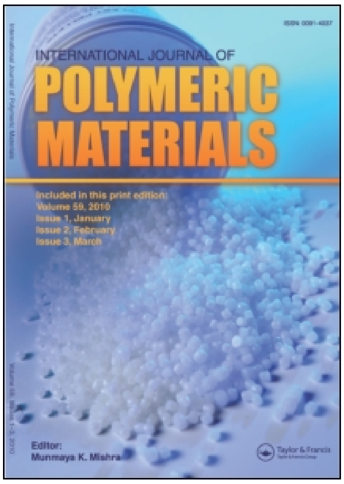

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Davydov, E. Ya. , Vorotnicov, A. P. and Toptygin, D. Ya.(1990) 'Influence of Structure-Physical Properties of Polymer Matrix on Kinetics of Inside Cell Radical Reactions', International Journal of Polymeric Materials, 13: 1, 187 — 194

To link to this Article: DOI: 10.1080/00914039008039473

URL: http://dx.doi.org/10.1080/00914039008039473

Intern. J. Polymeric Mater., 1990, Vol. 13, pp. 187–194
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Printed in the United Kingdom

Influence of Structure-Physical Properties of Polymer Matrix on Kinetics of Inside Cell Radical Reactions

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In polymethylmethacrylate and cellulose acetate the kinetics of triplet cyclohexadienone carbenes decay by 77–135 K including a hydrogen atom transfer from C—H bonds of macromolecules with the radical pair formation was examined. The kinetics of this process reflects the influence of peculiarities on a level of cells. The influence of external magnetic field on the decay of carbenes was established. The character of the magnetic is different in two polymers. It's determined by the cell recombination efficiency of radicals and the exchanged energy in radical pairs depending on mutual radical configurations. The structure-physical modification of polymers by aerosil filling connected with the formation of interfaces influences strong on the rate of carbenes conversions.

KEYWORDS: Radical reactions, cage effects, structure-physical properties, kinetics, mechanism, redical pairs

The reactions of radical pairs (RP) play the important role in chain free radical processes of the polymer degradation. The mechanism of RP conversion determines the efficiency of the initiation and the probability of the kinetic chain termination. It is known that in solid polymers the kinetics of radical reactions is connected with the physical structure of a matrix. Kinetic investigations of RP conversions represent the great interest to obtain informations about a physical structure on a level of elementary cells. The elucidation of the influence kind is important both to develop the radical reactions theory and to work out effective methods of polymer materials stability.

The decay of triplet carbenes in polymers by low temperatures is the example of the reaction with RP participation which includes the stage of the hydrogen atom transfer from C—H bonds of macromolecules on carbenes.[1] In this report kinetics dependences of triplet cyclohexadienone carbenes (CHC) conversions on the external magnetic field and the structure-physical modification by the filler are considered in polymethylmethacrylate (PMMA) and cellulose acetate (CA).

CHC were generated by photolysis ($300 < \lambda < 400$ nm, 77 K) of 2,6-ditretbuthylquinonediazide (QDA) in vacuum. The kinetics of CHC decay by

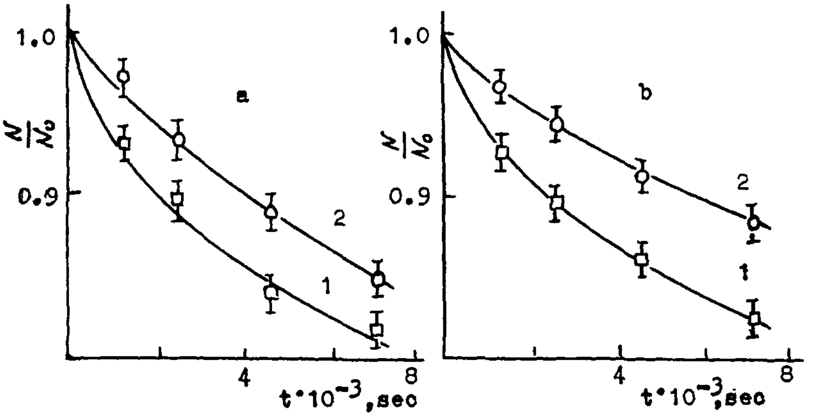

FIGURE 1 The kinetics of CHC decay (77 K) in PMMA (a) by zero (1) and 300 mT (2) fields and in CA (b) by zero (1) and 500 mT (2) fields.

77–140 K was studied by the decrease of ESR spectrum.[2] To investigate the magnetic field effect films of 50 μ thickness with QDA (~0.1 M) were used. As the filler the aerosil was used with the specific of 300 m^2/g and the particles size of 20 nm. The filled samples were prepared from 2% solution of polymers in chloroform containing the warmed 400°C aerosil. The QDA concentration in samples with the any filler quantity was composed ~0.1 M.

In Figure 1a, b kinetic curves of CHC decay by 77 K in zero and external magnetic fields are shown. The magnetic field as seen from figures influences noticeable on the process rate. As a characteristic of magnetic effects the time of 10% carbenes conversion in the magnetic field relatively that in the zero field ($W_H/W_{H=0}$) was chosen.

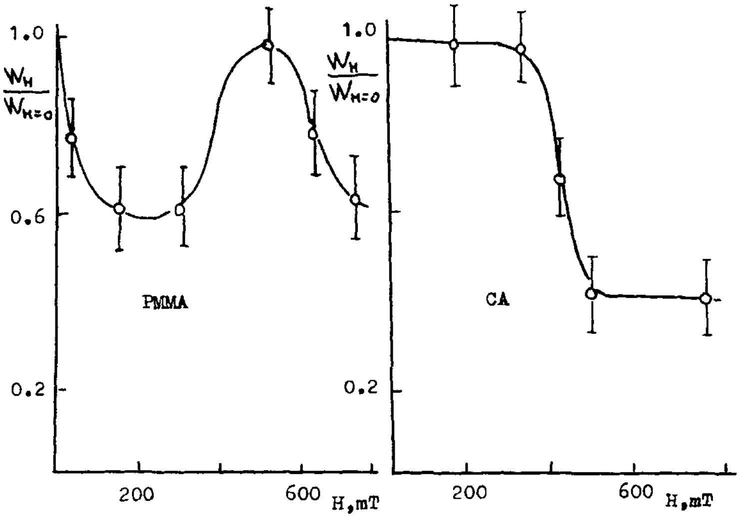

FIGURE 2 The rate dependence of CHC decay on the magnetic field strength.

Figure 2a, b give experimental dependences of $W_H/W_{H=0}$ in PMMA and CA. IN PMMA the magnetic effect has the maximum in zero and ~500 mT fields. In CA the rate is constant in the field region of 0–300 mT but in 300–500 mT the rate decrease was observed. To explain the magnetic effect one can propose the next mechanism that is analogous to Ref. 3.

In the primary stage of the hydrogen atom transfer on CHC the triplet RP is formed in which a singlet-triplet evolution takes place. RP in the triplet state are transformed into initial triplet carbenes by the back transfer and are able to recombine in the singlet state. Taking into consideration the steady state for RP one can obtain the following equation for the effective rate constant of CHC decay

$$K_{ef} = \frac{K_1}{\dfrac{K_{-1}P_T}{K_2P_S} + 1} \tag{2}$$

The efficiency of RP recombination influencing on the rate of CHC decay is determined by K_{-1}/K_2 and the relative population of triplet (P_T) and singlet (P_S) levels of pairs. There are very great differences in absolute values of K_2, K_{-1} and K_1 constants. This conclusion follows through the magnetic effect for the carbenes decay. In fact constants of RP conversions must be compared with the S–T transitions frequency ($\sim 10^8\,\mathrm{sec}^{-1}$). On the other hand K_{ef} in the polymer by 77 K is $\sim 10^{-4}\,\mathrm{sec}^{-1}$. Because of $K_{-1}P_T/K_2P_S$ values in different patterns are $1\text{–}30^3$ one can consider the primary hydrogen atom transfer (K_1) as the limiting stage of Ref. 3. This stage includes apparently the creation of CHC and C—H bonds favorable mutual arrangements for what a some energetic barrier must be overcome.

In the magnetic field the triplet level of RP is split by Zeeman interaction (T_0, T_+, T_-) therefore the probability of singlet-triplet transitions is changed. In enough great magnetic fields T_0 and $T_\pm$ sublevels are not mixed during spin evolutions. By these conditions the effective rate constant of CHC decay is the average meaning of effective constants corresponding to conversions of RP which are formed in primary acts on T_0, $T_\pm$ sublevels. Then Eq. (2) is transformed into

$$K_{ef} = K_1\varphi(H) \quad \text{where} \quad \varphi(H) = \frac{1}{3}\left(\frac{1}{\dfrac{K_{-1}P_{T_0}}{K_2P_S}+1} + \frac{1}{\dfrac{K_{-1}P_{T-}}{K_2P_S}+1} + \frac{1}{\dfrac{K_{-1}P_{T+}}{K_2P_S}+1}\right) \tag{3}$$

In (3) relative spin populations P_{T_+}/P_S and P_{T_-}/P_S depend on the magnetic field.

Figure 2a, b show unmonotonous dependences in which essential changes of the rate take place inside enough narrow field regions. Such character of field dependences indicates that the magnetic effect is connected with the exchanged interaction (J) of nonpair electrons in RP. In the field region determined by the resonance condition $2J = g\beta H/\hbar$ the intersection of T_+ or T_- and S levels and consequently the sharp rise of S level population are possible. This results in the observed increase of CHC decay rate.

On the base of the model examined approximate estimations of exchanged energies and the cell recombination efficiency were made. The relative spin populations of triplet and singlet levels in the magnetic field $P_T/P_S = 1 - P_S/P_S$ one can calculate by Eqns[4]

$$P_S(T_0 \leftrightarrow S) = \frac{a^2/8\tau^2}{1 + (a^2/4 + 4J^2)\tau^2} \tag{4}$$

$$P_S(T_\pm \leftrightarrow S) = \frac{a^2/4\tau^2}{1 + [a^2/2 + (2J + a/4 \mp g\beta H/\hbar)^2]\tau^2} \tag{5}$$

where τ is the life time of RP, a is the effective average square constant of STI. In a solid phase by low temperatures one can consider that $a^2\tau^2 > 1$. Then from (4) and (5)

$$\frac{P_{T_0}}{P_S} \simeq \frac{8}{a^2}(2J)^2 + 1 \tag{6}$$

$$\frac{P_{T_\pm}}{P_S} \simeq \frac{4}{a^2}(2J + a/4 \mp g\beta H/\hbar)^2 + 1 \tag{7}$$

Figure 3 shows dependences of the average RP recombination probability $\varphi(H)$ calculated by Eqns (3), (6) and (7). The shape of these curves depends on J and K_{-1}/K_2. By J compared with effective constants of STI ($J \leqslant 10$ mT) $\varphi(H)$ decreases monotonous to a plato and $\varphi(H_\infty) \simeq \varphi(H = 0)/3$. By enough great values of exchanged energy ($J \gg a$) the depndence has the maximum because of the S level population increase in RP by $H = 2J/\hbar g\beta$. If K_{-1}/K_2 is increased calculated dependences become more sharp and on the contrary.

The comparison of calculated dependences with the experience had showed that in PMMA the magnetic effect is described satisfactory by a supposition of two exchanged energy values: $2J \simeq 0$, $2J = 8.8 \cdot 10^{10}$ rad/sec. It was assumed that in PMMA $K_{-1}/K_2 = 1.6 \cdot 10^{-4}$. In CA the set of RP exists having $2J$ values from

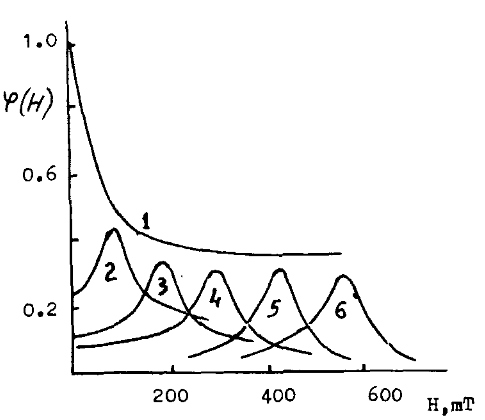

FIGURE 3 The dependence of RP recombination probability on the magnetic field strength by $2J = 0(1)$, $1.7 \cdot 10^{10}(2)$, $3.5 \cdot 10^{10}(3)$, $5.2 \cdot 10^{10}(4)$, $7.0 \cdot 10^{10}(5)$, $8.8 \cdot 10^{10}$ rad/sec (6); $K_{-1}/K_2 = 1.8 \cdot 10^{-3}$.

0 to $2J_{\max} \approx 7.0 \cdot 10^{10}$ rad/sec. The maximum value corresponds to the field in which the rate decrease is observed. The experimental magnetic effect in CA can be approximated by calculated dependences $\varphi(H)$ if to divide the exchanged energies region by five values $2J = 0$, $2J_{\max}/4$, $2J_{\max}/2$, $\frac{3}{2}2J_{\max}$, $2J_{\max}$ and if to consider $K_{-1}/K_2 = 1.8 \cdot 10^{-3}$.

Thus received date show the influence of the polymer matrix nature on kinetic dependences of the cell reaction from an external magnetic field. This effect is connected with differences of RP exchanged energies caused by differences of mutual radical configurations.[5] The reaction cells of CA are more unhomogeneous comparatively with PMMA. Such structure of CA cells results in the great exchanged energies set of unstable RP. The comparison of K_{-1}/K_2 values in PMMA and CA indicates also essential differences of the cell structure.

In this connection the influence of structure-physical modification of the matrix can be expected on the given process kinetics. It's known that the addition of a mineral filler causes the interfaces formation differing by the physical structure from the polymer phase in the volume. The maximum effect of structural changes is observed by some filler quantities when the polymer binder is turned into interface states fully.

Figure 4a, b show kinetic curves of CHC decay in PMMA and CA containing up to 65 weight parts of the aerosil. From these figures it's seen that the filler presence reduces essentially the rate of CHC conversion in that and other polymers. The filler effect is observed in all examined temperature region. The kind of the kinetic curves shows the evidently expressed kinetic unequivalence of CHC. The analysis of experimental dependences was carried out according to Eq.[6]

$$\frac{N}{N_0} = (1 - nK_0 t)^{-1/n} \tag{8}$$

where K_0 is the average effective rate constant of CHC decay and n is the number characterizing the distribution width by effective rate constants ($n > 0$). By 100–140 K kinetic curves are straightened satisfactory in coordinates of Eq. (8) $(N/N_0)^n - t$. As the example in Figure 5a, b anamorphoses of Figure 4a, b curves are shown in these coordinates.

Values of kinetic constants obtained by means of such analysis are collected in table. When the filler share is raised K_0 in PMMA and CA is decreased but the distribution width is not changed. The significant narrowing of the distribution width is observed by the termperature rise.

Figure 6a, b give changes of average constants from distances between filler particles. By $l > 20$ nm K_0 is decreased unsignificantly. When $l < 20$ nm K_0 is decreased more than a tenfold.

Together with the physical structure modification observed effects in principle could be caused by changes of the reaction mechanism on the filler surface. For example CHC decay by the reaction with the aerosil surface is possible and perhaps the rate in this case is smaller than that in the volume. Therefore the special experiment was made in which to prepare filled samples the modificated aerosil with QDA on its surface was used. It was shown that on the surface CHC is converted more effectively. Consequently if this possibility had been

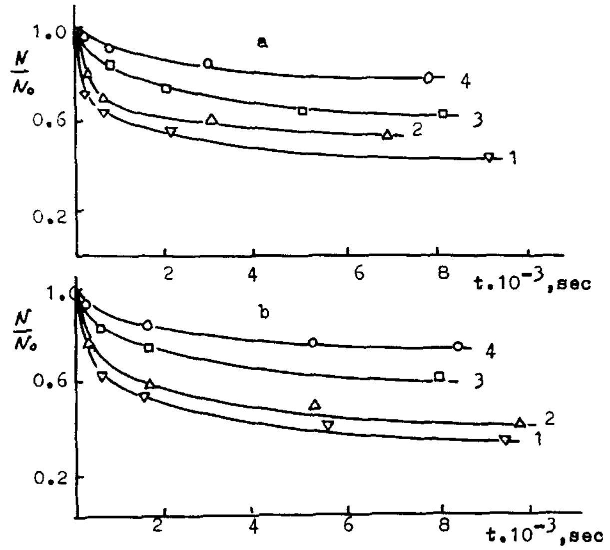

FIGURE 4 The kinetics of CHC decay by 100 K in filled PMMA (a) and CA(b) containing 1(1), 25(2), 40(3), 65(4) aerosil weight parts.

realized we should have observed opposite effects of the filler presence. Thus one can conclude that CHC decay in filled polymers takes place mainly by interactions with macromolecules but the essential decrease of this process rate is caused by structure changes connected with interfaces formations. By estimations of the given kinetic method the interface thickness is about 15–20 nm.

On the base of obtained date some suppositions were made of the structural reconstruction nature in filled polymers influencing on the cell reaction kinetics.

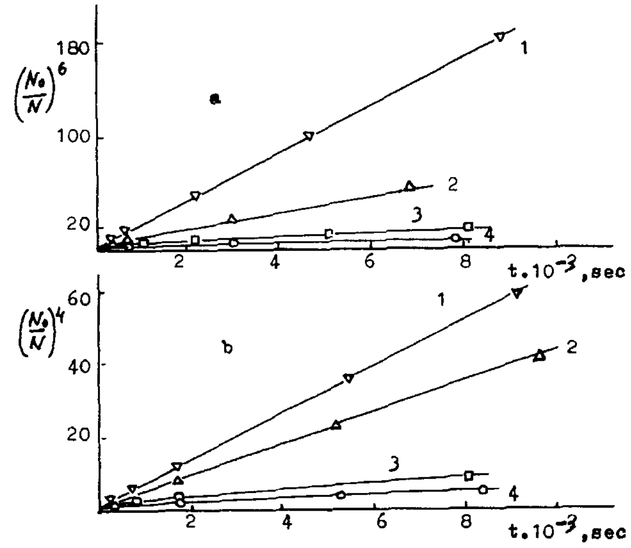

FIGURE 5 Anamorphoses of Figure 4a, b kinetic curves in Eq. (8) coordinates.

Kinetic parameters of CHC decay in filled PMMA and CA

PMMA						CA					
T,K	n	W_a, %				T,K	n	W_a, %			
		1	25	40	65			1	25	40	65
		$K_0 \cdot 10^4$, sec^{-1}						$K_0 \cdot 10^4$, sec^{-1}			
100	6	28,0	14,5	4,2	1,6	100	4	13,0	11,8	2,5	0,7
113	4	35,0	25,0	14,7	1,8	125	3	140	-	87	6,9
125	2	38,0	25,0	16,7	2,1	135	2	1000	580	200	12,0

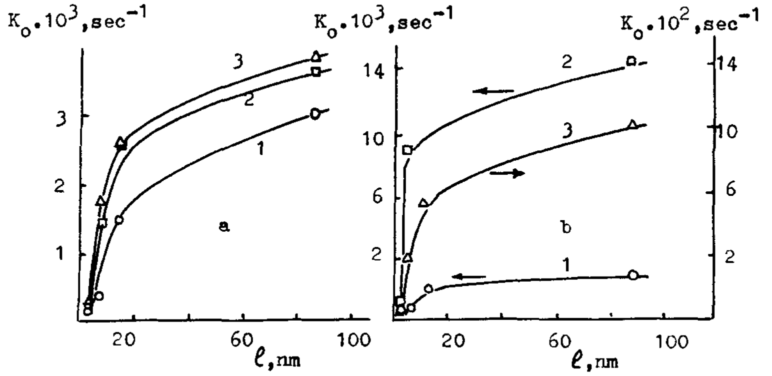

FIGURE 6 The dependence of K_0 on the average distance between aerosil particles in filled PMMA (a) by 100 K (1), 113 K (2), 125 K (3) and CA (b) by 100 K (1), 125 K (2), 135 K (3).

As the distribution by CHC activity becomes narrow by means of the temperature rise there is the connection between this distribution and the activation energy of small scale molecular motions. By the molecular motions defrosting the kinetic unequivalence of CHC is averaged considerably. It was noted above that the primary RP formation (K_1) is the limiting stage connected with the activation barrier availability. But fast stages of RP conversions do not require expenditures of the energy. Therefore we can consider that the kinetic unequivalence of CHC is conditioned by the activation energy distribution of the primary stage.

As by the polymer conversion into interfaces the distribution width is not changed structure-physical modifications do not influence on small scale molecular motions. It is confirmed also by the constancy of the effective activation energy of K_0 in PMMA and CA containing a filler different quantity. Perhaps structural changes determine the efficiency of RP conversions that is

$$\frac{1}{\dfrac{K_{-1}P_T}{K_2P_S}+1}.$$

It was revealed that owing to the difficulty of relaxation processes under the formation of amorphous filled polymers from solutions the packing density of macromolecules is decreased in interfaces.[7] Therefore alterations of RP geometrical configurations can arise as the filler is added. The RP geometry influences on the exchanged energy and consequently on relative spin populations of singlet and triplet states. For example the greater the discrepancy of nonpair electrons axises from perpendicular orientation the greater the exchanged energy and the greater population of RP triplet levels.[5] In this case $K_{-1}P_T/K_2P_S$ in (2) will be increased but accordingly K_{ef} is decreased.

Thus the kinetics of triplet carbenes reactions reflects structural peculiarities on the level of effective distances in RP (0.3–0.5 nm). The structure-physical modification affecting cells of such size can be registered by changes of kinetic parameters. Therefore the reaction of triplet carbenes apparently may be used to carry out thin structural investigations of solid polymers.

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