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Mechanisms of front propagation of photochemical reactions in polymer containing media: 1. Frontal regimes of photochemical reactions in polymer matrices with bleaching of specimen behind the front

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The propagation of conversion fronts and their forms are experimentally revealed by 9,10-diphenyl anthracene photo-oxidation in butyl methacrylate/methacrylic acid copolymer films, as an example. In addition to the absolute bleaching regime the partially bleached one was analysed and investigated. The latter case was realized by the addition of a u.v.-absorber–5-chloro-2-(2'-hydroxy-5'-methyl-3-*tert*-butylphenyl)benzotriazole. The method of allowing for light losses under routine photochemical experiments with non-rigorous parallel light beams was suggested. This method was used for a quantitative description of front propagation kinetics. Copyright © 1996 Elsevier Science Ltd.

(Keywords: photochemical front; butyl methacrylate/methacrylic acid copolymer; 9,10-diphenyl anthracene photo-oxidation)

INTRODUCTION

It has been shown theoretically[1-4] that photochemical reactions may proceed as typical frontal processes at high optical density and restricted mass transfer. The frontal reaction regime is interesting both from the theoretical and practical points of view because new possibilities arise to study the kinetics of complex processes and to produce materials with unusual properties. The investigation of frontal regimes seems to be important as they may be a very common occurrence in polymer photochemistry including degradation, cross-linking, discoloration and polymerization.

Although the theoretical equations obtained are not doubted there are paradoxically no experimental examples supporting their validity. This situation is caused both by the difficulty of choosing systems with proper optical characteristics as reagents and reaction products and by the possibility of polychronic character of photochemical reactions in polymer matrices[5-7].

In this work an experimental approach to the study of frontal photochemical processes in polymer matrices is proposed and applied to investigate typical cases of photochemical front propagation with absolute or partial bleaching of specimens.

EXPERIMENTAL

The copolymer of butyl methacrylate and methacrylic

acid (BMK-5, 20/1, $M_v = 4 \times 10^4$), 9,10-diphenyl anthracene (DPA, reagent grade) and 5-chloro-2-(2'-hydroxy-5'-methyl-3'-*tert*-butylphenyl) benzotriazole (HBT, Tinuvine 326, 'Ciba-Geigy' AG) were used without additional purification.

Films 0.1–0.4 mm thick were prepared by a slow evaporation of solvent from chloroform/acetone (1/1) solution of BMK-5 cast onto a cellulose support. After air-drying the films were peeled off by water. Additives were introduced into the polymer solution. The uniformity of film on thickness was checked by optical density of DPA and HBT, as well as by direct measurements with a micrometer. Maximum variations of film thickness in the working region estimated by these methods did not exceed 5%.

To perform photochemical reaction, the film was irradiated in air at room temperature with the light of a mercury high-pressure lamp DRSh-1000 with glass filters SS-15 and UFS-6 which isolated the wavelength $\lambda = 365$ nm. The i.r. radiation was reduced by using a water filter. The light intensity was determined by a thermocouple AT-50 and was equal to 5.5×10^{-9} Einstein $(cm^{-2} s^{-1})$. Two types of film plane orientation were used: (1) parallel to the incident light when studying front propagation, and (2) perpendicular to the incident light when studying the kinetics of DPA photo-oxidation in BMK-5 matrix. A special holder was used in the first case excepting the irradiation of the side surfaces of the film.
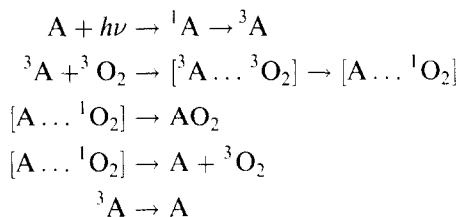
The absorption spectra in u.v. or visible regions were recorded by a spectrophotometer 'Specord UV-Vis'. The

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special device was used to measure the change of DPA concentration along the film sample. By this device the film was moved perpendicularly to the light beam of a spectrophotometer at a constant velocity and the optical density values were recorded simultaneously. The resolving power of the method of front analysis was about 0.1 mm and was determined by beam width of a spectrophotometer. The light losses due to light rays leaving outside the extended sample were taken into account in the front propagation study. These losses were due to deficient parallelism of the light beam obtained from the non-point light source.

RESULTS AND DISCUSSION

The well-known reaction of the auto-oxidation of aromatic hydrocarbons (A) with participation of the singlet oxygen[8,9] (in particular, photo-oxidation of 9,10-diphenyl anthracene[10,11]) was used to study the peculiarities of the photochemical front propagation. Under the assumption that $^1O_2$ reacts inside the cage $[A \ldots {}^1 O_2]$ the mechanism of the reaction at low concentrations of A may be represented by the scheme[8,12]

$$A + h\nu \rightarrow {}^1A \rightarrow {}^3A$$

$$^3A + {}^3O_2 \rightarrow [^3A \ldots {}^3O_2] \rightarrow [A \ldots {}^1O_2]$$

$$[A \ldots {}^1O_2] \rightarrow AO_2$$

$$[A \ldots {}^1O_2] \rightarrow A + {}^3O_2$$

$$^3A \rightarrow A$$

where ^1A and ^3A, $^1O_2$ and $^3O_2$ are the hydrocarbon and oxygen molecules in excited singlet and triplet states, and AO_2 is the product of the reaction (cyclic peroxide). A characteristic feature of this scheme is that reaction of AO_2 formation follows first-order kinetics.

As shown in *Figure 1*, during irradiation of thin film of BMK-5 in air with light incident perpendicularly to the film plane, DPA absorption decreases in accordance with first-order reaction kinetics. A minor deviation points to the very small contribution of bimolecular interaction of DPA with $^1O_2$ molecules that leave the cage[9]. The quantum yield of the reaction is equal to $(1.4 \pm 0.3) \times 10^{-2}$. The absence of the sharp rate decrease at deep stages
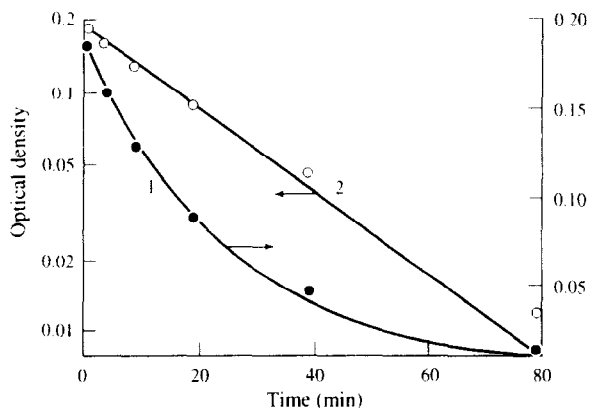

Figure 1 Kinetic curve of DPA consumption in course of irradiation of the BMK-5 films (1) and their linear anamorphosis in accordance with the first order reaction kinetics (2) at $c_{1,0} = 2.04 \times 10^{-3}$ mol l^{-1}. $\lambda = 365$ nm and $I_0 = 5.5 \times 10^{-9}$ Einstein (cm^2 s)$^{-1}$. The film plane is perpendicular to the light beam

of the reaction indicate that kinetic non-equivalence does not play any role in DPA consumption. This result is in close agreement with other data obtained at investigation of anthracene photooxidation[5,6] and for other photochemical reactions[13,14] in BMK-5. Hence it may be supposed that microheterogeneity determining the kinetic non-equivalence of reagents is absent in the polymer under consideration. The estimated inaccuracy in determination of front coordinate occurring due to deviation from first order kinetics at conversions more than 90–95% (see *Figures 1* and *2*) does not exceed 10%. Thus the photochemical auto-oxidation of DPA in BMK-5 is a suitable model reaction for experimental verification of theoretically predicted kinetics of frontal photochemical reactions within the scope of usual homogeneous kinetic schemes.

In the course of irradiation of samples with dimensions $0.4 \times 15 \times 60$ mm oriented parallel to the incident light so that the irradiated surface has dimensions 0.4×15 mm, the photochemical front is formed (*Figure 2a*) which may be seen as a bright blue luminescence stripe. In extended exposure to light this front moves along the film.

The differential equations and their solutions for the systems studied in limiting cases were given earlier[3]. In a more general case these equations have the form

$$\partial I(x,t)/\partial x = -\{\epsilon_1 c_1(x,t) + \epsilon_2 c_2$$
$$+ dg(x)/[g(x)dx]\}I(x,t) \quad (1)$$

$$\partial c_1(x,t)/\partial t = -\phi\epsilon_1 c_1(x,t)I(x,t) \quad (2)$$

at boundary and initial conditions

$$I(0,t) = I_0; \qquad c_1(x,0) = c_{1,0}$$

where $I(x,t)$ is light intensity, ϵ_1 and c_1 are DPA (reagent) extinction coefficient and concentration, ϵ_2 and c_2 are that of HBT (u.v.-absorber), ϕ is quantum yield of reaction, $g(x)$ is a function which defines light loss along the sample due to non-parallel behaviour of the light beam, and $g(x) = I(x)/I_0$ where $I(x)$ is a light intensity at point x for the non-absorbing and non-scattering sample.

The solution of equations (1) and (2) at $\epsilon_1 c_{1,0} \gg \epsilon_2 c_2$ and $\epsilon_1 c_{1,0} \gg dg(x)/[g(x)dx]$ (which corresponds to the experimental conditions chosen) is

$$c_1(x,t) = c_{1,0}/\{1 + \exp[-\epsilon_1 c_{1,0} x$$
$$+ \phi\epsilon_1 I_0 t \cdot g(x)\exp(-\epsilon_2 c_2 x)]\} \quad (3)$$

$$I(x,t) = [I_0 g(x)\exp(-\epsilon_2 c_2 x)]/\{1 + \exp[\epsilon_1 c_{1,0} x$$
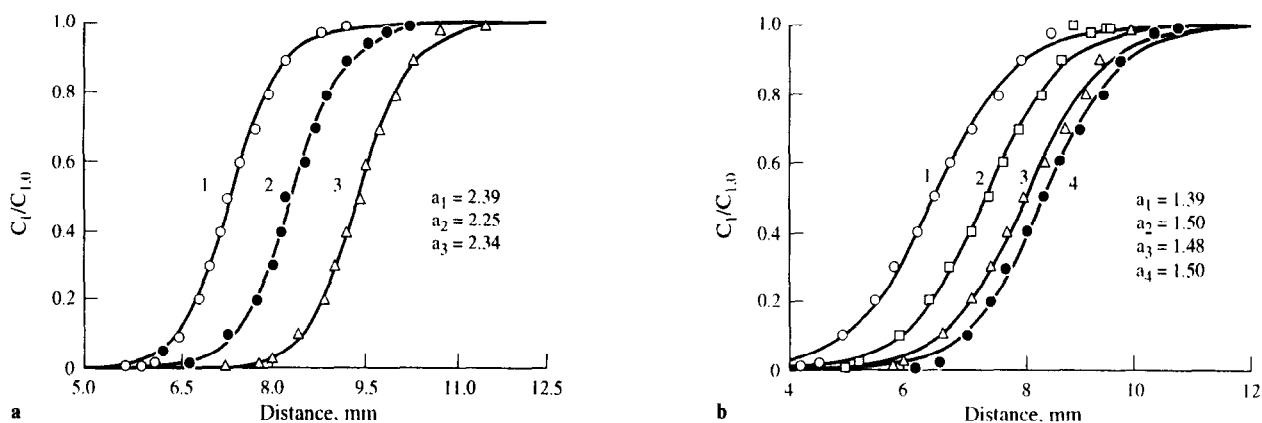$$- \phi\epsilon_1 I_0 t \cdot g(x)\exp(-\epsilon_2 c_2 x)]\} \quad (4)$$

The formula for the front propagation velocity taken as velocity of displacement of a point $c(x,t) = c_{1,0}/2$ follows from equation (3)

$$v = [\phi I_0 g(x)\exp(-\epsilon_2 c_2 x)]/c_{1,0} \quad (5)$$

The integration of equation (5) gives

$$x = (1/\epsilon_2 c_2) \cdot \ln\left\{\left[\epsilon_2 c_2 \phi I_0 \int_0^t g(x(t))\,dt\right]\Big/c_{1,0} + 1\right\}$$
$$(6)$$

The front width l at $\epsilon_1 c_{1,0} \gg \epsilon_2 c_2$ and $\epsilon_1 c_{1,0}$

Figure 2 (a) Reaction fronts in course of irradiation of BMK-5 films at $c_{1,0} = 1.64 \times 10^{-3} \, \text{mol} \, l^{-1}$, $t = 20$ (1), 30 (2) and 40 (3) h, $\lambda = 365$ nm and $I_0 = 5.5 \times 10^{-9}$ Einstein $(\text{cm}^2 \, \text{s})^{-1}$. Points are experimental data, curves are calculated by equation (8) at $a = 2.30$ (1), 2.25 (2) and 2.34 mm^{-1}. (b) Reaction fronts in course of irradiation of BMK-5 films at $c_{1,0} = 7.19 \times 10^{-4}$, $c_2 = 8.76 \times 10^{-5} \, \text{mol} \, l^{-1}$, $t = 19$ (1), 29 (2), 41 (3) and 50 (4) h, $\lambda = 365$ nm and $I_0 = 5.5 \times 10^{-9}$ Einstein $(\text{cm}^2 \, \text{s})^{-1}$. Points are experimental data, curves are calculated by equation (8) at $a = 1.39$ (1), 1.50 (2), 1.48 (3) and 1.50 mm^{-1} (4)

$\gg \mathrm{d}g(x)/[g(x)\mathrm{d}x]$ may also be estimated from equations (3) and (6) giving

$$l \sim 1/\epsilon_1 c_{1,0} \qquad (7)$$

As shown in *Figure 2a* the front profile in the case of reaction without u.v.-absorber is described by

$$c_1(x) = c_{1,0}/[1 + \exp(-ax + b)] \qquad (8)$$

This equation corresponds to

$$c_1(x, t) = c_{1,0}/[1 + \exp[-\epsilon_1 c_{1,0} x + \phi \epsilon_1 I_0 t]] \qquad (9)$$

which follows from equation (3) at $g(x) \sim 1$ and $c_2 = 0$. The mean value of parameters $a = 2.33 \, \text{mm}^{-1}$ is close enough to the value $\epsilon_1 c_{1,0} = 2.60 \, \text{mm}^{-1}$ calculated with experimental magnitude $\epsilon_1 = 1.54 \times 10^4 \, \text{l(mole} \cdot \text{cm})^{-1}$ determined for DPA at $\lambda = 365$ nm.

Equation (8) also describes the front profile in the presence of HBT (*Figure 2b*, $a = 1.11 \, \text{mm}^{-1}$, $\epsilon_1 c_{1,0} = 1.47 \, \text{mm}^{-1}$ because the experiment was carried out at the same condition $\epsilon_1 c_{1,0} \gg \epsilon_2 c_2$.

The front propagation in the sample with the absolute medium bleaching behind the front and under condition $g(x) = 1$ has to proceed with constant rate

$$v = \phi I_0 / c_{1,0} \qquad (10)$$

In practice, according to the reasons mentioned in the experimental part of the paper, $g(x) \neq 1$ and the front propagation rate decreases in the course of time and reaches a stationary level only at some distance from the irradiated surface (*Figure 3*, curve 1). As was mentioned above, a minor kinetic deviation of DPA consumption from the first order reaction (*Figure 1*) cannot lead to an appreciable variation of front propagation velocity. In particular, from equation (5), it follows that even in the case of complete kinetic cessation of reaction at the DPA conversion equal to 0.95 the reaction rate at a maximum distance from the irradiated surface $x_{\text{max}} = 10$ mm could only decrease by 12%.

As seen in *Figure 4*, curve 1, front propagation at partial sample bleaching is adequately described by

$$x = \alpha \cdot \ln(\beta t + \gamma) \qquad (11)$$

where α and γ are parameters. This equation corresponds formally to equation (6). For quantitative description of the process at such a mode it is necessary

to know the form of $g(x)$ which may be determined from experimental results (*Figure 3*, curve 1) obtained under absolute sample bleaching

$$g(x) = I(x)/I_0 = v(x)/v_0 \qquad (12)$$
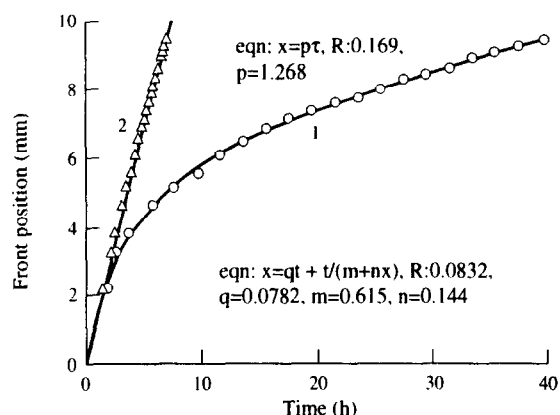
Figure 3 Dependencies of front coordinate on time (1) and on reduced time (2) for irradiation of BMK-5 film containing DPA. The straight line (2) is a theoretical dependence of the front propagation on characteristic time calculated at $\phi = 0.014$. Conditions are shown in the caption to *Figure 2a*
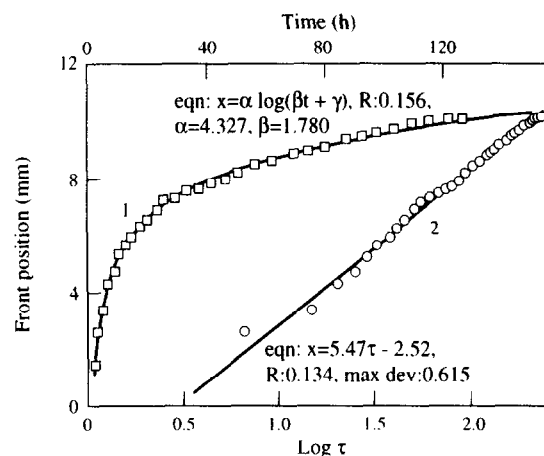
Figure 4 Dependences of front coordinate on time (1) and on the logarithm of the reduced time (2) for irradiation of BMK-5 film containing a mixture of DPA and HBT. Conditions are shown in the caption to *Figure 2b*

where $v(x)$ and v_0 are front propagation rates at point x and at irradiated sample surface.

As shown in *Figure 3*, the front propagation into the sample with absolute bleaching within the accuracy of measurement may be approximated by function

$$x(t) = qt + t/(m + nt) \qquad (13)$$

where $q = 0.0782$, $m = 0.615$ and $n = 0.144$ are parameters (curve 1). Using relation (13) and taking into account that $v(x) = \mathrm{d}x/\mathrm{d}t$, the function $g(x)$ at given conditions was obtained as

$$g(x) = \{q + m/[m + nt(x)]^2\}/v_0 \qquad (14)$$

where

$$t(x) = \{-(1 + qm - nx) + [(1 + qm - nx)^2$$
$$+ 4qmnx]^{1/2}\}/(2qn) \qquad (15)$$

Substituting calculated $g(x)$ in the expression (6) which describes the front propagation in the sample containing both DPA and HBT and introducing reduced time

$$\tau = \int_0^t g[x(t)]\mathrm{d}t \qquad (16)$$

we obtain (a) linear dependence of front position on reduced time τ for the case with absolute bleaching (curve 2 in *Figure 3*) and (b) logarithmic dependence of front coordinate on reduced time τ for the case of partial bleaching (curve 2 in *Figure 4*).

The slope (6.30 mm) of a straight line $x(\ln \tau)$ is practically the same as the value of the parameter $1/\epsilon_2 c_2 = 6.43$ mm, computed by using the values $c_2 = 8.8 \times 10^{-5}\,\mathrm{mol\,l^{-1}}$ (see *Figure 2*, caption) and $\epsilon_2 = 1.76 \times 10^4\,\mathrm{l(mol \cdot cm)^{-1}}$ (this magnitude was determined experimentally for HBT at $\lambda = 365$ nm). This agreement corroborates the validity of the analysis performed and together with linearity of $x(\tau)$ dependence is the principal experimental evidence of the exponential retardation of photochemical front propagation into the partially bleaching sample. It should be noted that the received data testify to an opportunity of use of investigation of front propagation for the analysis of mechanism of additives function. The coincidence of initial velocities of front propagation in the presence and in the absence of HBT and retardation on significant distances from the irradiated surface in the presence of HBT testifies that HBT does not act as quencher of exited states of DPA or $^1O_2$ but only as u.v.-absorber.

CONCLUSIONS

The frontal mechanisms are typical for photochemical reactions in optically dense polymer matrices. The main function of the polymer is to create the necessary conditions for front propagation which above all means the decreasing of mass transfer rate by means of

convection or diffusion. Thus frontal photochemical reactions in polymer matrices together with known examples of the frontal radical polymerization[15-18] are to some extent ideal objects for investigation of front propagation mechanisms. In this work for the first time conversion front propagation was studied by the direct methods for the representative limit cases of frontal photochemical reactions when front propagation is accompanied by absolute or partial bleaching of a system. The method developed may be used as a basis for further investigation of other typical cases and some specific peculiarities of reactions of considered type, in particular related to polychronic kinetics. The results obtained in this field are to be published in this series.

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