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EPR/ENDOR STUDY OF THE DECAY OF TRAPPED RADICALS IN PHOTOPOLYMERIZED BUTANE-1,4-DIOL DIACRYLATE

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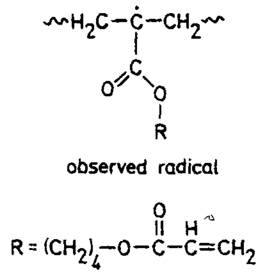
Long-lived trapped radicals produced during the photopolymerization of butane-1,4-diol diacrylate (BDDA) were studied by EPR and ENDOR spectroscopy and their thermal decay was followed by EPR measurements at different temperatures (40–120 °C) for kinetic study. The EPR signal showed the superimposition of two different patterns, a three-line and a single-line spectrum. Both EPR patterns decayed following first-order kinetics in the investigated temperature range. Activation parameters of the decay were obtained. The EPR patterns were attributed to the same radical species situated in fluid and in cross-linked regions of the photopolymerized BDDA. Radicals of the latter kind undergo electron spin exchange strong enough to wash out the hyperfine splitting. The single-line width is mainly determined by electron spin dipole–dipole interactions. The ENDOR response is only of the matrix kind, typical of radicals in a solid phase. The present model was also compared with recent literature reports.

INTRODUCTION

Trapped radicals in polymers produced by free radical polymerization of multifunctional acrylates were observed by EPR spectroscopy more than 30 years ago.[1] Many industrial applications of the photoinduced polymerization of multifunctional monomers have been developed recently,[2,3] and the properties of the polymer are strongly dependent on the irradiation conditions. This stimulated kinetic studies[3–6] of the photopolymerization process with several experimental techniques. It has been demonstrated that total conversion of acrylic groups is hardly attainable, owing to an early local gelation effect, and that diffusion restrictions are determinant both in the propagation and in the termination of the growing polymer chains.[4,5b] Trapping of radicals, due to the inhomogeneity of the system,[7] occurs from the early stages of photopolymerization, when a great amount of unreacted monomer is still present. The slow decay of radical species after irradiation is accompanied by further polymerization.

In an earlier paper[8] a model was proposed to account for the EPR spectra observed in photopolymerized hexane-1,6-diol diacrylate (HDDA) and tetraethylene glycol diacrylate (TEGDA) and for their decay with time at different temperatures. Experimental EPR spectra, fitted by an automatic non-linear least-squares procedure, turned out to represent the superimposition of a three-line and a single-line pattern, both attributed to the same radical in different environments. This should not be the propagation radical, but a mid-chain radical resulting from tertiary hydrogen abstraction from the polymer chain (see Scheme 1). The three-line spectrum, which shows an isotropic hyperfine splitting of about 25 G (2H), was attributed to radicals present in the fluid phase whereas the single-line spectrum was attributed to radicals in denser, cross-linked regions. The hyperfine interaction in these latter radicals is washed out of the EPR spectrum by electron spin–spin exchange between like radicals.



Scheme 1

ENDOR spectra were matrix[9] lines, typical of the solid state, split by hyperfine interaction; no ENDOR response was obtainable from the three-line EPR spectrum.

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The decrease with time of the EPR spectral areas at different temperatures was a first-order decay proceeding at the same rate as the parallel first-order conversion of double bonds, which was followed by chemical analysis.[8]

Recently several EPR studies on photopolymerized or free-radical polymerized acrylates have been reported,[10-12] and other workers have given different interpretations of their experimental results.[10,12] This prompted us to verify our model further by studying the radical decay of another photopolymerized diacrylate molecule, butane-1,4-diol diacrylate (BDDA). This monomer shows slightly different molecular characteristics to the previously investigated diacrylates, which have almost identical behaviour owing to the similarity of their chain lengths and mobilities.

EXPERIMENTAL

Sample preparation. Butane-1,4-diol diacrylate (BDDA) was a commercial product (UCB, Belgium) and was used without any further purification. Pure monomer, without any photoinitiating species, was irradiated for 12 min under vacuum in a quartz EPR tube, outside the spectrometer cavity. The previously described[8] apparatus and experimental procedure were employed. After the irradiation a transparent, colourless and apparently homogeneous solid was obtained.

Analysis of residual unsaturations was carried out by IR spectrometry on a Perkin-Elmer Model 1710 Fourier transform IR spectrometer. The peak at 812 cm^{-1} corresponding to the $CH_2{=}CH{-}$ twisting vibration of the acrylate group[13] was monitored. This revealed that, after the same standard irradiation time (12 min), BDDA samples reached the same degree of photopolymerization (68%) obtained with the previously investigated diacrylates.

Under the adopted experimental conditions, a degree of conversion higher than 68% could not be obtained even by longer irradiation of BDDA, whereas shorter irradiation times produced lower degrees of conversion.

EPR and ENDOR spectroscopy. EPR spectra were recorded by means of a Varian E-line Century Series EPR spectrometer equipped with a laboratory-built variable-temperature facility. EPR measurements were performed with BDDA samples photopolymerized under standard conditions (68% double bond conversion) within 15 min after the end of the irradiation. As the decay of trapped radicals is extremely slow at room temperature in the dark, no significant reaction occurred in this short lapse of time. The temperature of the samples was kept constant at the desired values to within ±1 °C by a flow of pre-warmed air. Digitized spectra were transferred to a Gould NP1 computer through an IBM PS/2 80, in order to fit them using the program EPR85.[14] The least-squares fitting procedure yielded width, hyperfine splitting, difference in g-factors and spectral area of each of the two overlapping patterns. The statistical error affecting each parameter was also calculated.

Radical decay kinetics were followed by monitoring the EPR intensity at temperatures ranging from 40 to 120 °C. The reaction is very slow at temperatures lower than 40 °C, so that kinetic runs are very time consuming. At temperatures higher than 120 °C the decay kinetics may become more complicated.[8]

Some runs were also carried out at 90 °C with lower initial degrees of conversion down to 50%. Samples with initial degrees of conversion lower than 50% gave an EPR signal that was too weak for kinetic study.

ENDOR spectra were recorded by means of a Bruker ESP300 spectrometer equipped with a Bruker ERO33C F/F lock, a Bruker EN810 ENDOR unit, a ENI A-900 radiofrequency (RF) 900 W power amplifier and a Bruker ER4111VT variable-temperature unit. The best ENDOR signal was obtained with a microwave power of 6.3 mW and 5 dB (900 W) RF power attenuation. The RF modulation depth was kept to 50 kHz to achieve a good resolution. Five scans were added for each spectrum. Low-temperature (100–200 K) ENDOR measurements were carried out by cooling the sample with a stream of cold nitrogen. ENDOR spectra were then transferred to an IBM PS/2 80 personal computer for subsequent analysis.

RESULTS

EPR spectra

Pre-irradiated samples kept in the dark exhibited stable EPR spectra. Like the previously investigated systems, photopolymerized BDDA yielded an EPR spectrum which turned out to be the superimposition of a single-line and a three-line pattern, both Lorentzian in shape, with the same g-factor. This was measured using DPPH as reference and was found to be 2·0028 at 40 °C. At the same temperature the hyperfine coupling constant of the three-line spectrum was $a_{2H} = 24{\cdot}51 \pm 0{\cdot}08$ G and the line width was $\Delta W_1 = 8{\cdot}2 \pm 0{\cdot}2$ G for the three-line spectrum and $\Delta W_2 = 32{\cdot}3 \pm 0{\cdot}9$ G for the single-line spectrum (see Figure 1). The single-line spectrum always showed an integrated signal intensity higher than that in the three-line spectrum. At 40 °C, the ratio between the spectral areas, measured at the end of irradiation, was 2·29.

Radical decay kinetics

In the range 40–120 °C, the decay of both signals of pre-irradiated BDDA followed first-order kinetics, characterized by the rate constants reported in Table 1. By comparing the present results with those obtained

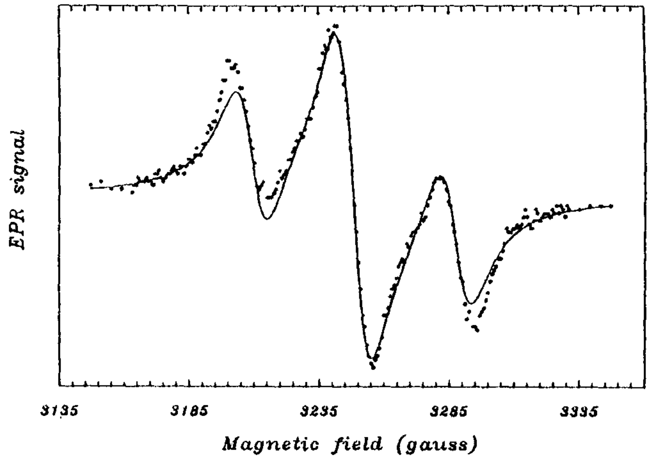

Figure 1. EPR spectrum of pre-irradiated BDDA at 40 °C. (*) experimental spectrum; (—) least-squares fitted spectrum. See text for the optimized parameters

with the previously investigated pre-irradiated monomers, we first note that a single relaxation expression can account for the kinetic data obtained at 120 °C with BDDA, whereas a multiple relaxation expression gave a better fitting for HDDA and TEGDA.[8] As in the latter two cases, the BDDA three-line spectrum decayed at higher rates than the single-line spectrum. For pre-irradiated BDDA, the first-order rate constants were lower than for the other two diacrylate systems at the same temperature. Moreover, they were independent of the initial degree of photopolymerization in the range 50–68%. The activation enthalpy, $\Delta H^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$, were also obtained from an Eyring plot of the kinetic data (see Table 2).

Spectral line widths vs concentration

As for photopolymerized HDDA and TEGDA, the three-line spectrum of BDDA did not undergo any significant line broadening on increasing the radical concentration, whereas the single-line spectrum showed a linear increase in width (see Table 3). However the slope of the line width vs concentration plot showed a threefold increase when the temperature was lowered from 120 to 40 °C, at variance with the previously investigated cases.

Table 1. First-order rate constants, k (10^{-4} min^{-1}), of radical decay from EPR measurements of pre-irradiated HDDA (from Ref. 8) and BDDA at various temperatures

	Three-line spectrum		Single-line spectrum	
T(°C)	HDDA	BDDA	HDDA	BDDA
40	2·7 ± 0·8	0·74 ± 0·04	2·3 ± 0·6	0·44 ± 0·05
60	11 ± 1	4·6 ± 0·2	9 ± 2	3·0 ± 0·2
90	55 ± 7	30 ± 3	27 ± 3	13 ± 2
120	—[a]	75 ± 11	—[a]	25 ± 7

[a] No single relaxation expression was found in this case.[8]

Table 2. Activation enthalpy, $\Delta H^{\ddagger}$, and activation entropy, $\Delta S^{\ddagger}$, for the radical decay of the single-line spectrum in different pre-irradiated diacrylate polymers

Monomer	$\Delta H^{\ddagger}$(kJ mol^{-1})	$\Delta S^{\ddagger}$(J K^{-1} mol^{-1})
HDDA[a]	39 ± 2	−222 ± 5
TEGDA[a]	40 ± 1	−219 ± 3
BDDA	56 ± 7	−148 ± 25

[a] From Ref. 8.

Table 3. Slopes of linear correlation of the width of the EPR single-line ΔW_2 with the radical concentration C in pre-irradiated BDDA at different temperatures[a]

T(°C)	q[G(arbitrary units)$^{-1}$]
40	33 ± 3
60	20 ± 2
90	16 ± 6
120	10 ± 7

[a] The regression equation is $\Delta W_2 = p + qC$, where C is the single-line integrated spectral area (arbitrary units) proportional to the concentration of the corresponding radical species.

ENDOR spectra

^{1}H ENDOR of pre-irradiated BDDA (see Figure 2) was detected with the magnetic field set at the centre of the EPR spectrum. ENDOR spectra recorded at different settings throughout the EPR absorption differed only in the absolute intensity. No significant change in the ENDOR spectrum was observed on increasing the temperature from 100 to 200 K, where the ENDOR signal was no longer detectable.

The ENDOR pattern, centred at the free proton frequency (14·5 MHz), is composed of a narrow single line and a doublet of broad lines. The overall spectrum spans about 3 MHz and is very similar to those obtained with pre-irradiated HDDA and TEGDA.[8]

This kind of ENDOR is known as matrix[9] ENDOR since it is due to matrix nuclear spins (protons in our case), which interact with the unpaired electron spin by hyperfine coupling. Theories of matrix ENDOR at different levels of sophistication have been proposed.[15] The assumption that the nuclear spin transitions are saturated allows the use of a simplified theory of matrix ENDOR proposed by Leniart *et al.*[16] In this model the ENDOR line position is determined by the free proton frequency and by the isotropic hyperfine constant a and the line shape is determined by the anisotropic (dipolar) hyperfine constant δ and by the width w of the Lorentzian function used in the convolution of the stick spectrum.

We performed extensive simulations of the proton ENDOR spectrum using a computer program[17] based on the above theory. All the parameters were varied widely until we obtained a satisfactory match between the experimental and simulated spectra (see Fig. 2). The best parameters for the doublet pattern are $a = 0{\cdot}13$ MHz, $\delta = 0{\cdot}28$ MHz and $w = 0{\cdot}23$ MHz. The single narrow line is too weak for a reliable simulation. Its width is about 0·04 MHz and it is affected by the RF modulation, the depth of which is 0·05 MHz. All we can say is that the hyperfine interaction of the nuclei giving rise to this line must be less than 40 kHz.

DISCUSSION

Our present and previous[8] experimental results must be compared with some recent literature reports. The EPR spectrum of pre-irradiated HDDA has been unequivocally identified as a mid-chain radical[18] surrounded by four β-methylene protons (see Scheme 1). The fact that only two of the four β-methylene protons show appreciable hyperfine interaction has recently been attributed[10] to a well defined conformation around the mid-chain polyacrylate radical. However, the experimental spectroscopic pattern could not be satisfactorily simulated by a single radical conformation. A good match between experimental and simulated EPR traces was obtained when a Gaussian spread around the most probable dihedral angle was assumed.

Two kinds of overlapped EPR spectra, in contrast, have been unequivocally observed for the bulk free-radical polymerization of methyl methacrylate initiated by ultraviolet light.[11] They have been attributed to free radicals in the liquid and to radicals trapped in the solid state.

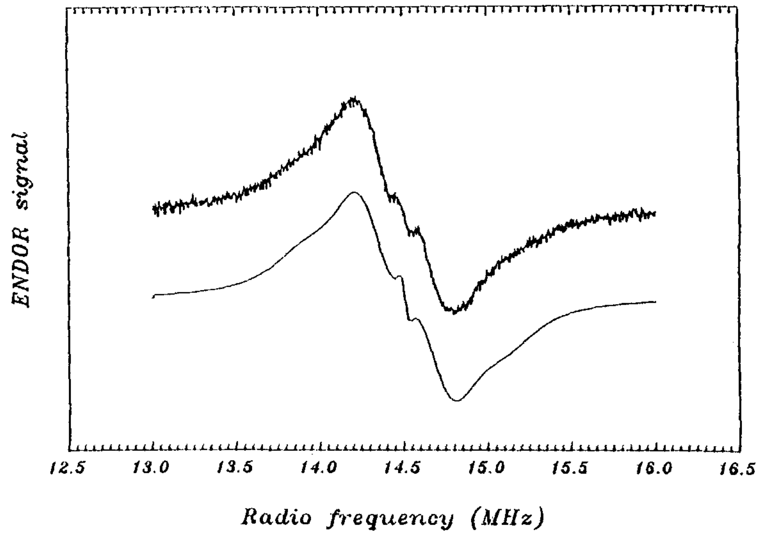

Figure 2. ENDOR spectrum of pre-irradiated BDDA at 100 K (−173 °C). The noisy trace is the experimental spectrum and the other trace is the spectrum simulated with the parameters given in the text. The free proton Larmor frequency is 14·5 MHz

Similar patterns are typical of the acrylate function in pre-irradiated multifunctional species.[3,5,10,12] It has also been reported that the hyperfine splitting observed by EPR in multiacrylate systems disappears and only a single line is detectable after prolonged thermal after-treatments[19] or after very long irradiation times.[12] This single line is attributable only to the mid-chain radical characteristic of photopolymerized multiacrylates[7,8] in a highly cross-linked environment and is not due to the presence of different radical species (e.g. radicals from the photoinitiator). In fact, this type of signal is not observable in the absence of acrylate functions.[12] As the three-line spectrum decays at a higher rate than the single-line spectrum, also in our kinetic runs only the latter is observable at long after-treatment times.

In our previous work,[8] the interpretation of the EPR spectra of pre-irradiated diacrylates as the overlap of two different patterns from the same radical species found further support in ENDOR studies; the ENDOR response, in fact, seemed not to be due to the radical species in the mobile phase generating the three-line EPR spectrum, but could be better attributed to the species producing the EPR single-line spectrum.

The EPR and ENDOR spectra observed with pre-irradiated BDDA are qualitatively similar to those already reported for HDDA and TEGDA.[8] Again, both the single- and the three-line spectra are due to the same type of radical, situated in different environments. The identity of the *g*-factor of both EPR patterns in photopolymerized BDDA supports this conclusion.

The decay rate constants of the three-line and the single-line spectra are always lower in BDDA than in HDDA and TEGDA (see Table 1) as a consequence of the lower mobility and flexibility of photopolymerized BDDA. A similar trend has been observed also in the first-order rate constants of double bond conversion occurring during the thermal after-treatment of photopolymerized diacrylates. Their values, determined on less photopolymerized BDDA samples,[20] were lower than those measured with pre-irradiated HDDA and TEGDA,[8] and fairly close to the radical decay rate constants reported for BDDA in Table 1. Then mid-chain radicals occluded in the polymer network can still produce some further polymerization, and both propagation and termination reactions are equally influenced by the local chain mobility.

The activation parameters obtained from Eyring analysis of the decay rate constants of the BDDA single-line spectrum along with activation parameters of HDDA and TEGDA[8] are reported in Table 2. A more rigid cross-linked phase is expected for BDDA than for HDDA and TEGDA, owing to a closer packing of polymer chains. This could be the reason why a larger value of the radical-decay activation enthalpy $\Delta H^{\ddagger}$ is measured for pre-irradiated BDDA than for HDDA (see Table 2). Results obtained with photopolymerized BDDA confirm that the three-line spectrum is due to a more mobile radical species, as it decays at a higher rate than the single-line spectrum, and its decay rate increases faster with increasing temperature. The activation entropy $\Delta S^{\ddagger}$ resulting from the kinetic data for pre-irradiated BDDA is smaller than that obtained with HDDA. This could again be attributed to a shorter distance between the reactive centres in the polymer network.

The lack of hyperfine splitting in the single-line spectrum is attributed to spin exchange between radicals in the cross-linked region. Since the spin exchange is effective on the radicals in the more viscous phase, it should not be caused by collisions of the paramagnetic centres, as usual in solution, but by the interaction between radicals at distances comparable to molecular diameters. This mechanism of spin exchange is expected in solids[21] and in concentrated solutions.[22] Clusters of radicals have been previously detected in γ-irradiated ethylene glycol dimethacrylate[23] and methyl methacrylate[24] polymers.

The line width of the three-line spectrum is constant when the radical concentration decreases. In contrast, the single-line width shows an appreciable decrease when the radical concentration decreases. These observations, as in the previously investigated cases, suggest that neither spin exchange nor electron spin dipole–dipole interaction takes place between the three-line radicals. This further supports the view that they are in the more mobile and less dense phase.

The behaviour of the single-line width is surprising at first sight. In fact, when spin exchange has washed out the hyperfine splitting, the exchange narrowing region is reached and any increase in radical concentration should lead to larger spin exchange and, consequently, to narrower lines. However, when the concentration of paramagnetic molecules is sufficiently high, the electron spin dipole–dipole interaction results in significant line broadening.[25] The contribution of the dipole–dipole interaction to the line width depends on the radical concentration and on the viscosity of the medium, since this interaction is averaged by the Brownian motion of spins. Low-viscosity solutions of radicals show an appreciable contribution to the EPR line width from dipole–dipole interactions only at very high radical concentrations. For example, an aqueous solution of radicals can be considered viscous from the point of view of averaging the dipole interaction[26] at radical concentrations higher than 10 mol dm^{-3}. In systems with very low molecular mobility (very high viscosity), as in the present case, the concentration-dependent line width is completely determined by dipole interactions[27] at any radical concentration detectable by EPR ($>10^{-5}$ mol dm^{-3}). The dipole broadening is proportional[26] to the radical concentration C:

$$\Delta W_2 = (\Delta W_2)_{\text{dip}} + (\Delta W_2)_0 = k_d C + (\Delta W_2)_0 \qquad (1)$$

where $(\Delta W_2)_0$ is the residual line width and k_d is the proportionality factor. The linear correlation of the single-line width with the radical concentration in BDDA (see Table 3), HDDA and TEGDA[8] supports the conclusion that the observed broadening with increasing concentration is due to electron spin dipole–dipole interactions. Unfortunately, k_d could not be calculated from the slope q of the plots since the radical concentration is known only in arbitrary units.

In fact, the electron spin dipolar interaction is partially averaged by Brownian motion or by spin flip-flops. This averaging is more effective at higher temperatures and results in a significant reduction of the slope q for BDDA from 40 to 120 °C. In this situation the line shape is Lorentzian only in its central part and the wings fall off more slowly than for a Lorentzian shape.[26] This can be seen in Figure 1, where the wings of the single line, overlapped by the outer lines of the other pattern, are underestimated by the least-squares fit. Even if a dipole-dipole interaction is predominant, other mechanisms of line broadening or narrowing, e.g. spin exchange, contribute to q. The dependence of the latter on temperature can be influenced by the temperature dependence of these minor contributions to the line width. The increase in q with temperature found in HDDA and TEGDA samples could be accounted for in this way.

Finally, the weak narrow ENDOR line can be reasonably attributed to protons far away from the unpaired electron, since their hyperfine interaction is less than 40 kHz. A lower limit for the distance between these protons and the unpaired electron can be estimated following Ref. 16 by the equation

$$\delta = 80/r^3 \qquad (2)$$

where δ is the dipolar constant in MHz and r is the proton–electron distance in Å. Since δ is less than 0·04 MHz, r is larger than 13 Å. The protons which give rise to the ENDOR doublet are closer to the unpaired electron and they experience a non-vanishing spin density. An average electron–proton distance of 6 Å can be estimated from the dipolar constant by equation (2). This value is close to that found with HDDA and TEGDA.[8] Then two shells of protons contribute to the ENDOR response. Protons in the outer shell are only weakly coupled to the electron spin whereas protons in the inner shell are coupled to the unpaired electron by both dipole–dipole and Fermi contact interactions. The similarity of ENDOR spectra detected with photopolymerized BDDA, HDDA and TEGDA suggests that the distribution of hydrogen nuclei in the cross-linked region does not depend much on the number of methylene groups between the two acrylate functions of each monomer.

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