

EPR Investigation of Radical Formation and Decay in Photopolymerization of Difunctional Monomers

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The formation of trapped radicals under UV irradiation during the photopolymerization of butane-1,4-diyl diacrylate in the presence of different amounts of photoinitiator, as well as the radical decay after the end of irradiation, have been studied by EPR spectroscopy. Direct evidence that higher photoinitiator radical concentrations greatly favour radical-radical encounters is obtained. The formation of the same radical species in two different polymeric phases, one essentially rigid and the other more fluid, is at the origin of the two observed superimposed EPR patterns. The ratio R between them decreases with increasing photoinitiator concentration, owing to the formation of shorter and consequently more mobile polymer chains. In contrast, the more rigid phase seems to dominate in photopolymerized diallyl 3-oxapentane-1,5-dicarbonate. ENDOR measurements further support the correlation proposed by us between EPR spectral shape and the rigidity of the polymeric phase.

In preceding papers a model has been proposed to account for the EPR spectra detected in photopolymerized difunctional acrylates and for their decay during post-irradiation polymerization.^{1,2} The EPR spectra have been interpreted as the overlap of a three-line and a one-line pattern, both due to the same mid-chain radical species, resulting from tertiary hydrogen abstraction from the polymer chain. The three-line spectrum is attributable to radicals in a more mobile phase, while radicals in a denser, crosslinked environment give a single-line pattern, as the hyperfine interaction is washed out in this case by electron spin-spin exchange between like radicals. The existence of two radical populations in the reacting mass, in terms of different radical environments, has also been suggested by other authors.^{3,4}

ENDOR spectra confirmed this model providing a matrix-line typical of the solid phase, when the single line was saturated. On the contrary, no ENDOR response was obtainable from the three-line spectrum.

All preceding investigations concerned the characterization and decay of EPR spectra obtained from diacrylates previously photopolymerized in the absence of any photoinitiating species. Aiming to find further support to our model, in the present paper we have extended our study to the effects of the presence of a photoinitiator. As photoinitiating species notoriously cause strong modifications in the characteristics of polymeric networks, we were interested in investigating their influence both on the formation of the two polymeric phases causing the two different EPR patterns and on the rate of radical decay during post-irradiation polymerization.

The kinetics of formation of radicals in butane-1,4-diyl diacrylate (BDDA) in the presence of different amounts of photoinitiator has thus been followed kinetically by irradiating the photoreactive mixture directly in the EPR cavity. The decay kinetics of EPR signals obtained in these conditions have then been studied after the end of irradiation.

Furthermore, we have studied radical systems trapped in a different polymeric network, in which one of the two phases would dominate the other, to see if, correspondingly, one of the two EPR patterns would dominate in this case. Our choice fell on diallyl oxydiethylene dicarbonate† (DADC), a monomer which is known to give rather rigid polymeric structures. Its

photochemical reactivity has been thoroughly investigated in our laboratories.⁵⁻⁸

Experimental

Materials.—Monomers and photoinitiator were commercial products. Butane-1,4-diyl diacrylate (BDDA), purchased from UCB, Belgium, was washed with 10% aqueous potassium hydroxide to remove inhibitor, followed by several washings with saturated NaCl. It was successively dried with anhydrous sodium sulfate and magnesium sulfate and then stored at 4 °C in the dark.

DADC (Enichem Synthesis, Italy) was purified as previously described.⁵ The photoinitiator, 2,2-dimethoxy-1,2-diphenylethanone, was purchased from BASF, Germany, and was used as received.

Sample Preparation.—In radical formation kinetics, BDDA mixed with photoinitiator (0–5 mol%) was sealed under vacuum in a quartz EPR tube and then irradiated directly *in situ* in the EPR cavity by means of a 400 W high pressure mercury arc lamps (Helios Italquartz, Italy). The polychromatic impinging photoenergy at the same distance as in irradiations *in situ* was measured actinometrically and found to be equal to 5.0×10^{-9} einstein $s^{-1} cm^{-2}$. We estimate that only half of the light incident on the instrument cavity can reach the EPR tube placed inside it.

In radical decay studies, photopolymerized BDDA samples were prepared by irradiating the monomer mixed with different amounts (1–5 mol%) of 2,2-dimethoxy-1,2-diphenylethanone directly in quartz EPR tubes, under the same experimental conditions as already described.^{1,2} IR analysis of residual unsaturations² showed that a conversion degree of double bonds of ca. 85% was achieved in the presence of photoinitiator.

Photopolymerized DADC samples were obtained by irradiating the monomer containing 4.7 mol% of photoinitiator for 2 h. By this procedure an EPR signal high enough to be studied kinetically could be obtained. No EPR response, however, was observed in the absence of photoinitiating species, even after longer irradiation times.

EPR and ENDOR Spectroscopy.—EPR and ENDOR spectra were recorded on a Varian E-line Century Series EPR and on a Bruker ESP 300 EPR/ENDOR spectrometer equipped with an

† Diallyl 3-oxapentane-1,5-dicarbonate.

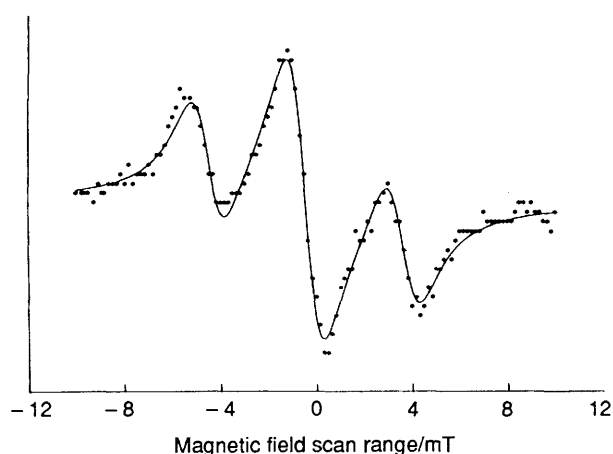


Fig. 1 EPR spectrum recorded after 170 min of UV irradiation *in situ* of pure BDDA. The computed spectrum (continuous line) represents the sum of the two EPR patterns. The former is due to two equivalent protons. The latter is composed of just a singlet. The hyperfine coupling constant of the former, the line-widths, the ratio between the two patterns are already reported in the text. The plot is reported *vs.* the magnetic field scan referred to the centre of the spectrum.

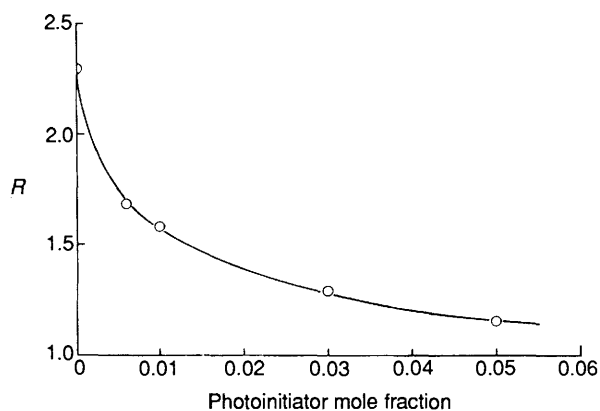


Fig. 2 Ratio R between spectral areas of the single-line EPR pattern over the three-line pattern as a function of photoinitiator concentration (mol%)

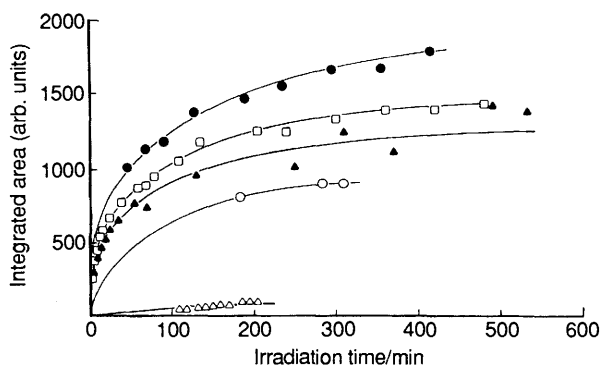


Fig. 3 Three-line pattern integrated area (arbitrary units) as a function of irradiation time, for BDDA (Δ) pure or photopolymerizing in the presence of (\blacktriangle) 0.6; (\bullet) 1; (\square) 3; (\circ) 5 mol% of photoinitiator

ENI A 500 (900 W) RF power amplifier. The temperature of the samples was kept constant at the desired value ± 1 K by circulation of pre-warmed air.

Digitized EPR spectra were transferred to a GOULD NP1 computer through an IBM PS/2 80, in order to fit them using the program EPR85.⁹ In this paper a model based on lorentzian spectral shapes has been adapted to make the results comparable with the ones already reported² for the decay of the

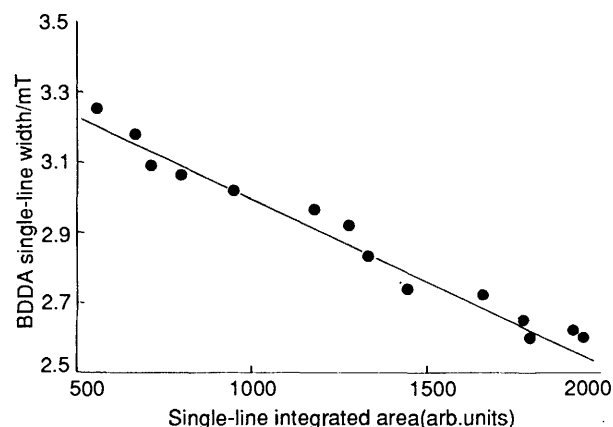


Fig. 4 Variation of the line-width ΔW_2 (mT) with the integrated spectral area (arbitrary units) for the single-line EPR pattern obtained under irradiation of BDDA photopolymerizing in the presence of 3 mol% of photoinitiator

same radical system. However, in many cases we also observed that a gaussian line shape is competitive in the fitting procedure of EPR spectra recorded during photopolymerization of BDDA.

Radical decay kinetics in pre-irradiated BDDA containing different amounts of photoinitiator were followed at 90 ± 1 °C, while in the case of pre-irradiated DADC the same study was carried out at five different temperatures, in the range 60–120 °C. Irradiations *in situ* were performed at 25 ± 1 °C.

The ENDOR spectrum of pre-irradiated DADC was recorded at 100 K under the experimental conditions reported in ref. 2. The ENDOR spectrum was then transferred to an IBM PS/2 80 for subsequent analysis and simulated by a computer program as already described elsewhere.¹⁰

Results

Radical Formation under Irradiation.—(a) *BDDA*. The EPR pattern obtained with BDDA irradiated *in situ* without photoinitiator was identical to that obtained under the same conditions but after irradiation² (see Fig. 1). In fact, all spectra recorded after different irradiation times were the superposition of single-line and three-line patterns with the same g -factor (2.0028). At 25 °C the hyperfine coupling constant of the three line spectrum was $a_{2H} = 2.44 \pm 0.01$ mT and the line-width was $\Delta W_1 = 0.88 \pm 0.03$ mT for the three-line spectrum and $\Delta W_2 = 3.4 \pm 0.1$ mT for the single-line spectrum. The ratio R between the spectral areas of the single-line pattern and the three-line pattern was 2.3 ± 0.3 and did not change with irradiation time.

When the photopolymerization of BDDA was performed in the presence of photoinitiator, however, the ratio R decreased with increasing photoinitiator concentration, down to a value equal to 1.15 ± 0.05 when 5 mol% of photoinitiator was present. The ratio R , however, was a constant for a given amount of photoinitiator, and did not change within each kinetic run of radical formation. Mean R values obtained with different amounts of photoinitiator are reported in Fig. 2.

The overall radical concentration, assumed to be proportional to the numerical integrated area of the EPR pattern, increased in the presence of photoinitiator by more than one order of magnitude, reaching its maximum value for 1 mol% of photoinitiator. As illustrated in Fig. 3, higher concentrations of photoinitiator are less effective in this respect. At higher radical concentration a narrower single-line spectrum (see for example Fig. 4) was also observed and this effect seems more evident at higher photoinitiator concentration. On the contrary, no significant line-width variation was measured at the highest radical concentration for the three-line pattern.

Table 1 First-order rate constants ($k/10^{-3} \text{ min}^{-1}$) at 90 °C of radical decay in BDDA pre-irradiated in the presence of I (mol%) of photoinitiator

I	$k/10^{-3} \text{ min}^{-1}$	
	Three-line spectrum	Single-line spectrum
0	3.0 ± 0.3	1.3 ± 0.2
1	3.7 ± 0.4	1.3 ± 0.2
3	6.5 ± 0.5	3.3 ± 0.3
5	8.9 ± 0.7	3.1 ± 0.6

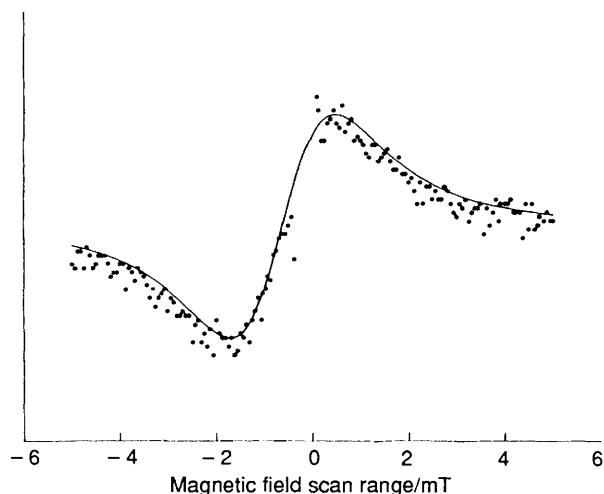
Table 2 Rate constants for initial radical decay from EPR measurements of pre-irradiated DADC

$T/^\circ\text{C}$	$k/10^{-3} \text{ min}^{-1}$
60	0.25 ± 0.03
75	1.01 ± 0.15
90	2.3 ± 0.5
105	3.9 ± 1.4
120	18.6 ± 3.7

Table 3 Activation enthalpy, ΔH^\ddagger , and activation entropy, ΔS^\ddagger , for the radical decay of the single-line spectrum in different pre-irradiated bifunctional monomers

Monomer	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$
HDDA ^a	39 ± 2	-222 ± 5
TEGDA ^a	40 ± 1	-219 ± 3
BDDA ^b	56 ± 7	-148 ± 25
DADC ^c	69 ± 7	-140 ± 20

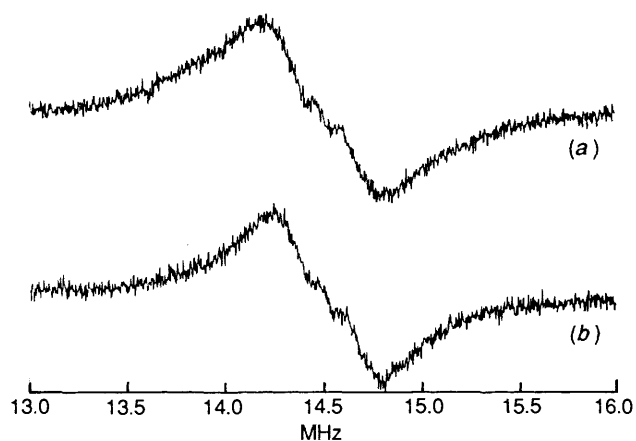
^a From ref. 1. ^b From ref. 2. ^c Only the initial radical decay has been considered.

**Fig. 5** EPR spectrum at the beginning of the decay run at 90 °C of pre-irradiated DADC. The spectrum is caused by just a single Lorentzian-shaped line (width = 1.75 ± 0.04 mT). The plot is reported vs. the magnetic field scan referred to the centre of the spectrum.

(b) *DADC*. DADC cannot be photopolymerized without photoinitiator, as it does not absorb enough light in the UV range. A rather weak EPR signal was detectable in the presence of photoinitiator but only after a long irradiation time.

Radical Decay after Irradiation.—(a) *BDDA*. A kinetic study has been already reported by us² for the decay of radicals produced in BDDA by UV irradiation without photoinitiator.

The decay of both EPR signals in the post-irradiation period followed first-order kinetics, characterized by the rate constants

**Fig. 6** ENDOR spectra at 100 K of (a) pre-irradiated BDDA and (b) pre-irradiated DADC

reported in Table 1. Clearly the decay of the species showing the three-line pattern becomes even faster with increasing photoinitiator concentration. This is also true for the single-line spectrum, but to a lesser extent.

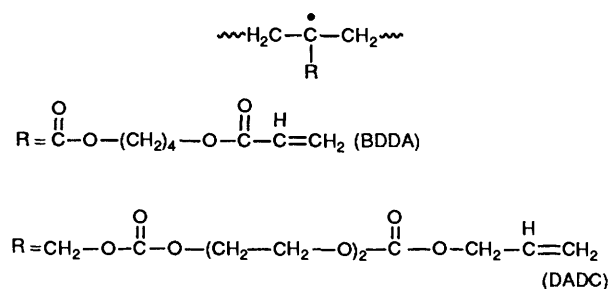
(b) *DADC*. The EPR spectra measured with this system have been obtained after a long UV irradiation time (2 h). On the basis of an EPR fitting procedure,⁹ they consist of just one Lorentzian-shaped line (see Fig. 5), the width of which (*ca.* 1.7 mT) is narrower than that of the single line already observed by us with BDDA, hexane-1,6-diyl diacrylate (HDDA) and tetraethylene glycol diacrylate (TEGDA).

The decay with time of this EPR pattern, followed at 60, 75, 90, 105 and 120 °C, resulted in a progressively self-decelerating process, characterized by a continuously increasing decay time. However, in order to compare the results of these kinetic studies with those obtained with the previously investigated diacrylates, we considered only the initial decay rate as following first-order kinetics. Table 2 reports the rate constants at different temperatures calculated in this way, while in Table 3 the activation parameters for radical decay in photopolymerized DADC are compared with the corresponding values for radical decay in pre-irradiated diacrylates.

Aiming to obtain a deeper insight in the nature of the radical species, we also performed an ENDOR investigation. The matrix-line ENDOR reported in Fig. 6(b) has been detected.

Discussion

Radical Formation under Irradiation.—It is worth noting, first of all, that the EPR spectra detected under irradiation of BDDA photopolymerizing in the absence of photoinitiator are similar to those obtained after the end of irradiation. This excludes any possibility of finding in the photoreacting system any radical species, such as propagation radicals, different from the mid-chain radical reported in Scheme 1.

**Scheme 1**

However, different mechanisms could affect the line-shape narrowing during the radical formation and decay processes. In fact in the former case a spin-spin exchange line-narrowing is observed for the single-line pattern at increasing radical concentration (see for example Fig. 4), while no effect of this kind is measurable during the radical decay runs (see below).

The addition of photoinitiator greatly increases the overall amount of trapped radicals, but at the same time it induces a change in the ratio R between spectral areas of single-line and three-line signals, as reported in Fig. 2. Two different hypotheses could in principle justify this trend. The photoinitiator could induce a relative decrease in the formation of species characterized by the single EPR line, or, on the contrary, it could induce an enhancement in the concentration of the species characterized by the three-line pattern.

The latter explanation seems the more reasonable. It is well known, in fact, that photoinitiators, upon irradiation, produce a great amount of radical fragments which can simultaneously initiate a large number of polymer chains. The average chain-length of the polymer is then reduced, favouring the more fluid phase with respect to the more rigid one.

On the other hand the higher fluidity of the system, together with the higher photoinitiator radical concentration, is at the origin of the decrease of the EPR integrated areas at photoinitiator concentrations higher than 1 mol%, as reported in Fig. 3. In fact, in this situation both radical-radical and photoinitiator fragment-radical encounters are favoured.

Radical Decay.—It has been shown above that a greater amount of more mobile radical species are formed in the presence of photoinitiator. This is also confirmed by the observation that radical decay is enhanced by its presence. In fact both three-line and single-line patterns decay faster at higher photoinitiator concentrations. This effect is most evident for the three-line spectrum, further supporting its attribution to the more mobile radicals.

However our model would be more completely confirmed if an opposite situation were experimentally observed, where a more rigid phase would correspond to an EPR pattern in which the single-line would dominate. This is what happens with photopolymerized DADC, in which a network more rigid than in photopolymerized BDDA causes an EPR pattern formed by just one single lorentzian-shaped line, the width of which is *ca.* 1.7 mT, nearly independent of temperature. In principle this line could also be attributed to different kinds of radicals,¹¹ such as ketyl or oxygen radicals, different from the mid-chain radical structure hypothesized in the previous cases in pre-irradiated HDDA, TEGDA and BDDA (see Scheme 1).

A correct attribution has been attempted by seeking a deeper insight into the nature of this single-line through an ENDOR analysis. In fact similar local environments of the unpaired electron should correspond to similar ENDOR patterns. For photopolymerized DADC a matrix line has been obtained [see Fig. 6(b)], quite similar to that already obtained for all the diacrylates¹⁻² [see for example Fig. 6(a)]. In all cases the spectrum is attributable to the same kind of shells of protons, 6 Å and 13 Å away from the unpaired electron.

This is what led us to suggest that radicals trapped in photopolymerized DADC have the same radical structure, reported in Scheme 1, as the previously investigated diacrylate radicals.

However, a difference must be underlined between the nature of the single EPR-line in diacrylates and in DADC. In the former systems first-order decay kinetics were observed.^{1,2} On the contrary, a self-decelerating rate is measured for the radical

decay in DADC. This difference can be interpreted as further confirmation that photopolymerized DADC has a structure more rigid than pre-irradiated diacrylates. This is in agreement both with the presence of just a single-line in the EPR pattern of DADC, as discussed above, and with the progressive inhibition observed with this polymeric system, but not with diacrylates, to a radical propagation and termination in the bulk.

Furthermore a different behaviour of the line-width with temperature has been noticed in the different investigated systems. In fact the single-line is always broadened at higher radical concentration during the decay runs, but this effect at higher temperatures is more evident with photopolymerized HDDA and TEGDA, whilst it is less pronounced for BDDA. No temperature influence, on the contrary, is observed on the change in single-line width with concentration during the decay of pre-irradiated DADC. The linear correlation of the single-line width with the radical concentration in HDDA, TEGDA and BDDA^{1,2} supports the conclusion that the observed line broadening with increasing radical concentration is due to electron spin dipole-dipole interactions.

However, the electron spin dipolar interaction is partially averaged by Brownian motion or by flip-flops. This averaging is more effective at higher temperatures and results in a significant reduction of the slope k_d of the line-width ΔW_2 vs. concentration C plot for BDDA from 40 °C to 120 °C. Nevertheless, even if dipole-dipole interaction is predominant, other mechanisms of line broadening or narrowing, *e.g.* spin exchange, may contribute to k_d . The dependence of the latter on temperature can be influenced by the temperature dependence of these minor contributions to the line-width. The increase of slope k_d with temperature found in pre-irradiated HDDA and TEGDA samples could be accounted for in this way.

Finally it seems that temperature does not influence the slope of the ΔW_2 vs. C plot in the case of DADC. In fact in this case just one kind of phase traps the radicals and so no temperature-dependent spin exchange between radicals trapped in different phases broadens the spectra. Furthermore the great rigidity of the medium inhibits any temperature dependent mechanisms of line-width variation. On the other hand, this is what made DADC particularly suitable to verify the nature of the EPR pattern in rigid systems.

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