln k \sim (1/T)$.

It should be noted that the dependence (10) is well described by the tunnelling mechanism of H atom transfer for the entire series of carbenes, as indicated by the similarity of temperature dependences for k_{max} and k_{min}. The corresponding representations of k_{max} and k_{min} in the reaction of DPC decay in PMMA are presented in Fig. 1 (curves *1′* and *2′*). These results show that the kinetic non-equivalence of carbenes in polymers is due to the same reason, *viz.*, the scatter of parameters (the width and height of the potential barrier) of the tunnelling transfer of the hydrogen atom. The width of carbene distribution with respect to these parameters is in turn determined by geometric heterogeneities of the reaction cages.

According to the tunnelling model of H atom transfer, a bond of the hydrogen-bond type is formed between the C–H bond of the matrix molecule and carbene.



Molecular oscillations in this complex result in changes in the permeability of the potential barrier to H atom transfer. The higher the temperature the larger the amplitude of intermolecular oscillations and the closer the reagents can come to each other and, consequently, the more probable is the tunnelling process. Thus, the effective potential barrier decreases as the temperature increases, and the rate of the process increases accordingly. Vorotnikov *et al.*[61, 66, 67] determined the values of parameters for the tunnelling of H atom to CHC and DPC in the same polypiperylene matrix. The height U and the width x of the potential barrier as well as the equilibrium distance (R_0) between carbon atoms of the active centre of carbene and the C–H groups of polypiperylene in the carbene–polypiperylene complex were determined from the kinetic data obtained at 77–133 K. The boundary values of these parameters, which correspond to the maximum and minimum rate constants of carbene decay, are presented in Table 1. These results indicate that the width and height of the potential barrier decrease with the increase in temperature. These values are somewhat higher for DPC than for CHC, which is indicative of the higher CHC activity in the reaction of H atom abstraction in the same polymeric matrix.

Also worthy of note is the proximity of parameters of the hydrogen atom tunnelling from macromolecules to triplet carbenes and the corresponding values of parameters of the H atom tunnelling to macroradicals in their low-temperature decay by the relay-race mechanism.[65]

The frequencies of intermolecular oscillations in a polymer which activate the H atom transfer were estimated from the KIE determined for the low-temperature decay of BCHC and DPC in common and perdeuterated PMMA and polystyrene (PS). The

Table 1. Parameters of the hydrogen atom tunnelling from the polypiperylene molecules to CHC and DPC.[67]

Carbene	T /K	U_{min} [a]	U_{max} [a]	x_{min} /nm	x_{max} /nm	R_0^{min} /nm	R_0^{max} /nm
CHC	~0	150	208	0.115	0.140	0.375	0.400
	77	125	150	0.100	0.115	0.375	0.400
	133	108	121	0.094	0.100	0.375	0.400
DPC	~0	167	188	0.120	0.130	0.360	0.370
	77	138	159	0.110	0.118	0.360	0.370
	133	121	138	0.103	0.110	0.360	0.370

[a] In kJ mol^{-1}.

KIE was shown to be dependent on the reactivities of carbenes. Ensembles of carbenes characterised by higher decay rate constants manifest lower KIE at a given temperature. At $T > 100-115$ K, the kinetic isotope effect virtually disappears. The regularities observed are explained in terms of the model of H atom tunnelling across a potential barrier which oscillates due to intermolecular vibrations.

It was shown that for a temperature increase in the range

$$\frac{\hbar\Omega}{4k} < T < \frac{\hbar M\Omega^2}{m\omega_{C-H}k}$$

[Ω is the characteristic frequency of intermolecular vibrations in the complex, M is the normalised mass of the carbene–CH (or CD) group complex] the KIE should decrease linearly in reactions of hydrogen atom transfer in conformity with the equation

$$\ln\frac{k_H}{k_D} = \left[\frac{\Theta^{1/2}R_0^2(m_D^{1/2} - m_H^{1/2})}{2\hbar}\right] - \left[\frac{\Theta R_0^2 kT(m_D - m_H)}{2\hbar^2 M\Omega^2}\right], \quad (11)$$

where $\Theta = m_H\omega^2_{C-H} = m_D\omega^2_{C-D}$ is the parameter characterising the rigidity of the C–H and C–D bonds; R_0 is the distance between the potential wells for the H and D atoms. At higher temperatures

$$T > \frac{\hbar M\Omega^2}{m\omega_{C-H}k}$$

KIE varies in conformity with the T^{-2} law:

$$\ln\frac{k_H}{k_D} \approx \frac{\hbar}{2\Theta^{1/2}}\left(\frac{1}{m_H^{1/2}} - \frac{1}{m_D^{1/2}}\right)\left(\frac{M\Omega^2 R_0}{kT}\right)^2. \quad (12)$$

Analysis of KIE in the reaction of BCHC decay in PMMA [66, 67] was performed using relations (11), (12) and the condition $T \approx \hbar M\Omega^2/m\omega_{C-H}k$, under which the linear temperature dependence is transformed into a T^{-2} dependence. The derived values of characteristic frequencies of intermolecular vibrations ($\Omega \approx 53$ cm$^{-1} \approx 10^{13}$ s^{-1}) correlate with the Debye frequencies for molecular crystals.[68] The difference of distances ΔR_0 between potential wells in the reaction of H(D) transfer in different kinetic ensembles of carbenes was also determined from the temperature dependence of KIE.[48, 66, 69] It turned out that the decrease in the rate constant of BCHC decay by one order of magnitude corresponds to $\Delta R_0 \approx 0.006$ nm. Such a drastic rate dependence on the distance between reagents is in agreement with the tunnelling mechanism of H atom transfer to triplet carbenes.

Unique information about the nature of the kinetic nonequivalence of carbenes in solid polymers can be obtained from studies of the magnetic field effect (MFE). Numerous literature data (see, *e.g.*, Refs 70–72) demonstrate the possibility of using this effect for the establishment of a detailed mechanism of processes involving RP. The application of a magnetic field was shown [46, 67, 69] to influence noticeably the rate of low-temperature decay of BCHC in PMMA and CTA (Fig. 2); however, the character of this influence is different. Based on experimental dependences $W = f(H)$, the effect of magnetic field is explained by the strong exchange interaction J between unpaired electrons and short-lived RP.[71] From the character of MFE, one can draw a conclusion about the existence in polymers of a set of RP differing in energies of exchange interactions. Poly(methyl methacrylate) is more homogeneous than cellulose triacetate, which is reflected in a smaller set of cages with different exchange energies in the radical pairs. The distribution of RP with respect to J corresponding to the scale of the observed effect is determined by the orientational factor associated with different angles of rotation of the axes of the orbitals of unpaired electrons relative to each other in RP.[73]

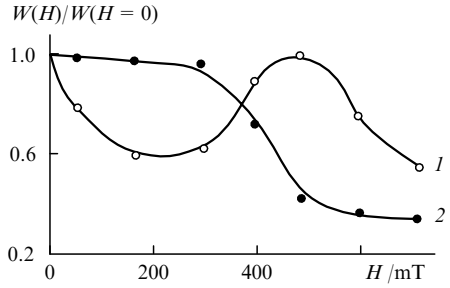
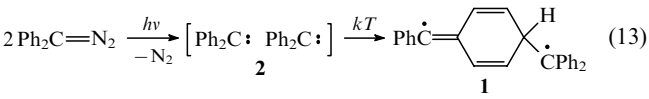


Figure 2. Effect of magnetic field on the rate of BCHC decay in PMMA (*1*) and CTA (*2*) at 77 K.[67]

The effect of magnetic field on the decay of carbenes in solid polymers is analogous to its influence on their decay in low-molecular-weight organic glasses; however, the scale of the MFE is different. This provides evidence that the extent of differences in the character of MFE is determined not only by the nature of RP, but also by the nature of the matrix. In low-molecular-weight glasses, the reaction cages are more homogeneous with regard to the structural-physical parameter J compared to polymeric matrices.

2. Determination of molecular-dynamic characteristics of polymers from the transformation kinetics of carbenes in clusters

Diazo compounds, like many low-molecular-weight additives, are irregularly distributed in solid polymers due to the existence of defects in the packing of macromolecules.[74] This leads to a higher concentration of diazo compounds in the regions with a decreased packing density of macromolecules, which can result in the formation of clusters. Thus EPR spectroscopy revealed that photolysis (at 77 K) of DDM in common and perdeuterated PMMA, PS and polycarbonate (PC) resulted in carbenes Ph_2C: formed in the matrix-isolated state and also biradicals **1** [75, 76] generated in the regions with a decreased packing density of macromolecules due to conversion of DPC dimers (**2**) in clusters according to the scheme



(13)

The EPR spectrum of biradicals generated in reaction (13) is shown in Fig. 3 *a*. It represents an anisotropic signal with the parameters of cleavage in a zero field $D_\perp = 11$ mT and $D_\parallel = 22$ mT. The mean distance between unpaired electrons is 0.63 nm. The formation of biradicals in reaction (13) is confirmed by the increase in their yields at higher DDM concentrations. At

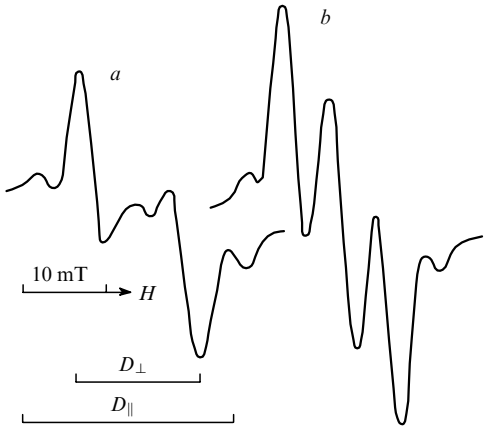
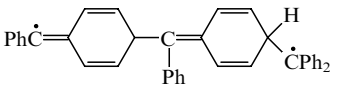


Figure 3. EPR spectra of biradicals generated in the photolysis of polymers supplemented with DDM at 77 K.[75] [DDM] (mol kg^{-1}): (*a*) 0.1; (*b*) 0.2.

sufficiently high [DDM] ($\sim$ 0.2 mol kg^{-1}) a signal of biradicals comprising three or more DPC fragments appears in the central part of the EPR spectrum (Fig. 3 *b*):



Such species arise in bulkier clusters, their proportion in PC and PMMA does not usually exceed 20% of the total quantity of biradicals.

Reactions of carbenes localised in clusters are interesting in two respects: the yield of biradicals **1** reflects the irregularity of the distribution of carbene precursors as regards their concentrations and this can also be used for the estimation of distribution of other low-molecular-weight additives as regards their concentrations in solid polymers. For example, an analogous distribution of bimolecular, trimolecular and larger clusters should apparently be expected for a number of photostabilisers, antioxidants and photosensitisers (salicylates, bisphenols, benzophenones).

In addition, the kinetics of biradical formation may be used to characterise the intensity of molecular mobility of the cluster surrounding. The kinetics of biradical generation in clusters at 77 – 120 K is well described by the logarithmic dependence on time. Analysis of experimental kinetic dependences performed by Davydov *et al.*[66, 75] made it possible to establish the distribution pattern of rate constants as regards the Arrhenius parameters. In general case, the reactivities of carbenes in clusters can be determined from the distribution with respect to both effective activation energies of reaction (13) and preexponents.[77]

Figure 4 shows the integral distribution functions $\Theta(E)$ and $\Theta(k_0)$ for the formation of biradicals involving DPC in polycarbonate. As the dependences shown in Fig. 4 are virtually linear, the functions of carbene distribution in clusters with respect to the Arrhenius parameters may be regarded as 'rectangular':

$$\frac{d\Theta(E)}{dE} = \frac{1}{(E_{max} - E_{min})}, \qquad E_{min} \leqslant E \leqslant E_{max};$$

$$\frac{d\Theta(k_0)}{d\log k_0} = \log\left(\frac{k_0^{max}}{k_0^{min}}\right), \qquad \log k_0^{min} \leqslant \log k_0 \leqslant \log k_0^{max}.$$

The limit values of the Arrhenius parameters in PC are as follows: E_{max} = 38 kJ mol^{-1}, E_{min} = 26 kJ mol^{-1}, $\log k_0^{max}$ = 14.4, $\log k_0^{min}$ = 12.8. The values of the activation energy are typical of the relaxation processes in RP determined by motions of monomer units of macromolecules. These values are in good agreement with the activation energies of the spin probe rotation.[78, 79] Thus, it may be concluded that the rate of reaction (13) in PC is controlled by the vibrational mobility of carbenes in clusters. Indeed, the values of $k_0 = 10^{13} - 10^{14}$ s^{-1} are comparable with the frequencies of motions of low-molecular-weight species in polymers. One should note a relatively narrow dispersion of the Arrhenius parameters in PC: ΔE = 12 kJ mol^{-1}, $\log k_0$ = 1.6.

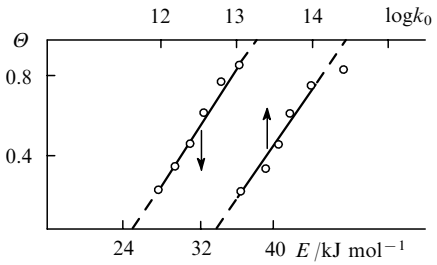


Figure 4. Integral functions of DPC distribution with respect to the Arrhenius parameters of biradical generation in PC.[75]

In PMMA, the limiting values of the Arrhenius parameters are as follows: E_{max} = 50 kJ mol^{-1}, E_{min} = 22 kJ mol^{-1}, $\log k_0^{max}$ = 16.0, $\log k_0^{min}$ = 10.5 kJ mol^{-1}. The mean values of these parameters (E_{mean} = 36 kJ mol^{-1}, $\log k_0^{mean}$ = 13.25) correlate with the activation energy of rotation and the correlation time of the spin probe in PMMA (E = 38 – 42 kJ mol^{-1}, $\log \tau$ = 13.2).[78] Of definite interest is a rather broad dispersion of parameters (ΔE = 28 kJ mol^{-1}, $\Delta \log k_0$ = 5.5), which seems to be due to a large set of molecular motions in PMMA at given temperatures. Indeed, the relevant calculations[80] show that the activation energy of rotational motions in the ester groups of PMMA with concomitant vibrations of the main chain segments near the equilibrium positions is 21.6 kJ mol^{-1}. This value correlates with the minimum activation energy of biradical formation. The activation barrier to rotation of the ester groups increases with the deviation of rotation angles of the main chain segments from their equilibrium values. Relevant calculations give a maximum potential barrier of 68 kJ mol^{-1} for the torque vibrations about the C – C bonds of the main chain.[80] Therefore, the increase in the activation energy of reaction (13) to 50 kJ mol^{-1} is indicative of the existence of ensembles whose reactivities are controlled by the mobilities of segments of the main macromolecular chain.

The results obtained[75, 76] make it possible to consider the reaction of biradical formation in DPC clusters as a specific probe for studying the molecular dynamics of macromolecules at low temperatures. The conventional method based on the use of a paramagnetic probe[79] is little suited for studies of molecular mobility in polymers at temperatures below the glass transition point. For $T < T_g$, EPR spectroscopy makes it possible to record only a part of the high-frequency spectrum of vibratory motions of the probe. The method based on measurement of the kinetics of DPC transformation in clusters extends considerably the temperature range for studies of the small-scale dynamics of macromolecules. This allows determination of molecular-dynamic characteristics of polymers in the temperature range 90 – 220 K where the use of other methods is problematic.

IV. Estimation of structural characteristics of filled polymers from the kinetics of cage reactions

Structural-physical modification of polymers at the macroscopic level has a strong effect on the reactivities of radicals in the cage. One of the most popular methods for the modification of the physical structure of polymers is to fill them with inorganic additives. Numerous studies have shown that the effect of polymer filling is associated with the formation of boundary layers[81 – 85] with structures noticeably different from the bulk structure of

polymeric medium. The effective width of the boundary layer measured experimentally was found to reflect the behaviour of the filled system in respect of the property under study, *i.e.*, this characteristic can be changed depending on the technique used for its measurement. Information about the boundary layers is as a rule derived from physicochemical parameters which are essentially dependent on the degree of filling, *e.g.*, from the heat capacity (in the range of glass transition temperatures),[86] density [83] and viscosity.[87] Due to a close relationship between the structural-physical properties of polymers and the kinetics of reactions occurring in them, investigation of kinetic dependences may also be regarded as an informative method for the determination of structural characteristics of filled polymers, in particular of the effective thickness of the boundary layers.

There is a large body of literature data devoted to the analysis of regularities of the thermal decay and thermal oxidation of filled polymers (see Bryk's monograph [88] and references cited therein). The available information points to a substantial role played by the filler in these processes. However, at high temperatures the kinetics can be influenced, in addition to the structural-physical factor, by the catalytic properties of the filler surface. From this viewpoint, the use of cage radical reactions occurring at low and moderate temperatures offers definite advantages for the estimation of the effect of the structural factor. The kinetics of these reactions should reflect peculiarities of the molecular organisation of boundary layers and the reactions must not be complicated by the interaction of radicals with the filler surface.

1. Effect of the filler on the kinetics of low-temperature decay of matrix-isolated carbenes

Filling of PMMA and TFC with Aerosil decreases the rate of low-temperature decay of BCHC in these polymers.[66, 89] This effect was observed at 100–140 K. The increase in the filler content decreases the limiting rate constants k_{max} and k_{min}; however, the width of the distribution as regards the rate constants $\log(k_{max}/k_{min})$ remains invariable and amounts to 6.8 in PMMA and 5.5 in CTA at 100 K. As the temperature increases, the distribution with respect to the constants becomes narrower. The constancy of the distribution with respect to the reaction rate constants under isothermal conditions is also confirmed by the approximation of the stepped kinetic curves to the equation

$$\frac{N}{N_0} = (1 + nk_0t)^{-1/n},$$

where n is the parameter characterising the distribution width of carbenes as a function of their reactivities and k_0 is the mean effective rate constant.[90] Despite different contents of Aerosil, the kinetics of low-temperature BCHC decay in PMMA and CTA is characterised by the parameter n which is constant at a given temperature.[69, 89]

Figure 5 shows the dependence of k_0 on the distance l between the filler particles. One can see from the graphs presented in Fig. 5 that k_0 varies little at $l > 20$ nm, though it decreases by more than one order of magnitude at $l < 20$ nm. Such a drastic drop of the process rate is related to changes in the physical structure of the polymeric matrix upon transition to the state of boundary layers. The structural rearrangement changes the ratio of the rates of individual stages of BCHC decay as well as the relative population density of the triplet and singlet states of the intermediate RP resulting from changes in their configurations and, consequently, in the exchange energies. All these factors lead to a lower k_0 constant. The kinetic data obtained indicate that the effective thickness of the boundary layers of the filler in PMMA and CTA ranges from 15 to 20 nm.

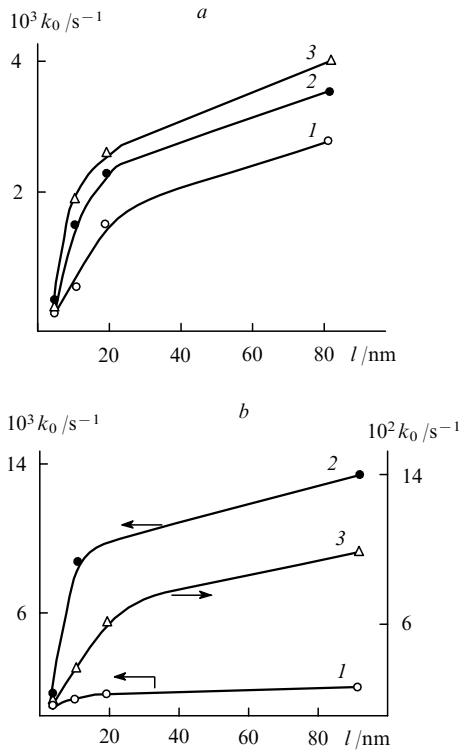


Figure 5. Dependence of the mean rate constant of BCHC decay on the distance between Aerosil particles in PMMA (*a*) and CTA (*b*);[89] (*a*) T = 100 (*1*), 113 (*2*), 125 K (*3*); (*b*) T = 100 (*1*), 125 (*2*), 135 K (*3*).

2. Effect of the filler on the kinetics of carbene transformation in clusters

In the example of filled PC, the reaction (13) of generation of biradicals in DPC clusters is shown to be noticeably influenced by the presence of a filler.[75, 76] Figure 6 shows the temperature dependence of the molecular mobility (the 'defrosting' curves), which reflects the reactivity of carbenes and biradicals in DPC clusters, on the Aerosil content in PC. The maximum quantity of biradicals is formed in the Aerosil-free PC at 130–150 K, while the molecular mobility is unfrozen for all ensembles of carbenes. In the filled samples, the maximum is shifted towards lower temperatures ($T \approx 120$ K), because at $T > 120$ K the biradicals

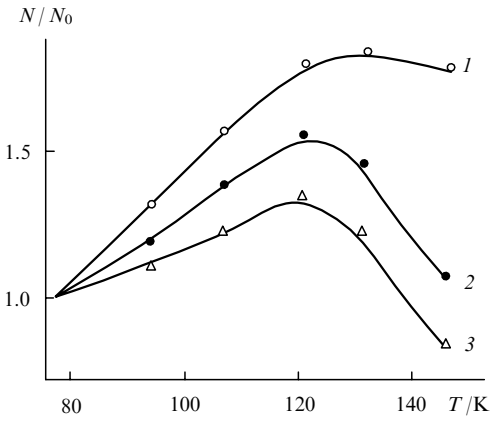


Figure 6. Temperature dependences of the yield of biradicals in the Aerosil-free (*1*) and Aerosil-filled (*2*, *3*) PC.[75] The content of the filler (mass %): 50 (*2*), 65 (*3*).

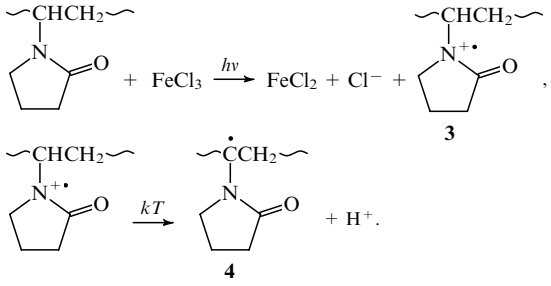
are thermally destroyed in these samples. The different time course of the unfreezing curves is determined by a considerable decrease in the thermostability of biradicals with the increase in the degree of polymer filling. The kinetics of biradical decay in PC at different filler contents may be used for the estimation of the effective thickness of boundary layers.[75] We give below the initial decay rates of biradicals (BR) in the filled PC at 146 K, relative to their initial concentration depending on the proportion (vol.%) of Aerosil V_a.

V_a (%)	0	22	30	40
$(W_0/[BR]_0) \times 10^4$ /s^{-1}	0.25	3	9	15

The non-additive character of the initial rate dependence on V_a and its dramatic increase at $V_a > 20\%$ are determined by the transition of the polymer to the structural state of the boundary layer. The boundary layer thickness was found to be 12 nm. This magnitude is rather close to the value derived from the filler effect on the decay kinetics of the matrix-isolated carbenes.

3. Effect of the filler on the transformation kinetics of macroradicals

Structural modification of polymers upon their filling is reflected in the kinetics of other elementary reactions, in particular of the monomolecular decay of macroradicals. Thus it was found that the kinetics of the radical decay of polyvinylpyrrolidone (PVP) initiated by photoreduction of Fe(III) additives at 77 K [49,91,92] is dependent on the presence of a filler.



(14)

Degradation of the radical cations **3** in the thermal stage results in the formation of macroradicals **4** which are identified from their EPR spectra. The effect of the Aerosil filler on the efficiency of generation of the radicals **4** is reflected by the unfreezing curves shown in Fig. 7. The maximum relative quantity of the radicals **4** is registered at 180–200 K. This characterises the proportion of their precursors, *viz*., radical cations **3**, which are stabilised in the low-temperature photolysis of samples. It follows from the plots shown in Fig. 7 that in highly filled PVP only 10% of the radical cations **3** are stabilised at 77 K, whereas their content reaches ~ 70% in non-filled samples. The non-linear character of variation of the radical concentration at a given temperature as a function of the filler content is determined by the structural transition occurring in PVP upon addition of definite amount of Aerosil, *i.e*., upon transition of the polymeric phase to the boundary layer state. The effect of structural modification on the efficiency of transformation of the radical cations **3** in reaction (14) is particularly strong where the amount of the filler is 50 mass%, which makes the distance between the filler particles equal to ~ 25 nm. This distance may be regarded as the effective thickness of the boundary layer. The observed effect seems to be caused by the formation of a looser molecular packing compared to that in the polymer bulk. The decrease in the molecular packing density favours the lowering of the energetic barrier to rehybridisation of the carbon atom [48] in macroradicals **4** from the sp^3 to the sp^2 configuration in the reaction (14). As a result, the activation energy of reaction (14) is decreased in the case of filled PVP compared to that in the non-filled polymer and the concentration of the radicals **4** increases accordingly in the photoinitiation at 77 K.

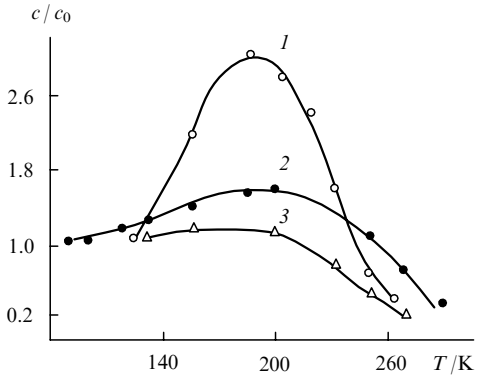
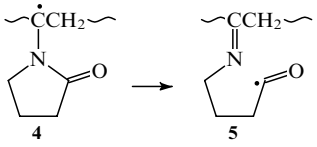


Figure 7. Temperature dependences of the yield of macroradicals **4** in the Aerosil-free (*1*) and Aerosil-filled (*2*, *3*) PVP. The filler content (mass %): 15 (*2*), 50 (*3*).[92]

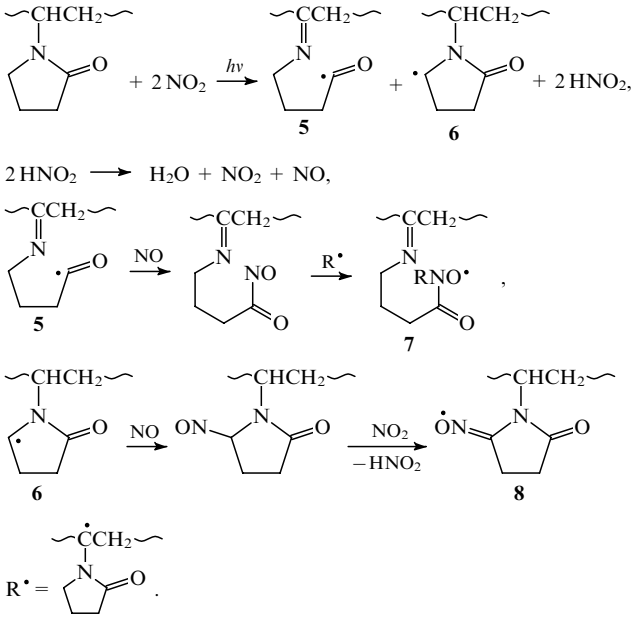
The application of the above reactions to the structural studies is limited to rather low temperatures. The expansion of the temperature range requires further search for radical reactions, the kinetics of which reflect the structural effect under conditions of usual and elevated temperatures and can be measured in a fairly simple manner.

From this standpoint, highly interesting are the reactions in which active radicals may be transformed into stable radicals which can be recognised by their characteristic EPR spectra. Thus dissociation of the radicals **4** leads to the pyrrolidone ring opening, which is accompanied by the formation of radicals **5**.



(15)

However, because of their low stabilities, radicals **5** could not be registered by EPR spectroscopy. For this reason, the course of reaction (15) was monitored by following the transformation of the radicals **5** into stable nitroxyl radicals under the action of nitrogen dioxide on the initial and Aerosil-filled (50 mass %) PVP.[93,94] Under these conditions, free-radical transformations of PVP occur according to the following scheme:[95]



These reactions result in the formation of two stable nitroxyl radicals, *viz*., **7** and **8**. The EPR spectrum recorded after exposure of PVP in NO_2 represents superimposition of the signals from these radicals (Fig. 8 *a*). The content of the radicals **7** is markedly

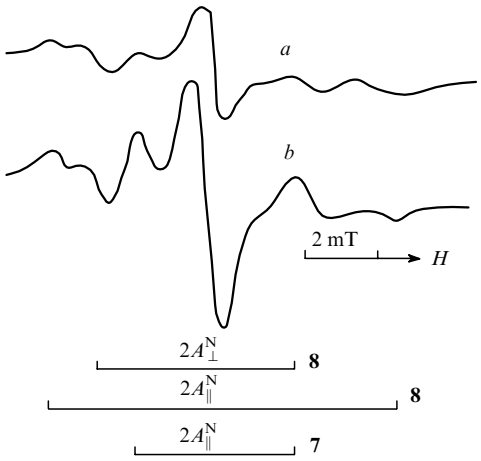
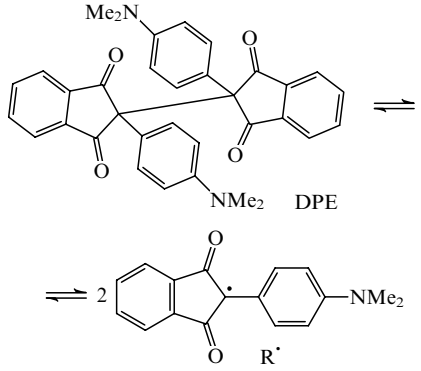


Figure 8. The EPR spectra of polyvinylpyrrolidone after its irradiation in the presence of NO_2.[94] (*a*) Aerosil-free PVP; (*b*) PVP with 50 mass % of Aerosil.

increased in highly filled PVP (Fig. 8 *b*). This fact points to an increase in the efficiency of formation of their precursors, *viz*., radicals **5**, in reaction (15) owing to a decreased density of molecular packing upon formation of boundary layers. Thus, the proportion of the signal from the radicals **7** in the overall EPR spectrum may be regarded as an indirect characteristic of the depth of the structural-physical modification of the filled polymer.

4. Kinetic features of the dissociation of radical dimers in filled polymers

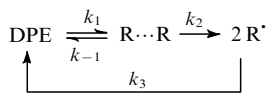
Structural characteristics of filled polymeric compositions can be estimated at relatively high temperatures using the cage reaction of thermal dissociation of diphthaloylethane (DPE) into two stable radicals.[96–98]



(16)

The reaction (16) is an equilibrium one in liquid state. However, kinetic studies of the DPE-free radicals system in CTA at 320–370 K pointed to a more complex mechanism of this reaction in the solid polymer matrix.[99, 100]

In the temperature range 320–334 K this process follows the scheme



In the first step, dissociation of DPE yields RP. The rigid cage surrounding it prevents the exit of radicals from the cage. Therefore, some radicals recombine in the cage, while those released into the bulk of the system are transformed into initial DPE as a result of diffusive collisions. At higher temperatures (344–364 K), the reaction scheme is different, which is related to the change in the mechanism of radical decay. In this case, the linear loss of radicals occurs instead of the quadratic loss.

$$\mathrm{DPE} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{R}\cdots\mathrm{R} \xrightarrow{k_2} \mathrm{R}^{\bullet} \xrightarrow{k_3'} \text{products.}$$

Taking account of the steady-state concentrations of RP and provided $k_{-1} \gg k_2$, the equations for the steady-state concentrations of radicals are expressed as

$$[\mathrm{R}^{\bullet}]_c = \sqrt{\frac{k_1 k_2 [\mathrm{DPE}]_0}{k_{-1} k_3}}, \tag{17}$$

$$[\mathrm{R}^{\bullet}]_c = \frac{k_1 k_2 [\mathrm{DPE}]}{k_{-1} k_3'}. \tag{18}$$

Structural modification of CTA upon its filling with Aerosil (up to 60%) influences the reactivity of the radicals $\mathrm{R}^{\bullet}$. This effect is demonstrated in Fig. 9, which shows the temperature dependences of the steady-state concentration of radicals in the original and Aerosil-filled CTA. At $T > 340$ K, the concentrations of $\mathrm{R}^{\bullet}$ in the filled samples are higher than those in the Aerosil-free samples. However, the reverse temperature dependence is observed in the high-temperature range. The increase in the steady-state concentration of radicals in the filled CTA at 320–344 K is associated with the decrease in the efficiency of radical decay and lower values of the parameters $k_{-1}k_3$ and $k_{-1}k_3'$ relative to the parameter k_1k_2 in equations (17) and (18). This is also evidenced by the results of measurement of the temperature dependence of the correlation time of the spin probe rotation.[99, 100] The effective activation energy of the probe rotary mobility increased from 4.6 kJ mol^{-1} in non-filled CTA to 7.6 kJ mol^{-1} in CTA containing 60 mass % of Aerosil, *i.e*., filling has a substantial effect on the molecular dynamics and hence on the ratio of rate constants in individual stages of the radical process.

Figure 9 shows that the temperature coefficient of the change in $[\mathrm{R}^{\bullet}]$ variation becomes negative for the highly filled CTA at $T > 340$ K. In CTA containing 30 mass % of Aerosil, an intermediate situation is realised in which only a decrease in the efficiency of radical formation was observed as the temperature was increased. These facts indicate that structural modification upon filling influences most effectively the decay of radicals. It is for this reason that the inversion of the dependence shown in Fig. 9 is observed in the region of transition of the quadratic decay of radicals to the linear one. The mean distance between the filler particles in CTA with 60 mass % of Aerosil is estimated as ~ 10 nm. This distance corresponds to the overlapping of boun-

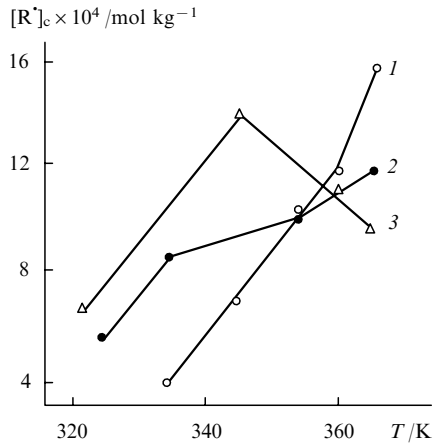


Figure 9. Temperature dependence of the mean radical concentration upon dissociation of DPE in Aerosil-free (*1*) and Aerosil-filled (*2*, *3*) CTA.[100]
Aerosil content (mass %): 30 (*2*), 60 (*3*).

dary layers and transition of the entire polymer to a new structural state. Thus, the exit of stable radicals from the cage in the process of thermal dissociation of DPE is rather sensitive to changes in the molecular organisation upon filling of the polymer and can characterise the degree of its structural-physical modification.

V. Conclusion

The kinetics of radical cage reactions demonstrates their clear-cut dependence on the physical structure of solid polymers and filled compositions. A distinctive feature of the processes considered above is their versatile character as regards their possible implementations in diverse polymers and composites over a wide temperature range (77 – 350 K), *viz*., from cryogenic to relatively high temperatures. A strong dependence of kinetic parameters on structural factors makes it possible to use such reactions as a sensitive tool for estimating the structural-physical modification of polymers. The results of kinetic studies of radical reactions in polymers can also be of independent significance in designing kinetic models of chemical processes characterised by their spatial-temporal disorder.[101 – 103]

Based on the results obtained up to now, it may be concluded that the kinetic regularities of the processes considered reflect physical structures of polymers both on local levels as well as on the scale which is much larger than the sizes of reaction cages. This is evidenced primarily by the results obtained in the studies of the reactions of triplet carbenes. For example, the effect of magnetic field on the kinetics of their low-temperature decay is determined by the distribution of intermediate RP with respect to geometric configurations defined by the nearest cage surrounding. It should be noted that the kinetics of this cage process is rather sensitive to relatively large-scale structural changes which involve the 15 – 20 nm thick interface layers in filled polymers.

The use of the above 'kinetic' approach in studies of the physical structures of polymers is undoubtedly limited. Today, based on the results obtained, one can speak solely about the possibility of comparative estimation of the extent of structural-physical modification reached in a definite way in a given polymeric material. Thus the dependences of kinetic parameters on the content of a filler may be instrumental in the establishment of polymer transition to a qualitatively different structural state (highly filled polymer) in which the boundary layers begin to overlap. Analogous conclusions about changes in the physical structure may be drawn by measuring yields of definite radicals in the reactions under study. In some cases, kinetic parameters can characterise indirectly the frequencies and energetics of the small-scale molecular mobility.

The difficulties encountered in the attempts to elucidate structural peculiarities based on kinetic data are often due to the fact that the mechanisms underlying the effect of molecular organisation of polymers on the reactivities of the reactants are obscure. Further search for processes which mimic the relationship between the kinetics and the physical structure seems to be in order. The search for the correlation between kinetic parameters and morphological forms of polymers determined by modern physical methods is of great significance for the advance in this direction.

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