ESR Study of Lophyl Free Radicals in Dry Films

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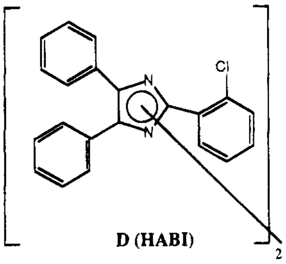
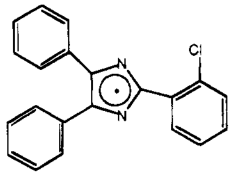
ABSTRACT: Photolysis of 2-(2′-chlorophenyl)-2′-(2′-chlorophenyl)-4,4′-5,5′-tetraphenylbisimidazoles (D) into corresponding lophyl free radicals ($R^\bullet$) was studied by steady-state and time-resolved (TR) CW ESR in dry films of poly(methyl methacrylate) (PMMA) at 6–400 K and in a frozen liquid solution at 77 K. Steady-state ESR experiments demonstrate the formation of spatially proximate electronically interacting radical pairs (RPs) $R^\bullet...R^\bullet$ as well as the formation of spatially isolated free radicals $R^\bullet$. The ratio of amounts of photogenerated $R^\bullet$ to $R^\bullet...R^\bullet$ depends upon the temperature and the properties of the film. This ratio increases with increasing temperature, and at the same temperature the ratio is larger in films containing a plasticizer (triacetin). At low temperatures (6–200 K) RPs are observed and are characterized by zero-field splitting (ZFS) values of $2\mathbf{D} \approx 250$ G (corresponding to intraradical distance of $r \approx 6$ Å) and $\mathbf{E} \le 10$ G. Films which do not contain a plasticizer demonstrate ESR spectra of RPs with $2\mathbf{D} \approx 100$ G ($r \approx 8$ Å) at room, and even at elevated, temperatures (up to 400 K) as well as ESR spectra of RPs of two types ($r \approx 6$ and 8 Å) at reduced temperatures. Thus, the measurement of ZFS parameters of RPs produced by the photolysis of D in films can be used to characterize photopolymer film. TR ESR spectra of the triplet state of D were observed in films at 53 K. Simulation of the spectra leads to estimates of $2\mathbf{D} \approx 2200$ G and $\mathbf{E} \approx 165$ G. Decay kinetics of the lophyl radicals in films was satisfactorily described by polychromatic second-order kinetics with a rectangular distribution of reactivity. The estimated maximum difference in activation energies for a film without a plasticizer is ca. 4 kcal/mol, suggesting a range of recombination rate constants of ca. 10^3.

1. Introduction

2-(2′-Chlorophenyl)-2′-(2′-chlorophenyl)-4,4′,5,5′-tetraphenylbisimidazoles (o-Cl-HABI and other hexaarylbisimidazoles are commonly termed HABIs) have been used as free-radical initiators in photopolymer imaging for more than 2 decades.[1] In the present work we investigate the photochemistry of a representative HABI, o-Cl HABI, abbreviated further as D. HABIs undergo thermolysis and direct and sensitized photolysis in both the liquid and the solid phase with the formation of corresponding lophyl radicals ($R^\bullet$).



D (HABI)



$R^\bullet$ (lophyl radical)

In the absence of hydrogen (electron) donors lophyl radicals recombine to D (eq 1). The lophyl radicals $R^\bullet$

$$\underset{\text{HABI}}{\mathrm{D}} \underset{2k_1}{\overset{h\nu\,(\Delta)}{\rightleftharpoons}} \underset{\text{lophyl radicals}}{2\mathrm{R}^\bullet} \tag{1}$$

undergo very slow recombination, similar to the well-known triphenylmethyl radicals and probably for the same reasons (steric hindrance);[2] typical values of $2k_1$ for lophyl radicals are ca. 10–100 $\mathrm{M}^{-1}\cdot\mathrm{s}^{-1}$ in solution at room temperature.[3] Slow recombination of $R^\bullet$ favors the observation of radical pairs (RPs) $R^\bullet...R^\bullet$ by ESR methods under moderate experimental conditions (i.e., without resorting to very low temperature) in viscous solvents. Geminate RPs are important initial intermediates produced by the photodissociation of D, and their self-reactivity (cage effect) will influence the efficiency of polymerization and thus the formation of an image in the photoimaging process.[1]

The present study is concerned with a steady-state and time-resolved (TR) CW ESR study of spectra and an investigation of the reactivity of photogenerated RP and $R^\bullet$ produced by photolysis of D in films consisting of poly(methyl methacrylate) (PMMA), D, and other ingredients commonly used in free-radical photoimaging systems. (More details on the properties of such films can be found in ref 1.)

2. Experimental Section

Reagents and Films. D was synthesized based upon a known procedure.[4] The following commercially supplied materials were used: PMMA (MW 350 000; ICI Acrylics, Inc.), 2-mercaptobenzoxazole (MBO; Eastman Kodak), trimethylolpropane triacrylate (TMPTA; UCB Radcure, Inc.), *N*-phenylglycine (NPG; Eastman Kodak), and leuco crystal violet (LCV; Eastman Chemical Co.). NPG was twice sublimed *in vacuo*. Solvents (Fisher) used as received were methylene chloride, triacetin (plasticizer in films), cyclohexanol, chloroform, toluene, and chlorobenzene. PMMA was used as a polymeric film-forming binder. The stock materials were binder and plasticizer dissolved in methylene chloride. Other ingredients (D, MBO, NPG, TMPTA, LCV) were dissolved in stock solutions for preparation of the films, which were then cast to a dry thickness of 25–50 μm. A number of PMMA films bearing different levels of triacetin, TMPTA, D, NPG, MBO, and LCV were studied. We found that the presence of triacetin and TMPTA had a profound effect on the parameters of the ESR spectra of $R^\bullet$ and their decay kinetics (see the Results and Discussion section). The compositions of four characteristic films is presented in Table 1.

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Table 1. Contents (Parts by Weight) of Films under Investigation

compd	film A	film B	film C	film D
PMMA	65	65	65	65
triacetin	35	0	0	0
TMPTA	0	35	35	35
D	5	5	5	5
NPG	0	1	0	0
MBO	0	0	1	0
LCV	0	0	0	1

For TR ESR experiments at room temperature the films were cut into strips measuring 15 mm in width by 30–40 cm in length. For steady-state ESR experiments and TR ESR experiments at low temperatures, the films were cut into narrow strips measuring ca. 2 mm in width.

Devices and Procedures. The steady-state CW ESR of R• (microwave power ca. 2 mW, modulation amplitude varying from 0.1 to 1 G) were recorded on a Bruker ES 300 spectrometer equipped with a variable-temperature accessory. The error limit of the temperature measurement was ca. ±1 K. A temperature of 77 K was obtained with liquid nitrogen as the coolant, and lower temperatures down to 6 K were obtained with liquid helium. The ESR spectra were taken in quartz ampules (3 mm diameter). Irradiation of the films in the steady-state ESR experiments was performed in the ESR cavity with the full light of a high-pressure mercury lamp passed through an aqueous filter. Irradiation of the sample usually lasted from half a minute to several minutes. Control experiments demonstrated that the temperature of the thermostated tube containing the films did not change under irradiation within the accuracy of the measurement of the temperature. A nanosecond excimer laser (Lambda Physik; λ 308 nm, ~ 30 mJ/pulse, 100 Hz) was employed as an additional source of light. Photoexcitation of the solutions (films) by either lamp or lasers used in the work leads to essentially the same results; the only difference between the two methods (i.e., the intensity of the signals) appears to originate from the difference in the intensity of the light sources.

The TR ESR apparatus used in studying the films and liquid solutions at room temperature has been described in detail.[5] The instrument consists of a Bruker ER 100 D spectrometer, a PAR Model 4402 digital boxcar integrator, a Quanta Ray DCR 2A Nd:YAG laser (8 ns fwhm), and a Bruker broad-band preamplifier with a response time of 60 ns. The ESR signals were detected at variable delay times after the laser pulse using integration times of 50–500 ns. The instrument response time was estimated to be ca. 200 ns. The experiments with liquid solutions were performed with a flow system employing a 0.5 mm quartz cell, and flow rates were around 5 mL/min. In experiments with dry films the latter were drawn through the cavity at a rate of 1–2 cm/min by a chart recorder in a manner similar to that described in the literature.[6] The third laser harmonic (λ 355 nm; laser energy ~ 30 mJ/pulse, 20 Hz) or the nanosecond excimer laser (λ 308 nm, laser energy ~ 30 mJ/pulse, 5Hz) was employed to excite the liquid solutions or moving films.

Low-temperature TR ESR experiments with the films were performed in the same way except that a Bruker ES 3000 instead of Bruker ER 100 D spectrometer was employed. Films were used in ampules, and excitation was performed with the excimer laser described above.

The decay kinetics of R• were monitored at the extremes of the CW ESR spectrum, putting the sweep width equal to zero. The time selected for acquisition of a spectrum was the time of observation of kinetics.

The samples were air-saturated.

Computer Simulation. The computer simulation of the observed TR ESR spectra at low temperatures was accomplished employing Kottis and Lefebrve's modification[7] of the scheme of Yager *et al.*[8] This scheme mixes the molecular frame spin sublevels as a function of orientation in the magnetic and microwave fields. The molecule's orientation can be described by two angles, θ and ϕ, where θ varies from 0 to π and ϕ varies from 0 to 2π. In the simulation, we solve for 100 angles of θ and 200 of ϕ. We assume that the spin–lattice relaxation and $S_0 \leftarrow T_1$ decay are negligible at the time of data acquisition (ca. 1 μs). We used a Levenberg–Marquadt minimization routine to the simulation scheme, and the uncertainties in the zero-field splitting parameters **D** and **E**, as well as in the population of sublevels P_x and P_y, are determined according to standard methods. A line width of 40 G was chosen for each possible transition. The signal of the free radicals (ca. $g = 2.00$) was ignored in the calculations. Further details of these calculations are available in the literature.[9]

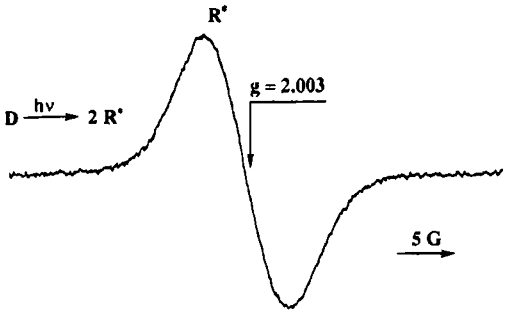


Figure 1. ESR spectrum of the photoirradiated film A at 293 K.

3. Results and Discussion

Steady-State ESR Spectra. a. Liquid Solutions. Prior to irradiation, solutions of D ($C \sim 10^{-3}$ M) in various solvents manifest weak ESR signals at room temperature and are typical of lophyl radicals. ESR spectra of R• are characterized by $g = 2.003$, line width of 9 G, which are very similar to those produced by the photolysis of hexaphenylbisimidazole (unsubstituted HABI).[3,10] Small hyperfine coupling constants (HFC) from the many magnetic nuclei (H, N, Cl) in R• lead to the observation of a broad envelope of the spectrum with poorly resolved HF structure. A decrease in microwave power and modulation amplitude as well as an increase in gain leads to better resolution of the HF structure. An increase in the temperature or the irradiation by lamp or laser of various liquid solutions of D leads to a significant increase in [R•] and in the intensity of the ESR signal.

In agreement with previous observations,[1] oxygen affects neither reaction 1 nor other parameters (e.g., ESR spectra) measured in this work.

b. Films and Frozen Solution. The investigated films (Table 1) did not exhibit ESR signals at room or elevated (up to 400 K) temperatures; however, irradiation of films containing a plasticizer at room or elevated temperatures led to an ESR spectrum that is experimentally indistinguishable from that observed in liquid solutions (Figure 1). Irradiation of such films at low temperatures ($T \leq 190$ K) leads to a different type of ESR spectrum, which can be described as a superposition of the ESR spectrum of R• (central component at $g = 2.003$) and a spectrum of at least one other species (Figure 2). The ESR spectrum of the other species is characteristic of a compound with spin $S = 1$ (RP or triplet state or biradical, etc.).[11,12] From the discussion that follows, we ascribe this spectrum to that of a RP, R•...R•. In accordance with procedures in the literature,[11,12] the distance (measured in gauss or in any energy units) between the outmost weak components of the ESR spectrum of RP corresponds to 2**D**, where **D** is the absolute value of the zero-field splitting (ZFS) parameter; cf. Figure 2. It is assumed that RPs are

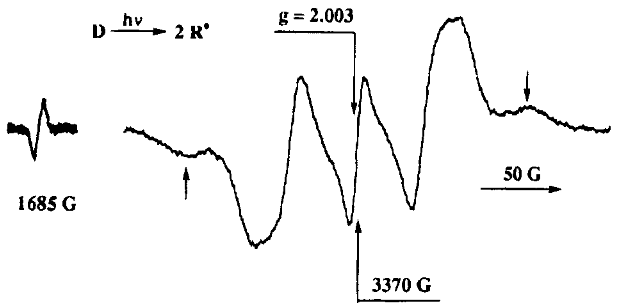


Figure 2. ESR spectrum of the photoirradiated film A at 157 K. The distance between the vertical arrows corresponds to 2**D**. The transition with $\Delta M_S = 2$ is shown; see text.

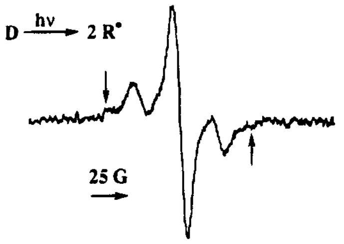


Figure 3. ESR spectrum of the photoirradiated film B at 293 K. The distance between the vertical arrows corresponds to 2**D**.

randomly oriented and the hyperfine structure is not resolved.[11,12] The indicated signals correspond to the allowed transitions with $\Delta M_S = 1$. Another characteristic feature of RPs is the presence of a "forbidden" weak transition ($\Delta M_S = 2$) at half-field.[11,12] This transition is easily observed for RPs which demonstrate relatively intense allowed transitions; cf. Figure 2. These RPs are assumed to have an approximate axial symmetry (because the second ZFS parameter $\mathbf{E} \approx 0$) because they do not show any additional splittings of the allowed transitions.[11,12]

Measurement of **D** allows one to estimate the distance r between unpaired electrons in RP using eq 2:[11,12]

$$r/\text{Å} = 30.3(\mathbf{D}/\text{G})^{-1/3} \qquad (2)$$

Most of the films and frozen liquid solutions demonstrate spectra with 2**D** of ca. 250 G (r of ca. 6 Å).

It was found that the presence of triacetin in the films clearly affects the experimental results. The films investigated can be roughly subdivided into two classes: "rigid" films, which contain a polymerizable plasticizer TMPTA, and "soft" films, which contain a nonpolymerizable plasticizer triacetin (cf. Table 1). Recombination rates as well as yields of lophyl radicals are higher in soft films compared to rigid films under similar conditions. All films contain a plasticizer, triacetin, or a monomer TMPTA (Table 1). Films containing nonpolymerized TMPTA may be considered as soft; however, after short irradiation, these films treated with TMPTA rapidly become rigid films due to photoinduced polymerization, and their IR spectra before and after irradiation demonstrate this polymerization (see below). Film B polymerizes very rapidly and behaves as a rigid film after very short (ca. 10 s) irradiation.

Rigid films (B and others) exhibit ESR spectra of RPs with 2**D** ≈ 100 G ($r \approx 8$ Å) at room (Figure 3) and elevated temperatures (up to 400 K) and also two types at reduced temperatures (Figure 4). The formation of two or more types of RPs in a polymer has been discussed in the literature.[13]

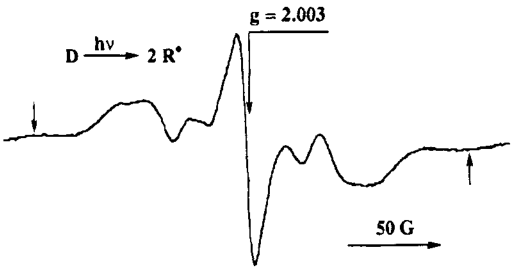


Figure 4. ESR spectrum of the photoirradiated film B at 154 K. The distance between the vertical arrows corresponds to the largest 2**D** value; see text.

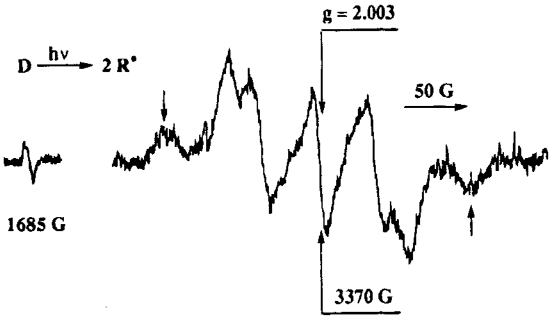


Figure 5. ESR spectrum of the photoirradiated solution of D (5×10^{-3} M) at 77 K in chloroform/toluene (50:50, v/v). The transition with $\Delta M_S = 2$ is shown; see text.

The relation between concentrations of R$^\bullet$ and RP depends upon the properties of the film; i.e., for the same film the relative intensity of the "allowed" ESR transitions corresponding to RP compared to that of free radical R$^\bullet$ increases with decreasing temperature. This observation is in accordance with the observation of ref 14b; we suggest that the species with $S = 1$ are not the triplet state of D[14b] but should be ascribed rather to the RPs (see the discussion below).

The 2**D** value can be determined with moderate precision from the observed spectra (cf. Figures 2–4). It is qualitatively clear that the value of 2**D** (or r) depends upon the temperature of the film. 2**D** varies from 250 G (r = 6.1 Å) at 6–50 K to 210–220 G (r = 6.3–6.4 Å) at 150–200 K (film A).

It is informative to compare the ESR spectra obtained in films with those obtained in a low-temperature glass. Figure 5 shows the ESR spectrum of a photoirradiated solution of D at 77 K in chloroform/toluene (50:50, v/v) glass. Formation of separated R$^\bullet$ and PRs is observed in the frozen solution as in films (cf. Figures 2–4 and Figure 5). The ESR parameters of the spectrum demonstrate that RPs do not possess symmetry axes; from the observed spectra[11,12] $\mathbf{E} \approx 10$ G. In agreement with previous interpretations,[10c] the spectra, which demonstrate signals characterized by $S = 1$ under photolysis of D, were assigned in the present work to RPs by the following arguments. (i) Spectra of the species with $S = 1$ are characterized by $2\mathbf{D} \approx 250$ G in the temperature interval of 6–170 K and, therefore, can be ascribed to the same species. The spectra do not change in time at $T \leq 100$ K and thus should be attributed to the poorly reactive RPs and not to the photoexcited triplet state of an organic molecule (^{3}D), which is expected to decay by a radiative or radiationless process in seconds or less.[15] (ii) The relative concentration of RPs compared to R$^\bullet$ varies with temperature. This relative concentration decreases with decreasing temperature. In fact, this observation agrees with the expectation that the decrease in temperature leads to a decrease in the

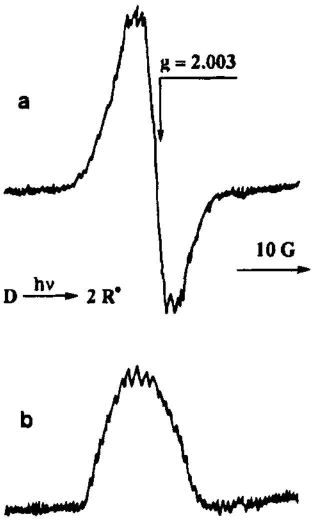


Figure 6. TR ESR spectra of D (5×10^{-3} M) in cyclohexanol taken at (a) 0.5 μs, A*/E pattern; (b) 6.0 μs, A pattern. The spectra are presented in the form of direct absorption/emission, not as a usual derivative.

mobility of the radicals and hinders the separation of RPs into free radicals. (iii) Two different species with $S = 1$ can be observed in certain films that are irradiated (cf. Figure 4). These species are attributed to RPs separated into different distances and cannot be attributed to ^{3}D. (iv) We have observed the TR ESR spectrum of photoexcited D, which can be ascribed to ^{3}D. This spectrum possesses a much larger value of 2**D** and decays in a microsecond time scale, properties expected for an organic triplet state (for details, see the TR ESR Experiments at Low Temperature section).

Our experimental observations are mainly in agreement with a literature report[14] of the ESR spectra of lophyl radicals at low temperatures (up to 5 K), but our interpretation is not. In the earlier report,[14b] the spectra with $S = 1$ were assigned to ^{3}D (the triplet state of HABI) based on the temperature independence of **D** (or r). Since the temperature interval examined was small (from 5 to 8 K), a temperature dependence may not be evident in this range (see above).[16] We suggest that the evidence provided in this report justifies a revision of this assignment.

Our ESR data on RPs corroborate previous observations and conclusions[17] that rigid films are microheterogeneous and have at least two phases in which dissolved species show "slow" and "fast" molecular mobility. We observed that the line width of the ESR spectra of RPs weakly depends upon temperature. An increase in the temperature results not in the averaging of molecular mobility in the film but in the decrease in relative volume (area) of the regions with slow mobility, where RPs are immobilized.

Irradiation of films containing TMPTA leads to the polymerization of the monomer. The polymerization manifests itself as the decrease or disappearance of the absorption band at 810 cm^{-1} (twisting vibrations of the ethylene group[18]) in the IR spectrum of irradiated films. Films containing LCV (film D, Table 1) visibly demonstrate a sensitivity to irradiation and even to their exposure to daylight. Upon irradiation they rapidly become blue with the appearance of film absorption at λ_{max} 600 nm from the formation of the dye crystal violet.

TR ESR Experiments with Liquid Solutions and Films at Room Temperature. TR ESR spectra of D in cyclohexanol are presented in Figure 6a. The spectra display an A/E (or A*/E) pattern, which is characteristic for a compound dissociating into a radical pair via the singlet state.[19] Indeed, it has been speculated that HABIs undergo photodissociation via the singlet state.[14] The observed TR ESR spectrum (Figure 6a) provides direct spectroscopic evidence that photolysis proceeds via the singlet state.

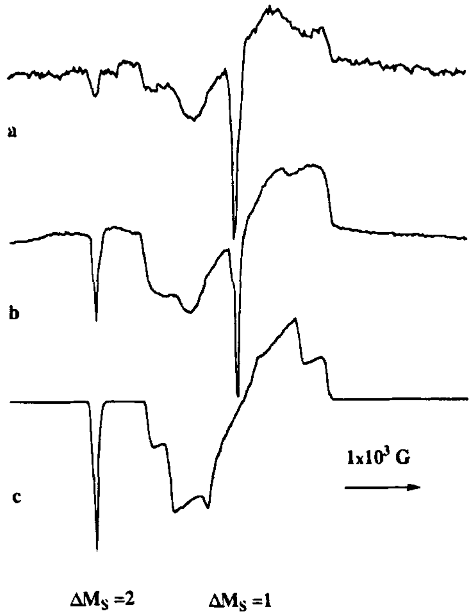


Figure 7. TR ESR spectra of films at 53 K: (a) rigid film B; (b) soft film A; (c) computer simulation of TR ESR spectrum of b; see the text for an explanation. The spectra are presented in the form of direct absorption/emission, not as a usual derivative.

This system demonstrates an A pattern due to the Boltzmann population of electronic levels in the magnetic field at the longest times (ca. 6 μs) of observation; cf. Figure 6b. Such an observation is expected for the systems investigated. In the absence of strong net (integral) polarization the observation of slow growth of the ESR signal is an evident result of spin relaxation.[20] The slow decay of R$^\bullet$ also facilitates the observation of the A pattern at longer times.

TR ESR spectra of soft films demonstrate a similar A/E or A*/E or A pattern (depending upon the time of observation) but with a relatively poor signal-to-noise ratio. In rigid films the signal-to-noise ratio was even poorer, and only very weak signals were observed.

TR ESR Experiments at Low Temperature. Figure 7 shows the TR ESR spectra of soft (A) and rigid (B) films at low temperature as well as a simulation of the spectrum of a soft film, showing better signal-to-noise ratio. Simulation of the spectra leads to the estimation of 2**D** $\approx$ 2200 and **E** $\approx$ 165 G. These values are ca. 10 times larger than the corresponding **D** and **E** values obtained for RPs (see the Steady-State ESR Spectra section). The distance between unpaired electrons is estimated by eq 2 to be ca. 3.0 Å, i.e., a significantly shorter distance. This TR ESR (Figure 7), which decays on the microsecond time scale, is assigned to the triplet state, ^{3}D.

Decay Kinetics of R$^\bullet$. The decay of lophyl radicals in films is determined mainly by recombination reactions of R$^\bullet$.[1,3] However, R$^\bullet$ will also react with certain additives in the film (LCV, NPG, MBO),[1,21] leading to polymerization and changing film viscosity. Short lamp irradiation (ca. 30 s) led to the production of relatively high concentrations of radicals, which mainly recom-

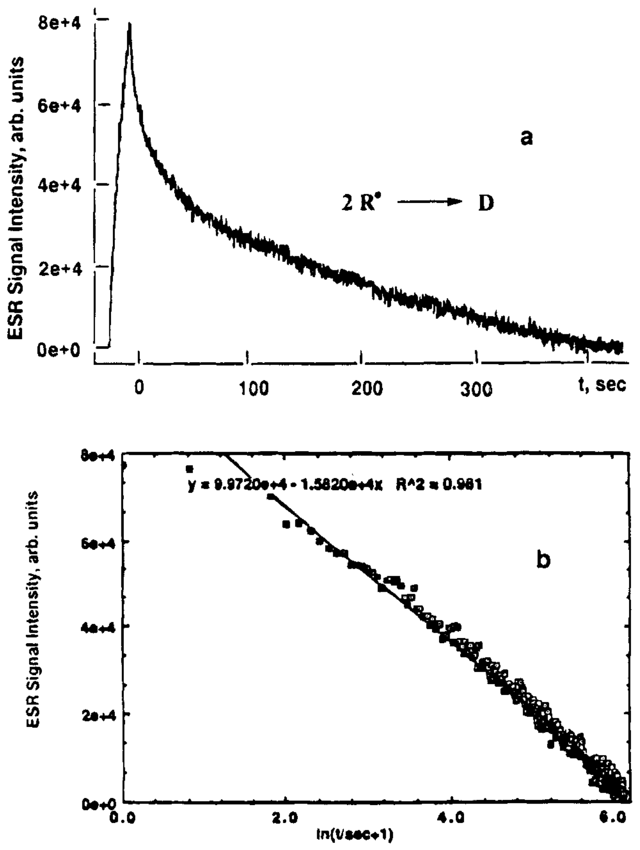


Figure 8. (a) Kinetics of growth and decay of R• at room temperature in film B under irradiation. Ascending part of the curve corresponds to irradiation of the film by the lamp; (b) decay kinetics of R• in coordinates corresponding to the second-order polychromatic kinetics; see text. The data corresponding to the descending part of the curve of Figure 6a were plotted.

bine; see eq 1. The subsequent irradiation of the same film after recombination of radicals during the same time leads to 98–99% of the concentration of R• obtained in every previous irradiation. So, the aforementioned 98–99% of the photogenerated lophyl radicals recombine. Study of the IR spectra of films subjected to such short irradiations demonstrates a 30–80% decrease in intensity in the double bonds of TMPTA due to a chain reaction of polymerization under such short irradiation.

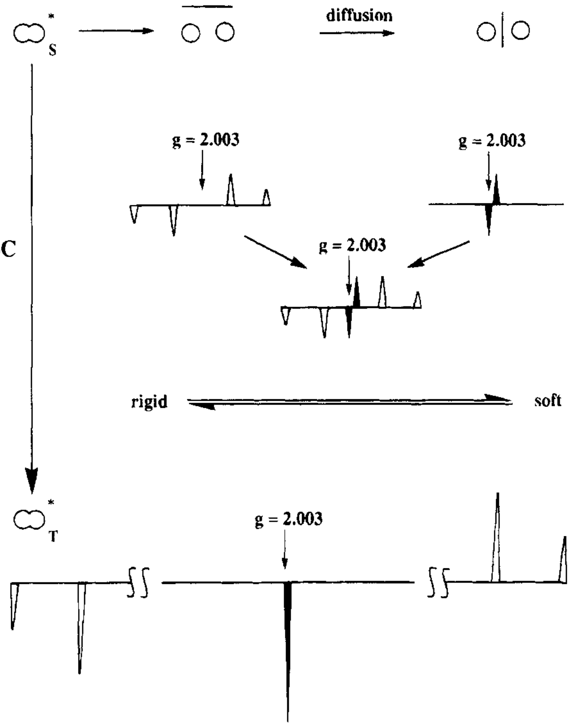
The decay kinetics of R• are not described by first- or second-order kinetics.[22] However, it is known that the kinetics of many elementary reactions in the solid state and in polymers are described by polychromatic kinetics, where the kinetic nonequivalence of chemically identical species (radicals) is accepted as a model for the analysis of the decay kinetics.[24] This nonequivalence remains unchanged throughout the reaction. The simplest assumption for an analysis with the model is that reagents have a rectangular distribution according to their activation energies E, i.e., $E_{\min} \leq E \leq E_{\max}$.[24,25] In such a case one should expect a linear dependence of [R•] *vs* ln t:[25]

$$[\mathrm{R}^\bullet] \sim -\ln t \qquad (3)$$

at relatively large t with a slope of $RT/(E_{\max} - E_{\min})$.

In fact, the decay kinetics of R• were satisfactorily described *via* the polychromatic kinetic model; cf. Figure 8. Deviation of the first several points from the straight line (Figure 8) is expected.[25] For the rigid film B the range of difference in activation energies $\Delta E = E_{\max} - E_{\min} \approx 4$ kcal/mol, which leads to a range of difference in rate constants of 3 orders of magnitude at 293 K.[26,27] The presence of triacetin, which replaces TMPTA in the film composition (Table 1), leads to enhanced reactivity (or recombination) or R•. As expected, R• has a higher reactivity in soft (A) rather than in rigid (B–D; cf. Table 1) films. For the soft film A it was estimated that $\Delta E \approx 2$ kcal/mol. Apparently, diffusivity and reactivity of other film components is higher in soft films.

Scheme 1



Although the rectangular distribution of reactivity of photogenerated lophyl radicals in films leads to a satisfactory description of their decay, the reconstruction of the real distribution of reactivity is a complicated mathematical problem.[28,29]

A quasi-stationary concentration of R• is reached under prolonged irradiation ($t \geq$ ca. 5 min) of films using a lamp at room temperature. This concentration slowly decreases with further irradiation. Interaction with the film components (chain-transfer agents[21]) and the enhanced reactivity of photoexcited free radicals[30] may be responsible for such a decay.

4. Conclusions

ESR spectra of photoirradiated films containing a representative HABI were investigated, and the photolysis of these films leads to the appearance of free R• as well as of radical pairs (RPs) in their ESR spectra. The spectrum of R• exhibits a single line (line width ca. 9 G) with nonresolved hyperfine structure. The relationship between concentrations of R• and RP depends upon the properties of the film; e.g., at low temperatures (6–200 K) RPs are observed, which are characterized by a zero-field splitting (ZFS) value of **2D** ≈ 250 G (or intraradical distance of $r \approx 6$ Å).

Rigid films demonstrate ESR spectra of RPs with **2D** ≈ 100 G ($r \approx 8$ Å) at room and elevated temperatures (up to 400 K); and at reduced temperatures, they show ESR spectra of two types of RPs. It is suggested that the measurements of the ZFS values of RPs in films can be used as a probe of the properties of a photopolymer film.

The TR ESR spectra of the triplet state of D were also observed. The spectrum of ^{3}D is characterized by a very short triplet decay (ca. microseconds) and 10 times larger values of **2D** and **E** than those for RPs; the distance between unpaired electrons in ^{3}D is estimated as $r \approx 3$ Å.

These results are summarized in Scheme 1.

Recombination kinetics of $R^•$ in films is satisfactorily described by polychromatic kinetics with a rectangular distribution of reactivities. Both ESR and kinetic results testify to the fact that films possess at least two phases with different reactivity (or diffusivity of $R^•$).

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(25) Under this assumption the following equation holds true for $[R^•]$:

$$[R^•]/[R^•]_0 = 1 - \frac{RT}{E_{\max} - E_{\min}} \ln\left(\frac{1 + 2k_{1(\max)}t[R^•]_0}{1 + 2k_{1(\min)}t[R^•]_0}\right) \qquad (4)$$

where $2k_{1(\max)}$ ($M^{-1}{\cdot}s^{-1}$) is the maximum value of $2k_1$ (corresponding to $E_{\min}$) and $2k_{1(\min)}$ ($M^{-1}{\cdot}s^{-1}$) is the minimum value of $2k_1$ (with $E_{\max}$); cf. ref 24a. The subsequent assumptions are the relatively large difference in $E_{\max}$ and $E_{\min}$ values and large times of observation of kinetics.[24a] In other words, one assumes that during the observation of decay kinetics, $2k_{1(\max)}t[R^•] \gg 1$ and $2k_{1(\min)}t[R^•] \ll 1$, which leads to eq 3. The greater the time of observation of the kinetics and the greater the difference between $E_{\max}$ and $E_{\min}$, the better eq 3 approximates eq 4.

(26) A reasonable estimation based on data for the liquid phase[3] is that $2k_1 = 10^7 \exp(-E/RT)$, where E varies from $E_{\min} = 7$ kcal/mol to $E_{\max} = 11$ kcal/mol for polymers and thus $2k_1$ varies from 10^{-1} to 10^2 $M^{-1}{\cdot}s^{-1}$ at room temperature.

(27) Our kinetic experiments have been conducted in the magnetic field of an ESR spectrometer, which affects the recombination rates. In the Earth's magnetic field one can expect ca. a 30% higher recombination rate for lophyl radicals in PMMA than in the magnetic field of an ESR spectrometer; cf. ref 23.

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