Dynamics of Biradicals Formation by Low Temperature Conversions of Carbenes in Polymers

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The kinetics of diphenylcarbene (DPC) conversions in clusters with biradicals (BR) formation has been studied in polycarbonate (PC) and polymethylmethacrylate (PMMA) at 77–125 K. The portion of carbene precursor-diphenyldiazomethane (DDM) localized in micropores has been evaluated from concentration dependences of BR yield. The correlation of kinetic parameters of BR low temperature formation with molecular dynamic properties of spin probe has been observed in studied polymers. The structural modification of PC by aerosil filling effects on conversion kinetics of BR.
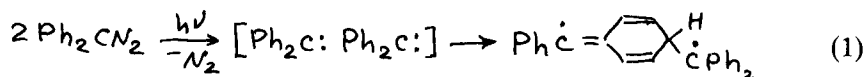
INTRODUCTION

The reaction of carbenes in ground triplet state with C—H bonds of surrounding molecules is typical process in solid phase. The intermediate radical pairs (RP) forming in this reaction are converted by following recombination in corresponding products.[1,2] The BR formation was registered by ESR for carbenes generated by photolysis of diazocompounds in polymers at 77 K. So the formation of BR is observed at cyclohexadienone carbene photogeneration in PMMA. These RP consisting of phenoxyl radical and PMMA macroradical have interradical distances 0.6 nm.[3] RP with distances 0.52 nm including diphenylmethyl radical and matrix radical were obtained in analogous conditions in polypiperylene.[4]

The cage reaction of hydrogen atom transfer on triplet carbene in the matrix isolated state is the basis of RP formation. As a rule ESR spectra of such RP are different in various solids and for different carbenes. However the appearance of radical particles with the identical ESR spectrum was discovered for DPC by photolysis of DDM in PMMA, polystyrene, deuterated PMMA-D_8 and polystyrene-D_8, PC. One can assert that they are not RP because of the same parameters of ESR spectra characterizing distances between radicals and HFI of unpair electrons.

As molecules of low molecular substances are in defects of polymer packing, that is parts with decreased density because of the relative arrangement disturbance

of macromolecules,[5,6] one can suppose that carbenes are accumulated both in matrix isolated states and in clusters of two or more DPC. Therefore the carbene dimer conversion products can be BR

$$2\,Ph_2CN_2 \xrightarrow[-N_2]{h\nu} [Ph_2C\!: \; Ph_2C\!:] \longrightarrow Ph\dot{C} = \underset{\underset{Ph_2}{\dot{C}}}{\overset{H}{\bigcirc}} \qquad (1)$$

The reaction of BR formation of carbenes localized in micropores is interesting in two aspects. The BR yield must reflect apparently the non-homogeneity of DDM distribution and can be used to estimate the distribution by concentrations of other low molecular additives in solid polymers. The kinetics of this process must depend on molecular organization of the micropore surrounding and the intensity of small-scale molecular mobility. In this connection the study of kinetic regularities of BR formation is important for the solution of fundamental problem the connection of the reactivity with structure-physical properties of polymers. In this report results of kinetics and mechanism study of BR formation in carbene cluster reactions in PMMA and PC are discussed. The effect of PC structure-physical modification by aerosil filling in the kinetics of BR formation and conversion is examined.

EXPERIMENTAL

PC with MM 30000 (PC-30), 100000 (PC-100) and PMMA with MM 125000 were used. The polymer films with DDM ([DDM] = 0.04–0.2 mol/kg) were obtained from solutions in methylenchloride. The aerosiel was warmed at 400°C and was added into 2% solution of PC in CH_2Cl_2. The diameter of aerosiel particles is about 20 nm. The solvent was evaporated to obtain filled polymers. DDM was added into samples by the swell from hexane solution. The concentration of DDM was 0.2 mol/kg in polymer phase at different content of aerosiel (40–60%). The samples were irradiated by light with $\lambda > 480$ nm in vacuum at 77 K.

RESULTS AND DISCUSSION

The same ESR spectrum of BR was registered at 77 K in irradiated PMMA and PC films (Figure 1a). This is anisotropic signal with parameters of the splitting in zero field $D_\perp = 11$ mT and $D_\parallel = 22$ mT. The average distance r between unpair electrons can be determined from parameters characterizing their dipol-dipol interactions by the equation

$$D_\perp = \frac{2.78}{r^3} \qquad (2)$$

In BR forming by the reaction (1) r is 0.63 nm. The BR formation mechanism is confirmed by the increasing of their yields, determined by ratio of initial rates
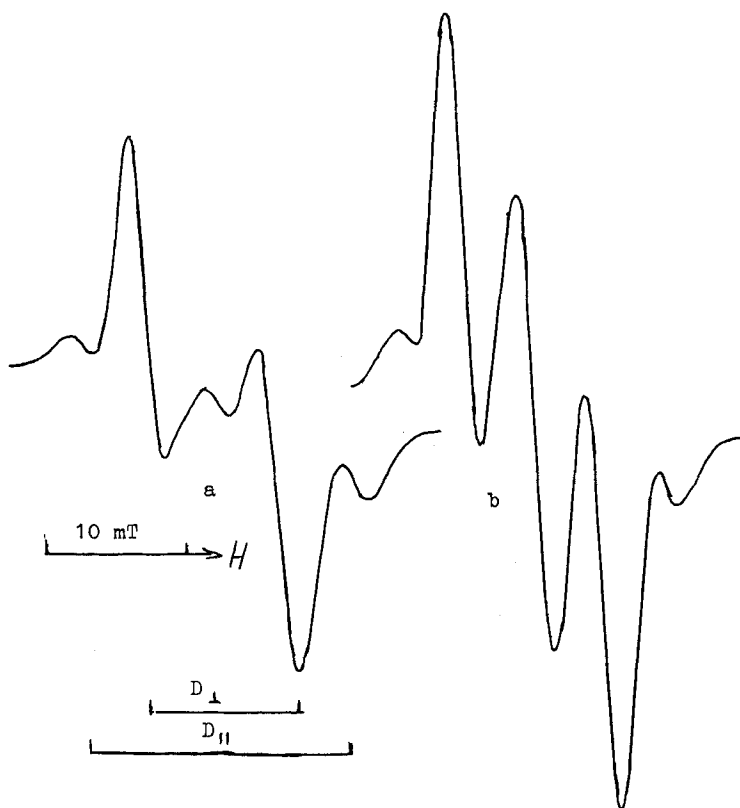
FIGURE 1   ESR spectra obtained by photolysis of DDM in PMMA, PC at 77 K: a—[DDM] = 0.1 mol/kg, b—[DDM] = 0.19 mol/kg.

of BR and isolated ^{3}DPC formation, with the increasing of DDM concentrations (Figure 2).

The dependence of BR yield on DDM concentration is described satisfactorily by the equation

$$\varphi = \frac{\varphi_x[DDM]}{C + [DDM]} \tag{3}$$

where φ_x = 0.005, C = 0.12 mol/kg. The top part of DDM dimers is $4\varphi_x$ = 0.2 as BR are formed from pairs of DDM molecules. The deviation of φ ([DDM]) from linearity is connected evidently with high filling of polymer micropores at [DDM] > C. The intense line belonging to BR with distances between spins 0.9–1.0 nm and more is appeared in central part of ESR spectrum at deep stages of DDM photolysis (Figure 1b). Such particles are formed if three DPC will react.
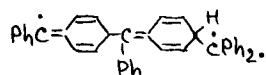
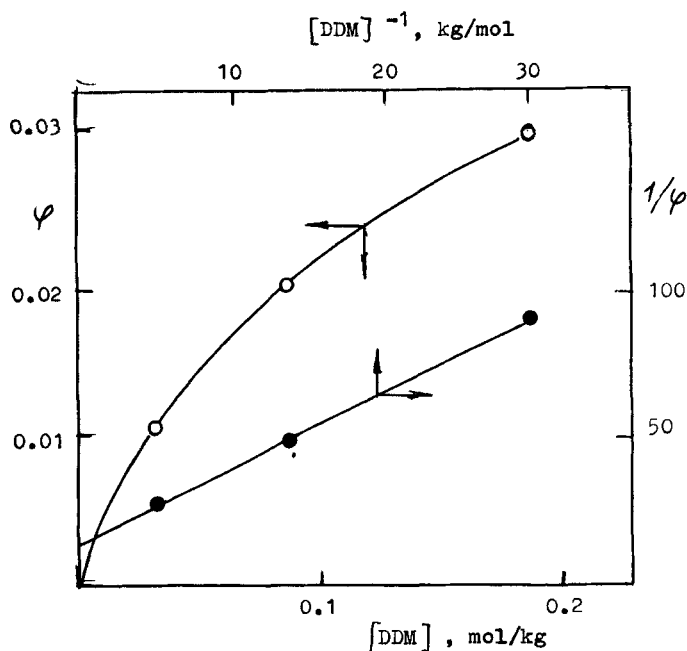FIGURE 2   The dependence of BR yield on DDM concentration and its anamorphosis in coordinates of Equation (3).

These BR can arise in bigger clusters. The ESR spectrum analysis shows that the portion of "polymeric" BR in PC and PMMA does not exceed 20% relatively to all quantity of BR.

The results obtained can be used to evaluate the non-homogeneity of low molecular additives like DDM by chemical structure. For example the analogous distribution of bimolecular, threemolecular etc. clusters must be in glass polymers for some photostabilizers, antioxidants, photosensibilizers (salicylates, benzophenones, bisphenols).

The influence of molecular organization of polymer matrix on microlevel is displayed in kinetics of BR photo- and thermal generations. Figure 3 shows kinetic curves of BR formation in PC with different MM at 77 K by light with $\lambda > 480$ nm at the same initial DDM concentration. In PC-30 the decreasing of BR yield relatively to that of isolated carbenes was observed if the photolysis time was increased. In this sample BR concentration achieves a limit for 120 min. The concentration of BR is increased twice by annealing of irradiated at 77 K samples up to 130 K. The repeated photolysis leads to essential decreasing of BR concentration. These results permit to consider that the process of BR formation from DPC at 77 K is convertible

$$2Ph_2C: \underset{K_{h\nu}}{\overset{K_{TTK}}{\rightleftarrows}} \quad Ph\dot{C} = \underset{\dot{C}Ph_2}{\langle = \rangle}\overset{H}{\diagup} \qquad (4)$$
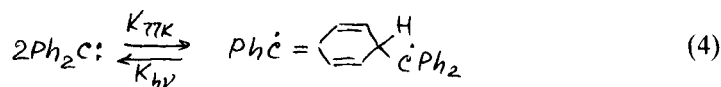
where K_{77K} is the rate constant of thermal BR formation from pairs of carbenes at 77 K, K_{hv} is the rate constant of BR decomposition. Since the maximum of BR concentration is twice comparatively with their stationary concentrations then $[2DPC]_{st}$ = $[BR]_{st}$ or $K_{77K} \approx K_{hv}$. The BR maximum concentration corresponds to initial concentration of DDM dimers. Therefore assuming that limiting stage of BR formation by DDM photolysis is thermal stage of carbene dimerization initial rates of BR formation and their photodecomposition by repeated light irradiation of samples must be equal. In fact this result is demonstrated by Figure 3 (2,2').

In PC-100 initial rate of BR formation is higher. The BR decay is much smaller for the same time of photolysis after the annealing of samples. These results can be explained by higher content of DDM dimers comparatively with PC-30.

The peculiarities of BR formation in course of thermal reaction are expressed by annealing curves of irradiated at 77 K samples shown on Figure 4. These curves were obtained by enduring of samples in isothermal conditions. In PC BR is 100% of initial quantity, in PMMA it is some lower (80%). The annealing curves are displaced relatively one another on 15–20 K that is the reactivity of carbenes in micropores depends on nature of polymer matrix. It was established that annealing curves characterized the distribution function of particles by reactivity.[7] The BR formation curves characterizing kinetic stop of process were obtained in temperature region 95–125 K. These curves in PC are shown on Figure 5. They are straightened in coordinates "concentration — lg t." This fact shows that the distribution function of carbenes is the straight-angle type[7] by activation energies of BR formation.

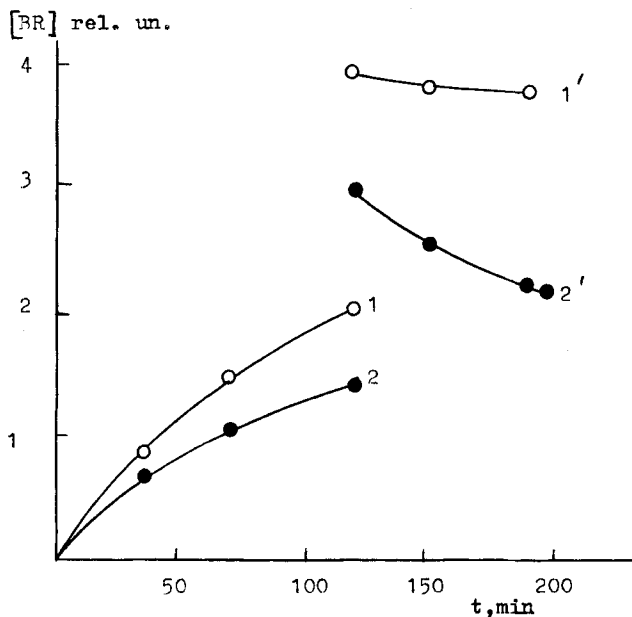FIGURE 3 The kinetics of BR photogeneration at 77 K (1,2) and photodecomposition at 77 K after heating of samples at 130 K (1',2') in PC-100 (1,1') and PC-30 (2,2'), [DDM] = 0.19 mol/kg.
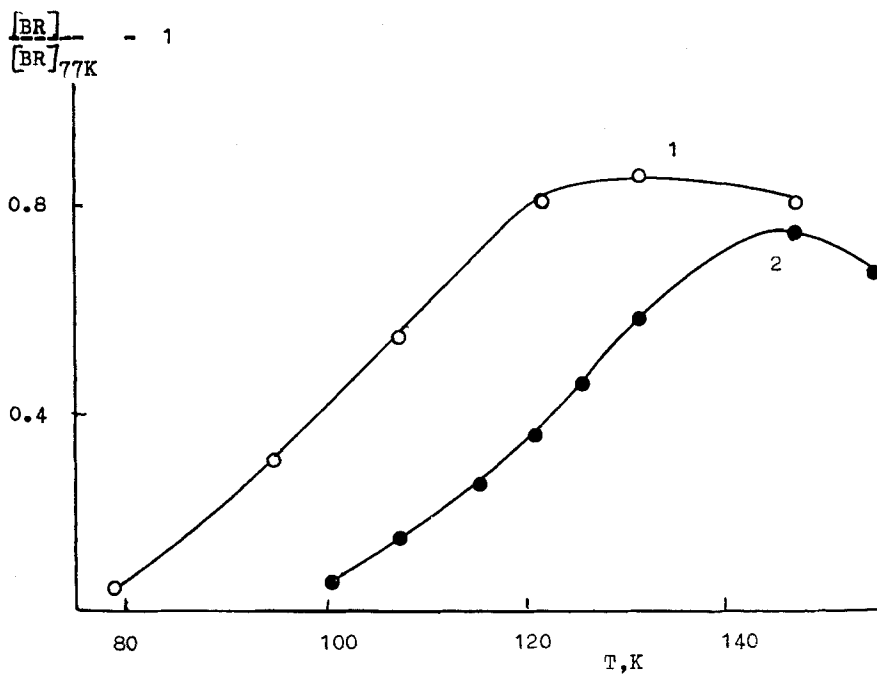
FIGURE 4   The annealing curves for BR formation in PC (1) and PMMA (2).
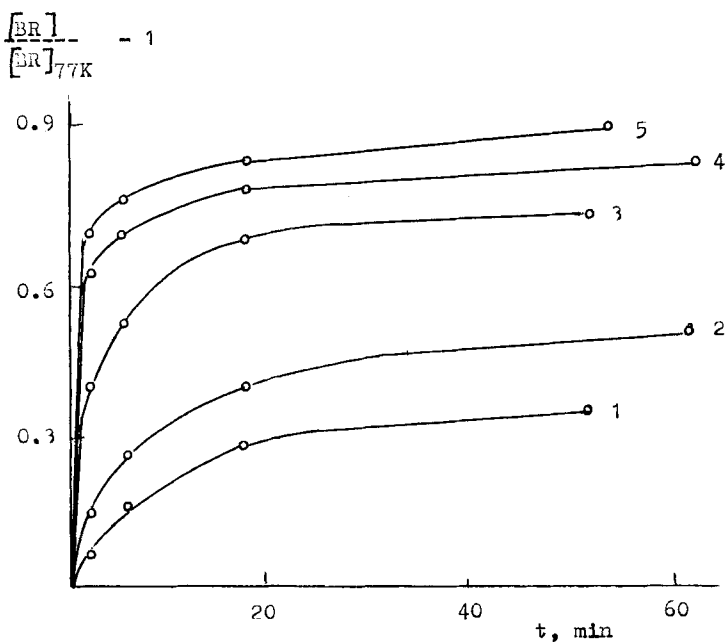

FIGURE 5   The kinetics of BR thermal formation in PC with DDM after photolysis ($\lambda > 480$ nm) at 77 K: 94K-1, 100K-2, 107K-3, 115K-4, 120K-5.

$$\rho(E) = \frac{1}{E_{max} - E_{min}}, \quad E_{min} \leq E \leq E_{max} \tag{5}$$

Then the distribution function by reaction rate constants is

$$\rho(K) = \frac{1}{K \ln(K_{max}/K_{min})} \tag{6}$$

where E_{max}, E_{min}, K_{max}, K_{min} are values of parameters characterizing the distribution width and the reaction kinetics is described by the equation

$$\theta = \frac{[BR] - [BR]_{77K}}{[BR]_{max} - [BR]_{77K}} = \frac{-\lg K_{min}t}{\lg(K_{max}/K_{min})} \tag{7}$$

which is valid for $1/K_{max} < t < 1/K_{min}$ (Figure 6).

The established kinetic non-equivalence of reaction cages in micropores indicates the distribution of reacting pairs of carbenes by kinetic ensembles. The gradual annealing of mobilities in carbene ensembles determines the character of temperature dependences of BR formation. In PC the annealing of all ensembles of reacting particles takes place at 130–140 K. In PMMA analogous effect is observed at 150 K. The analysis of kinetics with the rate constants dispersion permits to define the Arrhenius parameters distribution which in general case is connected with distributions both by activation energies and by preexponential factors.

The method stated in Reference 8 was used to determine the distribution by these parameters. By this method the kinetic curves set $\theta(t, T)$ (Figure 5) was cut by horizontal lines and values of rate constants $K(\theta, T) = t^{-1}(\theta, T)$ determining the reactivity of given ensembles were found. Then temperature dependences of obtained values $K(\theta, T)$ were constructed in Arrhenius coordinates and activation energies and preexponents were determined for different values.
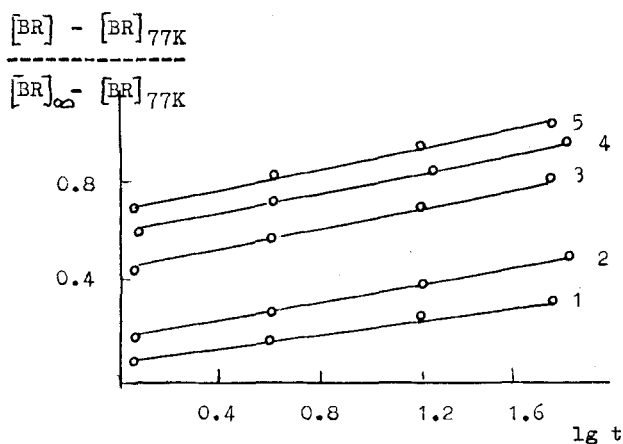

FIGURE 6   The anamorphosises of kinetic curves of BR formation in PC in coordinates of Equation (7).

The dependences $\theta(E)$ and $\theta(K_0)$ are integral distribution functions by corresponding parameters. These relationships are practical linear (Figure 7) that is distribution functions by Arrhenius parameters of carbenes in clusters can be considered as a straight angle type. The extrapolation of linear dependences (E, K) at 1 and 0 gives values of E_{max}, E_{min}, lg K^0_{max}, lg K^0_{min} determining the distribution width of carbenes by the reactivity. In PC these values are E_{max} = 38 kJ/mol, E_{min} = 26 kJ/mol, E_{min} = 26 kJ/mol, lg K^0_{max} = 14.4, lg K^0_{min} = 12.8.

The obtained values of activation energy are typical for relaxation processes in PC (40 kJ/mol) caused by motions of monomer links and side groups of macrochains. These values are adjusted with activation energy of the spin probe rotation.[9] In PC the reaction of BR formation is controlled by rotation of carbenes in micropores of polymers. In fact values K_0 = 10^{13}–10^{14} s^{-1} are compared with frequencies of orientational motions of low molecular particles in glassy polymers. One can note the small dispersion of Arrhenius parameters: lg K_0 = 1.5, E = 12 kJ/mol.

In PMMA limiting values are E_{max} = 50 kJ/mol, E_{min} = 22 kJ/mol, lg K^0_{max} = 16.0, lg K^0_{min} = 10.5. The average Arrhenius parameters of BR formation are lg K^0_{av} = 13.25, E_{av} = 36 kJ/mol. They correlate satisfactorily with activation energy and the rotation time of spin probes in PMMA: E = 38–42 kJ/mol, lg = -13.2.[9] But high dispersion of Arrhenius parameters attracts attention: lg K_0 = 6.5, E = 28 kJ/mol.

The result obtained can be explained by existence of wider scattering of hindered molecular motions in PMMA which are annealed with the increasing temperature. The theoretical calculation shows[10] that the activation energy of side ester groups rotation combined with rotational vibrations of main chain near equilibrium positions is 21.6 kJ/mol. This value agrees with that of minimum activation energy for BR formation. But the activation barrier of the ester groups rotation is increased with the increasing difference of rotational angles from their equilibrium values. The calculation gives maximum potential barrier 68 kJ/mol for torsional oscillations around C—C bonds of the main chain. Therefore, the increasing of BR formation activation energy to 50 kJ/mol corresponds to the transition of the carbene orientational dynamics to that controlled mainly by the macrochain links mobility.

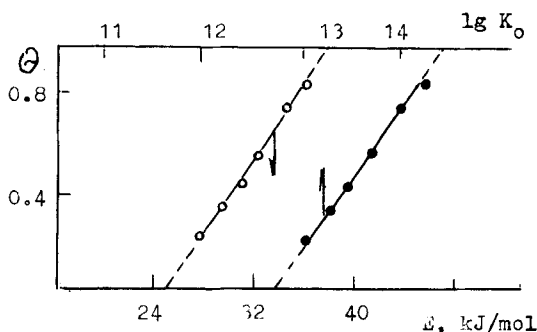Thus observed differences in kinetic regularities of BR formation in two polymers

FIGURE 7   The integral distribution functions of ^{3}DPC by Arrhenius parameters of BR formation in PC.

are caused by peculiarities of molecular organization of micropores environments. In the studied temperature region the distribution width of rate constants determined by $\lg(K_{max}/K_{min})$ is 1.5–2 times larger in PMMA than in PC. One can therefore conclude that the structural non-homogeneity of the micropore surrounding in PMMA higher than that in PC.

At $T > 130$–150 K BR thermal decay prevails over their formation (Figure 4). The kinetics of BR thermal decay express molecular dynamics defining reaction processes for larger particles as those of carbenes. The investigations of BR thermal decay in PMMA at 183–218 K show that BR are also unequal in reactivity. The kinetic curves of this process are straightened in coordinates $[BR]/[BR]_0 - \lg t$ (Figure 8). One can see that the inclination angle of anamorphosises does not change with the temperature. Hence the observed BR nonequivalence in given temperature interval does not correlate with the activation energy distribution. The rate dependence of BR thermal decay is treated by Arrhenius law. This yields the limiting constants $K_{max} = 5 \cdot 10^{12} \exp(-46 \pm 4/RT)s^{-1}$ and $K_{min} = 10^9 \exp(-46 \pm 4/RT)s^{-1}$.

From the obtained limiting values it follows that in PMMA activation energy of BR decay corresponds to the maximum activation energy of BR formation. The distributions of frequency factors are also overlapping. Thus, in the micropores the conversion of BR and carbenes with the lowest reactivity are controlled by the same molecular dynamics, the torsional movements of the main chains.

The presented data show the importance of rotational motions of carbenes concentrated in micropores of polymers in formation of BR. In this regard such reaction may be considered as a special probe to study the molecular dynamics at low temperatures. It is known that the spin probe method is used to obtain the reliable information about molecular motions near and above the glass temperature. At temperatures well below T_g a wide distribution of paramagnetic probe rotational frequencies appears. Here, the ESR method covers only the high frequency part. The development of ESR with the transfer of hyperhigh frequency saturation
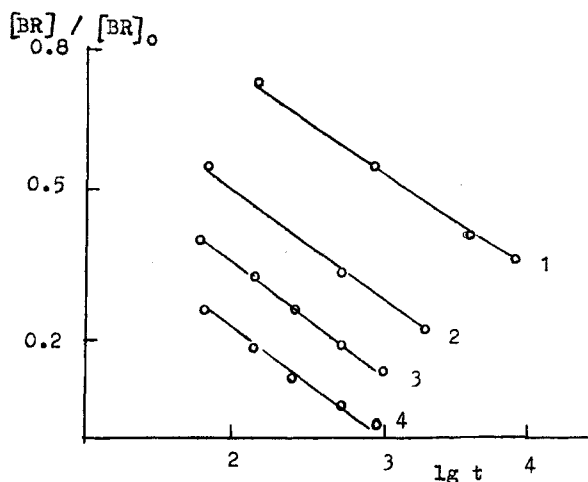

FIGURE 8   The anamorphosises of kinetic curves of BR decay in PMMA: 183K-1, 193K-2, 203K-3, 218K-4.

allowed us to extend the interval of reliable determinations of spinprobe correlation times to the region of slow motions ($\tau = 10^4$ s) at $T < T_g$. The method based on kinetic measurements of BR formation due to DPC conversions extends significantly the temperature region to investigate the macromolecules small scale dynamics. This method with the combination of BR thermal decay kinetics permits us to examine directly the reactivity distribution of particles associated with the non-homogeneity of the physical structure of polymers.

The effect of physical structure in the kinetics of carbene reactions in clusters is demonstrated by experiments with PC filled samples. Figure 9 shows considerable changes of annealing curves in PC having different aerosiel content. In samples without the filler the maximum of BR quantity is achieved at 130–150 K. In filled PC the maximum is shifted to lower temperature ($T = 120$ K) because of the effective thermal decay of BR at $T = 120$ K. The yield of BR is much higher in unfilled samples as compared with filled samples. Therefore, one can conclude that different kind of annealing curves result from a decrease in BR thermal stability with increase of filler content.

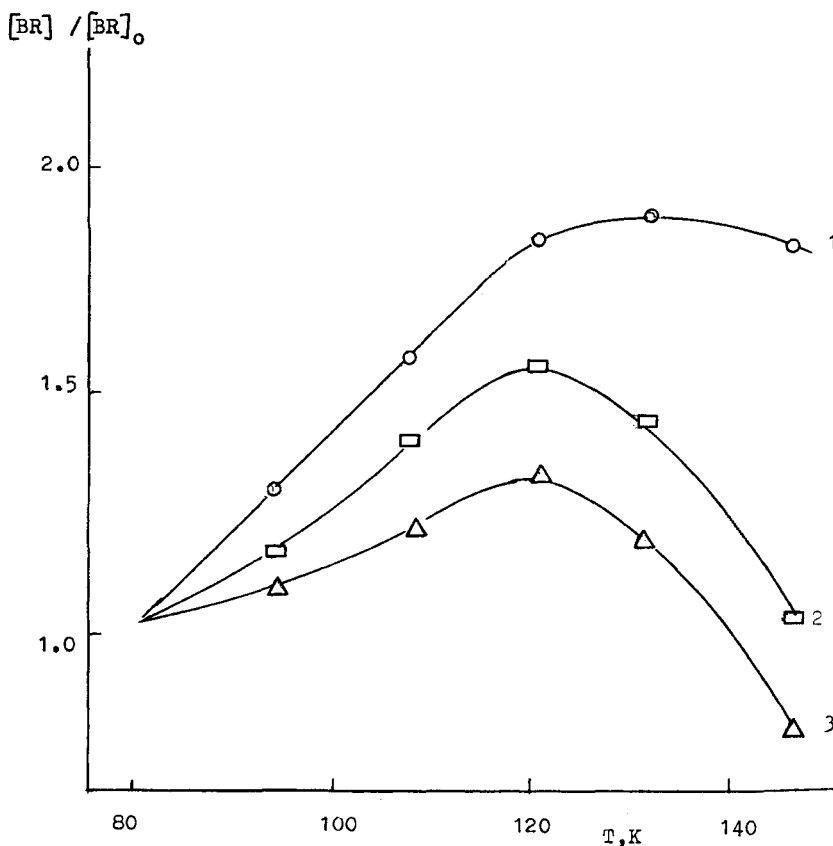The study of BR decay kinetics in PC at different filler contents permits us to

FIGURE 9   The annealing curves in processes of BR formation and decay in PC without filler (1) and with 50 weight % (2), 60% (3) of aerosil.
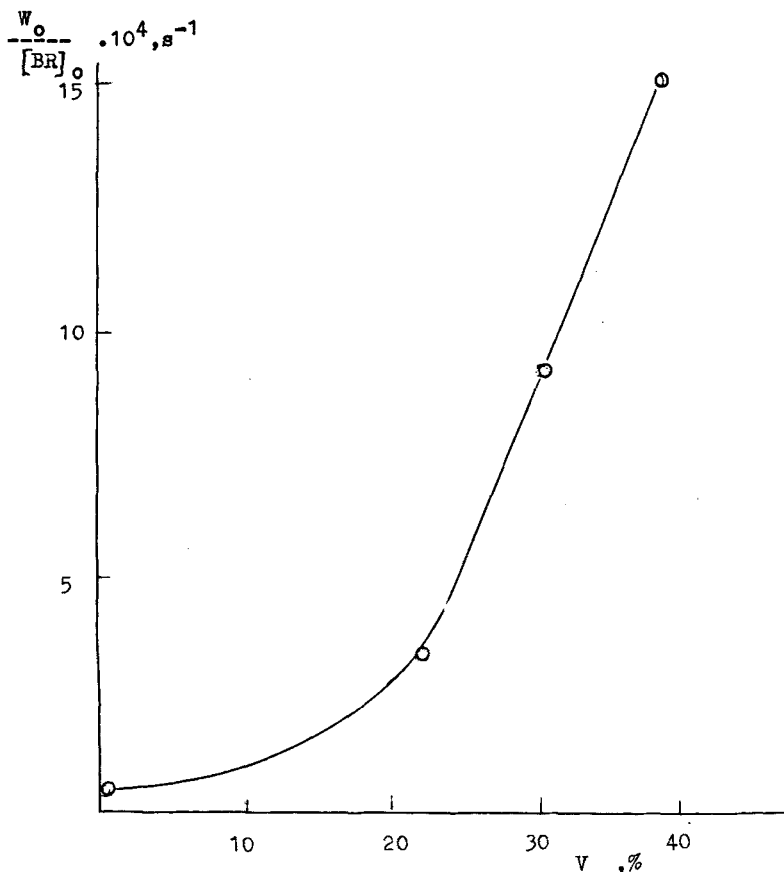
FIGURE 10   The dependence of initial rate of BR decay in PC on aerosil volume share.

estimate the effective thickness of interfaces. The samples irradiated at 77 K were heated at 120 K for 16 min to complete the BR formation, after that, they were annealed at 146 K. The addition of filler results in abrupt increase of BR decay rate.

The non-additive character of the initial rate dependence on the filler volume content $V_a\%$, and the abrupt growth of the rate at $V_a > 20\%$ reflect the polymer transition in the interface state where BR decay efficiency is high (Figure 10). The estimate of the interface thickness ℓ using equation[11]

$$\ell = d\left[\left(\frac{0.8}{1 - \eta}\right)^{1/3} - 1\right] \tag{8}$$

where d is the diameter of aerosol particles, η is the volume portion of aerosil in PC, gives the value of 12 nm.

Thus, the BR formation in micropores of polymer matrix is a specific low temperature reaction of acrylcarbenes. The BR yield is a quantitative characteristic of

unhomogeneous distribution of carbene precursors and other low molecular additives with similar sizes and shape of molecules. The kinetics of BR formation is controlled by rotational mobility of carbenes in the micropores. This reaction can serve as a probe to study small scale molecular dynamics of polymers between 90–220 K.

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